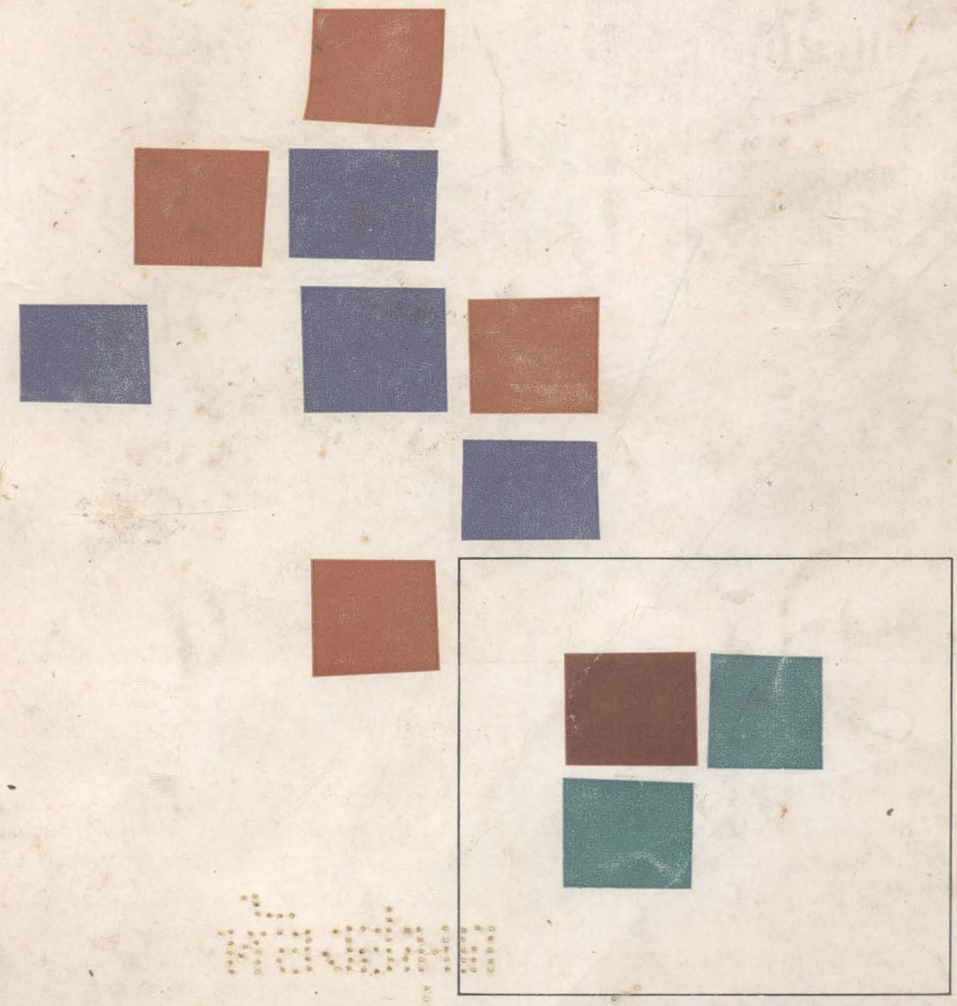
JULY 1963

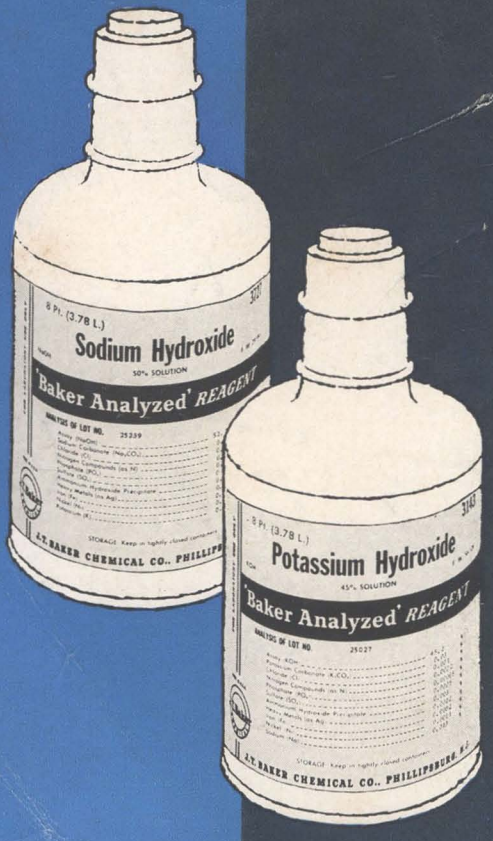
ANALYTICAL CHEMISTRY



NEW COMPANIES INVADE THE INSTRUMENT FIELD
25A

time-saving solutions

sodium hydroxide 50% solution



potassium hydroxide 45% solution

Designed for busy chemists, these two 'Baker Analyzed' Reagents are offered in easy-to-use **solution** form. You eliminate dissolving time and can quickly prepare accurate shelf and volumetric solutions by dilution.

Both J. T. Baker Solutions are labeled with the Actual Lot Analysis and Actual Lot Assay. Purity is precisely defined.

Your favorite Laboratory Supply House can supply both time-saving Solutions in 1-pint and 8-pint polyethylene bottles, and also the Sodium Hydroxide 50% Solution in a 60-lb. container. J. T. Baker Chemical Co., Phillipsburg, N. J.

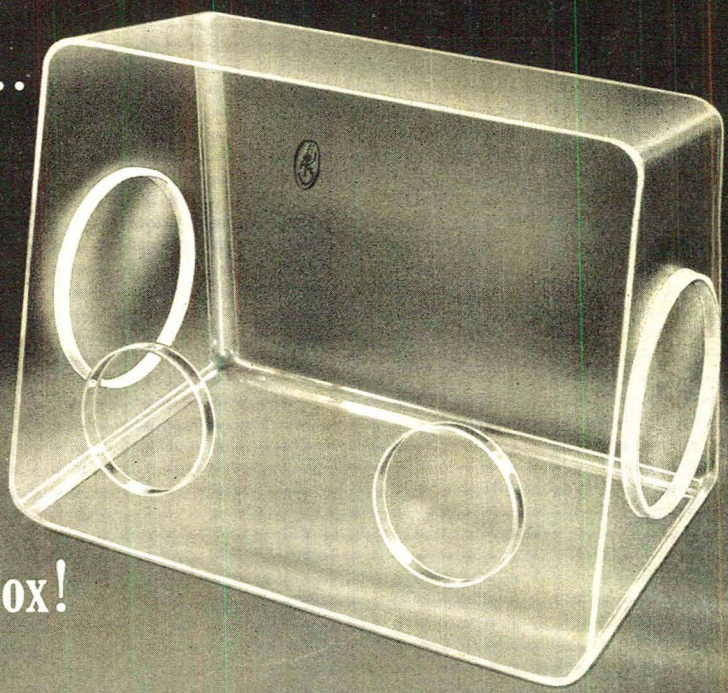
J.T. BAKER LABORATORY CHEMICALS

Circle No. 22 on Readers' Service Card

The features say –
$300 or $400 but...

$186

is the complete price of this Plexiglas® Glove Box!



NEW IMPROVED DESIGN! Now *completely hermetically sealed* with new rubber sealing technique... plus other features that compare favorably with boxes costing twice the price!

■ 100% visibility through transparent Plexiglas® walls ■ Rounded corners for ease of cleaning and complete accessibility ■ Boxes may be interconnected with simple slip-on adapter to make multiple units ■ Easy access through 12-inch diameter side entry openings with readily removable covers ■ 8-inch circular flanged hand holes accept standard GB-1700 gloves ■ New airlock accessory (optional extra) now available, as well as bellows gloves with replaceable hands, iris port, and coupling sleeves for joining two boxes. **GB-4000** Glove Box with two side access opening covers . . . **$186**

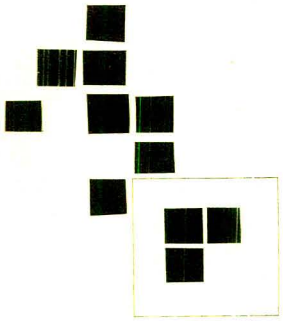
Write for Glove Box bulletin

MANOSTAT Corporation
A SUBSIDIARY OF GREINER SCIENTIFIC CORPORATION
26 North Moore Street, Dept. 521, New York 13, N. Y.

Circle No. 47 on Readers' Service Card

VOLUME 35, NUMBER 8 JULY 1963

ANALYTICAL CHEMISTRY



This Month's Cover is an artistic representation of the invasion of new companies into the ranks of established manufacturers of analytical instruments. For a discussion of the factors involved in this development, see the Report for Analytical Chemists, page 25 A.

© Copyright 1963
by The American Chemical Society
Issued June 21, 1963

MANUSCRIPT REQUIREMENTS, published in December 1962 issue, page 1853, outlines scope and copy requirements to be observed in preparing manuscripts for consideration. Manuscript (3 copies) should be submitted to the Editor, 1155 Sixteenth St., N.W., Washington 6, D. C.

The American Chemical Society assumes no responsibility for the statements and opinions advanced by contributors to its publications. Views expressed in the editorials are those of the editors and do not necessarily represent the official position of the American Chemical Society.

	1963 Subscription Rates		
	1 yr.	2 yr.	3 yr.
Members, domestic and foreign	$ 4.00	$ 7.00	$10.00
Nonmembers, domestic and Canada	5.00	9.00	12.00
Nonmembers, foreign except Canada	15.00	27.50	40.00

Postage: Canada, $0.70; Pan-American Union, $1.50, foreign, $2.50. Single copies: current, $1.50. Postage: Canada and Pan-American Union, $0.15; foreign, $0.20. Rates for back issues and volumes are available from Special Issues Sales Dept., 1155 Sixteenth St., N.W., Washington 6, D. C. Claims for missing numbers will not be allowed if received more than 60 days from date of mailing plus time normally required for postal delivery of journal and claim. No claims allowed because of failure to notify the Subscription Service Department of a change of address, or because copy is "missing from files."

Published monthly with review issue added in April by the American Chemical Society, from 20th and Northampton Sts., Easton, Pa. Executive offices, Editorial Headquarters, and Subscription Service Department, 1155 Sixteenth St., N.W., Washington 6, D. C. Advertising Office, 430 Park Ave., New York 22, N. Y. News Bureaus: 753 Third Ave., New York 17, N. Y.; 1725 Pennsylvania Blvd., Philadelphia 3, Pa.; 530 William Penn Place, Pittsburgh 30, Pa.; 36 South Wabash Ave., Chicago 3, Ill.; 1367 East Sixth St., Cleveland 14, Ohio; 57 Post St., San Francisco 4, Calif.; 422 South Western Ave., Los Angeles 5, Calif.; 1121 Walker St., Houston 2, Tex.; 1155 Sixteenth St., N.W., Washington 6, D. C.; Grosse Bockenheimerstrasse 32, Frankfort/Main, West Germany; 77 South Audley St., London, W.1, England.

Second class postage paid at Easton, Pa.

CHANGE OF ADDRESS: Notify Subscription Service Department, American Chemical Society, 1155 Sixteenth St., N.W., Washington 6, D. C. Such notification should include both old and new addresses and postal zone number, if any, and be accompanied by mailing label from a recent issue. Allow four weeks for change to become effective.

CONTENTS

REPORT FOR ANALYTICAL CHEMISTS

The business of making analytical instruments has attracted companies established in other fields. The factors involved in the decision to divert funds and know-how into instrument manufacture are many and include the ever-increasing rise in R&D expenditures and the influence of foreign markets.....**25 A**

NEWS SECTION

Scientific meeting and university course schedules are given..**41 A**

EDITOR'S COLUMN

Some highlights from the President's Science Advisory Committee report on "Science, Government, and Information" are given. .....**65 A**

LABORATORY OF THE MONTH

Varian Associates has added an Applications Laboratory at the Pittsburgh Airport building to its worldwide facilities. These laboratories aid in the design and utilization of nuclear magnetic resonance and electron paramagnetic resonance spectrometers. .....**81 A**

INSTRUMENTATION

Studies of the Hall effect undertaken since the advent of improved semiconductors have resulted in the development of numerous useful devices and instruments.....**91 A**

BOOKS...49 A

BRIEFS...9 A

CALENDAR OF EVENTS... 42 A

NEW CHEMICALS...113 A

EDITORIAL...937

FUTURE ARTICLES...128 A

MANUFACTURERS' LITERATURE...114 A

PRODUCT CAPSULES...119 A

NEW PRODUCTS...101 A

READERS' INFORMATION SERVICE...98 B

Scientific Communications

Quantitative Immunofluorescein Titration of Human and Bovine Gamma Globulins. R. P. TENGERDY . 1084

Voltammetry and Electron Paramagnetic Resonance Spectra of Halonitrobenzene Anion Radicals. TOYOKICHI KITAGAWA, T. P. LAYLOFF, and R. N. ADAMS 1086

Preparation and Isolation of Isomeric Ketones by the Girard Reaction. I. C. NIGAM and LEO LEVI. . . 1087

Mercury-Coated Platinum Electrodes. LOUIS RAMALEY, R. L. BRUBAKER, and C. G. ENKE 1088

Quantitative Measurement of Hydrogen Types by Integrated Nuclear Magnetic Resonance Intensities. **J. L. Jungnickel and J. W. Forbes** 938

The Physical Basis of Analytical Atomic Absorption Spectrometry. The Pertinence of the Beer-Lambert Law. **Keiichiro Fuwa and B. L. Valle** 942

Application of Time of Flight Mass Spectrometry and Gas Chromatography to Reaction Studies. **E. J. Levy, E. D. Miller, and W. S. Beggs** 946

Separation of Some Alkaloids, Steroids, and Synthetic Compounds by Thin-Layer Chromatography. **B. P. Korzum, Louis Dorfman, and S. M. Brody** 950

The Chromatographic Determination of Trace Amounts of Polynuclear Hydrocarbons in Petrolatum, Mineral Oil, and Coal Tar. **William Lijinsky, Irving Domsky, Gloria Mason, H. Y. Ramahi, and Taher Safavi** 952

Detection and Identification of Mercaptans by Gas Liquid Chromatography. **K. F. Sporek and M. D. Danyi** 956

A High Sensitivity Scanning Coulometer with Automatic Background Correction and Proportional Scan Rate. Titration of Plutonium and Other Redox Species. **R. C. Propst** 958

Electrolysis Cell for Continuous External Generation of Reagents in Reagent-Addition Analyzers. **R. B. Kesler** 963

Polarographic Analysis of a Series of Metal Ion 1-Hydroxypyridine-2-thione Systems. **A. F. Krivis, E. S. Gazda, G. R. Supp, and M. A. Robinson** 966

The Dead-Stop Titration of Indium. **L. S. Martens and Herschel Frye** 969

Determination of Trinitrotoluene in Warhead Exudates by Linear Sweep Polarography. **G. C. Whitnack** 970

Potentiometric Titration of Acids in an *N,N*-Dimethyl Fatty Amide. **C. A. Reynolds, James Little, and Merle Pattengill** 973

Determination of Hexafluorophosphate by Amperometric Titration with Tetraphenylarsonium Chloride. **H. E. Affsprung and V. S. Archer** 976

Polarographic and Coulometric Determination of Technetium. **G. B. S. Salaria, C. L. Rulfs, and P. J. Elving** 979

Liquid-Liquid Extraction of Pertechnetate Ion with Methyltricaprylammonium Chloride. **G. B. S. Salaria, C. L. Rulfs, and P. J. Elving** 983

A Scheme for the Separation of Platinum, Palladium, Rhodium, and Iridium by Solvent Extraction. **G. H. Faye and W. R. Inman** 985

Behavior of Dialkyl Phosphorodithioic Acids in Liquid Extraction Systems. **R. H. Zucal, J. A. Dean, and T. H. Handley** 988

Di-*n*-butyl Phosphorothioic Acid as an Extractant for Metal Ions. **T. H Handley** 991

Anion Exchange Studies in Tartrate Medium. The Separation of Manganese(II), Cobalt(II), Zinc(II), Copper(II), and Iron(III). **G. F. Pitstick, T. R. Sweet, and G. P. Morie** 995

The Determination of Plutonium by (Ethylene dinitrilo)-tetraacetic Acid Titration. **W. B. Brown, D. R. Rogers, E. A. Mershad, and W. R. Amos** 1000

A Continuous Photometric Fluorine Analyzer. **C. W. Weber and O. H. Howard** 1002

The Ultraviolet Spectrometric Determination of the Three Isomeric Toluenesulfonic Acids in Excess of Aqueous Sulfuric Acid. **Hans Cerfontain, H. G. J. Duin, and Leo Vollbracht** 1005

Spectrophotometric Hydroperoxide Determination by the Use of Triphenylphosphine. **R. A. Stein and Vida Slawson** 1008

Spectrophotometric Titration of Some Divalent Metals in Chloroform–Isopropyl Alcohol Solvent Mixture. **R. K. Behm and R. J. Robinson** 1010

Spectrophotometric Determination of Aldrin. **H. O. Friestad** 1012

Comparison of Two Colorimetric Methods for Determination of Copper in Mineral Oils. **J. M. Howard and H. O. Spauschus** 1016

Quantitative Radiochemical Procedure for Analysis of Polonium-210 and Lead-212 in Minerals. **H. T. Millard, Jr.** 1017

General Applicability of the Channels Ratio Method of Measuring Liquid Scintillation Counting Efficiencies. **E. T. Bush** 1024

Neutron Activation and Radiochemical Determination of the Molybdenum, Chromium, and Iron Content of Individual Stainless Steel Microspheres. **P. A. Benson and C. E. Gleit** 1029

Novel Radiotracer Method for Fluoride Determination. **F. L. Moore** 1032

CONTRIBUTED ARTICLES

Fluorescence Techniques in the Microdetermination of Metals in Biological Materials. Utility of 2,4-Bis-[*N,N'*-di-(carboxymethyl)aminomethyl] Fluorescein in the Fluorometric Estimation of Al^{+3}, Alkaline Earths, Co^{+2}, Cu^{+2}, Ni^{+2}, and Zn^{+2} in Micromolar Concentrations. **D. F. Hoelzl Wallach and T. L. Steck** . . 1035

The Separation and Fluorescent X-Ray Spectrometric Determination of Zirconium, Molybdenum, Ruthenium, Rhodium, and Palladium in Solution in Uranium-Base Fissium Alloys. **J. O. Karttunen** 1044

X-Ray Emission Analysis of Plutonium and Uranium Compound Mixtures. **Oscar Menis, E. K. Halteman, and E. E. Garcia** 1049

Inert Gas Fusion Determination of Oxygen in Vanadium, Niobium, and Tantalum. **G. J. Kamin, J. W. O'Laughlin, and C. V. Banks** 1053

Semimicro Determination of Molecular Weight with a Dew-Point System. **Angelo De Ros, Oliviero Fagioli, and Piero Sensi** 1054

The Use of Perchloric Acid in Propellants Analysis. **J. B. Macorkindale and J. J. Lamond** 1058

Rapid Titrimetric Determination of Orthophosphate with Cerous Ion. Applications to Technical Grade Inorganic Phosphates. **T. A. Taulli and R. R. Irani** . . 1060

Assay of Aziridinyl Compounds. **R. C. Schlitt** 1063

Elimination of Chloride Interference in the Chemical Oxygen Demand Test. **R. A. Dobbs and R. T. Williams** 1064

Determination of Surface Areas of Phosphates from Adsorption Measurements in Nonaqueous Media. **R. E. Mesmer and R. R. Irani** 1067

Spectropolarimetry. Acid-Base Titrimetry with Asymmetric Indicators and Determination of Metal Ions and Asymmetric Substances. **Stanley Kirschner and D. C. Bhatnagar** 1069

Radioactivation Analysis of Sodium by Counting Photoneutrons. **Saadia Amiel and Max Peisach** 1072

Diffuse Reflectance Spectra of Potassium Iodate and Some Mercuric Iodide Complexes. **T. R. Griffiths** . 1077

Anion Exchange Separation of Magnesium and Calcium with Alcohol–Nitric Acid. **J. S. Fritz and Hirohiko Waki** 1079

Correspondence

(Ethylene dinitrilo)tetraacetic Acid Titration of Lead(II) in the Presence of Orthophosphate and Alkaline Earths. **F. H. Blood and W. H. Nebergall** . . 1089

The Use of Raney Nickel in the Rapid Determination of Small Concentrations of Nitric Acid in Sulfuric Acid. **Charles Wankat, D. A. Keyworth, and V. A. Brand** 1090

Quantitative Study of Gas Chromatographic Analysis of Head Space Gas of Dilute Aqueous Solutions. **Süheyla Özeris and Richard Bassette** . . . 1091

A Polarographic Study of the Copper(II) Complexes of Mono, Di-, and Triethanolamine. **P. E. Sturrock** 1092

Determination of Nitrogen Impurity as Uranium Nitrides in Fused Uranium Dioxide (UO_2). **H. J. Anderson and J. C. Langford** 1093

Determination of Rhodium in Rhodium–Uranium Alloys by Precipitation with Hydrogen Sulfide. **E. J. Maienthal** 1094

Rapid Extraction and Spectrophotometric Determination of Vanadium(V) with 2-Thenoyltrifluoroacetone **A. K. De and M. S. Rahaman** 1095

An Improvement of the Amperometric Titration of Thiols at the Rotating Platinum Electrode. **H. C. Börresen** 1096

The Quantitative Recovery of Germanium by Distillation from Hydrochloric Acid in the Presence of Sodium Chloride. **H. B. Rayner** 1097

Determination of Aluminum in Organo-Aluminum Compounds by X-Ray Fluorescence. **H. F. Smith, and R. A. Royer** 1098

Correction for Anomalous Fluorescence Peaks Caused by Grating Transmission Characteristics. **R. M. King and D. M. Hercules** 1099

Chronopotentiometric Investigation of the Adsorption of Iodine at Platinum Electrodes. **R. A. Osteryoung** 1100

Gravimetric Determination of Silica as Quinolinium Molybdosilicate in Phosphate Rock. **J. A. Brabson, R. D. Duncan, and I. J. Murphy** 1102

Spot Test for Beryllium Based on the Color Reaction with Eriochrome Cyanine R. **P. R. Mohilner** . 1103

Aids for the Analyst

A New Automatic End Point Detector for Constant Current Coulometric Titrations. **C. B. Roberts and H. A. Brejcha** 1104

A Simple, Inexpensive, Heated Infrared Gas Cell. **E. A. Burns** 1106

An Automatic Programmer for Chromatographic Eluents. **S. R. Lerner** 1108

Multiple Hydrogenation Insert. **R. A. Eisenhauer and R. E. Beal** 1110

Safe, Simple Method of Opening Irradiated Silica Ampoules. **Ray Porritt and Malcolm Thackray** 1111

A Partition Sampler for Vapor Analysis by Gas Chromatography. **E. R. Colson** 1111

A Convenient Mass Reference Plate for Use in Spark Source Mass Spectrography. **F. N. Hodgson, Michel Desjardins, and W. L. Baun** 1112

Digitize Your Chart Record for only $585

Any standard strip chart recorder can be equipped with a Disc Chart Integrator to deliver an accurate digital interpretation of chart areas for chromatography, electric power, flow rates, temperature, pressures, etc. The continuous permanent record of the integrator output directly below the curve can be translated to digits, or the digits can be read directly from a counter.

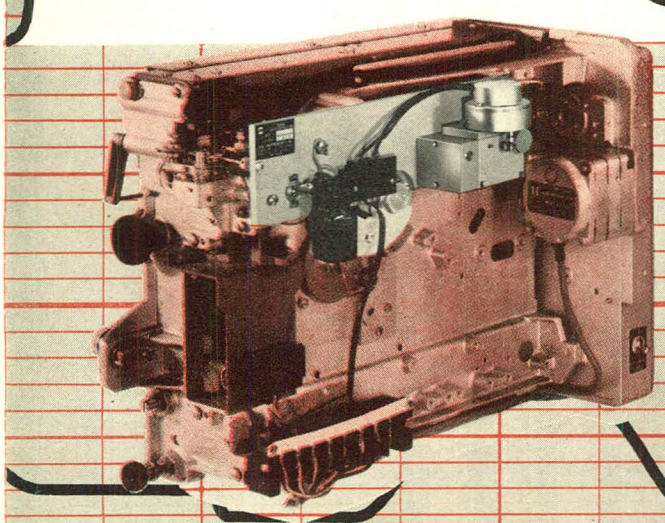
Highly accurate, the integrator will measure the actual area of the recorded chart trace within ±0.1% full scale. Exceptionally stable, it will not drift or change in its accuracy characteristics over years of operation. Practically no maintenance is required outside of filling the ink bottle.

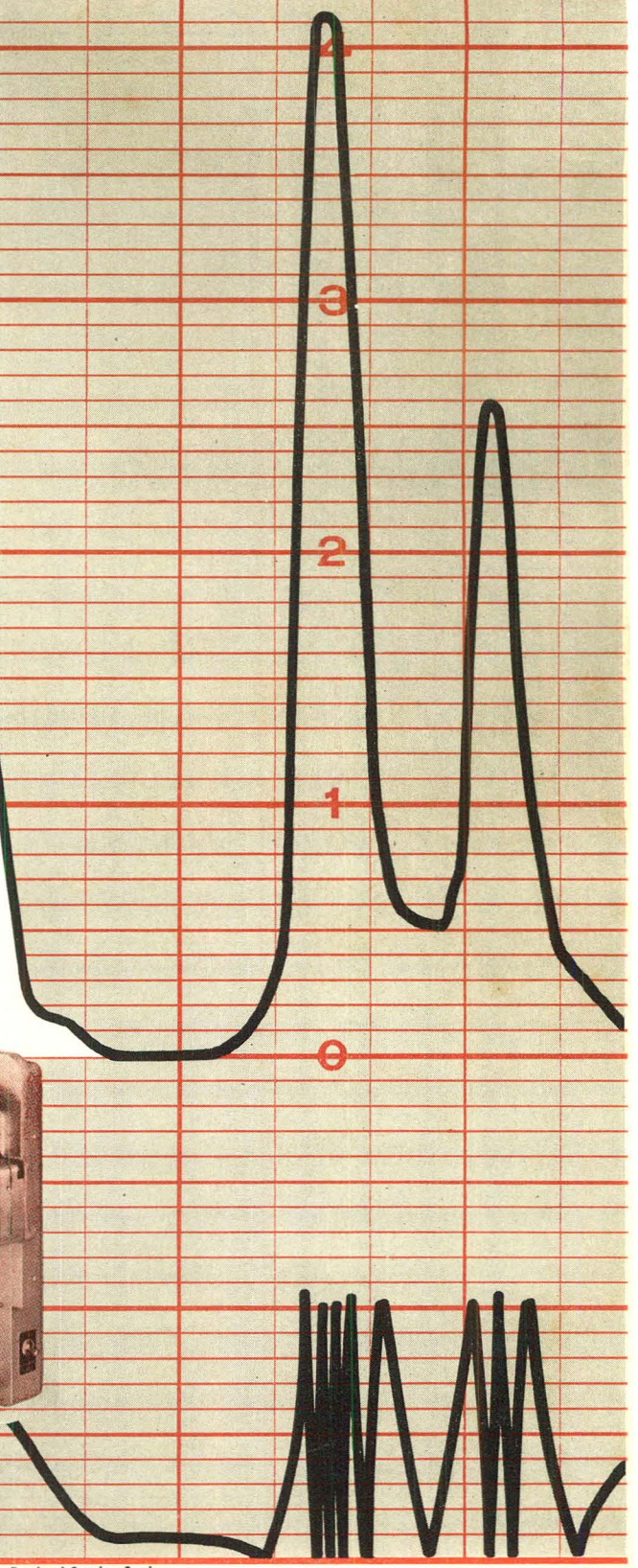
The Series 200 Integrator is available with new recorders, or may easily be installed on recorders in service. Order from laboratory apparatus dealers, recorder manufacturers, or direct. Complete details in Specification S-200.

DISC

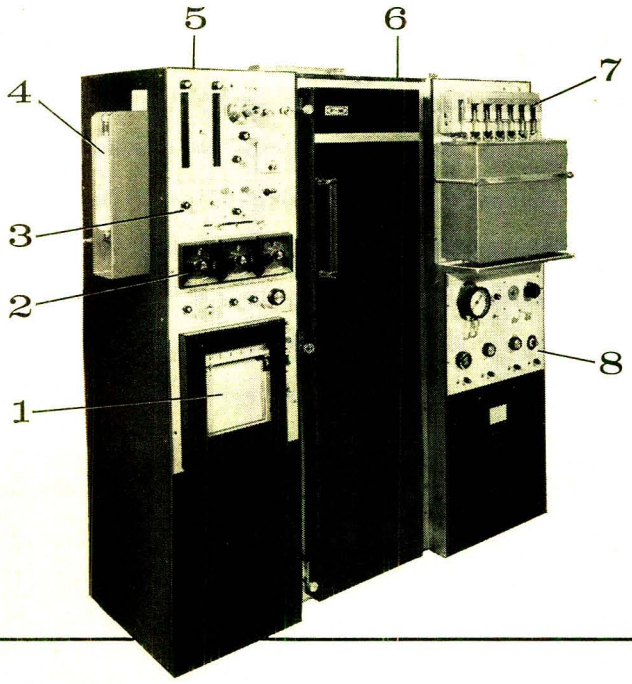
DISC INSTRUMENTS, INC.

3014-B So. Halladay, Santa Ana, Calif.
National Dial 714, KI 9-0345





Circle No. 39 on Readers' Service Card



1. Integral Strip Chart Recorder for ease and accuracy in interpreting preparative or analytical results
2. Adjustable Delay Timers (for pre- and post-injection and upper limit delays)
3. Programmed or Isothermal Operation; Manual or Automatic (8 programming rates from 0.5 to 10°C/min)
4. Pressurized 300 ml Sample Reservoir
5. Independent Analytical System for column scouting or checking the purity of collected fractions
6. Column Flexibility (¼ to ¾" OD; up to 48'; series or parallel operation)
7. Six High-Efficiency Collection Traps
8. Independent Temperature Control of column oven, detector, injection port and manifold heaters.

fully automatic / large capacity

MODEL 770 PREPARATIVE GAS CHROMATOGRAPH

The F & M Model 770 is a high-performance, fully automatic preparative gas chromatograph, designed and built for the automatic collection of large quantities of high-purity components. Although the Model 770 has literally dozens of significant features, they all exist only to advance the instrument's three most important characteristics:

- **Fully Automatic**—The Model 770 can be operated completely unattended, overnight or through a weekend. Injection, programming, collection, re-injection: all are automatic.
- **Large Capacity**—The 770 automatically injects from 0.25 to 12 ml at each cycle, and provides facilities for the collection of any six components of a complex mixture in the 75 cc traps.
- **High Purity**—Collected component purities of 99.9+% are the rule. Because the 770 is controlled by system parameters, there is no possibility of the component contamination that is common to instruments operating on a timed cycle.

For more information on the Model 770 Automatic Preparative Gas Chromatograph, write or call F & M Scientific Corporation, Route 41 and Starr Road, Avondale, Penna., 215-COlony 8-2281.
European subsidiary: F & M Scientific Europa N. V., Leidsestraat 67, Amsterdam, The Netherlands.

F&M

F & M SCIENTIFIC CORPORATION
AVONDALE / PENNSYLVANIA

SALES OFFICES: Atlanta • Boston • Chicago • Dallas • Cleveland • Houston • Los Angeles • New York • Pittsburgh • St. Louis • Toronto • Washington

Circle No. 42 on Readers' Service Card

new PICKER **2 in 1**

SPECTRO DIFFRACTOMETER

x-ray emission / x-ray diffraction

always ready for either technique

two permanently mounted x-ray tubes preclude changeover downtime

use this tube for fluorescence analysis

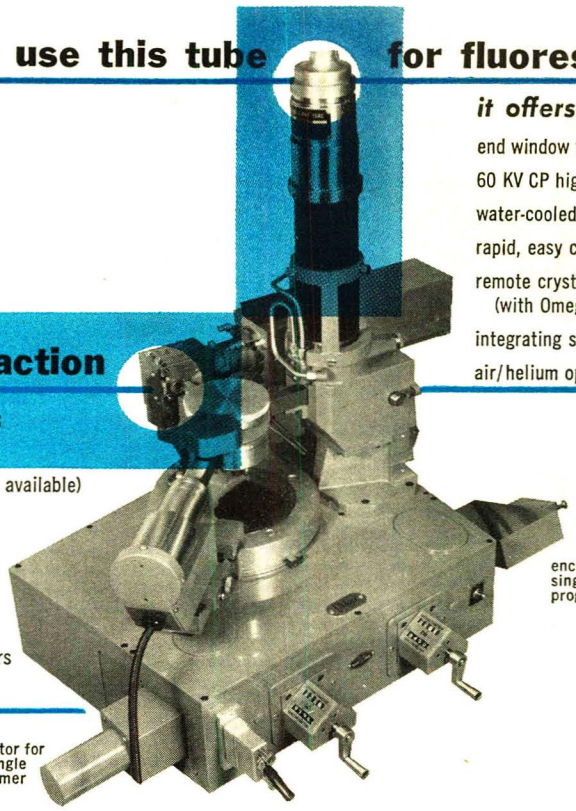
it offers these advantages

- end window type with W, Mo, Cr, or Pt target
- 60 KV CP high intensity radiation
- water-cooled specimen chamber
- rapid, easy crystal changing
- remote crystal tuning (with Omega motor)
- integrating specimen spinner
- air/helium operation (10 second flush)

this for x-ray diffraction

it offers these advantages

- constant potential operation
- variety of focal spots (.4, .75 and 1.5 mm available)
- both Omega and 2-Theta scanning
- electrically operated shutters
- take-off angle easily adjustable (without disturbing beam alignment)
- track-mounted specimen and detector supports
- complete set of slits or pinhole collimators



encoder for single-angle programmer

slew motor for single-angle programmer

The Picker Two-in-One SPECTRODIFFRACTOMETER provides uniquely versatile technical resources for a minimal outlay. It will find particular welcome in the laboratory where both diffraction and emission analyses may be required on the same specimen: one can follow the other by simple switchover (no need to interchange and/or align components). The instrument's instant readiness to tackle either job commends it to the small laboratory where scant space or stringent budget permits investment in only one goniometer.

To get the detailed story of these remarkable instrumental advances, call any local Picker representative or write PICKER X-RAY CORPORATION, WHITE PLAINS, N.Y.

another advance ...

automatic single-angle programming

The attachments seen jutting from the diffractometer base in the picture above are the slew motor and encoder for the Picker Single-Angle Programmer.

The programmer will automatically analyze

up to 10 elements by x-ray emission techniques

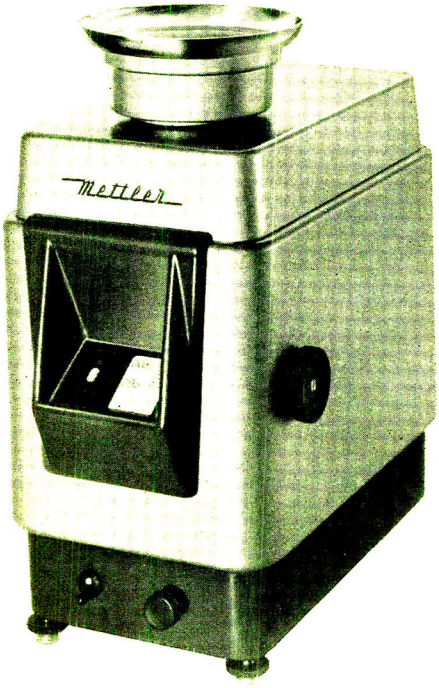
or up to 5 pairs of Bragg angles by diffraction

Operating unattended, it can save countless manhours in situations where much sequential work is to be done.

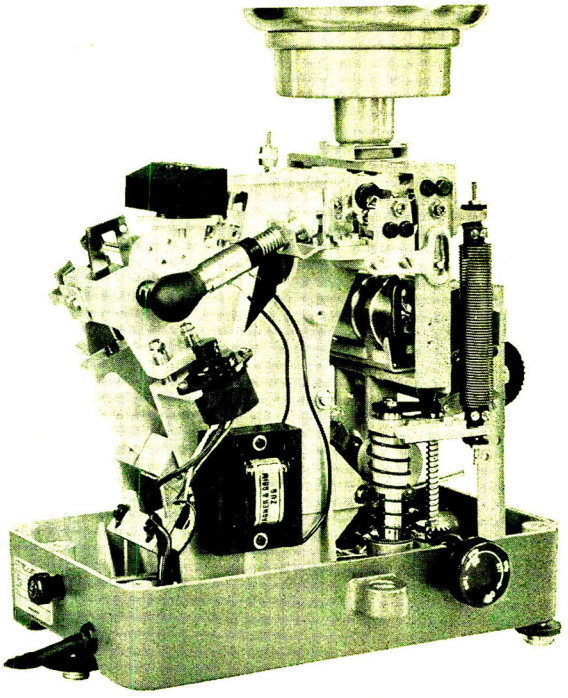
look to **PICKER** *for* **NEW** *THINKING*

in x-ray instrumentation

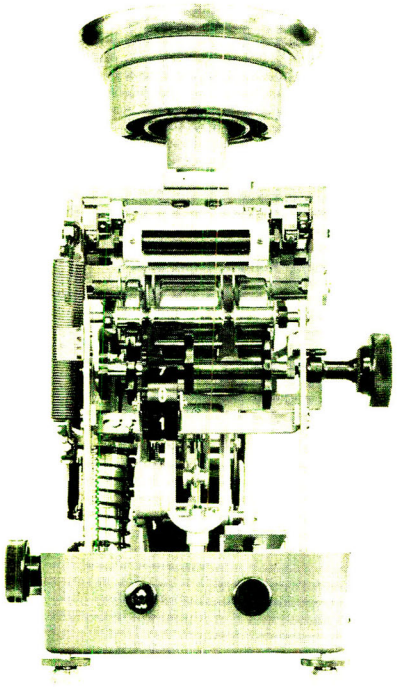
Circle No. 76 on Readers' Service Card



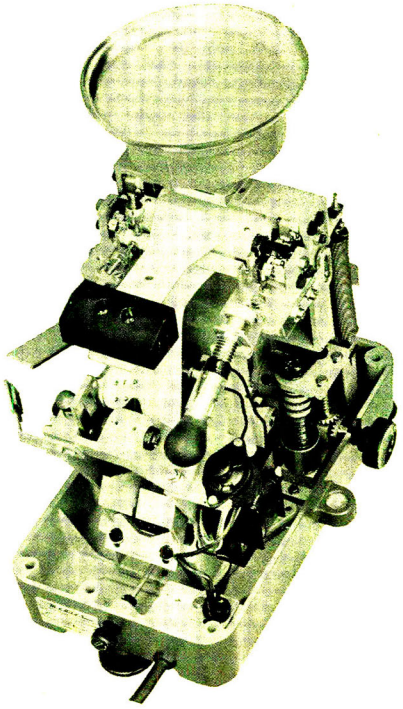
in a balance . . .



it's the mechanism . . .



that measures . . .



no matter how you look at it!

See the Mettler "K" Balance for yourself. Write for demonstration or particulars to:
Mettler® Instrument Corporation, 20 Nassau Street, Princeton, New Jersey

Circle No. 66 on Readers' Service Card

AC BRIEFS

Highlights of the scientific and technical articles in this issue

Quantitative Measurement of Hydrogen Types by Integrated Nuclear Magnetic Resonance Intensities

Absorption bands for nonequivalent groups of protons in 26 selected pure compounds were integrated to determine percentages of total hydrogen content. The results were compared with theory. The effect of r.f. field strength on the integrals was studied.

J. L. JUNGNICKEL and J. W. FORBES, Shell Development Co., Emeryville, Calif.

Anal. Chem. 35, 938 (1963)

The Physical Basis of Analytical Atomic Absorption Spectrometry. The Pertinence of the Beer-Lambert Law

The Beer-Lambert law is used as a model for a study of atomic absorption. It is shown that the sensitivity of measurement is a function of the length of the absorbing flame path and of the reflectivity of the surrounding cell surfaces. The described absorption cell increases the sensitivity of detection of many elements.

KEIICHIRO FUWA and BERT L. VALLEE, Biophysics Research Laboratory of the Division of Medical Biology, Department of Medicine, Harvard Medical School, and the Peter Bent Brigham Hospital, Boston, Mass.

Anal. Chem. 35, 942 (1963)

Application of Time of Flight Mass Spectrometry and Gas Chromatography to Reaction Studies

The described technique is applicable to any thermal, photochemical, or catalytic reaction carried out in a flow stream. Gas chromatographic peaks are identified with the mass spectrometer while quantitative analysis is determined by chromatographic peak areas.

E. J. LEVY, E. D. MILLER, and W. S. BEGGS, The Atlantic Refining Co., Philadelphia, Pa.

Anal. Chem. 35, 946 (1963)

Separation of Some Alkaloids, Steroids, and Synthetic Compounds by Thin-Layer Chromatography

Preparative thin-layer chromatography is used to separate alkaloids, steroids, and synthetic compounds in amounts of 100 to 500 mg. A detailed account of the procedure, equipment, and examples of application is given.

B. P. KORZUN, LOUIS DORFMAN, and S. M. BRODY, Research Department, CIBA Pharmaceutical Co., Division of CIBA Corp., Summit, N. J.

Anal. Chem. 35, 950 (1963)

The Chromatographic Determination of Trace Amounts of Polynuclear Hydrocarbons in Petrolatum, Mineral Oil, and Coal Tar

Analysis of petrolatums, mineral oils, and coal tar for polynuclear hydrocarbons by adsorption chromatography, solvent partition, and paper chromatography is discussed. Gas chromatography appears more sensitive than other analytical methods for polynuclear hydrocarbons.

WILLIAM LIJINSKY, IRVING DOMSKY, GLORIA MASON, HUSNI Y. RAMAHI, and TAHER SAFAVI, Division of Oncology, The Chicago Medical School, 2020 West Ogden Ave., Chicago 12, Ill.

Anal. Chem. 35, 952 (1963)

Detection and Identification of Mercaptans by Gas Liquid Chromatography

The mercaptan sample is treated with iodine to form disulfide; a second portion of the sample is spiked with a known mercaptan and this is converted to a mixture of disulfides. The technique provides nearly absolute identification of the mercaptans.

K. F. SPOREK and M. D. DANYI, Owens-Illinois Technical Center, Toledo 7, Ohio

Anal. Chem. 35, 956 (1963)

A High Sensitivity Scanning Coulometer with Automatic Background Correction and Proportional Scan Rate. Titration of Plutonium and Other Redox Species

Coulomb-potential curves of reversible processes under nearly equilibrium conditions are recorded with a scanning coulometer. The instrument is used for the direct determination of plutonium in irradiated nuclear fuel at the 2- to 5-μg. level with a precision of 2.1%.

R. C. PROPST, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, S. C.

Anal. Chem. 35, 958 (1963)

Electrolysis Cell for Continuous External Generation of Reagents in Reagent-Addition Analyzers

The cell features single-piece, strong, compact construction; low generator-electrolyte consumption; and attainment of high current values for reagent generation at 100% current efficiency. It is capable of producing standard iodine solutions of about 0.08N concentration and bromine solutions of about 0.2N concentration.

RICHARD B. KESLER, Engineering and Technology Section, The Institute of Paper Chemistry, Appleton, Wis.

Anal. Chem. 35, 963 (1963)

Polarographic Analysis of a Series of Metal Ion 1-Hydroxypyridine-2-thione Systems

A polarographic study is reported on the copper-, zinc-, cadminum-, iron-, and nickel-1-hydroxypyridine-2-thione systems. In the copper, zinc, and cadmium cases, the polarograms showed separate waves for the complexed and uncomplexed organic moieties, and for the complexed and uncomplexed metal ions.

ALAN F. KRIVIS, EUGENE S. GAZDA, GEORGE R. SUPP, and MARTIN A. ROBINSON, Central Analytical Laboratories, Olin Mathieson Chemical Corp., New Haven, Conn.

Anal. Chem. 35, 966 (1963)

The Dead-Stop Titration of Indium

Indium is determined by dead-stop titration with hexacyanoferrate(II). Mole ratios of five indium(III) to four hexacyanoferrate(II) were obtained, in agreement with previously reported ratios.

L. S. MARTENS and HERSCHEL FRYE, Department of Chemistry, University of the Pacific, Stockton 4, Calif.

Anal. Chem. 35, 969 (1963)

Precise measurement of radioactivity in gas chromatography effluents

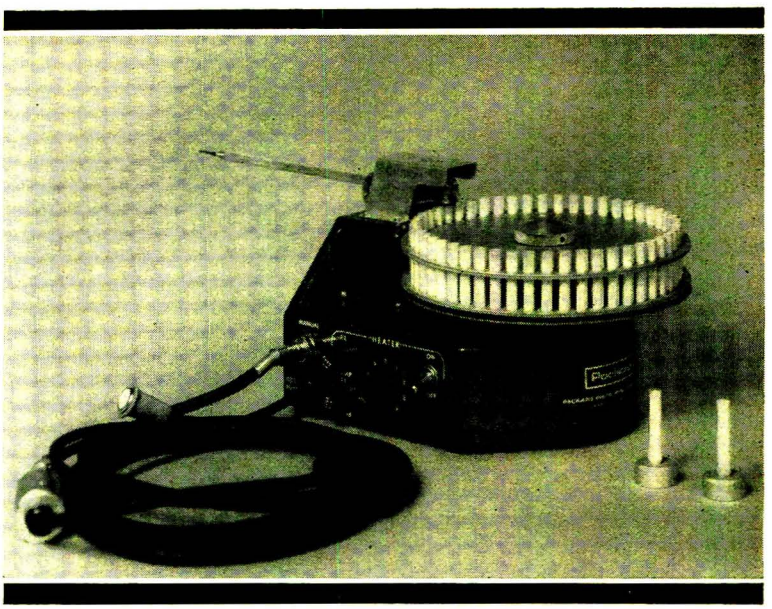
The Packard Model 830 Tri-Carb® Gas Fraction Collector enables quantitative collection of the individual organic components in a gas chromatographic effluent stream. It is suitable for use with any gas chromatograph using a non-destructive mass detector. Precise measurement of the radioactivity in component peaks can be made after collection.

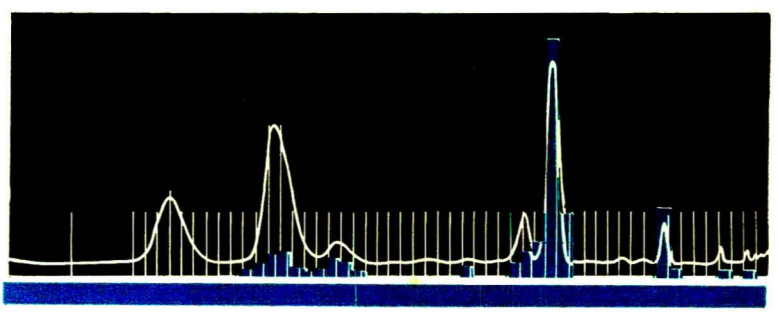
An 8″ diameter turntable holds up to 50 Tri-Carb Cartridges, each packed with silicone-coated scintillation crystals. Vapors leaving the gas chromatography mass detector pass through the heated gas injection nozzle of the collector and condense on the coated surfaces of the scintillation crystals. Cartridges may be changed by actuating a pushbutton or automatically according to a preset time. Changing takes only a fraction of a second.

After sample collection, the cartridges are counted in an Automatic Tri-Carb Liquid Scintillation Spectrometer. No sample preparation is necessary.

Counting efficiency for C^{14} is over 50% and backgrounds are extremely low. Consequently, even peaks with very low activity can be accurately measured in short counting periods.

For more information call your local Packard Sales Engineer—or write for descriptive literature.





Analysis of methyl esters labeled with carbon-14. The curves represent the output of a mass detector. The white vertical lines represent the times at which the fraction collector was actuated. The bar graph represents the radioactivity in each fraction in counts per minute, determined by a 10-minute count. *(Ref.: Journal of Lipid Research 3, No. 1, 44, January, 1962)*

Packard

PACKARD INSTRUMENT COMPANY, INC.
BOX 428 • LA GRANGE, ILLINOIS • HUNTER 5-6330

Circle No. 72 on Readers' Service Card

Determination of Trinitrotoluene in Warhead Exudates by Linear Sweep Polarography

The method is based on the presence of only microgram amounts of TNT in a 25% acetone and 75% 0.1*M* lithium chloride solution and depends on the measurement of the wave produced by the TNT at —0.66 volt *vs.* a Hg pool in this solution. TNT can be determined in a few minutes using an X-Y recorder with a linear sweep polarograph.

GERALD C. WHITNACK, Chemistry Division, Research Department, U. S. Naval Ordnance Test Station, China Lake, Calif.

Anal. Chem. 35, 970 (1963)

Potentiometric Titration of Acids in an *N,N*-Dimethyl Fatty Amide

In the method a conventional glass indicating electrode is used with a saturated calomel reference electrode modified by replacing the saturated potassium chloride with a saturated aqueous solution of lithium chloride. The solvent is shown to be effective, especially for differentiating titrations.

CHARLES A. REYNOLDS, JAMES LITTLE, and MERLE PATTENGILL, Department of Chemistry, University of Kansas, Lawrence, Kan.

Anal. Chem. 35, 973 (1963)

Determination of Hexafluorophosphate by Amperometric Titration with Tetraphenylarsonium Chloride

The indicating ion is tetraphenylarsonium, and supporting polarographic data on the method is given. The results from the method are shown to agree well with those of the Nitron determination of this fluoride complex.

HAROLD E. AFFSPRUNG and VERNON S. ARCHER, Department of Chemistry, The University of Oklahoma, Norman, Okla.

Anal. Chem. 35, 976 (1963)

Polarographic and Coulometric Determination of Technetium

Technetium in any oxidation state can be readily converted to Tc(VII), so the determination of Tc(VII) will cover most situations in which technetium is to be determined. The polarographic determination of Tc, based on the measurement of wave I at pH 2, provides optimum selectivity and sensitivity. However, Tc can also be determined by measurement of wave I, II, or III at pH 13.

G. B. S. SALARIA, CHARLES L. RULFS, and PHILIP J. ELVING, The University of Michigan, Ann Arbor, Mich.

Anal. Chem. 35, 979 (1963)

Liquid-Liquid Extraction of Pertechnetate Ion with Methyltricaprylammonium Chloride

The formation of a 1:1 pertechnetate–organic cation adduct seems to be necessary for the extraction at any pH. The competition of the chloride ion in the liquid-liquid anion exchange system described was studied.

G. B. S. SALARIA, CHARLES L. RULFS, and PHILIP J. ELVING, University of Michigan, Ann Arbor, Mich.

Anal. Chem. 35, 983 (1963)

A Scheme for the Separation of Platinum, Palladium, Rhodium, and Iridium by Solvent Extraction

The iodide complexes of platinum and palladium are extracted with tributyl phosphate, thereby separated from rhodium and iridium. Modifications of existing methods are used for the separation of palladium from platinum and for the separation of iridium from rhodium.

G. H. FAYE and W. R. INMAN, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada

Anal. Chem. 35, 985 (1963)

Behavior of Dialkyl Phosphorodithioic Acids in Liquid Extraction Systems

The solubility and acidity of the diethyl, diisopropyl, di-*n*-butyl, and diisobutyl esters of phosphorodithioic acid in water and the distribution of each between CCl_4, methyl isobutyl ketone, or *n*-amyl acetate and HCl-NaCl solutions was studied. Acid dissociation constants and partition coefficients were calculated.

RAQUEL H. ZUCAL and JOHN A. DEAN, Department of Chemistry, University of Tennessee, Knoxville, Tenn., and THOMAS H. HANDLEY, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Anal. Chem. 35, 988 (1963)

Di-n-butyl Phosphorothioic Acid as an Extractant for Metal Ions

A study was made of the extraction of metal ions from aqueous solutions of HCl or H_2SO_4 using di-*n*-butyl phosphorothioic acid. Of 32 metal ions studied, 18 extracted in significant amounts.

THOMAS H. HANDLEY, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Anal. Chem. 35, 991 (1963)

Anion Exchange Studies in Tartrate Medium. The Separation of Manganese(II), Cobalt(II), Zinc(II), Copper(II), and Iron(III)

Radioisotopes were used for batch equilibrium studies at various pH values and tartrate concentrations and also for following the column separations. Mn(II), Co(II), Zn(II), Cu(II), and Fe(III) were successfully separated with Dowex 2-X8 resin in the tartrate form.

GERALD F. PITSTICK, THOMAS R. SWEET, and GERALD P. MORIE, Department of Chemistry, The Ohio State University, Columbus 10, Ohio

Anal. Chem. 35, 995 (1963)

The Determination of Plutonium by (Ethylene dinitrilo) tetracetic Acid Titration

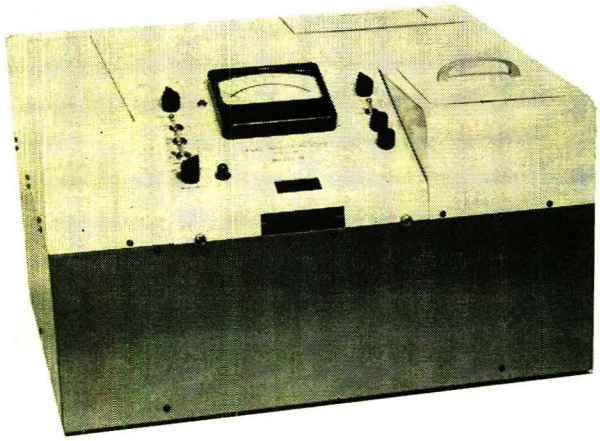
In a direct procedure a solution containing 8 to 40 mg. of plutonium is buffered between pH 2.5 and 3.0, heated to boiling, and titrated with EDTA to a Cu—1-(2-pyridylazo)-2-naphthol end point. An indirect procedure is given which is a continuation of the direct procedure. Standard deviation data are given.

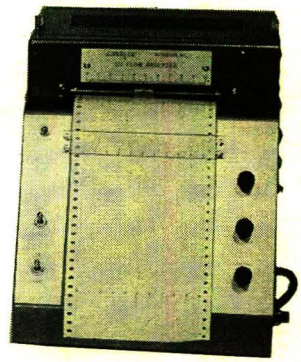
W. B. BROWN, D. R. ROGERS, E. A. MERSHAD, and W. R. AMOS, Monsanto Research Corp., Mound Laboratory, Miamisburg, Ohio

Anal. Chem. 35, 1000 (1963)

FOR COLUMN CHROMATOGRAPHY AND OTHER FLOW SYSTEMS

FULLY AUTOMATED





UV-VISIBLE

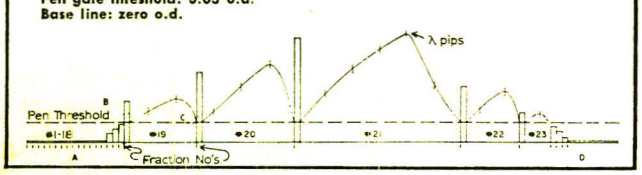
SPECTRAL CURVE ANALYSIS

The new **"MODEL M" FLOW ANALYZER** by Canalco offers these exclusive benefits:

- UV and visible wavelength range
- 1 mu resolution
- two-wavelength ratios
- spectral curve scans
- manual or automatic control
- timer-controlled repetitive spectra of kinetic reactions
- automatic chart marking for both fraction change and wavelength
- full accuracy and sensitivity in gradient elutions using absorbing solvents
- %T or o.d. readout
- recorded spectra of each fraction over wavelength span of your choice from 200-800 mu

A TYPICAL CHART PRESENTATION

Monitor wavelength: 280 mu
Scan limits: 240-300 mu
Pen gate threshold: 0.03 o.d.
Base line: zero o.d.



For full interpretation, request UVA Bulletin

Write for complete details:

CANALCO

Canal Industrial Corporation
4935 Cordell Avenue, Dept. A-71
Bethesda, Maryland

Circle No. 31 on Readers' Service Card

A Continuous Photometric Fluorine Analyzer

Elemental fluorine in gas mixtures is measured by passing the sample stream through hot sodium chloride. The fluorine quantitatively liberates chlorine, which is measured at 360 mμ in a pressure-controlled flow colorimeter cell. The relative standard deviation of the analyzer is about ±1.5% above 0.8% fluorine. The standard deviation is about ±0.04 at lower levels.

C. W. WEBER and O. H. HOWARD, Technical Division, Oak Ridge Gaseous Diffusion Plant, Union Carbide Nuclear Co., Oak Ridge, Tenn.

Anal. Chem. 35, 1002 (1963)

The Ultraviolet Spectrometric Determination of the Three Isomeric Toluenesulfonic Acids in Excess of Aqueous Sulfuric Acid

The procedure involves the multicomponent spectrophotometric analysis of the sulfuric acid solution based on the ultraviolet absorption of the sulfonic acids. The absorbances of the unknown mixture and of its constituents, gathered at a large number of wavelengths, are subjected to a least square treatment by an electronic computer.

HANS CERFONTAIN, HERMAN G. J. DUIN, and LEO VOLLBRACHT, Laboratory for Organic Chemistry, University of Amsterdam, The Netherlands

Anal. Chem. 35, 1005 (1963)

Spectrophotometric Hydroperoxide Determination by the Use of Triphenylphosphine

The decrease in absorbance at 260 mμ when triphenylphosphine is oxidized to triphenylphosphine oxide by a hydroperoxide is a quantitative measurement of the hydroperoxide present. The procedure is compared with iodometric and ferric thiocyanate methods.

ROBERT A. STEIN and VIDA SLAWSON, Department of Biological Chemistry, University of California, Los Angeles 24, Calif.

Anal. Chem. 35, 1008 (1963)

Spectrophotometric Titration of Some Divalent Metals in Chloroform—Isopropyl Alcohol Solvent Mixture

Dimethylglyoxime was used as a titrant. Spectrophotometric titrations of 0.4 to 4 μmoles of Ni(II) in 40 ml. of 1:1 chloroform–isopropyl alcohol solvent gave an overall precision of 3 parts per thousand. Co(II) in amounts of 1 to 4.5 μmoles was titrated with a precision of 2.5 parts per thousand. The influence of other metal ions was studied.

R. K. BEHM and R. J. ROBINSON, Department of Chemistry, University of Washington, Seattle 5, Wash.

Anal. Chem. 35, 1010 (1963)

Spectrophotometric Determination of Aldrin

Aldrin is converted to dihydroaldrin nitrosochloride. This compound forms dihydrochlorketoaldrin, which in turn, reacts with *m*-dinitrobenzene and potassium hydroxide to give a violet-red chloroform-extractable derivative. The resulting solution obeys Beer's law over the range 0 to 100 μg.

HAKON O. FRIESTAD, Department of Pharmacology and Toxicology, The Veterinary College of Norway, Oslo, Norway

Anal. Chem. 35, 1012 (1963)

Comparison of Two Colorimetric Methods for Determination of Copper in Mineral Oils

The carbamate method is compared with the neocuproine method for copper in the range of 2 to 200 μg. of copper. The carbamate method is more sensitive but requires modification if iron is present. Precision and accuracy data are given.

J. M. HOWARD and H. O. SPAUSCHUS, Major Appliances Laboratories, General Electric Co., Louisville, Ky.

Anal. Chem. 35, 1016 (1963)

Quantitative Radiochemical Procedure for the Analysis of Polonium-210 and Lead-212 in Minerals

The procedure involves spontaneous electrodeposition on silver for the isolation of polonium-210 and controlled-potential electrogravimetric separation of lead-212 plus added lead carrier. Amounts of deposited nuclides are then determined by alpha counting. The method was applied to four zircon samples and one uranothorite sample.

H. T. MILLARD, Jr., Division of Geological Sciences, California Institute of Technology, Pasadena, Calif.

Anal. Chem. 35, 1017 (1963)

General Applicability of the Channels Ratio Method of Measuring Liquid Scintillation Counting Efficiencies

The behavior of the curves of efficiency *vs.* channels ratio is examined as a function of small changes in photomultiplier and discriminator voltages, and the over-all accuracy of the method is assessed. Advantages of the channels ratio method over internal standardization or dilution techniques for determining efficiency are discussed.

ELIZABETH T. BUSH, Nuclear-Chicago Corp., 333 East Howard Ave., Des Plaines, Ill.

Anal. Chem. 35, 1024 (1963)

Neutron Activation and Radiochemical Determination of the Molybdenum, Chromium, and Iron Content of Individual Stainless Steel Microspheres

Diameters of stainless steel microspheres, weighing between 4.7×10^{-9} and 3.9×10^{-8} gram, are measured by optical microscopy. After encapsulation in lead foil and irradiation with an intense flux of neutrons, radiochemical procedures are used to isolate Mo^{99}, Cr^{51}, $Fe^{55,59}$, and Np^{239}. The sources of errors in the method are reported.

PHILIP A. BENSON and CHESTER E. GLEIT, Tracerlab, Divison of Laboratory for Electronics, Richmond, Calif.

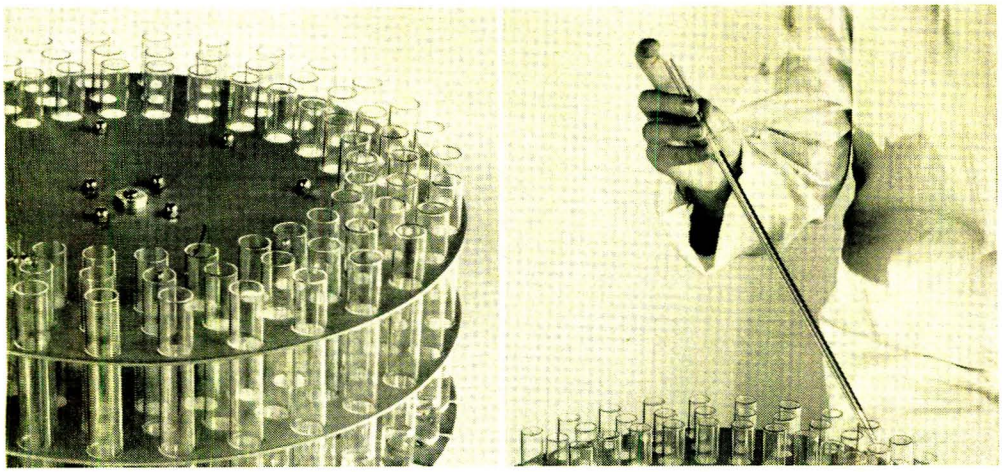
Anal. Chem. 35, 1029 (1963)

Novel Radiotracer Method for Fluoride Determination

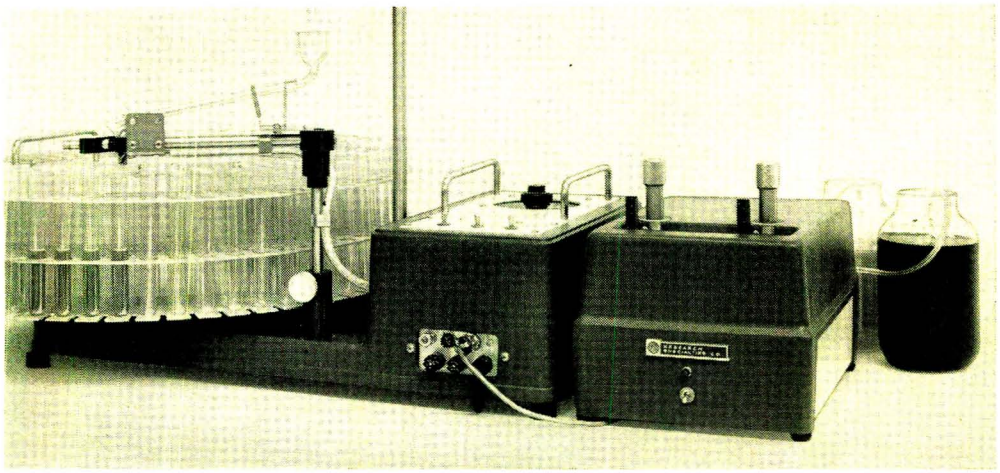
Using selective conditions, tantalum-182 is extracted from 6.5*M* sulfuric acid solution as a fluoride complex into diisobutylketone. The radioactivity of the extractant is proportional to the fluoride ion concentration. Applications of the method are discussed.

FLETCHER L. MOORE, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Anal. Chem. 35, 1032 (1963)



Are you collecting fractions...then adding reagents?



Now do both at once—automatically.

RSCo's NEW REAGENT DISPENSING FRACTION COLLECTOR completely automates these two operations. Without supervision (at night when the lab is closed), it makes up to 500 cuts, adds two reagents simultaneously. Saves time, improves accuracy and reproducibility. Use it with drop counting, timed flow, or volumetric siphoning. ☐ Buy the complete system or either component. You can add the new RSCo Reagent Dispenser to your present RSCo fraction collector or to many other fraction collectors. ☐ Our Model 1205 Fraction Collector is available for volumetric siphoning, or with time base and drop counting accessories. Rugged. Compact. Dependable in both laboratory and cold room. ☐ Available from your RSCo Dealer. Or write us for more information.

RESEARCH SPECIALTIES CO.

200 SOUTH GARRARD BLVD. • RICHMOND, CALIFORNIA

Circle No. 80 on Readers' Service Card

Fluorescence Techniques in the Microdetermination of Metals in Biological Materials. Utility of 2,4-Bis-[*N,N'*-di-(carboxymethyl)aminomethyl] fluorescein in the Fluorometric Estimation of Al^{+3}, Alkaline Earths, Co^{+2}, Cu^{+2}, Ni^{+2}, and Zn^{+2} in Micromolar Concentrations

Spectral and fluorescent changes accompanying the reaction of aluminum, the alkaline earth metals, cobalt, copper, nickel, and zinc with 2,4-bis-[*N,N'*-di-(carboxymethyl)aminomethyl] fluorescein have been studied as a function of pH and of concentration of the reactants.

DONALD F. HOELZL WALLACH and THEODORE L. STECK, Harvard University Medical School, Boston 15, Mass.

Anal. Chem. 35, 1035 (1963)

The Separation and Fluorescent X-Ray Spectrometric Determination of Zirconium, Molybdenum, Ruthenium, Rhodium, and Palladium in Solution in Uranium-Base Fissium Alloys

Palladium is precipitated with dimethylglyoxime, the precipitate is extracted with chloroform. The aqueous portion, made 6*M* in HCl, is passed through a Dowex 1-X8 anion exchange resin. Zirconium and rhodium do not adsorb, uranium is eluted with 0.03*M* HCl, ruthenium and molybdenum with 8*M* HNO_3. The elements are then determined by x-ray fluorescence.

J. O. KARTTUNEN, Argonne National Laboratory, Argonne, Ill.

Anal. Chem. 35, 1044 (1963)

X-Ray Emission Analysis of Plutonium and Uranium Compound Mixtures

Refractory oxide mixtures or alloys are fused in a flux of potassium pyrosulfate. The flux mixture is cast in such a way as to provide slow cooling. $L\alpha$ lines of uranium and plutonium produced by x-ray emission are measured. Thorium is used as an internal standard.

OSCAR MENIS, E. K. HALTEMAN, and E. E. GARCIA, Advanced Materials Center, Nuclear Materials and Equipment Corp., Apollo, Pa.

Anal. Chem. 35, 1049 (1963)

Inert Gas Fusion Determination of Oxygen in Vanadium, Niobium, and Tantalum

Oxygen in vanadium is determined by a platinum flux technique, while oxygen in niobium and tantalum is determined with a mixed nickel–platinum bath with a platinum flux technique. The method permits determination of oxygen contents from 100 to 1000 p.p.m. with a relative standard deviation of 3% for vanadium and 5% for niobium and tantalum.

GEORGE J. KAMIN, JEROME W. O'LAUGHLIN, and CHARLES V. BANKS, Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa

Anal. Chem. 35, 1053 (1963)

Semimicro Determination of Molecular Weight with a Dew-Point System

The method described, based on the vapor pressure lowering of a solution, is easy to perform and is shown to provide good precision and accuracy. Molecular weight determinations below 500 have been made. Solvents having boiling points between 40° and 120° C. can be used.

ANGELO DE ROS, OLIVIERO FAGIOLI, and PIERO SENSI, Research Laboratories, Lepetit S.p.A., Milan, Italy

Anal. Chem. 35, 1054 (1963)

The Use of Perchloric Acid in Propellants Analysis

After oxidation of propellants in hot perchloric acid, lead, aluminum, copper, and potassium can be determined easily and precisely. The sulfate content can be estimated by precipitation as barium sulfate from the perchloric acid solution. The described procedure has proved to be safe.

J. B. MACORKINDALE and J. J. LAMOND, Chemical Inspectorate, Royal Arsenal, Woolwich, London, S.E. 18, England

Anal. Chem. 35, 1058 (1963)

Rapid Titrimetric Determination of Orthophosphate with Cerous Ion. Applications to Technical Grade Inorganic Phosphates

Orthophosphate is titrated with cerous ion in a buffered medium at pH 7.0 to 9.5 using Eriochrome Black T indicator. Accuracy and precision data on the method are given, and the interfering ions are considered.

T. A. TAULLI and R. R. IRANI, Research Department, Inorganic Chemicals Division, Monsanto Chemical Co., St. Louis, Mo.

Anal. Chem. 35, 1060 (1963)

Assay of Aziridinyl Compounds

Methanol-soluble aziridinyl compounds are assayed by reacting them with excess thiocyanic acid, generated in situ from potassium thiocyanate and *p*-toluene sulfonic acid, and back-titrating with methanolic potassium hydroxide.

R. C. SCHLITT, Methods Development Section, Chemical and Materials Laboratory, Aerojet-General Corp., Sacramento, Calif.

Anal. Chem. 35, 1063 (1963)

Elimination of Chloride Interference in the Chemical Oxygen Demand Test

The procedure requires the addition of mercuric sulfate to the sample forming a soluble mercuric chloride complex that resists oxidation under conditions of the chemical oxygen demand test. Results are presented on pure organic solutions and various sewage effluents containing known amounts of chloride.

RICHARD A. DOBBS and ROBERT T. WILLIAMS, Robert A. Taft Sanitary Engineering Center, 4676 Columbia Parkway, Cincinnati 26, Ohio

Anal. Chem. 35, 1064 (1963)

แผนกห้องสมุด กรมวิทยาศาสตร์

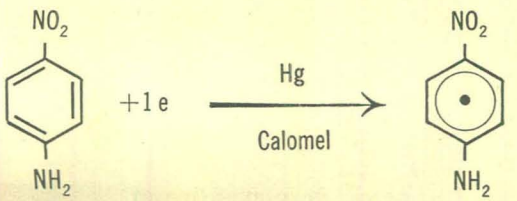
NUMBER 3 IN A SERIES

Chemists seeking to detect the presence of free radicals in chemical systems will find EPR Spectrometry the most sensitive and rapid technique available. The ability of Varian EPR Spectrometers to detect as low as 2×10^{11} free radicals (10^{-8} molar concentrations), and to respond in times less than 100 microseconds, has rendered all other techniques obsolete.

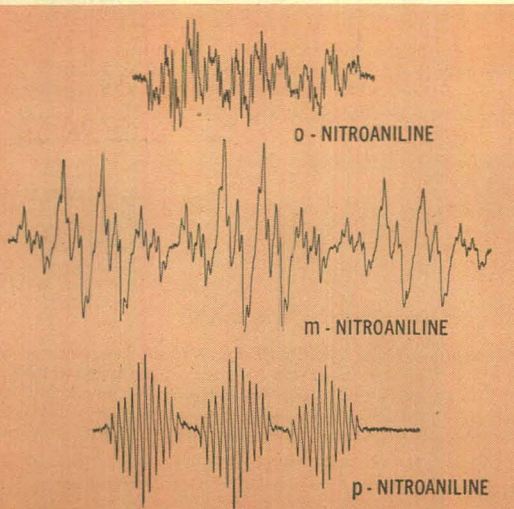
This ability to detect, and in many cases to identify free radicals is inherent in the basic phenomenon of Electron Paramagnetic Resonance, since EPR Spectrometers respond **only** to chemical systems containing unpaired electrons.

EPR IN THE WORLD OF CHEMISTRY

UNIVALENT OXIDATION-REDUCTION BY ELECTROLYSIS



Cyclic voltammetry can be an effective tool for studying univalent oxidation-reduction reactions of organic molecules, provided one observes a split wave in the typical current-potential curve. Very often these split waves are not resolved and an uncertainty arises as to whether one or multiple electron steps are occurring. EPR has eliminated the necessity of observing split waves in such measurements by direct detection of the one-electron intermediate (free radical ion) resulting from a univalent oxidation-reduction.



In situ generation and detection of univalent intermediates in an EPR cavity allow not only positive detection of intermediates in a complex organic electrode reaction, but also permit direct study of the nature of the intermediate.

Fig. 1 illustrates typical one-electron intermediates as detected by EPR in the **in situ** electrolytic reduction of ortho, meta and para nitroaniline in 0.1M KC1 solutions.

Attention is called to the radically different EPR spectra obtained for these three intermediates whose molecular structures differ only by the position of substitution of the amino group. It is this difference in the number of lines and spacings of lines (hyperfine pattern) that allows positive identification of these intermediates. How to identify free radicals by means of their "EPR hyperfine pattern" will be discussed in a later number of this series.

Detection and identification of free radicals are not the only results obtainable from the EPR spectrum, however. It is also possible to measure the rate of free radical formation for studies of complete reaction kinetics.

Varian EPR Spectrometer systems and accessories are designed for a wide range of applications in the fields of chemistry, biology, medicine and physics. For additional information about the example above and other chemical applications of EPR, please write: INSTRUMENT DIVISION.

VARIAN associates
PALO ALTO 4, CALIFORNIA

BRIEFS

Determination of Surface Areas of Phosphates from Adsorption Measurements in Nonaqueous Media

The method is based on the Langmuir equation for adsorption and it utilizes common laboratory reagents and equipment. Phosphates with surface areas between 1.3 and 71 sq. meters per gram are determined in acetic acid—toluene solutions.

R. E. MESMER and R. R. IRANI, Research Department, Inorganic Chemicals Division, Monsanto Chemical Co., St. Louis, Mo.

Anal. Chem. 35, 1067 (1963)

Spectropolarimetry. Acid-Base Titrimetry with Asymmetric Indicators and Determination of Metal Ions and Asymmetric Substances

A high-precision photoelectric spectropolarimeter is used to determine optical rotation at many different wavelengths. The instrument is applied to the titration of acids or bases using optically active substances as indicators. Metal ions, asymmetric coordinating agents, and ligand-metal ion ratios in coordination compounds can be determined.

STANLEY KIRSCHNER and DINESH C. BHATNAGAR, Wayne State University, Detroit, Mich.

Anal. Chem. 35, 1069 (1963)

Radioactivation Analysis of Sodium by Counting Photoneutrons

Na^{24} is assayed by counting photoneutrons emitted from deuterium by the 2.75-m.e.v gamma ray, in an assembly consisting of D_2O and neutron detectors. Microgram quantities of sodium were analyzed with a precision of 2%. Sensitivities better than 0.1 μg. are indicated.

SAADIA AMIEL and MAX PEISACH, Israel Atomic Energy Commission, Soreq Research Establishment, P. O. B. 527, Rehovoth, Israel

Anal. Chem. 35, 1072 (1963)

Diffuse Reflectance Spectra of Potassium Iodate and Some Mercuric Iodide Complexes

Diffuse reflectance spectroscopy in the UV was studied using KIO_3 variously diluted with an inactive diluant, LiF. Results of a semiquantitative nature at wavelengths down to 220 mμ were obtained by using some precautions.

T. R. GRIFFITHS, North East Essex Technical College, Colchester, England

Anal. Chem. 35, 1077 (1963)

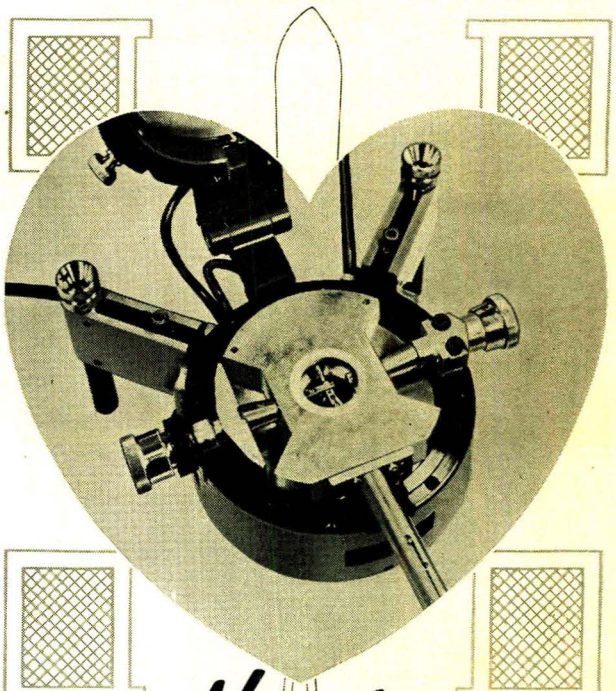
Anion Exchange Separation of Magnesium and Calcium with Alcohol–Nitric Acid

A "column separation factor" is proposed and used in selecting the best eluting medium for the anion exchange separation of magnesium and calcium. A solution of 0.5*M* nitric acid in 90% isopropyl alcohol is the eluent, and Amberlyst XN-1002 is used as the anion exchange resin.

JAMES S. FRITZ and HIROHIKO WAKI, Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa

Anal. Chem. 35, 1079 (1963)

The Heart of the Norelco Electromagnetic Optical System



Norelco®

EXCLUSIVE

"IMMERSION" OBJECTIVE LENS

with rod-type holder allows specimen—to be "immersed" directly into the heart of objective lens • to be easily manipulated for stero orientation studies, high/low temperature studies, and tensile studies • to be dry-box loaded and transferred to microscope without atmospheric contact • to be simultaneously compared with another specimen.

PHILIPS ELECTRONIC INSTRUMENTS Norelco®

PHILIPS ELECTRONIC INSTRUMENTS

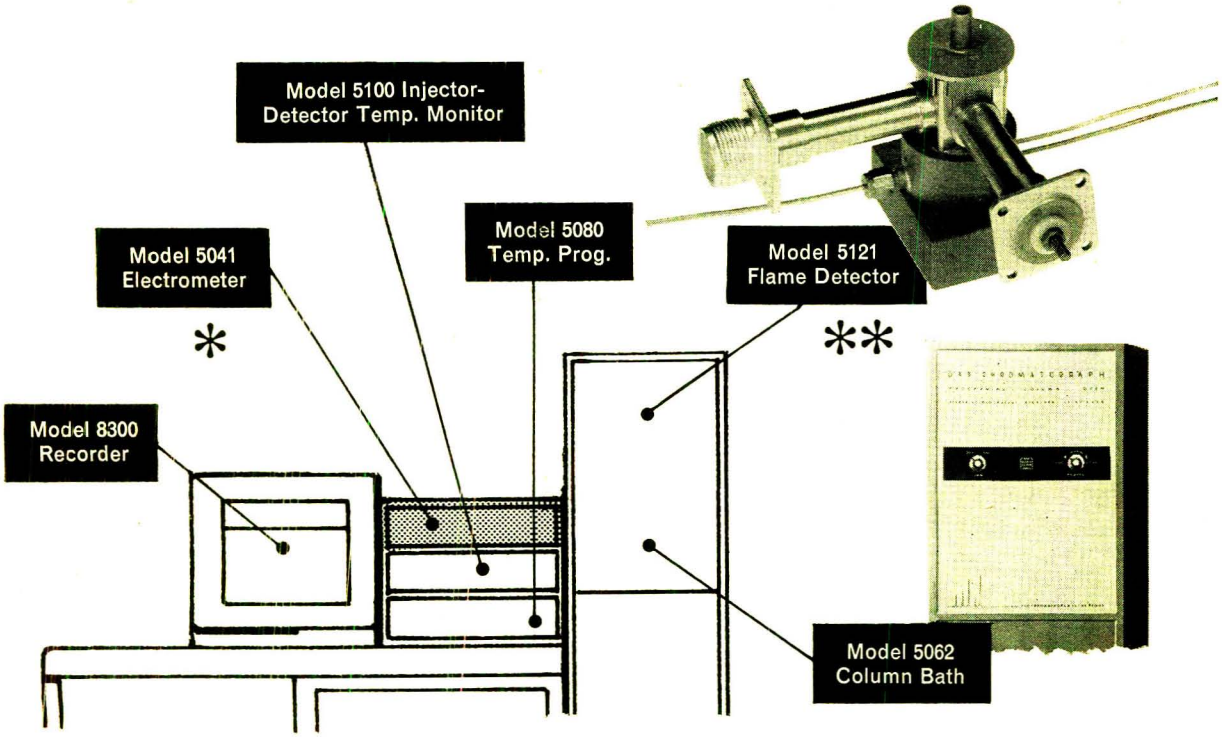
A Division of Philips Electronics and Pharmaceutical Industries Corp.

Dept. EO-33, 750 South Fulton Avenue, Mount Vernon, N. Y.

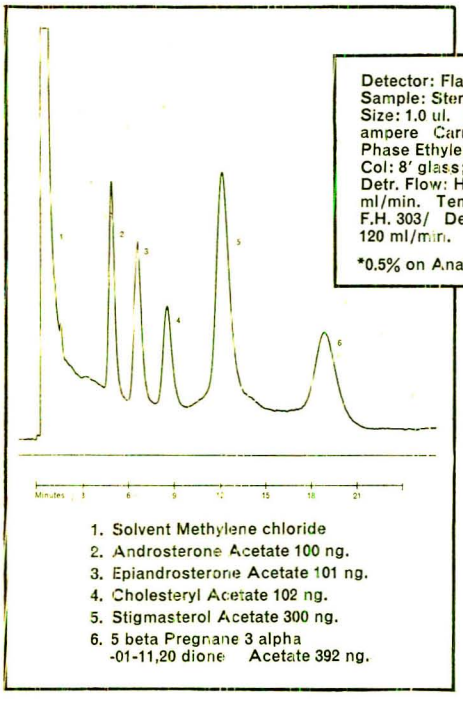
INDUSTRIAL RADIOGRAPHIC EQUIPMENT · X-RAY DIFFRACTOMETERS
X-RAY SPECTROGRAPHS · PROCESS CONTROL INSTRUMENTATION
ELECTRON PROBE MICROANALYZERS · NUCLEAR INSTRUMENTATION

Circle No. 162 on Readers' Service Card

←Circle No. 155 on Readers' Service Card



...for Analysis of Steroid Derivatives Specify Series 5000 Selecta-System Gas Chromatographs



Detector: Flame Model 5121
Sample: Steroid Acetates
Size: 1.0 ul. Range: $9x10^{-12}$ ampere Carrier N_2 15 psi Liq. Phase Ethylene Glycol Isophthalate*
Col: 8' glass; OD 7mm; ID 5 mm.
Detr. Flow: H_2 44ml/min; Air 225 ml/min. Temp. °C: Col 215/ F.H. 303/ Detr. 240. Col. Flow 120 ml/min.

*0.5% on Anakrom ABS, 80/90 mesh

1. Solvent Methylene chloride
2. Androsterone Acetate 100 ng.
3. Epiandrosterone Acetate 101 ng.
4. Cholesteryl Acetate 102 ng.
5. Stigmasterol Acetate 300 ng.
6. 5 beta Pregnane 3 alpha -01-11,20 dione Acetate 392 ng.

* **Featuring Model 5041 Electrometer for low noise**

** **Featuring Model 5121 Flame Detector for low noise at high temperature**

Barber-Colman's Selecta-System, Series 5000, offers the analyst an extremely flexible system for keeping abreast of a dynamic technology. The system suggested above has the following advantages: High temperature operation to 500°C with minimum noise level. ■ Flexibility of carrier gas flow rate ranges allows use of capillary and packed columns — noise level is constant with flows from 1 to 200 cc/min. and flame is operative to 250 cc/min. ■ Detector noise level is as low as 10^{-14} ampere under optimum conditions. Closed detector design avoids fluctuations due to drafts. ■ Easy to operate and clean. Call any of our nation-wide network of Sales and Service Offices, or contact us at Rockford.

BARBER COLMAN

BARBER-COLMAN COMPANY

Dept. S, 15104 Rock Street, Rockford, Illinois, U.S.A.

BARBER-COLMAN of CANADA, Ltd., Dept. S, Toronto & Montreal • Export Agent: Ad. Auriema, Inc., N.Y.

Circle No. 24 on Readers' Service Card

Convince yourself—
ask for a demonstration

New Torsion 1,000 gram balance speeds laboratory work

Only Torbal 1/10 gram PL-1 offers all these features

- *Fast, accurate readings optically projected to 1/10 gram*
- *No-knife edge construction eliminates friction and wear*
- *Greater taring range*
- *Remains unaffected by out-of-level conditions*
- *Oil dampened to speed weighings*

Price only $525.

To give you more convenient, accurate readings, Torsion has designed the PL-1 with a fine-reading vernier to 1/10 gram and a capacity of 1 kilogram. The balance has an optical range of −10 grams to +110 grams.

The heart of the mechanism in the new PL-1 is the Torsion no-knife edge construction. This eliminates friction and wear, insures lifetime accuracy and speeds weighing. The balance will operate accurately even in severely corrosive or dust-laden atmospheres.

Taring through a 125 gram range is accomplished with a built-in knob on the side of the balance. By using the second pan the balance can be made to tare up to 325 grams. Torsion's optical projection Model PL-1 offers a sharp image with a high degree of illumination for easy reading and an oil damper to speed up weighing.

ASK YOUR LABORATORY SUPPLY SALESMAN FOR A DEMONSTRATION OR WRITE FOR BULLETIN TB-100.

Circle No. 140 on Readers' Service Card

THE
TORSION BALANCE
COMPANY

TORBAL

TO MEET YOUR CHANGING NEEDS FASTER AND EASIER

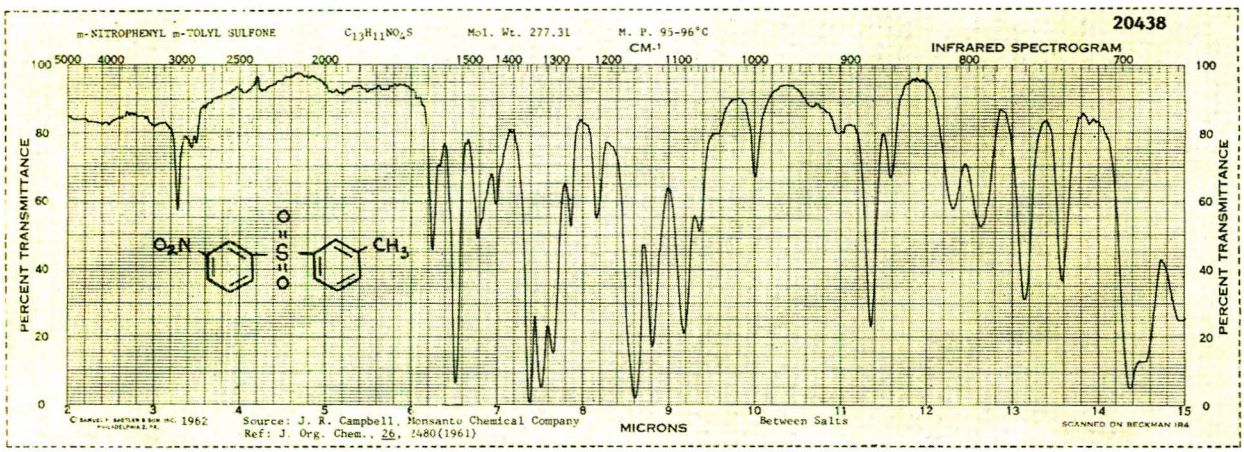
HOW TO IDENTIFY 22,000 IR SPECTRA QUICKLY EASILY ACCURATELY

You can locate and interpret an infrared spectrum in minutes by using the Sadtler Standard Reference Spectra. The Sadtler SPEC-FINDER lists Sadtler Standard Spectra in a numerical absorption-band system. The comparison spectrum for an unknown is found simply by turning to the section of the index listing the strongest band. Location of some of the remaining bands then gives the serial number of the standard spectrum. You are also given the chemical name, empirical formula, molecular structure, source of test sample, size and nature of sample, and more.

Sadtler Standard Reference Spectra are available in 25 volumes covering 22,000 spectra.

SADTLER SPECTRA ARE INDEXED BY:

ALPHABETICAL—Chemical Abstract nomenclature, classified by parent compounds, followed by substituent derivatives ■ MOLECULAR FORMULA—increasing order of carbon, hydrogen and other atoms ■ CHEMICAL CLASS—permitting location of any single spectrum or class by functional group ■ NUMERICAL —by Sadtler Serial Number ■ SPEC-FINDER—for Standard IR or Commercial IR. Systematic classification of each by major absorption bands in each micron region and strongest band per spectrum. Coded numerically to locate unknown spectra from more than 30,000 in the Sadtler series. Also indexed in the Sadtler Computer System and the ASTM-IBM cards.



302R

Write today for free brochure including sample spectra to:

SADTLER RESEARCH LABORATORIES, INC.

1517 VINE STREET, PHILADELPHIA 2, PA. • *AGENTS IN PRINCIPAL COUNTRIES OF THE WORLD*

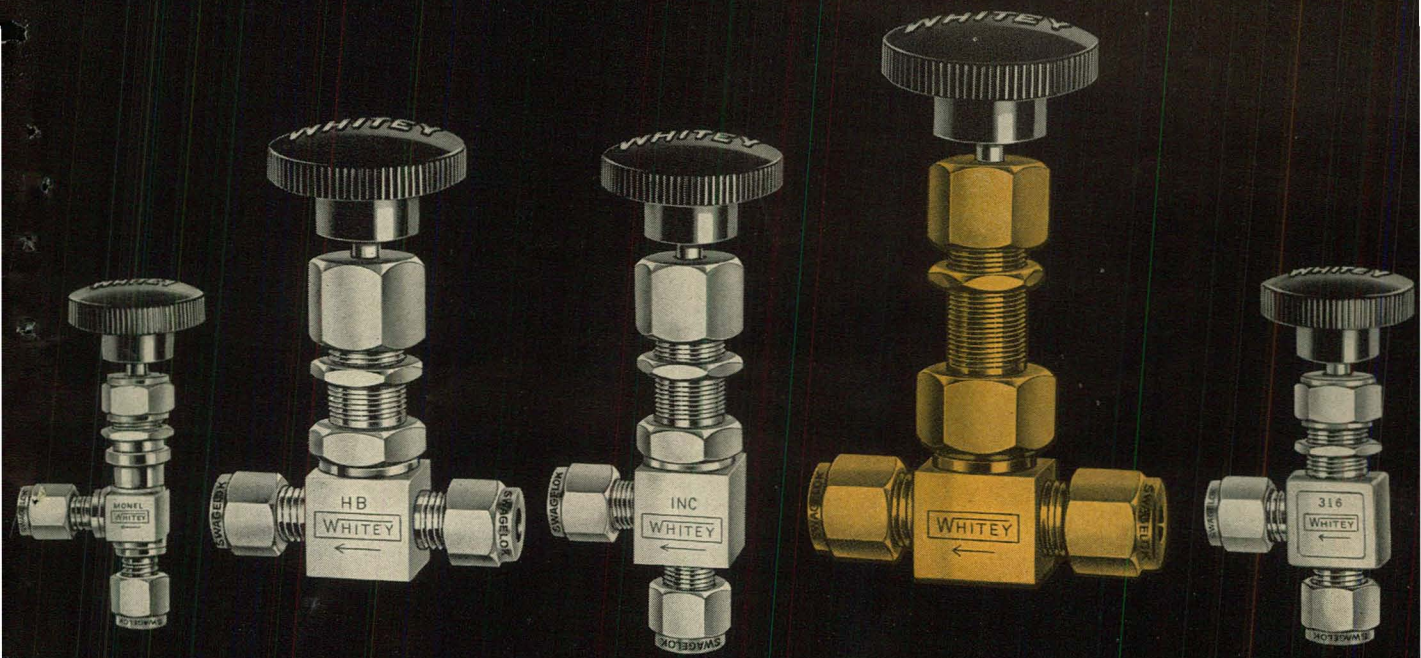
Circle No. 77 on Readers Service Card

Circle No. 8 on Readers' Service Card →

FOR EXACTING SERVICE WHITEY®

CONTROL VALVES

for 1/8" through 1/2" O.D. Tubing feature usual and unusual metals with Swagelok Tube Fitting Connections



• MONEL • HASTELLOY B • INCONEL • BRASS • 316 S.S.

For years, WHITEY RESEARCH TOOL CO. has used exceptional machining and engineering skill to produce valves in new alloys that most manufacturers hesitate to machine. Monel, Hastelloy, Inconel and Nickel require top skill. It is through this manufacturing skill that quality performance is combined with quality appearance to provide precision, leak-tight WHITEY Valves to meet your most exacting system requirements.

WHITEY Valves are available in straight and angle pattern styles with 1/8" through 1/2" SWAGELOK Tube Fitting connections or 1/8" through 1/2" male and female pipe connections.

Panel mounting; Teflon* cylinder packing; micro-regulating and non-regulating stems are standard features on all WHITEY Valves. Colored handles, to permit color coding, can be specified when ordering.

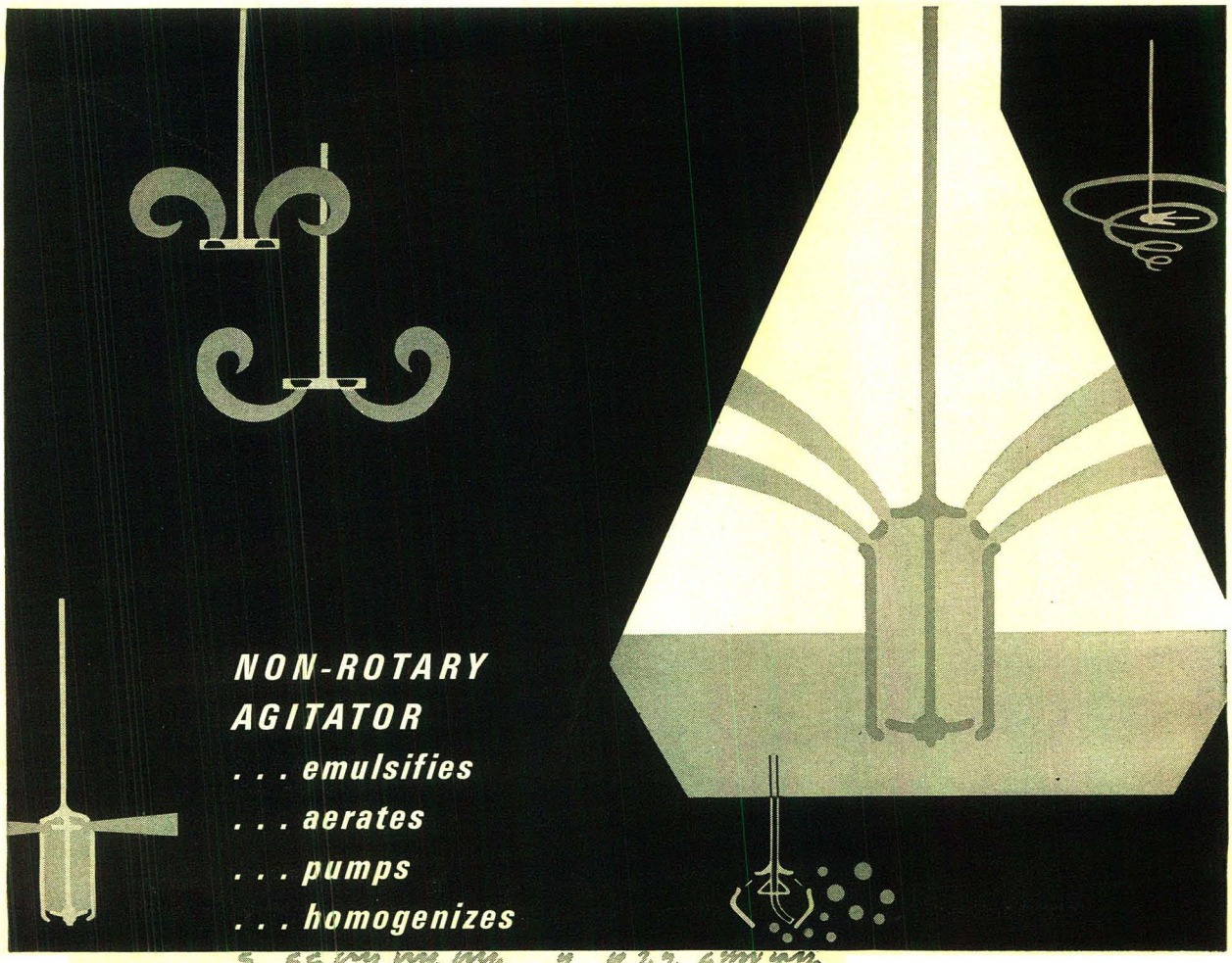
Pressure ratings of WHITEY Valves range from 3,000 p.s.i. to 5,000 p.s.i. All WHITEY Valves are available with SWAGELOK Tube Fitting connections for efficient, leakproof installation.

COMPLETE TECHNICAL DATA ON ***WHITEY*** VALVES AVAILABLE ON REQUEST.

*Dupont Trademark

WHITEY RESEARCH TOOL CO.
5525 MARSHALL STREET
OAKLAND 8, CALIFORNIA

WHITEY®

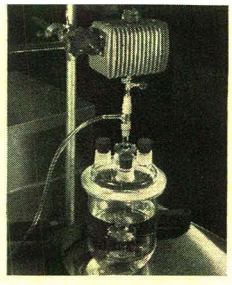


CROWN VIBRO-MIXER

How many kinds of standard apparatus would be required to carry out the above functions? Quite a few, obviously. But the Vibro-Mixer, with a few simple attachments on one basic unit, will do them all.

With its selection of specialized pumps, membrane seals, flask shaking devices and impellers, the Vibro-Mixer will do anything a whole battery of other equipment can do — and more — pumping liquids and gases, defoaming, agitating in virtually any container, hydrogenation or other gas reactions. Action is vibratory, not rotary, and can be controlled in intensity. Sparkless drive mechanism is safe when used in explosive atmospheres.

For details see your Aloe Scientific representative or write Aloe Scientific, [B] Division of Brunswick, 1831 Olive Street, St. Louis 3, Mo.



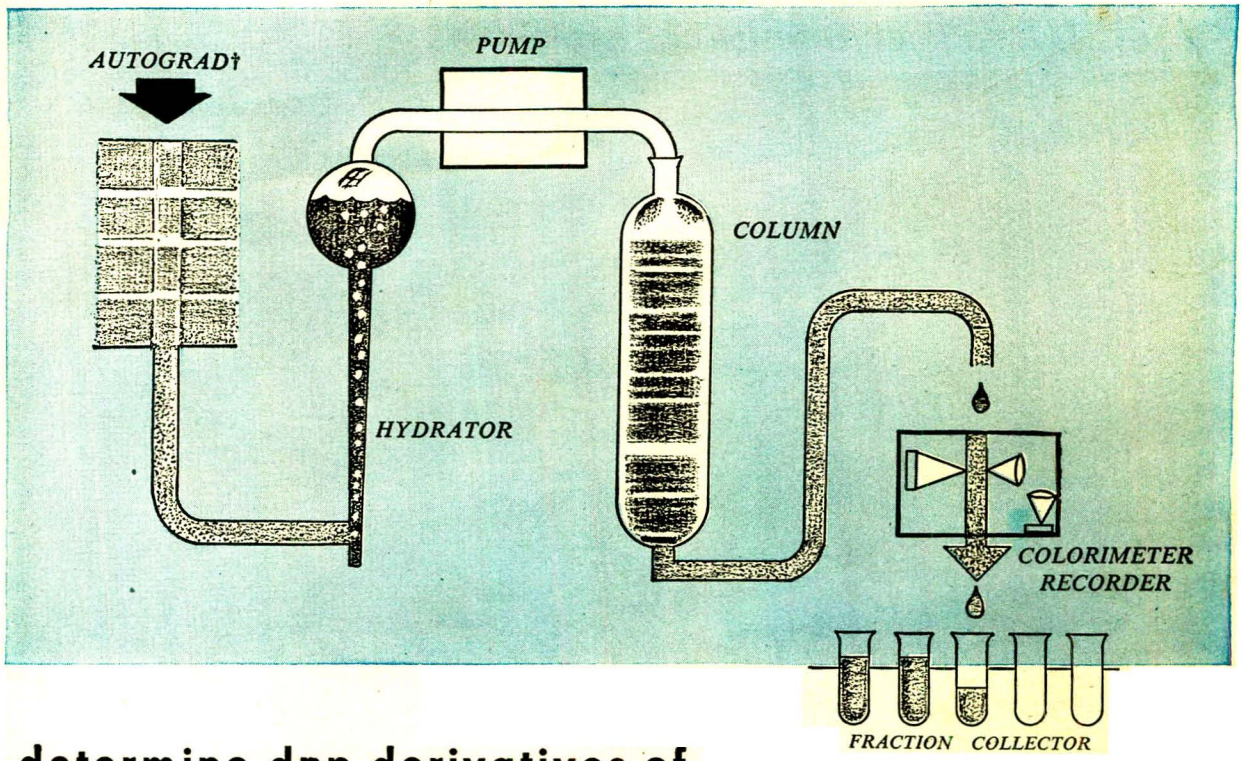
Especially valuable for sealed atmosphere applications — agitating or pumping within closed systems. No rotary parts, no stuffing boxes.

Serving the Sciences that Serve Mankind

ALOE SCIENTIFIC

Circle No. 18 on Readers' Service Card

automatic...



determine dnp derivatives of

PEPTIDES and amino acids*

The determination of N-terminal amino acids, automated by use of Technicon AutoAnalyzer system and Sanger's reagent, assays DNP amino acid derivatives from protein hydrolysates in 4 hours... more than 30 DNP derivatives plus peptides can be determined automatically in an overnight run, continuously and with no interruption.

HOW THE SYSTEM OPERATES:

An organic solvent gradient prepared in the Autograd® elutes the bands from the column by partition. Both the ether and water soluble derivatives of amino acids and peptides are resolved on a single silica gel column. The colored compounds are continuously assayed by a Colorimeter and the concentration automatically recorded. Because no destructive reaction is necessary, effluent may be collected after analysis for further study.

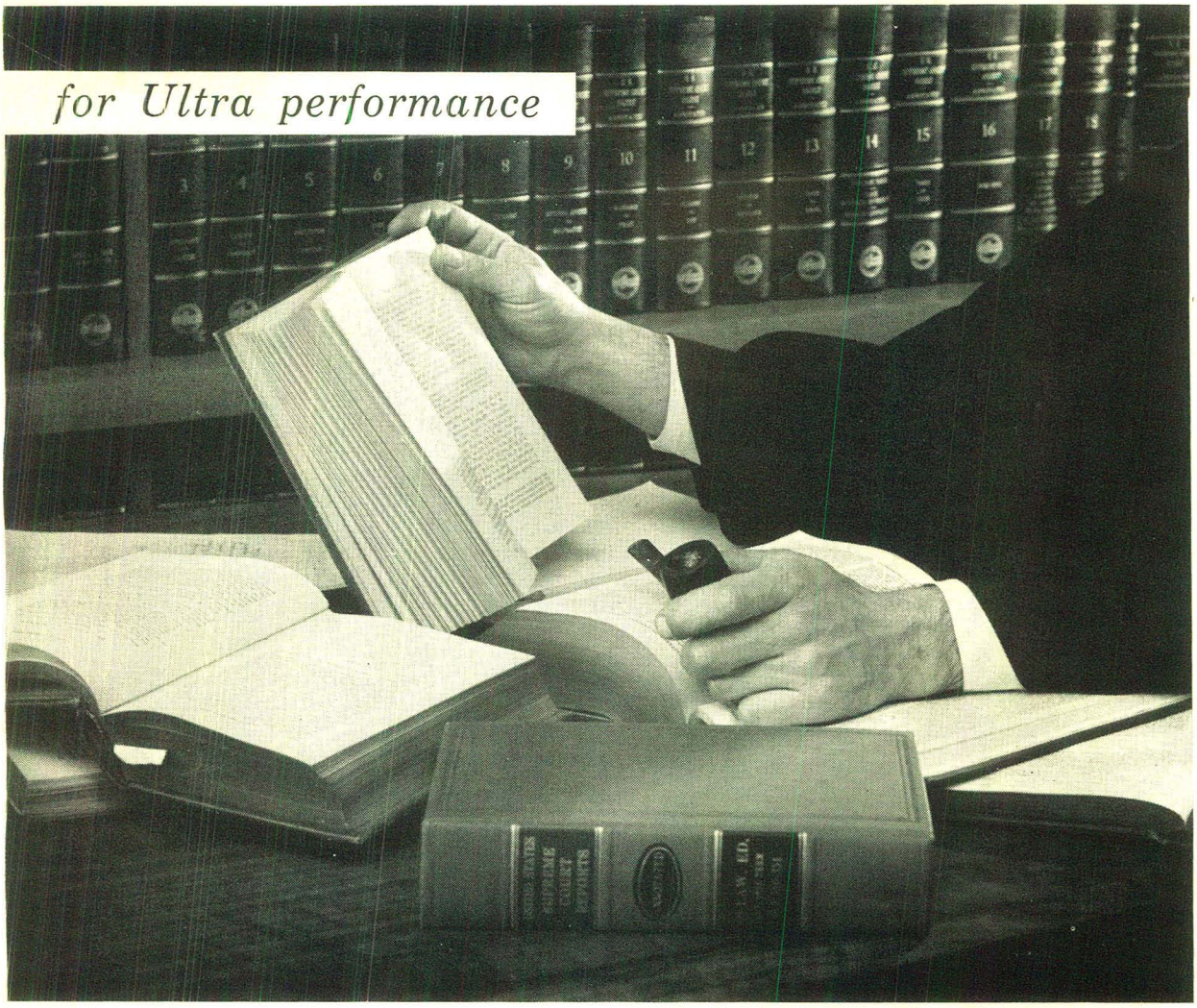
TECHNICON®
AutoAnalyzer®

Technicon Chromatography Corp.
Research Park · Chauncey, New York

* *REF.: "Automatic Column Chromatography of Ether and Water Soluble DNP-Derivatives of Amino Acids, Peptides, and Amines", L. Kesner, E. Muntwyler, G. E. Griffin, J. Abrams, State Univ. of New York, Downstate Medical Center. Anal. Chem., Vol. 35, No. 1, Jan. 1963.*

† *(Ref. E. A. Peterson and H. A. Sober, Anal. Chem., Vol. 31, No. 34, May 1959)...Developed at the National Cancer Institute, National Institutes of Health, U S. Department of Health, Education, and Welfare, Public Health Service, Bethesda, Maryland.*

Circle No. 138 on Readers' Service Card



The jurist uses many references

Creative jurisprudence is the result of research,
for the judge studies many references.
Each similar case increases his background.

The rapidly growing sophistication of the spectrographic art challenges today's true professional. Only through creative analytical techniques aimed at the specific problem can he achieve success. He cannot afford to compromise his standards nor let an inadequate selection of electrodes limit his ability.

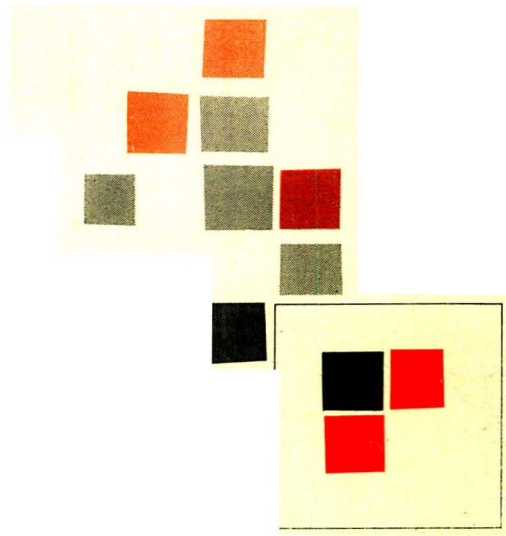
That's why *Ultra Carbon* not only offers an entire family of stock electrodes from low to high densities . . . but also will make any design in your choice of grade.

ULTRA CARBON® CORPORATION

FORMERLY UNITED CARBON PRODUCTS CO.

Write for complete data and samples from our wide selection of custom and stock electrodes today. P. O. Box 747-A, Bay City, Michigan.

Circle No. 1 on Readers' Service Card



NEW COMPANIES INVADE INSTRUMENT FIELD

A NUMBER OF NEW FIRMS have decided to enter the business of making analytical instruments in recent years. Many of these newcomers are diverting capital and manpower from fields where they have established reputations to become tyros in this exacting new craft. This report attempts to bring into focus the various factors which prompt a firm to diversify into manufacturing analytical instruments.

While it is impossible to pinpoint dollar sales volumes for analytical instruments, the total is large now and is growing at a rapid clip. The bulk of the information on instrument shipments comes from Commerce Department data on the five Standard Industrial Classification (SIC) categories which comprise the so-called scientific and process control instrument industries. This group includes electric, mechanical, optical, and scientific instruments. Its combined sales have grown at an annual rate of

REPORT FOR ANALYTICAL CHEMISTS

about 11% compounded in the period 1946 to 1962. This rate, if continued, will more than triple sales every ten years.

According to the United States Department of Commerce, Business and Defense Services Administration, about 3000 firms produce over 100,000 different types of scientific and process control instruments. About 50% of these instruments have been developed since World War II.

R&D Spending

The reason for the health of the scientific instrument industry is not difficult to spotlight. The driving force behind its growth is this nation's increasing emphasis on research and development. Research and development expenditures by government, industry, and university sources have continued to increase every year for the past two decades (Figure 1). The bulwark of the analytical instrument business, therefore, is the seemingly inexorable rise of R&D expenditures.

In 1962 funds spent for basic and applied research and development in this country totaled about $15 billion—a fourfold increase over 1952's outlay of $3.7 billion. It is a valid, if not conservative, assumption that sales of analytical instruments have kept pace with this over-all R&D growth.

Another sign of the R&D growth syndrome is the number of persons that now find employment in this field. According to the National Science Foundation, 37% of the 201,292 scientists in the U. S. in 1960 were occupied in research, development, or design.

Government Outlays Climb

Since 1958, the Federal Government has sponsored about 65% of the total expenditures for R&D. In contrast, 1941—the year prior to our entry into World War II, government expenditures for R&D only accounted for about 41% of the total from all sources.

Understandably then, many of the instruments found in analytical laboratories today were spawned under the aegis of government research and development programs; and it is to be expected that this trend will continue. For example, the Bendix Corp.'s time-of-flight mass spectrometer stems from the firm's work on radar and microwave systems since World War II.

There is also little doubt that with time, a new generation of instruments for the analytical chemist will spring from the dragon's teeth of this nation't involvement in the space race. Recently, in Bloomington, Indiana, Aerospace Research Applications Center was formed to seek industrial uses for knowledge acquired in space research. The organization is sponsored by both government and private industry.

While the merits of defense contracts can be debated at length, it

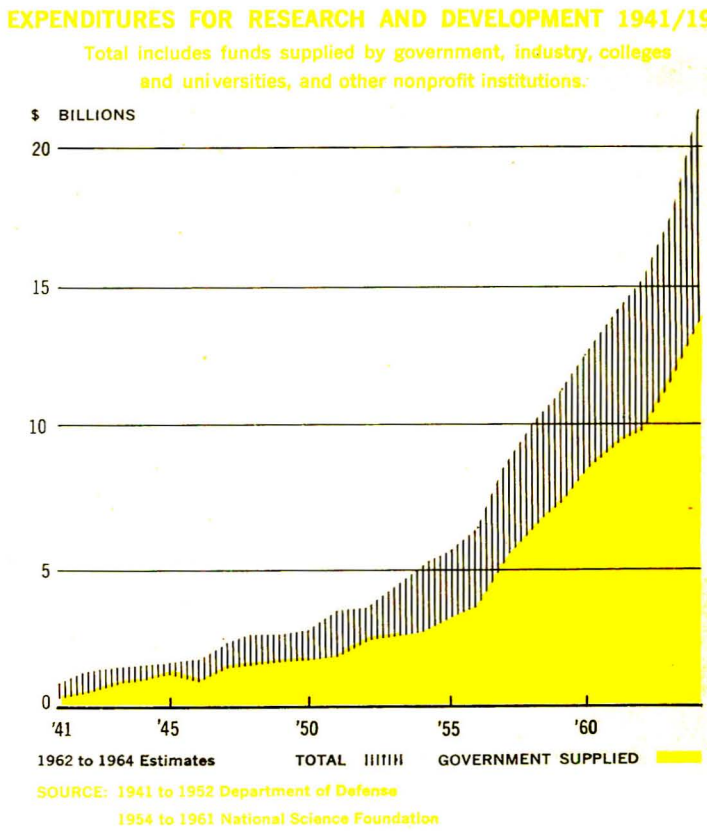


Figure 1

seems probable that instrument firms that deploy a large proportion of their resources to government R&D work have a head start in developing new instruments. These firms are able to make a judgment very early in the history of a development regarding its potential in the marketplace.

It is likely that a passel of aerospace devices such as Texas Instrument's Lobometer—an infrared sensing device for measuring the surface temperature of planets from space probes—may someday evolve into instruments that strengthen the arsenal of the analytical chemist.

In the same vein, it is also to be expected that the massive dollar outlays by the Federal Government for R&D will shift the breeding grounds for new instruments away from the university campus to the company laboratory and the industrial research institute.

Already analytical instrument makers are using such recent developments as lasers. Jarrell-Ash showed a Laser Microprobe at the 1963 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. Of real significance is the closing of the time gap between the discovery and commercialization of lasers.

It is clear that a major reason companies decide to manufacture analytical instruments is that the continuous rise in R&D spending over the past 20 years augurs well for the future of the industry. Many firms now entering into the business of making analytical instruments are noteworthy for the fact that they have traditionally concentrated on other markets. Du Pont and Bendix Corp. probably best typify large firms that have decided to diversify through the manufacture of analytical instruments.

Emphasis on R&D

Both Du Pont and Bendix cite as the bedrock reason for their entrance into instruments the high technological levels that exist within their respective companies. Both firms are committed to extensive R&D programs. During 1962 Du Pont's expenditures for pioneering research were about $61 million excluding the cost of laboratories and equipment. Bendix in 1962 spent $145 million for R&D and engineering.

Du Pont's fledgling Instrument Products Division had a large number of Du Pont-developed analytical and process instruments to choose from for its initial offering. Before the division decided to introduce its differential thermal analyzer and its 400 photometric analyzer, it screened over 200 different instruments. These instruments had been internally developed for uses that couldn't be satisfied with commercially available hardware. The instrument business looked like a good way to cash in on this reservoir of know-how.

ALL YOU NEED

FAST U. S. DELIVERY

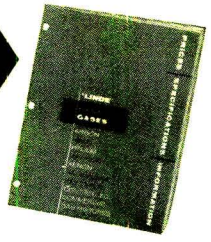
MIXED GASES

FOR X-RAY FLUORESCENCE SPECTROSCOPY AND NUCLEAR COUNTERS

- For other applications, such as: bridge control gas for instrumentation . . . calibration standards use in laboratories and production control. Mixtures for gas-filled tubes.
- Mixed to your precise specifications and tolerances — over a wide range of variations.
- Quality based on more than 50 years of rare gas know-how.

SEND FOR NEW 24-PAGE ONE-SOURCE RARE GAS BOOKLET

First comprehensive price and specification list for most gases and mixtures.



CLIP COUPON ATTACH TO BUSINESS LETTERHEAD

Linde Company, Dept. ALC-7
Division of Union Carbide Corporation
270 Park Avenue, New York 17, N. Y.

☐ Please send a copy of your booklet listing prices, specifications, and information on LINDE Atmospheric Gases.

☐ Please have a representative contact me.

UNION CARBIDE

LINDE COMPANY

"Linde" and "Union Carbide" are registered trade marks of Union Carbide Corporation.

Circle No. 3 on Readers' Service Card

Bendix manufactures a wide variety of products for the aviation, automotive, electronics, and space industries. All products have a high technological content. The depth of this technical base was a big factor in the firm's decision to enter the instrument business.

Another factor which prompted Bendix to diversify was its desire to lessen its dependence on military markets. About 72% of the corporation's sales came from military contracts in 1962.

Bendix would like to increase its sales of products to commercial markets. A larger commercial market base will give the firm increased stability to weather changes in defense spending. One step toward that end was the acquisition of Greenbrier Instruments, Inc., last year.

Bendix intends to increase its instrument sales ratio of the company's total revenues by any or all of the following routines:

1) Purchasing instrument firms or forming joint ventures.
2) Licensing instruments developed by other instrument firms.
3) Distributing instruments manufactured by other instrument firms.
4) And by internal development of instruments stemming from its own investment in R&D. These so-called internal developments can come either from Bendix Research Division labs or from various research companies or universities employed by Bendix.

Another method used by Bendix to enlarge its line of new instruments is through developments arising out of so-called paid engineering contracts the company selectively agrees to perform. Paid engineering contracts may provide Bendix with proprietary rights to new products which might be uncovered.

Acquisitions

One of the most popular routes for companies to take when diversifying into instruments is to acquire an already successful firm. This has been a very satisfactory arrangement in many cases. The smaller instrument company may badly need an injection of capital at a crucial stage in its growth.

Last year, Du Pont acquired a minority interest in Block Engineering, Inc., a Cambridge, Mass., producer of specialized devices used principally in space and defense applications. More recently, the company loaned an undisclosed sum of money to Dana Laboratories, Inc., Santa Ana, Calif., which has a product line that includes precision digital voltmeters and direct current amplifiers for test and data-gathering systems. The loan is convertible into Dana common stock up to a 40% holding. Du Pont has also purchased a minority interest in Cryogenic Engineering Co., Inc., Denver, Colo., a maker of equipment for producing, storing, and handling liquid hydrogen and helium.

Milton Roy Co., St. Petersburg, Fla.—a manufacturer of controlled volume metering pumps—has expanded into the instrument field both by research and with its purchase of Serfass Corp. Research developed a line of colorimetric analyzers and the Serfass acquisition gives Milton Roy a line of palladium diffusion hydrogen purifiers. Milton Roy metering pumps have often been used for sample flows to analytical instruments. Instruments, therefore, are a logical extension of the company's activities.

There are, of course, a host of other reasons why firms widen the scope of their operations to include the manufacture and sale of analytical instruments. In some cases, it is to spur production of an instrument after the slowing down in growth of its markets. For example, General Electric began making an x-ray spectrograph for analytical chemists when sales of its similar equipment for x-ray inspection of metal parts reached a plateau. Since the facilities and skills were already available, it was a straightforward step for G.E. to modify its design to produce an x-ray spectrograph.

Others come into the business to open up new uses for their principal product. For instance, Corning Glass is always on the lookout for new uses for glass. The firm now makes a laboratory water still.

Many times the commercial manufacture of an instrument by a firm stems from a special request by an analytical chemist who requires an instrument that's not available. Firms find that such demands from their customers stimulate much of their research activity and can lead to attractive new markets.

Foreign sales are a very important aspect of the instrument business today. Firms must carefully consider the potential of foreign markets when mapping their strategy.

Some idea of the impact of foreign markets on a U. S. firm's revenues can be gained from the fact that exports coupled with foreign manufacturing accounted for 24% of Perkin-Elmer's sales volume in 1961–62. This is up from 22% the year earlier. About 17% of Beckman's sales in fiscal 1962 were accounted for by its international operations with foreign manufacturing operations representing about one fourth that amount.

Exports Continue Steep Gains

U. S. exports of all types of scientific instruments (instruments used principally in scientific research activities of all kinds) soared to $343 million in 1962 (Figure 2). This represents a 62% gain over 1961's total of $212 million. The U. S. Department of Commerce, Business and Defense Services Administration further predicts that exports of all types of scientific, industrial, and component instruments are expected to increase to a new high of $750 million in 1963. Exports of all types of instruments totaled $562.8 million last year—a 35% increase over 1961's $416 million.

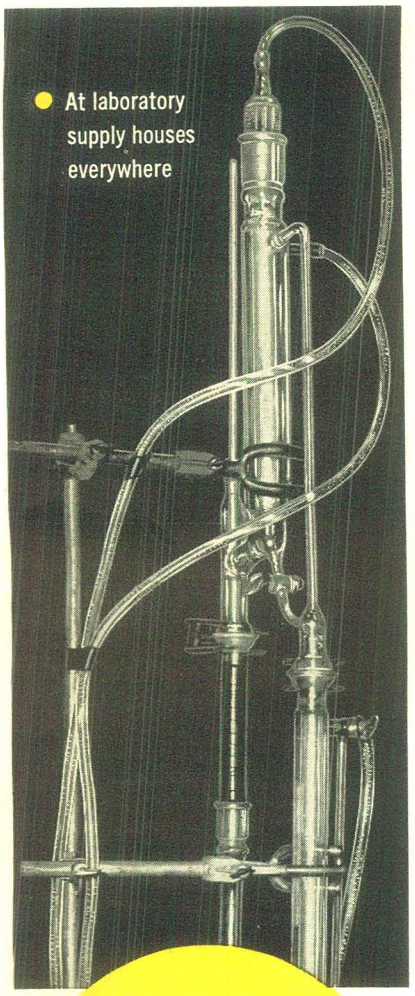
The major foreign markets for U. S. instruments are Canada, West Germany, Japan, France, and the United Kingdom.

Instruments manufactured in the United States, although higher priced, compete successfully with instruments manufactured abroad because of their technical superiority. It can be claimed that U. S. manufactured instruments are generally 3 to 5 years ahead of their foreign-made counterparts.

MODERN EFFICIENCY-MINDED LABS are turning to corrosion-resistant Nalgene® labware. Strictly a product of twentieth century research and technology, plastic labware has really come of age. Not only less costly than glass, but endowed with superior qualities . . . unbreakable, lighter-in-weight and ever-so-much safer. They're so easy to handle, and shatter-proof. Nalgene wash bottles, for instance, have many unique design features. Blow-molded, with dispensing tube set in a boss on the shoulder of the bottle. Tip the bottle, the tube is always in the fluid. Fill the bottle, tubing is not exposed to contamination. Use Nalgene plastic labware, available in a multitude of items. See how really efficient a laboratory can be. Ask your laboratory supply dealer or write for your copy of Catalog L-926 Dept. 1131, The Nalge Co., Inc., Rochester 2, New York.

NALGENE LABWARE
Leader in quality plastic labware since 1949

Circle No. 71 on Readers' Service Card



TYGON®
Clear Flexible Plastic
TUBING

The world over, more laboratories have standardized on Tygon plastic Tubing than on any other brand. No other tubing is "just as good as" Tygon. For your protection, every foot is permanently branded with the name TYGON and the formulation number.

225-H

Plastics & Synthetics Division
U. S. STONEWARE
AKRON 9, OHIO

Circle No. 141 on Readers' Service Card

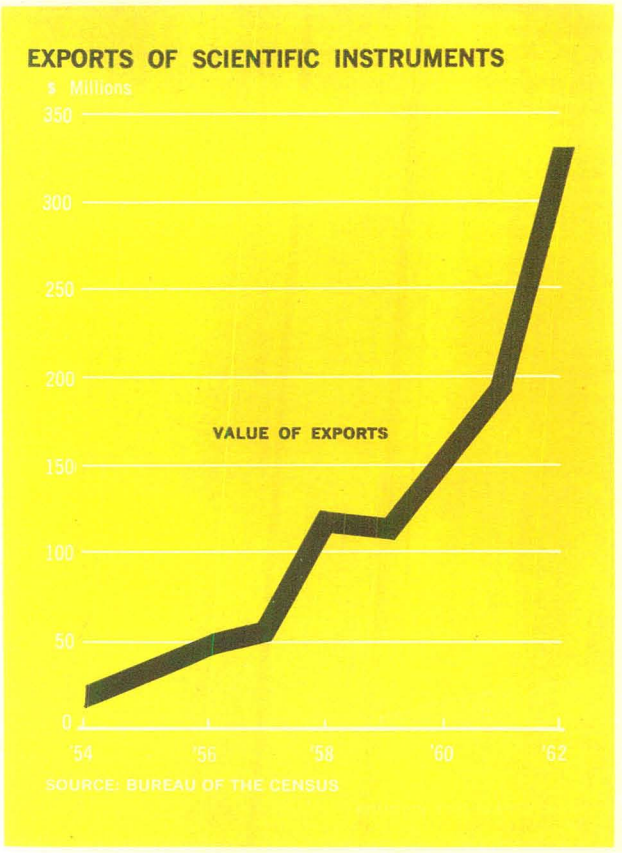


Figure 2

Du Pont and Bendix are newcomers that are fortunate in having extensive foreign operations from which to mass an attack on this burgeoning market. This also was an important factor in their decisions to manufacture instruments. Bendix's foreign royalty receipts amounted to about $3.3 million last year—an increase of 9% over 1961's total. Bendix holds about 430 license agreements with over 130 companies in various countries of the free world. If the total sales represented by Bendix's license agreements and the sales of its foreign affiliates were added to Bendix's export sales, the total would exceed $250 million.

Total Du Pont foreign business, including business conducted by nonconsolidated foreign affiliated companies, amounted to $388 million in 1961. About 29% was in Europe, 31% in Canada, 24% in Latin America, and 16% elsewhere in the world.

Analytical instrumentation is an esoteric business which demands topflight scientific, technical, sales, and market talent. These skills are not easily obtained and there is much which can only be learned by experience.

Bendix has attacked the problem of building up a sales organization for its instrument line by a number of means. Probably the most important step the firm made toward rounding out its distribution network for instruments was the Greenbrier acquisition. Bendix now has the ability to sell through any of the following channels:

1) Distributors, dealers, and lab supply houses.
2) Manufacturers representatives.
3) Direct via Bendix sales and sales engineering offices.
4) Direct mail.

Others may not desire this sales flexibility. Du Pont prefers to bypass the first two groups to concentrate on its company directed sales offices. Du Pont doesn't plan to

use distributors or sales representatives, except in special cases.

Pitfalls

Marketing and pricing are often serious problems. Even established instrument companies can misgage the size of the market for a new instrument. Market information is very difficult to obtain in this industry. It is also easy to put the wrong price tag on an instrument and scuttle its chances.

Production has not been a major problem to firms breaking into the business. While most have their own production facilities, even this isn't necessary. Du Pont has several fabricating shops in the Wilmington area under contract to manufacture to Du Pont specifications. Later, the firm may decide to phase into manufacturing.

Du Pont's Instrument Products Division faces a couple of novel problems due to the competitive business of its parent company. The division has to prove to other chemical firms that it will not carry back their confidential process and research information to Du Pont's operating division. The division foresees no problem in convincing customers of its integrity.

Competition is a two-edged sword and Du Pont's Instrument Products Division may also have to come to terms with the problem of getting the parent firm to release instruments for commercialization which the manufacturing divisions may prefer to keep under wraps. For example, an instrument may give Du Pont a big edge in product quality. Management may object to permitting competition to have the same advantage in its product quality. Du Pont doesn't have a general rule which blankets this potential situation. Each case will be judged on its own merits.

The analytical chemist today has much to gain from the various forces at play in the instrument industry. He stands before a cornucopia of new instruments spurred along by R&D efforts on the one hand, and vigorous commercial exploitation by the instrument community on the other.

END ■

Serum, plasma or urine determinations quickly and accurately... from a single drop

THE NEW AO TS METER* requires just one drop of sample to provide immediate, accurate determinations of total solids, specific gravity, refractive index, protein concentration or water concentration in serum, plasma and urine.

MINUTE SAMPLE REQUIRED: As little as 0.02 ml . . . a single drop . . . of sample is sufficient for the most precise determinations.

TEMPERATURE COMPENSATED: Unique, hermetically-sealed liquid prism eliminates error due to temperature changes. Samples, whether at body or refrigerated temperatures, can be read immediately when the ambient temperature of the instrument is between 65-95° F.

URINE SPECIFIC GRAVITY: No more "Q.N.S." reports. Ideal for pediatrics, oliguric patients and in collections from ureteral catheters. Readings are consistently obtained with a degree of accuracy, speed or reproducibility significantly better than those obtained with urinometers, the falling-drop method or with instruments uncompensated for temperature.

SERUM PROTEINS: Ideal for rapid screening of serum proteins. Samples as small as those obtained from a microhematocrit tube are ample.

DIRECT READINGS: You make an immediate analysis directly from the built-in scale . . . readings to 0.1 percent total solids . . . without references to graphs, tables or thermometer readings.

**Total Solids Meter. This method of analysis using the Goldberg Refractometer was developed in close cooperation with Dr. A. V. Wolf, Head of the Department of Physiology, University of Illinois, College of Medicine, Chicago, Ill.*

American AO Optical
COMPANY

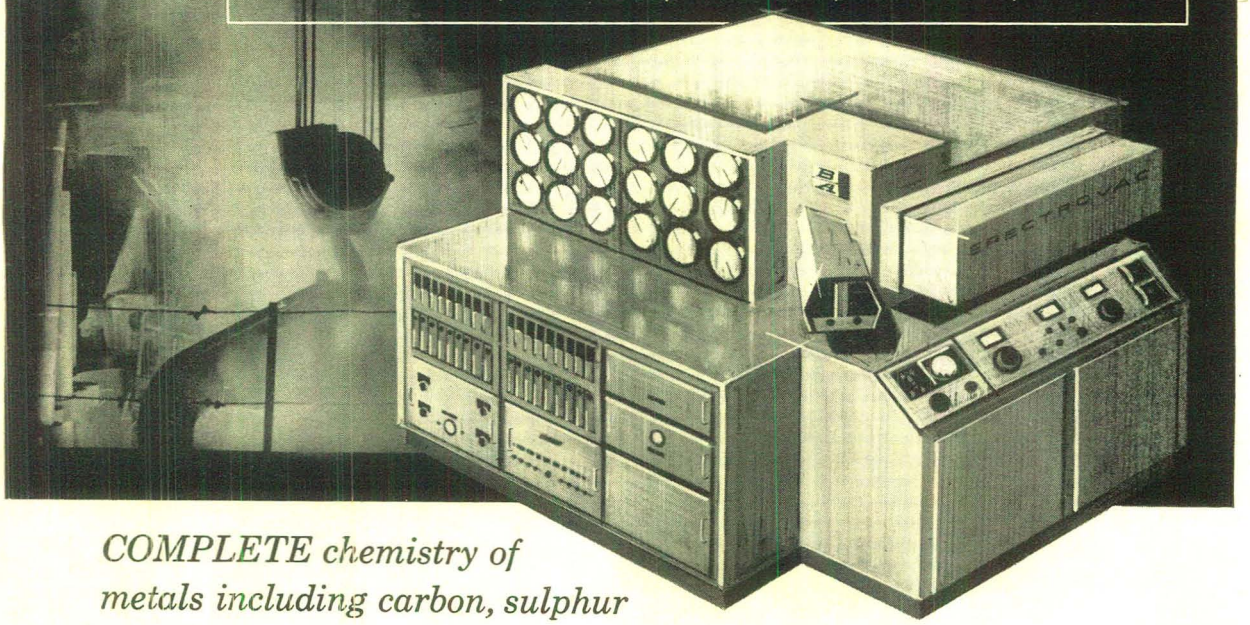
INSTRUMENT DIVISION, BUFFALO 15, NEW YORK
Circle No. 19 on Readers' Service Card

Introducing... B/A SPECTROVAC®

A VACUUM DIRECT-READING SPECTROMETER

SPECTROVAC OFFERS MORE

	Baird-Atomic Spectrovac	Competitive Vacuum Spectrometers A	B	C
Focal Length	3 Meters	2 Meters	1.5 Meters	1.5 Meters
Grating (Grooves/inch)	30,000	30,000	30,000	24,400
Dispersion	2.76 A/mm	4.1 A/mm	5.5 A/mm	6.95 A/mm
Wavelength Range	1450-4300A	1625-4025A	1750-3450A	1600-3300A
Focal Curve	40″	24″	12″	9¾″
Argon Consumption (Liters/Sample)	Less than 3	Less than 3	Less than 3	6 — 9
Automatic Servo Monitor	Yes	No	No	No
Readout	Simultaneous	Sequential	Sequential	Sequential



COMPLETE chemistry of metals including carbon, sulphur

The Baird-Atomic Spectrovac incorporates new principles of optical, mechanical and electronic design to give metallurgy its most versatile analytical instrument. Covering a wavelength range from 1450 – 4300A, with linear reciprocal dispersion of 2.76 A/mm, the Spectrovac permits observation of more sensitive lines, with higher resolution, than any other Schumann region apparatus.

Only the Spectrovac offers Rowland-mounted optics which assure both maximum linearity and perfect symmetry of dispersion. The patented Automatic Servo Monitor insures continuous optical alignment. The high vacuum maintained within the chamber permits 99.99% transmission of the vacuum region wavelengths.

Compare the parameters of performance of Spectrovac and all other direct reading vacuum spectrometers. Then write for complete details on how you can get faster, more accurate, more efficient metallurgical analysis with Spectrovac.

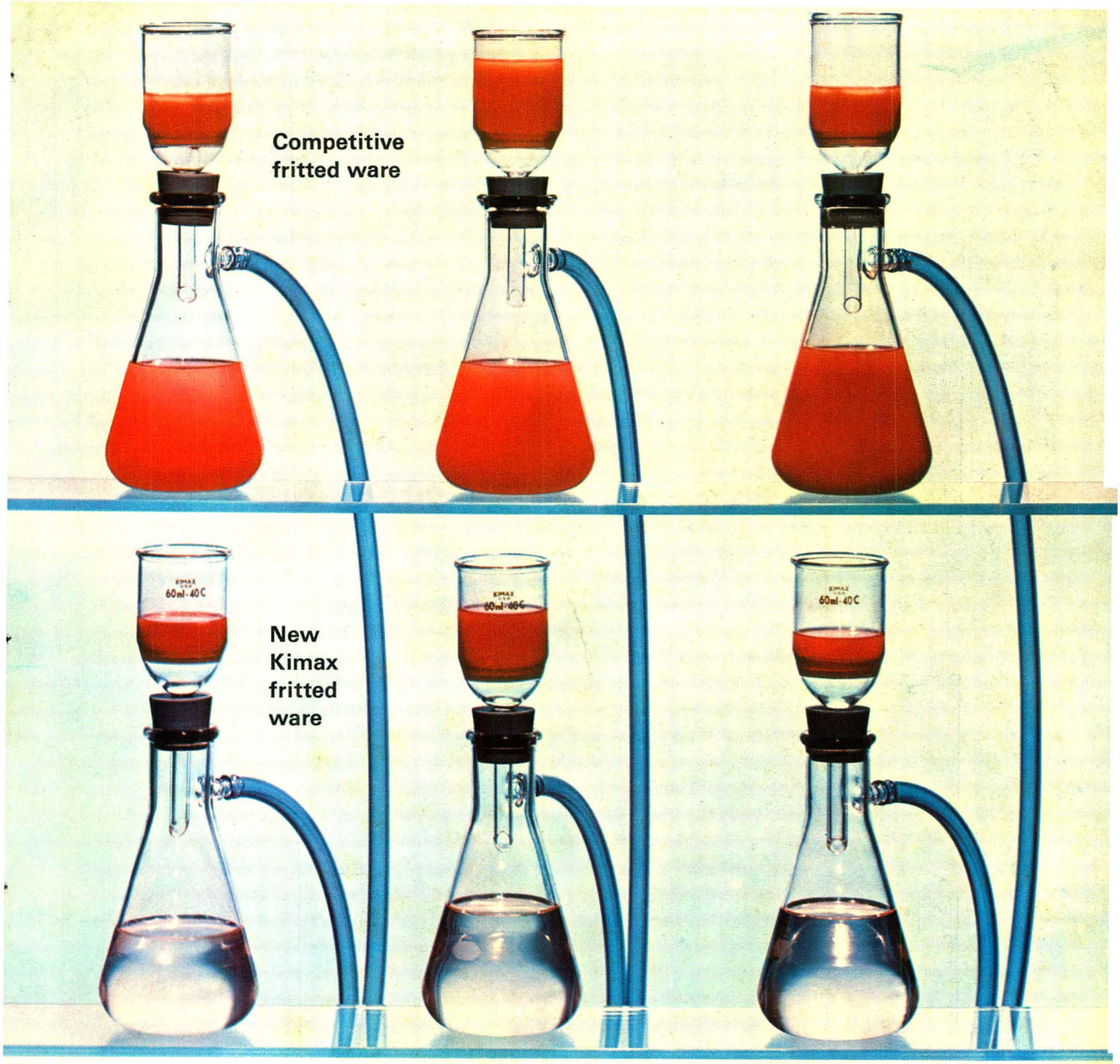
Engineers and Scientists: *Investigate challenging opportunities with B/A. Write Industrial Relations Director. An equal opportunity employer.*

B/A **BAIRD-ATOMIC, INC.**

33 University Road · Cambridge 38, Mass.

Circle No. 103 on Readers' Service Card

Circle No. 5 on Readers' Service Card →



Buchner funnels with filters of the same labeled porosity were taken from stock and tested, using identical solutions.

If you think **FRITTED WARE** is all the same . . . compare Kimax®

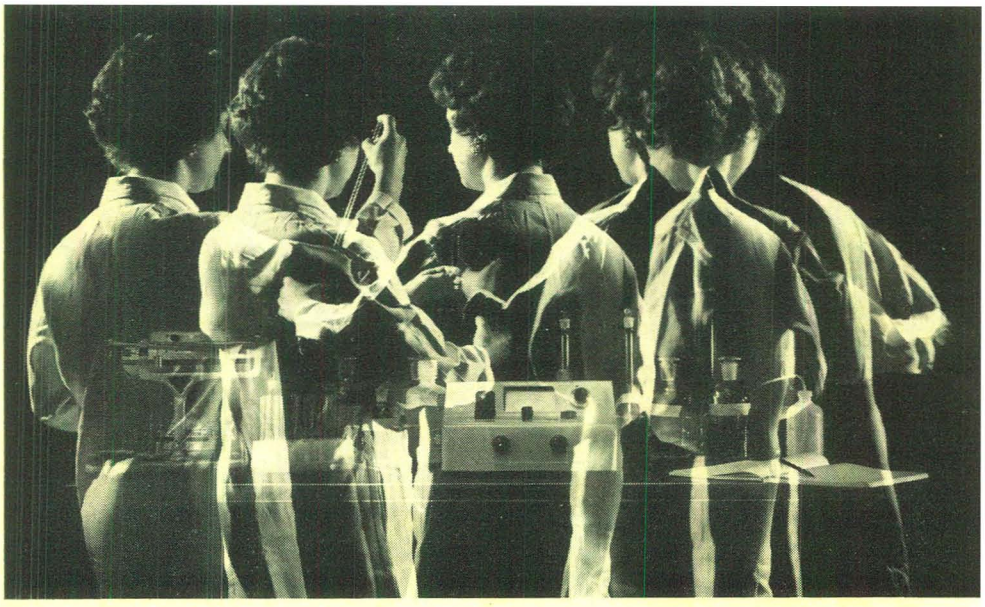
Compare. Filtrations indicate there is a difference. From one test to the next, other brand porosities may vary as much as 100%. Kimax does not. In manufacture, Kimble keeps pore sizes within maximum and minimum *specifications*. Every disc. Every piece of fritted ware. Every shipment. Every time.

Consider. Here's what Kimax fritted ware's controlled porosities, inspected in every batch, mean to you: uniform dispersion or scrubbing of gas in liquid, exact filtration results, controlled blocking in bacteriological work—accurate analyses that can be duplicated time after time. The same accuracy is built into every piece of Kimax fritted ware and every fritted disc. Catalog supplement SC-180 contains specifications and prices.

You get more of the better things first from Kimble.

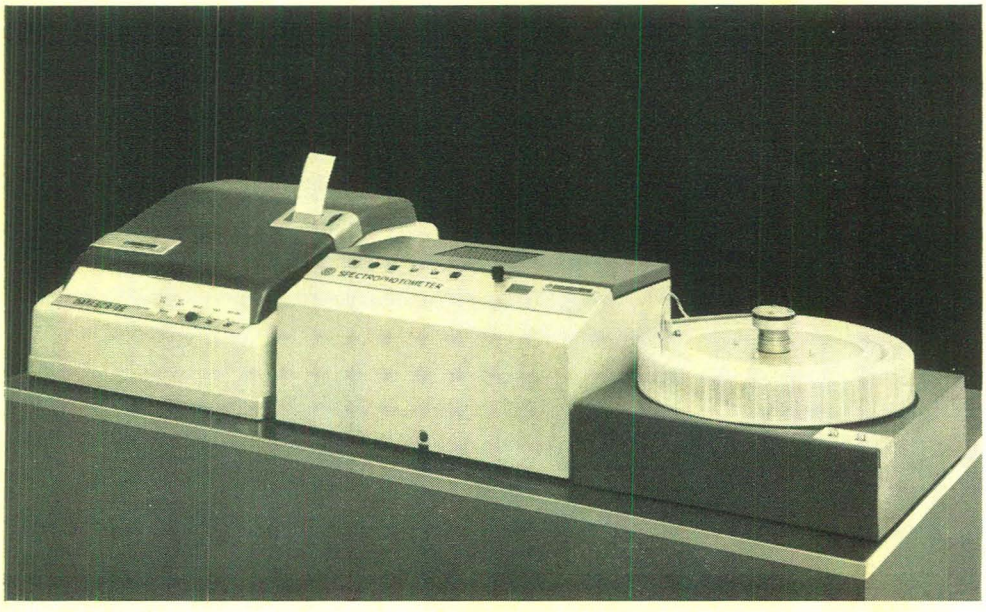
KIMBLE LABORATORY GLASSWARE
AN (I) PRODUCT

OWENS-ILLINOIS
GENERAL OFFICES • TOLEDO 1, OHIO



In spectrophotometry, would you prefer six chances for error...

or none?

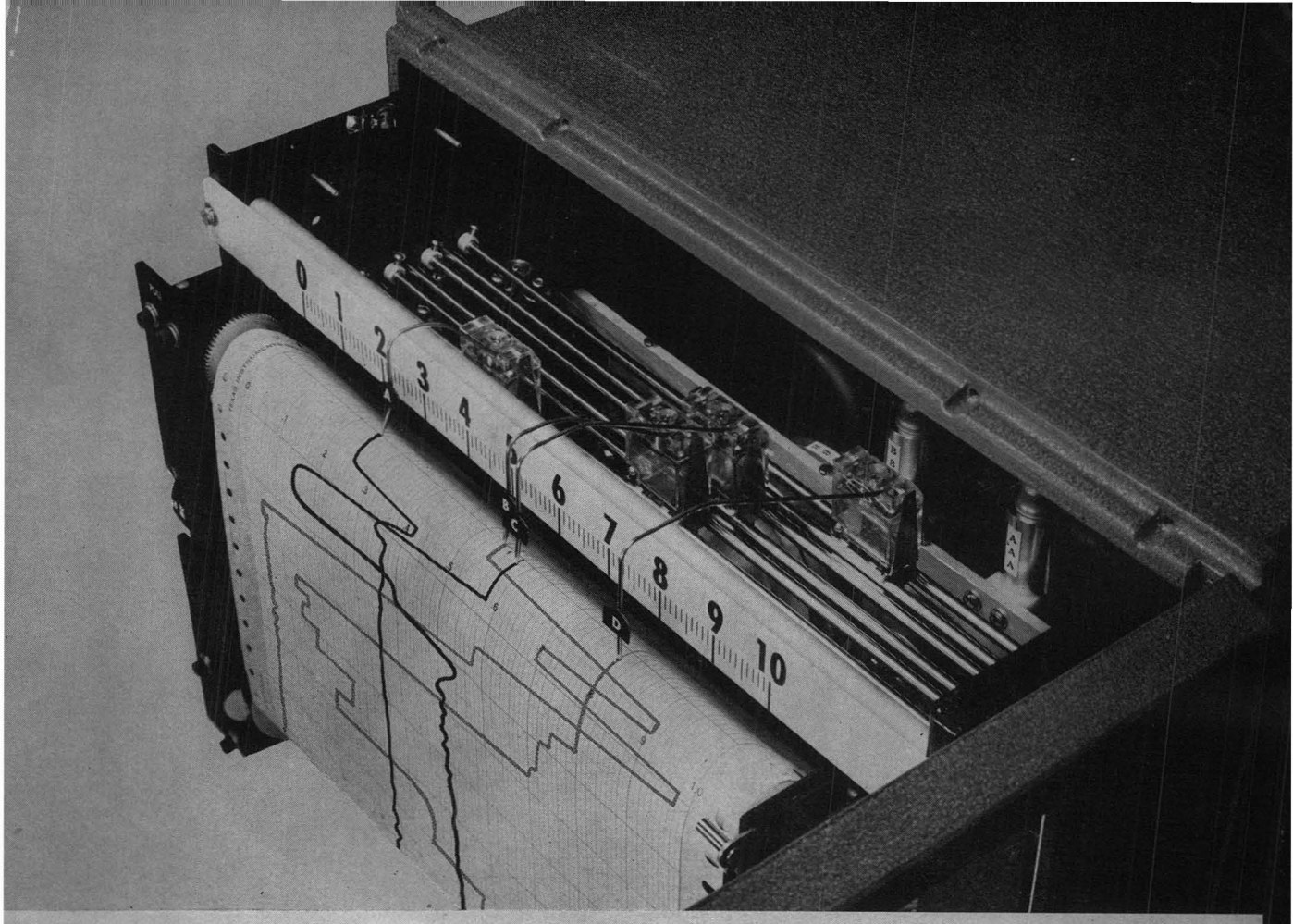


☐ **RSCo's NEW AUTOMATED SPECTROPHOTOMETRY SYSTEM** eliminates the chance of human error. Simply load the turntable. Push the button labeled START. RSCo automation does the rest. ☐ Our fully automated spectrophotometry system presents each sample (up to 52 of them), measures light absorbance, converts this measurement to constituent concentration, and prints the result opposite an identifying sample number. Automatically. Unattended. Without operator variability. ☐ Three separate units make up the system: The Automatic Turntable, Programmed Operation Spectrophotometer, and DATA-SCRIBE™ Printing Converter. Components of the system may also be purchased for semi-automatic operation or for use with other instruments. ☐ Want to improve your lab's productivity, reduce expenses, and get more reliable results? Please write. We'd like to send you detailed information.

RESEARCH SPECIALTIES CO.

200 SOUTH GARRARD BLVD. • RICHMOND, CALIFORNIA

Circle No. 146 on Readers' Service Card



only servo/riter* recorders offer uninterrupted multi-channel recording with wide chart resolution

OVERLAPPING PENS

For the first time in a potentiometric instrument, **continuous** recording of up to six variables can be made on a single chart. Up to four channels of data can be recorded with the high resolution attained only on a 9¾" grid — all four overlapping pens record across the full chart width.

TWO TO SIX CHANNELS

Five and six channel ***servo/riter*** recorders utilize overlapping pens on dual side-by-side 4½" grids. Two and three channel recorders are offered in both narrow and wide chart configurations with all pens writing on only one sheet of chart paper.

REMOTE AMPLIFIERS

Amplifiers are separate from the recorder and may be mounted as far as 15 feet from the recorder chassis. An optional assembly places amplifiers in a standard rack-mounting case to be located adjacent to the recorder.

CHOICE OF INPUTS

There is an industry-proved ***servo/riter*** recorder for every application. Single and dual channel, narrow and wide grid, portable, flush-mounting and multi-channel instruments — all offered in the widest selection of high impedance or high rejection input ranges with mercury or Zener regulated reference and other options.

WRITE FOR COMPLETE INFORMATION.

*A Trademark of Texas Instruments

INDUSTRIAL PRODUCTS GROUP
STRIP CHART RECORDERS
TEST EQUIPMENT
DATA SYSTEMS
TRANSDUCERS

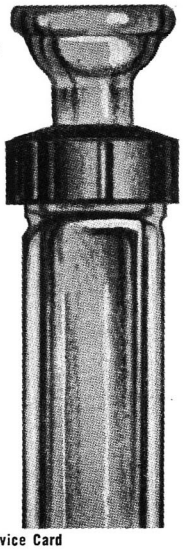
TEXAS INSTRUMENTS
INCORPORATED
3609 BUFFALO SPEEDWAY
P. O. BOX 66027 HOUSTON 6, TEXAS

Circle No. 41 on Readers' Service Card

ONE
TWO
THREE
COMPLETE
AMINO ACID ANALYSES IN 24 HOURS

with the
PHOENIX MODEL K-8000-B
AMINO ACID ANALYZER

If you are conducting amino acid analyses but need to increase the number of analyses per day, write to Department K for Bulletin K-8000-B.



PPI

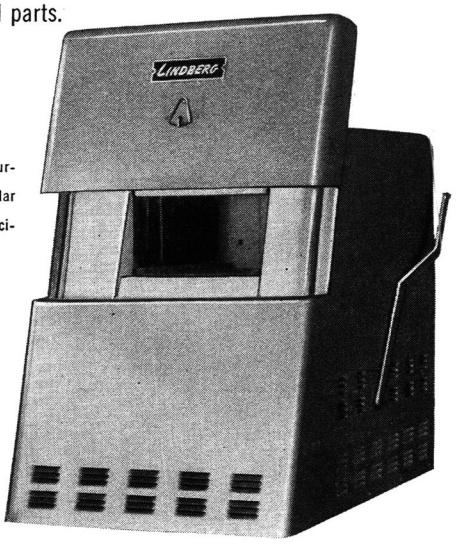
PHOENIX
PRECISION
INSTRUMENT
COMPANY

3801-05 North Fifth Street
Philadelphia 40, Penna.

Circle No. 131 on Readers' Service Card

This Lindberg quality **LABORATORY FURNACE** is available in two sizes. Either is ideal for a variety of uses such as **ASH DETERMINATIONS, FUSIONS, ASSAYING** and **HEAT TREATING** small parts.

Lindberg Type B-6 Furnace. Type B-2 is similar in appearance. See specifications below.



THE DETAILS: In both furnaces shell is fabricated from heavy sheet steel and finished with high temperature gray baked enamel. Manually operated door is counter-weighted for easy operation. A built-in transformer and control circuit contactor for supplying and controlling the low voltage to the heating element are located in the lower section of the furnace housing. Work chamber is heavily insulated and equipped with a high temperature refractory hearth plate. Heat is provided by a heavy, one piece, rod type nickel chromium element, easy to remove and replace. Available with either Automatic Controller Pyrometer or Manual Input Control.

	Model B-2	Model B-6
Overall length	25″	30¼″
Overall width	19″	22″
Overall height	22″	26″
Chamber depth	10¼″	14¼″
Chamber width	4¼″	7½″
Chamber height	4″	5″
Power rating	1800 W	4000 W
Max. Temperature	2000°F.	2000°F.

Lindberg Laboratory Equipment is sold only through **LABORATORY EQUIPMENT DEALERS.** For full information on the B-2 and B-6 Furnaces ask your dealer for Lindberg Bulletin No. 1055. Laboratory Equipment Division, Lindberg Engineering Company, 2455 West Hubbard Street, Chicago 12, Illinois.

LINDBERG
heat for industry

Circle No. 4 on Readers' Service Card

(Reprint in above photo is exact duplication of original ad.)

Tooting a 6 year old horn?

You could call it that.

We ran this ad in 1957 to introduce our new, sturdy and functionally "straight" ground outer joints.

They caught the industry with their "bulges" showing.

Now, 6 years later, others have adopted designs that *look* strikingly similar to the Kontes original.

This presents a problem.

Recognition.

Our joints are the sturdy, straight ones that don't leak. They can be identified by small crowns and very satisfied users.

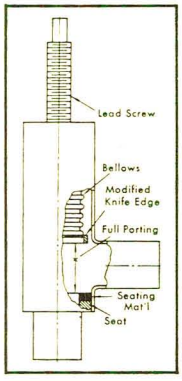
In fact, we think so much of our ground joints that we put them on only the finest technical glassware.

Try some.

You'll do a little horn tooting of your own.

KONTES
GLASS COMPANY
Vineland, New Jersey

Circle No. 121 on Readers' Service Card



Non-work-hardening indium alloy seat that is reflowable and a slip clutch on the drive screw to control depth of knife edge penetration into the seat contribute to the long-life performance of KEL valves. After 200 or more closures, the seat can be reflowed in minutes without removing valve from system. Indium alloy has vapor pressure less than 10^{-10} mm Hg at room temperature; 10^{-9} mm Hg at 450° C. 1″, 1½″, and 2″ sizes. Angle and cross type. Standard flange assemblies available.

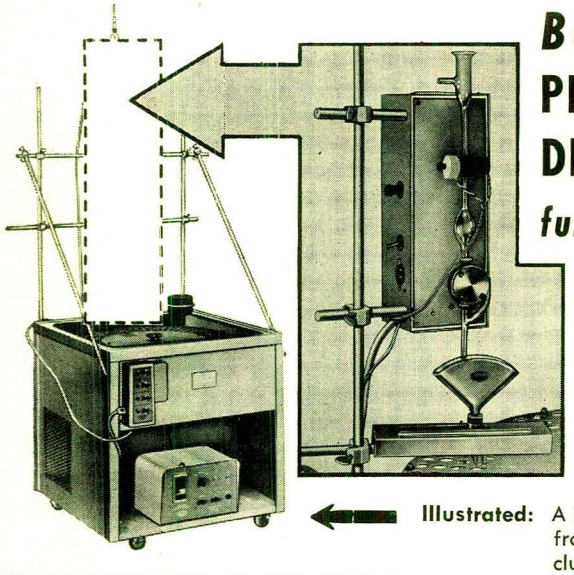
Other KEL Ultra High Vacuum Components . . .
MOLECULAR SIEVE TRAPS • STAINLESS STEEL BELL JARS & BASE PLATE COLLARS

Bakeable Ultra High Vacuum Valves with Unlimited Seat Life

KANE
KANE ENGINEERING LABORATORIES
845 Commercial Street, Palo Alto, California (415) 321-2487 TWX 415-492-9478

Circle No. 55 on Readers' Service Card

NOW! PRECISE VOLUME CUTS *of any solution . . . organic or aqueous*



Buchler PHOTOELECTRIC VOLUMETRIC DISPENSING HEAD *perfects the function of* FRACTION COLLECTING

Works equally well with organic or aqueous solutions . . . Permits accurate collection of preset volumes from 1–20 ml. per fraction . . . No mixing of eluent. Complete drainage. All glass and teflon components prevent contamination.

Operating Principle: Liquid rising in collecting tube acts as a lens and increases amount of light striking photocell; this activates a teflon stopcock to release exact volume.

DISPENSING HEAD USEABLE WITH BUCHLER AND ANY OTHER MAKE OF FRACTION COLLECTORS

Illustrated: A Buchler Refrigerated Model (the "mobile cold room"), cooled from column to test tubes. Complete line of 25 models including short-run, continuous, sectional or special purpose fraction collectors described in **Bulletin A 3-4000.**

Other **BUCHLER** *Items:*

Flash Evaporators • Rotary Evapomix • Micropump • Varigrad • Uviscan • Water Booster • Electrophoresis Apparatus • Chloridometer • Densigrad

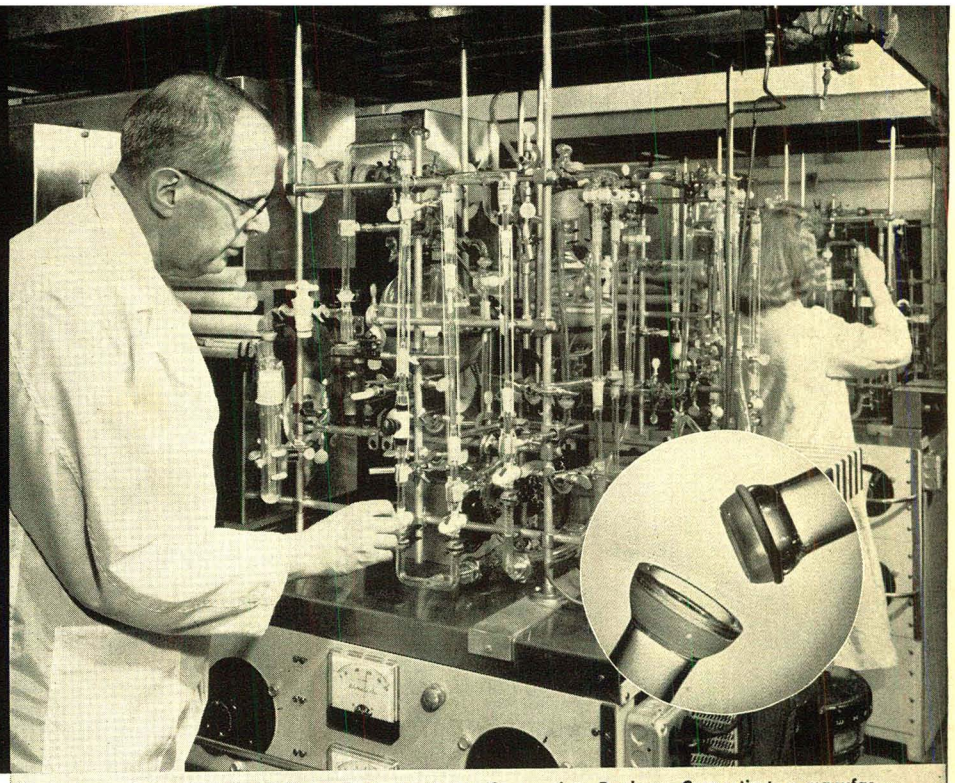
LABORATORY APPARATUS
BUCHLER INSTRUMENTS
PRECISION INSTRUMENTS

BUCHLER INSTRUMENTS, INC.
1327 16th Street, Fort Lee, New Jersey
Phone 201-945-1188 or call N.Y.C. direct LO 3-7844

Circle No. 107 on Readers' Service Card

VACUUM TIGHT!

"HVS" (High Vacuum Seal) JOINTS*



another "SGA" exclusive!

Dr. M. Schneider of the National Semiconductor Corporation, Danbury, Connecticut, a manufacturer of high quality silicon semiconductor devices, is shown regulating a Gyco stopcock on "SGA" glassware which incorporates "HVS" joints. Our high vacuum seal joints solved the problem of leakage formerly experienced with conventional joints.

In addition to being vacuum tight, "HVS" Joints do not require any lubrication. Furthermore, since the unique design features an O-ring seal *above* the ground joint, you never have to worry about contamination. (The ground joint surface protects the O-ring from solvents and vapor; the tight seal prevents the atmosphere from attacking the system!)

"HVS" Joints may be incorporated into any apparatus fabricated from hard borosilicate glass. They're easily assembled and disassembled. Buna-N O-rings are standard, but silicone and Viton† are available.

All Inter-Joint® glassware in "SGA" Combined Catalog 63 can be supplied with "HVS" Joints *at no extra charge.* Ask us for details.

*Patent Applied For †DuPont Trademark

JJ-1280X "HVS" SPHERICAL JOINTS. Ball member supplied with "Buna-N" O-Ring. Please specify catalog number and size:

⅌ No.	12/1	12/2	12/3	12/5	18/7	18/9
Ball, each	$2.09	$2.09	$1.76	$1.76	$1.82	$1.82
Socket, each	2.48	2.48	1.98	1.98	2.04	2.04
Complete	4.57	4.57	3.74	3.74	3.86	3.86

⅌ No.	28/12	28/15	35/20	35/25	50/30	65/40
Ball, each	$2.09	$2.09	$2.48	$2.48	$3.85	$6.33
Socket, each	2.31	2.31	2.70	2.70	4.24	6.44
Complete	4.40	4.40	5.18	5.18	8.09	12.77

JJ-3755X "HVS" ⅌ JOINTS. Inner member supplied with "Buna-N" O-Ring. Please specify catalog number and size:

⅌ No.	10/18	12/18	14/20	19/22	24/25	29/26
Inner, each	$1.50	$1.50	$1.40	$1.50	$1.60	$1.80
Outer, each	1.70	1.70	1.65	1.75	1.85	2.00
Complete	3.20	3.20	3.05	3.25	3.45	3.80

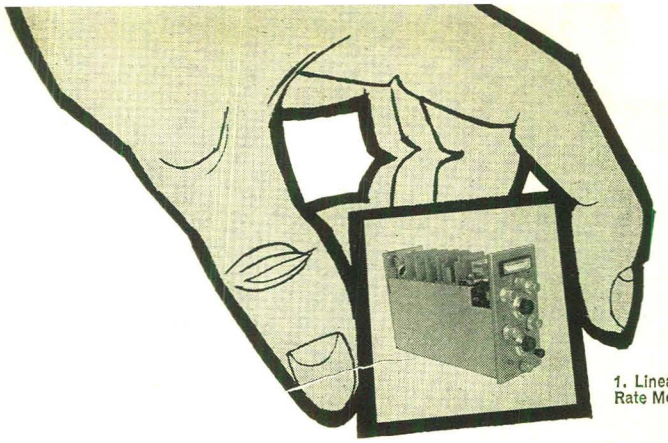
⅌ No.	34/28	40/35	45/35	55/35	71/40
Inner, each	$2.25	$2.75	$3.45	$4.50	$6.15
Outer, each	2.50	3.30	3.85	5.10	7.00
Complete	4.75	6.05	7.30	9.60	13.15

SCIENTIFIC GLASS APPARATUS CO. INC
BLOOMFIELD, NEW JERSEY

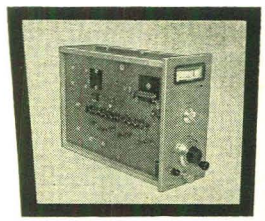
LABORATORY...
♦ APPARATUS
♦ INSTRUMENTS
♦ CHEMICALS
♦ GLASSWARE

Branches: Boston 16, Mass. • Elk Grove Village, Ill. • Fullerton, Calif. • Philadelphia 2, Pa. • Silver Spring, Md. • Syracuse 2, N.Y.

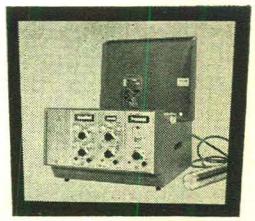
Circle No. 82 on Readers' Service Card



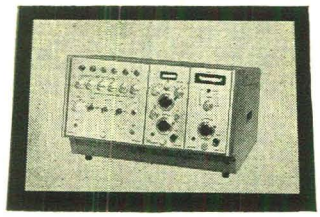
1. Linear-Log Count Rate Meter



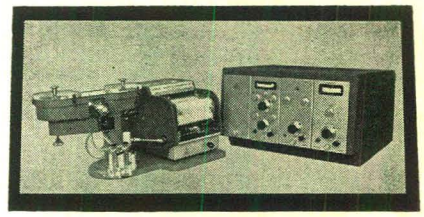
2. High Voltage Power Supply



3. Blank Panel, Linear Count Rate Meter, Single Channel Analyzer, High Voltage Power Supply



4. Printing Scaler-Timer, Single Channel Analyzer High Voltage Power Supply



5. Chromatograph Scanner, Linear-Log Count Rate Meter, Linear Amplifier, High Voltage Power Supply

BUILD YOUR INSTRUMENTATION SYSTEM AS YOUR BUDGET PERMITS

With transistorized building-block modules available individually or in combinations

PROGRESS REPORT: Start with a simple module (linear amplifier, single channel analyzer, or count ratemeter) add the power supply, detector and read-out device and you have the simplest of spectrometer systems. As funds permit, you can add another module (quickly substituted for the blank panel in the chassis) and perform the additional experiments you desire.

When you are ready for automatic scaling or counting of your spectra, the double module scaler-timer can be added. You can simultaneously add a print-out facility to integrate the total energy under a peak automatically or to record this energy as a digital output. Depending upon the selection of the read-out device, simultaneous chart recording is also possible.

The widest possible choice of input and output devices is available. G-M or Scintillation detectors can be accommodated by simply reversing the printed circuit card in one of the modules. More advanced devices for automatic sample counting, gas flow counting, or paper chromatograph counting also are available.

Each instrument features transistorized reliability; modular construction; built-in electronic gating circuits; and plug-in etched circuit boards. Individual modules may be interchanged or combined to provide unsurpassed measurement capability. In addition, etched circuit boards may be substituted within individual modules to produce extreme flexibility and versatility of application. **For full details write:**

RCL **RADIATION COUNTER LABORATORIES, INC.** A SUBSIDIARY OF ALLIED RESEARCH ASSOCIATES, INC.

5120 West Grove Street, Skokie, Illinois, U.S.A., TWX: 9675150, Cable Address: RACOLAB / Phone YOrktown 6-8700

Circle No. 79 on Readers' Service Card

NIH Symposium and Exhibit

The National Institutes of Health, Bethesda 14, Md., announces the 13th Annual Instrument Symposium and Research Equipment Exhibit, October 7 to 10.

The symposium on recent developments in research methods and instrumentation will cover the following topics:

RESEARCH APPLICATIONS OF LASER BEAMS

ATOMIC ABSORPTION SPECTROSCOPY

AUTOMATION IN BIOCHEMICAL ANALYSIS

METHODS OF MOLECULAR STRUCTURE ANALYSIS

NEW METHODS IN IMMUNOLOGY AND IMMUNOCHEMISTRY

HIGH RESOLUTION MICROSCOPY

RADIATION BIOLOGY

ADVANCED X-RAY AND ELECTRON TECHNIQUE SPECTROSCOPY

MOLECULAR SEPARATION BY SIZE AND CHARGE

PHYSIOLOGICAL MONITORING

Dr. Fred Alt, National Institutes of Health, is chairman of the symposium. Louis Heiss, American Instrument Co., Inc., 8030 Georgia Ave., Silver Spring, Md., is chairman of the Committee of Manufacturers' Representatives of the exhibit, while James B. Davis of the National Institutes of Health is exhibit manager.

AOAC Meeting

The 77th Annual Meeting of the Association of Official Agricultural Chemists will be held at the Shoreham Hotel, Washington, D. C., October 14 to 17.

Scientific reports and papers from members and nonmembers on analytical methodology will be presented on many areas such as animal feeds, antibiotics, analytical entomology, alcoholic beverages, cacao products, carbohydrates, cereals, color and food additives, cosmetics, dairy products, decomposition and filth in foods, drugs, extraneous materials in foods, fats, and oils, fertilizers and liming materials, flavors, foods, gums, marine products, meats, nutritional adjuncts, pesticide formulations and residues, plant materials, preservatives in food, tobacco, and vegetable products.

Important events include the presidential address, a business session, and a banquet. Dr. E. L. Butz, formerly Assistant Secretary of Agriculture and now Dean of the College of Agriculture, Purdue University, an outstanding speaker, will address the banquet. The Harvey W. Wiley award will also be presented at the banquet to a scientist who has contributed notably to development of analytical methods. A highlight of the meeting will be an address by Professor Paul Kirk, famed scientific criminologist, University of California.

Several laboratory equipment and supply firms will exhibit many of their items of special interest to analytical and research chemists.

Registration is free. All interested scientists from federal, state, and local agencies, universities, agricultural experiment stations, and industrial and commercial firms are invited to attend and participate. All correspondence and requests for information should be addressed to Mr. Luther G. Ensminger, Association of Official Agricultural Chemists, Box 540, Benjamin Franklin Station, Washington 44, D. C.

New Date for Environmental Symposium

The Environmental Measurements Symposium, announced in April ANALYTICAL CHEMISTRY, page 47 A, will be held Sept. 4 to 6 instead of the earlier announced date (Aug. 26 to 28). This change became necessary because of unanticipated conflicts with international meetings, according to the Division of Air Pollution, Public Health Service, sponsors of the symposium.

Gas Chromatography Symposium—1964

The Fifth International Symposium on Gas Chromatography to be organized by the Institute of Petroleum Gas Chromatography Discussion Group will be held from Sept. 8 to 10, 1964, at Brighton, England.

Those wishing to submit papers and those wishing to attend this meeting should write to: The Organizing Office, Fifth International Symposium on Gas Chromatography, 61 New Cavendish St., London, W. 1., England.

ACS Southeastern Regional Meeting

The 1963 Southeastern Regional Meeting of the ACS will be held at Charlotte, N. C., on Nov. 14 to 16. This meeting, sponsored by the Carolina-Piedmont Section, has the rapid growth of the chemical industry in the South as its theme.

The general chairman is C. R. Holtzclaw, Southern Dyestuff Co., while the program chairman is J. B. Gallent of Davidson College. The general sessions will include papers on analytical chemistry as well as other fields.

More information is available from V. S. Salvin, Celanese Fibers Co., P. O. Box 1414, Charlotte, N. C.

Hot Laboratory Conference

The Eleventh Hot Laboratory and Equipment Conference will be held Nov. 18 to 21, in New York City as part of the winter meeting of the American Nuclear Society. The meeting covers the design, construction, operation, and management of hot laboratories and includes specialized equipment which operates in hostile environments and which are now used or are likely to be used for handling radioactive materials. Further information is available from the American Nuclear Society, 244 E. Ogden Ave., Hinsdale, Ill.

Committee D-9 of ASTM

ASTM Committee D-9 will have a symposium and meeting on Electrical Insulating Materials, October 21 to 23, at the Cavalier Hotel, Virginia Beach, Va. More information is available from C. L. Craig, Materials Engineering Dept., 1A36 Sperry Gyroscope Co., Great Neck, L. I., N. Y.

Design of Experiments

Purdue University, Lafayette, Ind., announces a short course on design of experiments to be held September 9 to 19. This course is for statisticians, quality control personnel, engineers, and others concerned with planning and interpreting experiments. The course fee is $225. More information is available from C. R. Hicks, Purdue University, Lafayette, Ind.

CALENDAR OF EVENTS

July 10 to 17	**XIX International Congress of Pure and Applied Chemistry.** London, England. *Contact:* The Honorary Secretary, XIX IUPAC Congress, 14 Belgrave Square, London, S. W. 1, England. Page 47 A, Jan.
July 17 to 19	**Society for Analytical Chemistry, Microchemistry Group.** London, England. *Contact:* D. W. Wilson, Sir John Cass College, Jewry St., Aldgate, London, E. C. 3, England. Page 49 A, June.
July 17 to 23	**5th International Pesticides Congress.** London, England. Includes special session on pesticide residue analysis. *Contact:* 5th International Pesticides Congress, Honorary Secretary, 14 Belgrave Square, London S. W. 1, England. Page 47 A, Jan.
July 18 to 20	**Conference on the Vibrational Spectra of High Polymers.** Milan, Italy. *Contact:* Dr. Giuseppe Zerbi, Istituto di Chimica Industriale del Politecnico, Piazza L. Da Vinci 32, Milan, Italy. Page 51 A, May.
July 22 to 26	**Microscopy Symposium.** Brighton, England. McCrone Research Institute. *Contact:* Mrs. Elizabeth Bitoy, McCrone Research Institute, 451 East 31st St., Chicago 16, Ill. Page 52 A, Dec.

Coming Events

Aug. 7 to 9—**12th Annual Conference on Applications of X-Ray Analysis.** Albany Hotel, Denver, Colo. *Contact:* Dr. W. M. Mueller, Denver Research Institute, University of Denver, Denver 10, Colo.

Aug. 19 to 23—**Fifth International Congress of Clinical Chemistry.** Detroit, Mich. *Contact:* Dr. D. G. Remp, Henry Ford Hospital, Detroit 2, Mich. Page 54 A, Mar.

Aug. 20 to 23—**Fourth Australian Spectroscopy Conference.** Australian National University, Canberra, Australia. *Contact:* Prof. A. N. Hambly, Australian National University, Canberra, Australia. Page 56 A, Mar.

Aug. 26 to 30—**Gordon Research Conference on Analytical Chemistry.** New Hampton School, New Hampton, N. H. *Contact:* Dr. W. George Parks, Director, Gordon Research Conferences, University of Rhode Island, Kingston, R. I. Page 47 A, May.

Aug. 27 to Sept. 4—**Second World International Federation of Automatic Control Congress.** Basle, Switzerland. Sponsor: Swiss Federation of Automatic Control. *Contact:* Dr. Anton von Schulthess, Wasserwerkstrasse 53, Zürich 6, Switzerland.

Aug. 28 to 31—**21st Annual Meeting of the Electron Microscope Society of America.** Denver-Hilton Hotel, Denver, Colo. *Contact:* Prof. F. W. Boswell, Dept. of Physics, University of Waterloo, Waterloo, Ontario, Canada. Page 100 A, Feb.

Sept. 4 to 6—**Symposium on Environmental Measurements.** Cincinnati, Ohio. Sponsor: U. S. Public Health Service. *Contact:* John S. Nader, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio.

Sept. 8 to 13—**American Chemical Society, 145th National Meeting.** New York, N. Y.

Sept. 9 to 12—**18th Annual Instrument-Automation Conference and Exhibit.** McCormick Place, Chicago, Ill. Sponsor: Instrument Society of America. *Contact:* T. A. Abbott, Instrument Society of America, Penn-Sheraton Hotel, 530 Wm. Penn Pl., Pittsburgh 19, Pa.

Sept. 9 to 14—**Society of German Chemists Annual Meeting.** Heidelberg, Germany. Includes analytical chemistry sessions. *Contact:* Gesellschaft Deutscher Chemiker, Gerschäftstelle, Postfach 9075, 60000 Frankfurt (Main) 9, Germany. Page 48 A, May.

Sept. 16 to 18—**Tenth Ottawa Symposium on Applied Spectroscopy.** Ottawa, Canada. *Contact:* Mr. John Kelly, The Steel Company of Canada, Ltd., Wilcox St., Hamilton, Ontario, Canada. Page 48 A, May.

Sept. 30 to Oct.4—**XI International Conference on Spectroscopy.** Beograd, Yugoslavia. *Contact:* Colloquium Spectroscopicum Internationale, Sekretarijat, Prirodno-matematički fakultet, Fizičkohemijski zavod, Beograd, Studentski trg 16, Blok C, Jogoslavija. Page 49 A, May.

Oct. 7 to 10—**National Institutes of Health 13th Annual Instrument Symposium and Research Equipment Exhibit.** NIH, Bethesda 14, Md. *Contact:* Dr. Fred Alt, National Institutes of Health, Bethesda 14, Md. Page 41 A, July.

Oct. 8 to 10—**Seventh Conference on Analytical Chemistry in Nuclear Technology,** Sponsor: Oak Ridge National Laboratory. Conference subject: Analytical Instrumentation. *Contact:* C. D. Susano, Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tenn. Page 49 A, June.

Oct. 14 to 17—**77th Annual Meeting of the Association of Official Agricultural Chemists.** Shoreham Hotel, Washington, D. C. *Contact:* Mr. Luther G. Ensminger, Association of Official Agricultural Chemists, Box 540, Benjamin Franklin Station, Washington 44, D. C. Page 41 A, July.

Oct. 14 to 18—**Second National Meeting of the Society for Applied Spectroscopy.** San Diego, Calif. *Contact:* Earl P. Wadsworth, Jr., San Diego State College, San Diego 15, Calif. Page 53 A, Apr.

Oct. 16 to 18—**Tenth National Vacuum Symposium.** Statler Hilton Hotel, Boston, Mass. Sponsor: American Vacuum Society. *Contact:* G. H. Bancroft, 398 Kilbourn Rd., Rochester 18, N. Y. Page 56 A, Apr.

Oct. 21 to 23—**Eleventh Detroit Anachem Conference.** McGregor Memorial Conference Center, Wayne State University, Detroit, Mich. *Contact:* Mr. C. M. Gambrill, Ethyl Corp., 1600 West 8 Mile Rd., Detroit 20, Mich. Page 53 A, Mar.

Pittsburgh Diffraction Conference

The annual Pittsburgh Diffraction Conference will be held November 6 to 8 at Mellon Institute, Pittsburgh, Pa. Sessions will be devoted to instrumentation and techniques, structures, metals and alloys, defect lattices and/or radiation damage with special sessions on transmission microscopy, electron probe microanalysis, lattice dynamics, and/or neutron diffraction. Professor Caroline MacGillavry of the University of Amsterdam will be the guest speaker for the Thursday evening meeting. A placement service will be available. Further information can be obtained from W. M. Biagas, Crucible Steel Company, P. O. Box 7257, Pittsburgh 13, Pa.

Industry Items

Beckman Instruments, Inc., and **Sharp Laboratories, Inc.,** announced agreement on the Beckman acquisition of the La Jolla, Calif., developer of nuclear instrumentation. The proposal is subject to approval of Sharp shareholders and rulings by regulatory bodies.

Coleman Instruments, Inc., Maywood, Ill., manufacturer of analytical instruments, has acquired the **Electro-Mechanical Development Co.,** Houston Texas. The new subsidiary, EMDECO manufactures hospital and laboratory equipment.

The Glass Products Division of **Fischer & Porter Co.,** has been expanded and renamed "The Lab-Crest Scientific Division." This division will offer a line of scientific and analytical instruments, in addition to glassware and conventional laboratories supplies.

General Electric, Schenectady, N. Y., offers a nationwide service for the maintenance and repair of measurement and control equipment. The Service Shops Dept. will repair process control, industrial, and laboratory instruments of all manufacturers. Plans call for 40 different shops staffed with 200 technicians. The service maintains highly accurate standards based on reference to standards certified by the National Bureau of Standards.

Schuco Scientific, 250 West 18th St., New York City, has been appointed as a distributor of **Nonius** x-ray diffraction equipment. The Dutch firm manufactures a range of instruments including goniometers, microdensitometers, cameras, and other analytical equipment.

New catalog now ready!

Regional Editions for fast service from 4 plants on most complete line of compressed gases, gas mixtures, fluid controls and accessories

Among the new listings:
Phosphorus Pentafluoride
Sulfuryl Fluoride
Neon 99.7%

Neon-Helium . . . for spark-chamber spectroscopy

Doping Gases, including Stibine and Arsine

Certified Moisture Mixtures

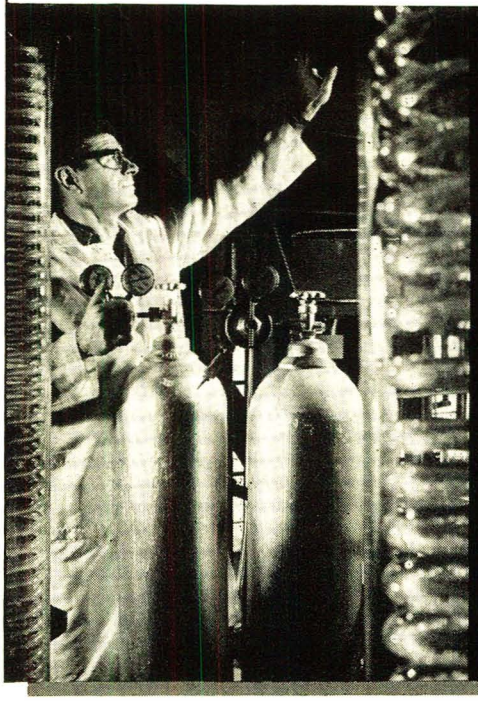
Gas and Liquid Purifier— for removal of oil, water and 5-12 micron size particles

---

New Bench-Type Cylinder Holder
New Line Regulator

Write for your new Regional Edition. It lists special localized price and shipping data for your area.

1963 / Matheson
Compressed Gases and Fluid Controls
The Matheson Company, Inc. / P.O. Box 85 / East Rutherford, N.J.
Area Code: 201 933-2400 (In New York, Enterprise 6869) TWX-RFD 840
Joliet, Illinois / La Porte, Texas / Newark, California / Whitby, Ontario



Gas Regulating Equipment Section
Starts on Page 39.

ADAPTORS
AUTOMATIC PRESSURE REGULATORS
including Chromatography, Corrosion Resistant, High Pressure, Regulator Flowmeter
FLOWMETERS
GAS PURIFIERS
LECTURE BOTTLE ACCESSORIES
MANIFOLDS
MANUAL CONTROLS
SAFETY DEVICES
VALVES
for every laboratory purpose

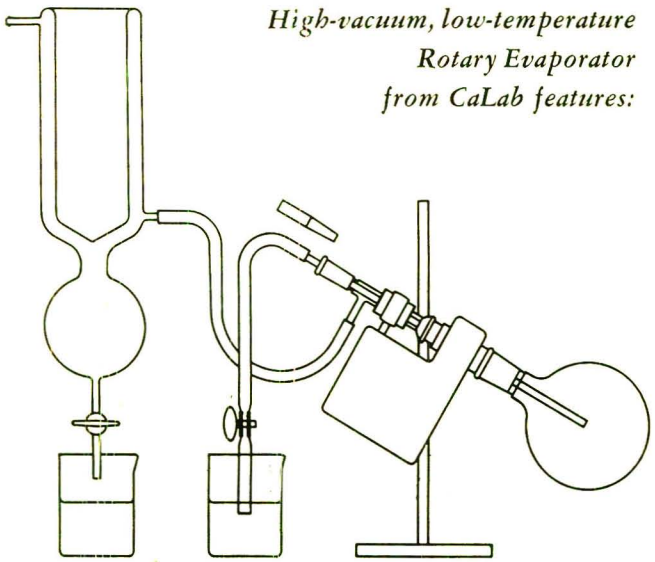
The Matheson Company, Inc., P. O. Box 85, East Rutherford, N. J.
☐ Please send me your 1963 Gas Catalog

Name_____
Firm_____
Address_____
City_____ State_____

The Matheson Company, Inc.
Compressed Gases and Regulators / East Rutherford, N. J. / Joliet, Ill. / La Porte, Texas / Newark, Calif.
Matheson of Canada, Ltd. Whitby, Ont.

CALAB

MODEL C ROTARY EVAPORATOR



High-vacuum, low-temperature Rotary Evaporator from CaLab features:

All glass and Teflon surfaces: No metal, rubber or grease to react with sensitive materials.

Greaseless vacuum seal: Teflon ball joint in stationary glass socket joint forms seal that maintains 0.1 mm vacuum while flask and shaft rotate.

Continuous addition: Easily adapted for either continuous addition rotary evaporation or flash evaporation.

Heavy-duty motor: Fully enclosed Bodine induction motor powers unit with sparkless, quiet, cool-running operation.

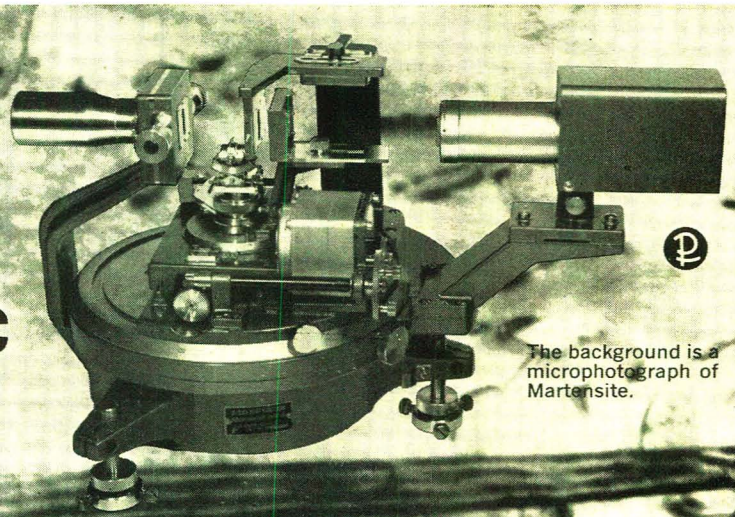
For full information on the Model C Rotary Evaporator, write for Brochure AE.

California Laboratory Equipment Company

1717 Fifth Street • Berkeley 10, California

Circle No. 108 on Readers' Service Card

THE RIGAKU LANG X-RAY MICROGRAPHIC CAMERA



The background is a microphotograph of Martensite.

. . . a scanning type camera used for studying such defects as dislocation, or segregation of impurities in a crystal. The specifications of the Rigaku Lang Camera are as follows: resolution, 1 micron or better; accuracy, ±2 seconds, zero lag; specimen holder, x-y orientation with goniometer; enlargement, up to 500X, photographically. Berg-Barrett topographical studies can also be made with the versatile new Rigaku Lang Camera.

ERB & GRAY SCIENTIFIC

A Division of the Perkin-Elmer Corporation

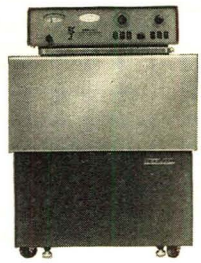
LOS ANGELES · HOUSTON · CHICAGO · NEW YORK

Circle No. 115 on Readers' Service Card

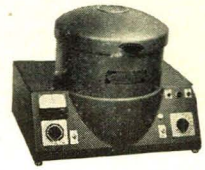
Assisting Biological Researchers...

Around the World

RC-2 Automatic Superspeed Refrigerated Centrifuge* — 17,500 rpm — 37,000 x G
Accepts six different rotors on Gyro-Action direct drive

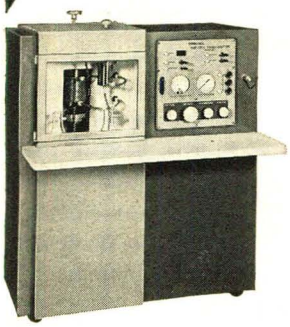


RC-3 Automatic Refrigerated Centrifuge — 5,000 rpm — 5,140 x G — 70 seconds to top speed.
Ideal for routine operations.

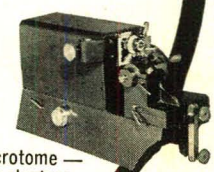


SS-3 Automatic Superspeed Centrifuge*
— 17,000 rpm — 34,800 x G
with push-button simplicity and armor-plate safety

SS-4 Enclosed Superspeed Centrifuge*
— 17,000 rpm — 34,800 x G with removable control panel for cold room or fume hood use

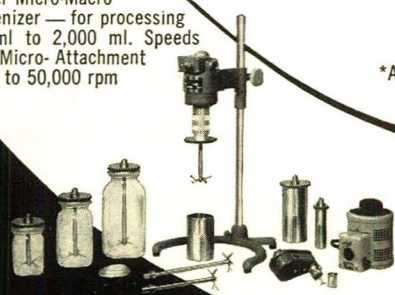


Ribi Refrigerated Cell Fractionator — for isolating cell walls and subcellular particles of the cytoplasm



"Porter-Blum" MT-1 Ultra-Microtome —
1/40μ to 1/2μ — for electron and light microscopy

Omni-Mixer Micro-Macro Homogenizer — for processing 0.5 ml to 2,000 ml. Speeds with Micro- Attachment up to 50,000 rpm



*Adaptable to "Szent-Gyorgyi & Blum" Tube Type Continuous Flow System

"Porter-Blum" MT-2 Ultra-Microtome
— 100 A to 4μ — automatic operation
— the finest instrument of its kind in the world

Researchers in every branch of the life sciences in more than thirty different countries rely on the Centrifuges and Laboratory Instruments with the SERVALL trademark.

Centrifuges offering a full range of forces up to 37,000 x G, and a wide selection of angle, horizontal and special purpose rotors, provide the researcher with the utmost in versatility. Models include refrigerated, non-refrigerated, automatic, manual, remote control, and continuous flow.

SERVALL's unequalled quality of design and reliability is available also in the prize-winning Ribi Refrigerated Cell Fractionator, "Porter-Blum" Microtomes, and the Omni-Mixer Micro-Macro Homogenizer.

Ivan Sorvall, Inc.
NORWALK • CONNECTICUT

For descriptive literature on the above please ask us for Bulletin AC-7GCW

Circle No. 136 on Readers' Service Card

From A to Z

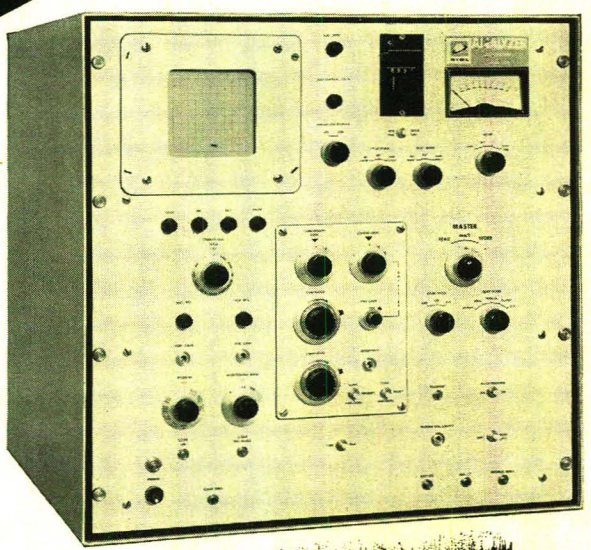
THE 34-12B

RIDL Analyzers are used in every known analyzer application from Activation Analysis to Zoology.

Widest Range of Inputs

Internal Amplifier
External Transistor Amplifier
External Vacuum Tube Amplifier
Sampling Input for Mössbauer Correlation Studies, etc.

The RIDL Model 34-12B 400 Channel Analyzer has the widest selection of flexible features and options available. These features and options, some of which are listed here, provide the most *economical* means to meet your requirements of today and the future.



Widest Range of Accessories and Options

2 to 8 Channel Mixer Systems
Single Channel/Multi-Channel Coincidence Gating
Paper Tape Read-in
Complete Time Mode Systems
Time Base Generator for Time Mode
Log Display and Analog Output
Off-line Typing
Magnetic Tape Read-in
Transfer Indicator
10^6 Counts/Channel
Access to Parallel Data Transfer
8-50 Channel Subgroups
Blinker
Solid State Detector Preamplifiers
50 Cycle
Temporary Storage System
Analyzer Accessory Cart
Random Access to Address Register
Probes and Preamplifiers

Widest Range of Outputs

Typewriter
IBM Card Punch
Parallel Printer
Adding Machine
Tape Punch
Magnetic Tape
Digital Meter
Strip Chart Recorders
X-Y Recorders
Built-in 5" CRT

RIDL

Radiation Instrument Development Laboratory

4501 WEST NORTH AVENUE • MELROSE PARK, ILLINOIS • MU 1-2323 • CABLE: RADILAB • TWX: 312-681-3448

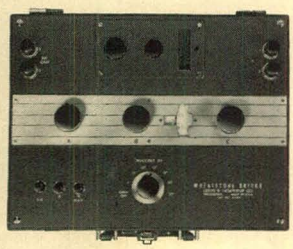
DIVISION OF NUCLEAR-CHICAGO CORPORATION

Circle No. 133 on Readers' Service Card

2 NEW WHEATSTONE BRIDGES

4283 COMPACT D-C WHEATSTONE BRIDGE

For wide-range resistance measurement in plant or laboratory. Covers 0 to ∞ ohms in six ranges. Limit of error, ±1% of reading. Sensitivity, 1% or better when measuring resistances between 0.3 and 300,000 ohms. Completely self-contained with galvanometer, batteries and binding posts for connecting external standards for ratio measurements. Metal case with handle, 7" x 6" x 5"; Weight, 4½ lb.



4289 PRECISION D-C WHEATSTONE BRIDGE

For general resistance measurements with laboratory accuracy. Range, 1 ohm to 11.01 megohms. Limit of error, ±0.05% of reading or better. Sensitivity, better than 0.05% for measurements up to 1 megohm. Completely self-contained with light-beam galvanometer, batteries and central readout. Metal case with handle and slip-hinged removable lid, 14¼" x 11½" x 7½" overall; Weight, 21 lb.

For additional information contact your nearest L&N office or write for literature to Leeds & Northrup Company, 4906 Stenton Avenue, Philadelphia 44, Pa.

Pioneers in Precision

LEEDS & NORTHRUP CO

Circle No. 63 on Readers' Service Card

This is the WILD* M-11 MICROSCOPE

For the laboratory, industrial or educational, that demands highest precision and versatility from a moderate investment. Fine Swiss optics and flawless craftsmanship, plus many attachments, make the instrument well adapted for research. **For field investigations,** its light weight, sturdy steel hood, and easy portability make it an ideal companion for student or scientist. **And for medical students,** the M-11 offers professional features, and a high degree of versatility.

Write for Booklet M-11.

*The first name in Surveying Instruments, Photogrammetric Equipment and Microscopes.

WILD® HEERBRUGG

Full Factory Services

WILD HEERBRUGG INSTRUMENTS, INC.
PORT WASHINGTON, NEW YORK
In Canada: Wild of Canada Ltd.,
881 Lady Ellen Place, Ottawa 3, Ontario

Circle No. 97 on Readers' Service Card

SPRINGER-VERLAG
Berlin · Göttingen · Heidelberg

ACADEMIC PRESS
New York and London

Ready summer 1963

Thin-Layer Chromatography

A Laboratory Handbook

Edited by **Egon Stahl**

Contributions by
H. R. Bolliger, M. Brenner,
H. Gänshirt, H. K. Mangold,
H. Seiler, Egon Stahl, D. Waldi

With 197 figures and 2 tables in colour
Approx. 560 pages 8vo. 1963
Plastic binding DM 68.–
$ 17.—; £ 6.1.5

The new method, by which minute quantities of inorganic or organic substances are rapidly separated, is employed now in so many fields of natural science and medicine, and the amount of information available is so extensive, that its compilation in the form of a handbook meets a great need. Prominent specialists with relevant knowledge and laboratory practice associated for the purpose of composing a handbook for the practice, which will be of actual assistance to beginners as well as specialists. At the present developmental stage of "thin-layer" chromatography, it is a fact of special value, that the associated authors included numerous own studies, which have not been published before.

From reviews of German edition

"Although in many laboratories experts are still trying hard to improve the method, E. Stahl is to be congratulated upon his initiative in editing, in collaboration with a group of prominent co-workers, this excellent laboratory-handbook. This book is designed, primarily, for the practician." *Chimia*

"The author of this first, truly collective, handbook, Prof. Egon Stahl, does not claim at all to be the only inventor of the 'thin-layer' chromatography, but he doubtless has the great merit to have 'put things in order', and to have established systematic working procedures." *Laboratoriu rs-Praxis*

■ **Pamphlet on request!**

Circle No. 151 on Readers' Service Card

NEW BOOKS

Mass Spectrometry. *Klaus Biemann. xii + 370 pages. McGraw-Hill Book Co., Inc., 330 West 42nd St., New York 36, N. Y. 1962. $13.75.*

Reviewed by F. W. McLafferty, Eastern Research Laboratory, The Dow Chemical Co., Framingham, Mass.

Although the techniques for obtaining mass spectra of complex organic molecules have been available for some time, most organic chemists are not particularly aware of the unique and varied potentialities of mass spectrometry in their field. This excellent text "by an organic chemist for organic chemists" provides a needed tool to help both the student and the experienced scientist become aware of these potentialities.

The types of instruments and their operation are summarized, with a large part of this section appropriately devoted to sample introduction techniques. The general ion fragmentation processes which produce the mass spectrum are organized in a logical and useful manner. There is a thorough, excellent discussion on techniques for converting milligram samples to chemical derivatives which can give additional mass spectral information, and also on the labeling of sample molecules with stable isotopes as tracers. Most of the remaining third of the book is devoted to the mass spectra of particular natural products, with exhaustive (and excellent) discussions of indole alkaloids and amino acids and peptides, and relatively brief reviews of steroids, fatty acids, carbohydrates, and other compounds.

The extensive coverage of the spectra of multifunctional natural products will be a real improvement over previous texts for many readers, although it is regrettable that the spectral characteristics of many appropriate references for other interpretations or further information on particular topics are neglected. The majority of examples are from the author's own research, (including much excellent, previously-unpublished work), making them alive and accurately detailed, although placing considerable emphasis on certain narrow areas of chemistry.

Inexactness is frequently found in descriptions involving physics ("cleavage of a bond will occur if the energy transferred exceeds the ionization potential"—p. 200) or physical-organic chemistry ("a *low* electron affinity of X permits rupture" of the C—X bond in CH_3CH_2X—p. 108). Calculation of empirical formulas from natural isotopic abundances (p. 60) emphasizes errors from variations in natural abundance with no mention of instrument discrimination, although this is stressed as important for labeled molecules (p. 214). Metastable ions observed are described as formed before acceleration is complete, with ion acceleration assigned an inordinately long time (10^{-4} sec.). Negative ions are dismissed as of little usefulness, without mention of the considerable work of Melton and co-workers.

The printing, binding, and illustrations are excellent. Graphic spectra used as examples have ordinates based on both the most abundant ion and the total ion abundance, a very useful feature. A sizable number of mistakes and typographical errors were found.

For a large variety of complex organic molecules, the author has been able to derive vital and unique structure information from the individual mass spectra. This has been done through logical mechanisms of degradation, not empirical correlations, which should demonstrate to the careful reader the broad potential of the method for types of complex organic compounds as yet unstudied. This book is strongly recommended for scientists in organic chemistry and allied fields, as well as for mass spectrometrists.

Kolorimetrie. Photometrie und Spektrometrie. *Gustav Kortum. viii + 464 pages. Springer-Verlag, Heidelberger Platz 3, Berlin-Wilmersdorf, West Berlin, Germany. 1962. DM 48.*

Reviewed by E. J. Rosenbaum, Drexel Institute of Technology, Philadelphia, Pa.

This book is characterized by its breadth of coverage and its completeness within the limits set by the author. The range of topics includes general methods and instrumentation for ultraviolet, visible and infrared absorption, Raman spectroscopy, fluorescence spectroscopy, nephelometry, and reflectivity measurements. The main emphasis is on optical components and on the principles, design, and limitations of apparatus in this broad field. There is no descriptive material on sample preparation or on specific

No. 37 in the ADVANCES IN CHEMISTRY SERIES

Reactions of Coordination Ligands and Homogeneous Catalysis

The 18 papers in this volume explore an area which has recently taken on renewed life. All given before the Symposium In Homogeneous Catalysis and Reactions of Coordinated Ligands held by the Division of Inorganic Chemistry at the 141st ACS National Meeting in March 1962, they represent timely material.

Coordination chemists now are paying more attention to the ligands. Major developments which spotlight this area are (1) biochemical research which reveals the role of coordinated metal ions in biochemical synthesis and in energy storage and transfer, (2) the search for polymers which can withstand high temperatures, in turn, uncovering interesting ligand reactions, and (3) the discovery of the oxo- and the Ziegler-Natta catalytic syntheses which focus interest on coordination compounds as reaction intermediates.

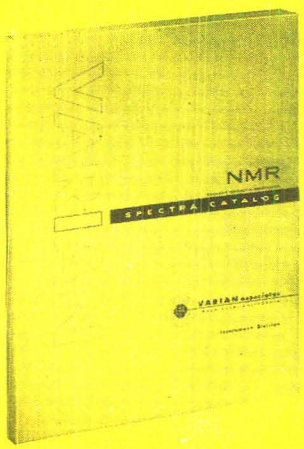
Further investigation into ligand reactions is bound to b- fruitful. If you are working anywhere in this field, you will need this volume as part of your literature.

255 pages. Paper bound. Price: $7.00

Order from:

Special Issues Sales
American Chemical Society
1155 Sixteenth Street, N.W.
Washington 6, D. C.

NMR
NUCLEAR MAGNETIC RESONANCE
SPECTRA CATALOG
NOW AVAILABLE



- BASIC NMR REFERENCE
- AID TO INTERPRETATION
- 368 ORGANIC COMPOUNDS
- FULLY CROSS-INDEXED

The Varian NMR Spectra Catalog is now available for use by chemists everywhere as a basic reference and as an aid to interpretation of new NMR analyses. It has been made possible by the use of spectra obtained on pre-calibrated charts from the Varian A-60 Analytical NMR Spectrometer, and represents a significant contribution to the field of organic chemistry.

This catalog contains the spectra of 368 organic compounds as well as a brief introduction explaining its use. All spectra are fully cross-indexed by molecular name, functional group, and NMR chemical shift value.

Copies of the Varian NMR Spectra Catalog are available at $5.00 each. Orders for 10 or more catalogs earn a quantity price of $4.00 each. Single copy price for students is $4.00. Please send orders to the INSTRUMENT DIVISION.

VARIAN associates
611 HANSEN WAY · PALO ALTO, CALIFORNIA

applications of the methods under discussion. No reference is made to the determination of color coordinates.

For each major type of measurement there is a careful analysis of the associated errors and a discussion of calibration methods. Chapters are devoted to visual and photographic methods. In contrast, some instrumental developments published in 1961 are included. The newer material has been thoroughly integrated into the portions carried over from the previous edition.

The fact that this book has appeared in a fourth edition is a commentary on its acceptance in its country of origin. This reviewer is not aware of any single work in English which matches this one in range and depth. It is highly recommended.

Fundamentals of Analytical Chemistry. *Douglas A. Skoog and Donald M. West. xii + 786 pages. Holt, Rinehart and Winston, Inc., 383 Madison Ave., New York 17, N. Y., 1963. $8.50.*

Reviewed by Garry A. Rechnitz, Department of Chemistry, University of Pennsylvania, Philadelphia 4, Pa.

This book represents a detailed statement of the extreme classical viewpoint in analytical chemistry. Primary emphasis is placed on manipulations and descriptive material; for the most part, important principles and theoretical points are presented only as statements of fact with very little discussion to show how these generalizations arose and may be confirmed.

There can be no question that the book is ably written and clearly organized. It contains compilations of useful reference material and is largely free of typographical and other errors. The six main sections of the book are entitled: Introduction, Gravimetric Analysis, Volumetric Analysis, Electroanalytical Methods, Optical Methods of Analysis, and The Complete Analysis. The authors state in the preface that they aim "to minimize the rather arbitrary distinction between so-called classical and instrumental methods . . ." but have met with little success in this endeavor except to append some descriptive details of instrumental methods to the more usual material dealing with "wet" analytical chemistry. Since it contains neither new material nor a fresh approach to analytical chemistry, this lengthy book has little to recommend itself over already existing texts.

It is particularly unfortunate that such a carefully written book should so completely fail to convey anything of the changing and exciting nature of modern analytical chemistry—unfortunate because the exhaustive sections of descriptive detail are definitive and, if combined with some more recent theoretical and even speculative material, might have resulted in an outstanding textbook for analytical chemistry.

Methods of Organic Elemental Microanalysis. *Gerald Ingram. xvi + 511 pages. Reinhold Publishing Corp., 430 Park Ave., New York 22, N. Y.*

Reviewed by J. A. Kuck, American Cyanamid Co., Stamford, Conn.

The author, who is well qualified to write about quantitative microanalysis by virtue of his long association with the field, has written a good book. He has managed to include some account of recent developments as well as a substantial body of basic information. There is much of value for both specialist and beginner. Several illustrations of interesting pieces of apparatus from the author's laboratory are included in addition to a large number of instructive diagrams.

The book is well organized, and contains three main sections. Of these, Part 1 is devoted to analytical procedures for those elements that one deals with in normal practice. Here appear suitable methods for C & H, O, N, S, and halogens. There is also a brief treatment of special combustion topics such as the mechanics of the rapid C & H, carbon in F-containing compounds, and the problem of "simultaneous" determination. Part 2 of the book deals with metals and nonmetals, some of which the analyst may meet but once in a lifetime; others more often. Part 3 is entitled "microgram analysis." It is a good start at dealing with this rapidly growing field where methodology is still fluid. Unfortunately, however, in this area the author was unable to keep abreast of current developments; several new procedures appeared after his book went to press.

One specific criticism might be leveled at the book: it might be argued that it is occasionally too narrow in outlook. That is to say, some of the apparatus described is too provincial and there is a tendency to slight good foreign ideas. Take the discussion of automatic combustion on p. 13 for example. Conspicuously absent here is any mention of furnaces which embody the segmented, stationary, sample-burner instead of the traveling one, or of the general idea of achieving a flash

← Circle No. 156 on Readers' Service Card

ignition with a series of fast heating zones. Yet many analysts have abandoned the traveling burner and a number of laboratories, Russian, Czech, German, or American, report considerable success with "zone combustion" for fast operation. This manner of burning is perhaps the coming thing and may be the only way to complete automation.

In the category of minor shortcomings we feel obligated to point to the following: There is no systematic treatment of the current trend toward instrumentation in the determination of C & H, N, O, or S, although some of these methods have been out for several years. Also, in the discussion of the quartz fiber balances several other well known makes beside the excellent one described receive no mention. And again, the instructions at the top of page 293 for taking the rest point of the quartz fiber balance do not apply to the instrument in the illustration on the opposite page; with the balance shown you observe a pointer instead of matching images of the two opposite ends of the index fiber as the author directs.

The author writes in a smooth, clear and iterative style and the book is written in a bold type that is easy to read. We were not happy, however, with the publisher's stylization of the printed page; no indentation for paragraphing is a psychological annoyance for fast readers and a hazard for one attempting to follow laboratory directions. The eye sighting down the left-hand margin never sees a break in the line and paragraph separation can be recognized only by scanning the right of the page for a double spacing that may be either long or quite short. Hence the fashion of no indentation should be discouraged!

1962 Index to ASTM Standards. *234 + x pages. American Society for Testing and Materials, 1916 Race St., Philadelphia 3, Pa. Paper Cover. Single copies on request, additional copies $1.*

This publication contains two listings. In the first, the 1812 ASTM Standards and 1306 Tentatives in effect as of December 1962 are indexed under key words. In some cases Proposed Methods are indexed. The second listing contains a complete list of these standards and tentatives in numeric sequence.

Also included in the book are lists of ASTM technical committees, compilations of standards, and special technical publications with prices, and a schedule of ASTM national meetings for the next five years.

Spectrochemical Abstracts. Vol. VIII. 1958–61. *E. H. S. Van Someren, F. Lachman, and F. T. Birks. 95 pages. Hilger & Watts., Ltd., 98 St. Pancras Way, London, N. W. 1, England. 1963. Paperbound. 42s, postage 9d.*

In this volume 423 papers have been abstracted. Papers have been selected which contribute some development to the subject beyond a mere record of spectrochemical results. The abstracts are organized under the following headings: Substances Analysed, Apparatus, Methods, Source Theory, Bibliographical, and Indexes.

U. S. Government Publications

The following can be obtained from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.

Calibration of Volt-Ampere Converters. *E. S. Williams, National Bureau of Standards. Technical Note 188. 22 pages. April 1963. 20 cents.*

A voltage comparator, described in this paper, simplifies the d.c. standardization tests of volt-ampere converters. The construction of the comparator and the procedure for its use are described.

Transistorized Building Blocks for Data Instrumentation. *R. L. Hill, National Bureau of Standards. 77 pages. Technical Note 168. April 1963. 77 pages. 55 cents.*

This technical paper describes a number of modular transistorized digital circuits that can be connected together systematically so as to accept raw data from experimental equipment and transpose these data into a form suitable for input to a high-speed computer.

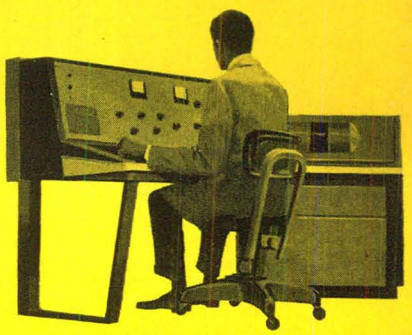
The following can be obtained from the Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C.

Methods of Microanalysis V. Oxygen Flask Combustion of Chemical Agents. *J. M. Corliss, Army Chemical Center, Md. 32 pages. April 1962. Order AD 278 160. $3.60.*

Oxygen flask combustion is followed by modified volumetric methods per-

Circle No. 157 on Readers' Service Card ⟶

A-60 NMR
APPLICATIONS
LABORATORY



A-60 NMR ANALYSES OF YOUR OWN SAMPLES AT NO COST

Whether your primary interest is advanced research, analytical chemistry or routine process monitoring and control, here is your opportunity to explore the applicability of the Varian A-60 NMR Spectrometer to your own particular chemical problems...to discover what chemical insights the A-60 can reveal about your own hydrogen-bearing samples.

The professionally staffed A-60 Applications Laboratory will perform NMR analyses for all interested parties and will provide an analysis of a maximum of three samples for each customer at no charge. Additional analyses will be performed for a nominal fee.

For additional information about this service, including detailed instructions on sample preparation, please write Dr. Donald P Hollis, A-60 Applications Laboratory, Instrument Division, Varian Associates, 611 Hansen Way, Palo Alto, California.

VARIAN associates
611 HANSEN WAY · PALO ALTO, CALIFORNIA

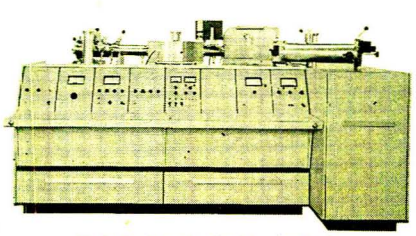
Need to spark a solid analysis?

(CEC's Mass Spectrometer 21-110 gives high resolution on solids. Liquids and gases, too.)

Whatever advance materials you plan making . . . solids, liquids or gases . . . you can analyze them *all* — at high resolution — with CEC's 21-110. Here's a uniquely versatile mass spectrometer.

That's because both ends of the 21-110 are modular. You can interchange the radio frequency spark source (as shown above) with a gas source, Knudsen Cell, or surface ionization source. And, photographic and electrometer/electron-multiplier type collectors are interchangeable as well. What's more, conversion from one type analysis to another doesn't inhibit the high performance of the basic analyzer system.

But versatility isn't the only story: the 21-110 gives you high resolution, too. This double-focusing mass spectrometer employs a resolving system much more powerful than any other instrument of its kind . . . better than 1/2500 at m/e 28 for solids, and 1/7000 for liquids and gases. Sensitivity is in the part-per-billion range.

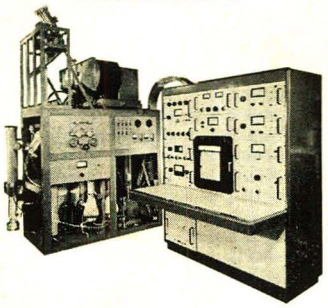


Circle No. 34 on Readers' Service Card

For complete information, call your CEC office. Or, write for Bulletin CEC 21110-X15.

CEC Analytical & Control Division
CONSOLIDATED ELECTRODYNAMICS
A Subsidiary of **Bell & Howell** • Pasadena, California

3 more reasons to measure with CEC



Studying thermo-dynamic equilibrium, heat of vaporization, or isotopic composition? You can't get better help than the kind CEC's 21-703 Mass Spectrometer offers you. This versatile sector instrument has two basic configurations: Knudsen Cell or surface ionization source. And other sources are readily installed. You can depend on its high performance, convenient operation, and total versatility. Because CEC, leader in mass spectrometry, has been building, improving, perfecting mass spectrometers for more than 25 years.

In addition to the 21-703 above, the 21-110 on opposite page, CEC offers two others: the 21-103C for qualitative analysis of complex mixtures, and the 21-130, a most versatile, medium-priced instrument. For more data, call your nearby CEC office, or write for CEC Kit 3406-X2.

CEC

Analytical & Control Division

CONSOLIDATED ELECTRODYNAMICS

A Subsidiary of Bell & Howell • Pasadena, Calif.

Circle No. 35 on Readers' Service Card

formed on absorption solutions. Halides and sulfur were analyzed on statistical numbers of samples. Recovery data, calculated to indicate the accuracy and reliability of the methods, show that the methods compare favorably with other analytical techniques.

Infrared Spectra of Some Oils, Greases, Additives, and Related Materials. *L. D. Smithson and M. S. Matta, University of Cincinnati for the U. S. Air Force. 51 pages. August 1962. Order AD 287 756. $1.25.*

Infrared spectra from 2 to 16 microns has been determined for 82 oils, greases, additives, and related materials of interest to the Air Force. "Fingerprint identification" is possible by matching unknown spectra with those in this collection.

USSR Research Reports: A Report Bibliography. *E. H. Hall, Armed Services Technical Information Agency. 330 pages. October 1962. Order AD 289 550. $5.*

This is a list of translated USSR technical literature cataloged from 1952 through 1962 and contains 2149 references covering 33 subject matter divisions. Part I refers to translated material; Part II refers to English material on USSR technical literature.

Automatic Analysis of Moist Helium in Nuclear Reactors. *D. L. West, E. I. du Pont de Nemours Co., for the U. S. Atomic Energy Commission. 15 pages. August 1962. Order DP 754. 50 cents.*

The Greenbrier Chroma-matic 112a, an automatic gas chromatograph with three chromatographic columns, is used to determine the amount of deuterium, oxygen, nitrogen, deuteromethane, carbon dioxide, and carbon present in moist helium.

Techniques for the Determination of Tritium. *A literature search. M. S. Feldman, Savannah River Laboratory for the U. S. Atomic Energy Commission. 56 pages. June 1962. Order DP-511. $1.25.*

This bibliography lists about 160 references on the physical and radiometric methods for the quantitative determination of tritium. Primary divisions are devoted to Geiger-Mueller and proportional counters, ionization chambers, scintillation counters, spectrometric techniques, and general references.

An Improved Titrimetric Method for the Precise Detemination of Uranium. *O. A. Vita, C. F. Trivisonno, and C. R. Walker, Goodyear Atomic Corp. for the U. S. Atomic Energy Commission. 10 Pages. November 1962. Order GAT-471. 50 cents.*

Basis of the described method is the addition of solid, primary standard potassium dichromate to oxidize the uranium(IV) to uranium(VI) and a slight excess. This excess is determined colorimetrically with diphenylcarbazide. The uranium content is then determined by calculation of the amount of potassium dichromate consumed in the oxidation reaction.

Identification of Microconstituents in Superalloys. *C. H. Lund and H. J. Wagner, Battelle Memorial Institute for the Dept. of Defense. 22 pages. November 1962. Order AD 289 664. 75 cents.*

The costs and skills needed to analyze for carbon, nitrogen, boron, zirconium, and other microconstituents in superalloys are discussed in this memo. Methods covered include optical microscopic examination, electron transmission, x-ray diffraction, and electron beam microprobe techniques.

Nukleonika. *Polish Academy of Sciences, 1960. Translated 1962. 760 pages. Order 62-11074. $7.75.*

Twelve issues of "Nukleonika," a journal devoted to nuclear energy, were translated and printed as a single volume. Included are about 100 articles. Subjects included of special interest to analytical chemists are: determination of radioactive iodine in rainwater, separation and determination of uranium, gamma ray dosage as measured by film, strontium-90 level in milk and bones of human beings and cattle, and the first Polish symposium on the use of radioisotopes.

Rapid Methods to Estimate the Molecular Weight Distributions of Polymers. *R. G. Griskey and S. Y. Fok, University of Cincinnati, for the U. S. Air Force. 48 pages. December 1962. Order AD 294 355. $1.25.*

A comparative study of three rapid inexpensive methods for determination of polymer molecular weight distribution carried out on 66 nylon samples is described. Of the three methods: cumulative precipitation fractionation, swelling, and turbidimetric titration, the latter was found to be the most rapid and precise.

Below, left to right: GERALD NEVILLE — Sales Product Manager, Chromatography • FREDERICH BRECH — Vice President, Research • RICHARD JARRELL — President, Jarrell-Ash • JOHN UDALOY — Vice President, Operations • WADE JONES — Marketing Consultant • ALLEN ANDREWS — President, Andrews Associates, Advertising

How Analytical Chemistry Helps Jarrell-Ash Sales Exceed $5,500,000

"During 1962, over twenty-five percent of our space advertising budget was allocated to Analytical Chemistry magazine. And for good reasons: not only does Analytical Chemistry cover the research market best, but it produces the largest number of bona fide sales leads. Of over $5,500,000 in sales last year, a healthy percentage resulted from contacts gained through our ads in Analytical Chemistry.

"To date we have received dozens of unsolicited letters from satisfied users of Jarrell-Ash

THORNTON LABORATORIES, INC.
ANALYTICAL AND CONSULTING CHEMISTS
1145 EAST CASS STREET
TAMPA 1, FLORIDA

R. P. THORNTON, PRES.
C. C. THORNTON, SEC-TREAS.

TELEPHONE 2-2641
P. O. BOX 2880

December 27, 1962

Mr. G. J. Neville, Manager
Chromatography Division
Jarrell-Ash Company
26 Farwell Street
Newtonville 60, Mass.

Dear Charlie:

We have for sometime been involved in the analysis of insecticide residues on fresh vegetables, citrus, and citrus products. Up to now we have had to employ wet chemical analyses, which, as you probably know, are tedious, time consuming, and leave much to be desired.

In order to provide faster and better service to our clients, we have been investigating the various commercially available gas chromatographic units.

Some time ago, I had talked with Mr. John Schuch and Gene Roberts of your Atlanta office about spectrographic equipment. I had no idea that Jarrell-Ash manufactured gas chromatographic equipment until I read your advertisement in the November issue of Analytical Chemistry. This was a pleasant surprise, as Gene Roberts had been very kind and helpful in the past. I phoned Gene the same day, requested more detailed information, and as you know, within one week we had purchased a Model 700.

After the thorough short course in gas chromatography held at your office in Newtonville, I am anxiously awaiting delivery of our unit.

Best wishes for the coming year, and give my regards to that yankee-Irishman, Larry O'Brien.

Sincerely,

THORNTON LABORATORIES, INC.

By James A. North

James A. North
Laboratory Director

JAN/jc

HONEYWELL

Minneapolis-Honeywell Regulator Company

Military Products Group

AERONAUTICAL DIVISION • 2600 RIDGWAY ROAD • MINNEAPOLIS 40, MINNESOTA • STERLING 1-8011

IN REPLY, REFER TO DEPT. 630

April 12, 1963

Mr. G. J. Neville, Manager
Chrom. Division
Jarrell-Ash Company
26 Farwell Street
Newtonville 60, Massachusetts

Dear Mr. Neville:

For some time the Materials Laboratory at Minneapolis-Honeywell Aeronautical Division has been interested in the use of materials for space systems. One phase of this program involves the study of atmospheric contamination from non-metallic materials. We felt this study required the use of gas chromatographic techniques.

Being unfamilar with all the manufacturers of gas chromatographs, I made a brief survey of the recent issues of Analytical Chemistry for such information. From this survey I obtained a list of several possible companies, including Jarrell-Ash Co. We were aware of the Jarrell-Ash capability in the field of spectrographic equipment, but we had no idea that they made gas chromatographic equipment.

After seeing the Jarrell Ash Model 700, and talking with your representative, Mr. Golay, we decided on the purchase of a Model 700 for our work.

Shortly after my training at your office in Newtonville, we received our instrument and placed it in immediate use. The instrument is at the present in constant use around the clock.

The instrument has given us valuable information and shows great promise for the future.

Yours very truly,

Norman T. Gonnella

Norman T. Gonnella
Associate Chemist
Materials Engineering

NTG:cch

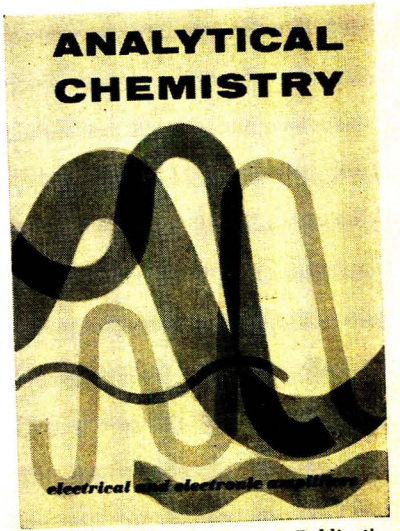
instruments . . . customers who might not have learned about us without Analytical Chemistry. Above are two examples. Is it any wonder that we are convinced that regular advertising in Analytical Chemistry gets our message across to the most prospects, in the most economical manner?"

Sincerely,

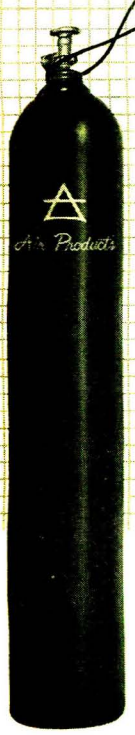
R. F. Jarrell

R. F. JARRELL, *President*
Jarrell-Ash Company

Jarrell Ash



An American Chemical Society Publication
Advertising Management:
REINHOLD PUBLISHING CORP.
430 Park Ave., New York 22, N.Y.



CERTIFIED

Calibration Gases

Certified Analysis Supplied with each Cylinder

The industry's broadest line of span, zero, and multi-component gas mixtures of extremely high purity are now available from Air Products and Chemicals, Inc. To provide maximum quality control and superior analysis, each calibration gas mixture is prepared to order using all appropriate compressibility (Z) factors, and is thermally blended prior to analysis.

Air Products precision-blended mixtures have the following accuracy of analysis:

Percent of Component in Standard	Analysis Accuracy
10-50%	±0.5%
5-10%	±0.2%
less than 5%	5% of component value

Air Products has been producing calibration gases for over five years for intracompany consumption. Advanced R & D programs required extremely accurate analyses of gas mixtures . . . difficult to purchase on a commercial basis. This line of Air Products certified precision-blended mixtures is now available commercially for your calibration requirements.

UNANALYZED GAS MIXTURES
Unanalyzed gas mixtures for controlled atmospheres and other less critical applications are also available from Air Products.

For information on Air Products individually blended calibration gases for your specialty programs, please write Specialty Gas Department.

Air Products and Chemicals INC.
ALLENTOWN, PENNSYLVANIA

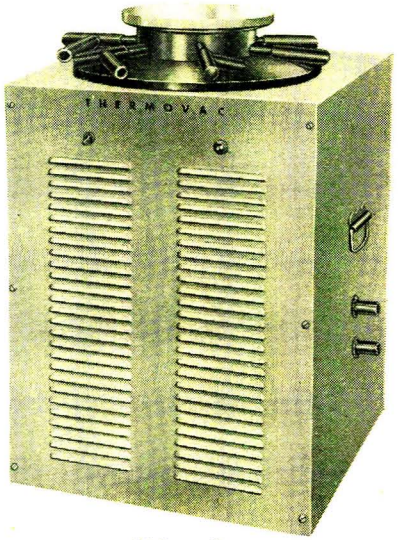
NEW DIMENSIONS IN GAS TECHNOLOGY

Circle No. 17 on Readers' Service Card

you're looking at the only

MECHANICALLY REFRIGERATED PORTABLE FREEZE-DRYER

on the market today...



it's also the lowest priced!

Just look at these startling features:

The condenser chamber is different

- It's easily accessible and visible during the entire process
- In just 5 minutes defrosting and cleaning can take place

The unit is complete

- Bulk chamber freeze drying and manifold freeze drying can be done at the same time
- Inside of drum can be fitted with removable tray rack with controlled heating

Write for further information and comprehensive specification sheet

A complete line of Mechanically Refrigerated Freeze Dryers from $550.
PAT. PEND.

Dept. AC-7
THERMOVAC INDUSTRIES CORP.
654 Henry Street, Brooklyn 31, New York

Circle No. 89 on Readers' Service Card

BEST BUY: MODEL 139

NEW MODEL 139 ULTRAVIOLET-VISIBLE SPECTROPHOTOMETER —BY ANY STANDARD GIVES MORE PERFORMANCE AT LESS COST

At no extra cost [1] Full coverage of ultraviolet and visible ranges. [2] Transistorized line-operated power supply. [3] High dispersion diffraction grating optics. [4] Direct reading in transmittance and absorbance. [5] Precision scale expansion. [6] Linear wavelength output. Normal operating range is 205 to 800 millimicrons for transmittance measurement.

Optional All attachments for ultraviolet and visible spectral analysis, plus such *exclusive* attachments as atomic absorption and emission photometry.

Pooling two decades of experience in spectroscopic equipment, Perkin-Elmer and Hitachi Limited have joined to create this modern spectrophotometer.

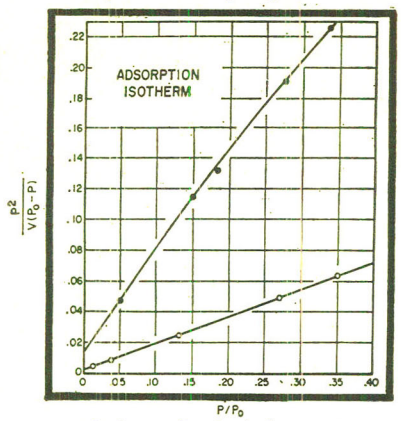
We believe that the result of this joint effort is the finest instrument of its type available anywhere in the world. Price: $2300 delivered to your laboratory anywhere in the United States.

Please write for a complete brochure and price list on this new instrument to Instrument Division, Perkin-Elmer Corporation, 751 Main Avenue, Norwalk, Conn.

Circle No. 125 on Readers' Service Card

ABSOLUTE SURFACE AREA MEASUREMENTS

by **BET** gas adsorption techniques on materials with surface areas as low as 0.1 square meter per gram



reported results include a plot of the adsorption isotherm

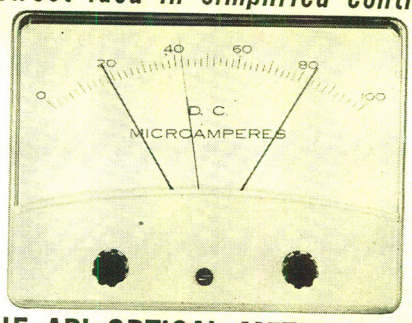
For complete details write to

ISOTOPES, INC.

123 Woodland Avenue, Westwood, New Jersey

Circle No. 54 on Readers' Service Card

Newest idea in simplified control:



THE API OPTICAL METER-RELAY

With the API optical meter-relay, you can get simplified control of any electrically measurable variable. Operating on a beam of light channeled through a fiber-optic light circuit, this new kind of meter-relay will respond to signal changes as small as 0.0125 microamps or millivolts—without amplification. The fiber-optic light system eliminates contacts, makes possible continuous indication, through set-point and beyond, without affecting meter reading. Other features are noted below; for full specifications and prices, write for Bulletin 33.

- Full-scale sensitivity to 5 microamps or millivolts.
- Standard accuracy: ±2% DC, ±3% AC.
- Super-Calibrated accuracy: to ±0.5%.
- One or two set-points with fail-safe circuitry.
- Three forms of control: on/off or limit, time-proportioning, and modulating with an SCR.
- Seven sizes from 3¼" to 6" in the new API Stylist/Panelist Series.
- Taut-band and pivot-and-jewel models.
- Also available in ten pyrometer ranges.

api ASSEMBLY PRODUCTS, INC. • CHESTERLAND 82, OHIO

SA2814

Circle No. 21 on Readers' Service Card

SNAP-IN A STERILE PIPETTE!

Now . . . rapid insertion and removal of serological pipettes with

• SPEED • EASE • ACCURACY

in a quick, simple

ONE HAND MOVEMENT

Piggy-Back Pipetter

Model PB10

SOME SPECIAL USES:

- With Plugged Pipettes
- Transfer of Infectious Liquids or Radio-Isotopes
- Serial Dilution, as in Serum or Virus Titrations
- Pipetting of Acids • Routine Pipetting
- Large Scale Titrations

NOW YOU CAN ELIMINATE DANGEROUS MOUTH PIPETTING WHILE UTILIZING GRADUATED AND/OR UNGRADUATED PIPETTES!

Piggy-Back Pipetter is available in both a 2 cc and 10 cc size. Order today!

AT YOUR LABORATORY SUPPLY DEALER

another quality product of

Scientific Industries INC

Dept. AC763, 220-05 97th Avenue • Queens Village, N.Y.

Circle No. 11 on Readers' Service Card

ἀπιεζον* = APIEZON®

APIEZON = *The Finest Oils, Waxes and Greases for High Vacuum Work*

Preferred by leading scientists for high vacuum equipment and systems where low pressure process is used at one or more stages.

- Vacuum coating units and vacuum furnaces for degassing of metals
- Metallurgical vacuum distillation of light metals
- Lyophilic drying of penicillin, vitamins and other substances
- Preparation of vitamin concentrates
- Dehydrated food
- Blood serum drying
- The electron microscope

As exclusive distributor in the United States, we offer immediate delivery from stock on the complete range of Apiezon oils and compounds.

For details on applications, working characteristics and list prices, write for Bulletin 43-AC.

*from the Greek meaning "without pressure"

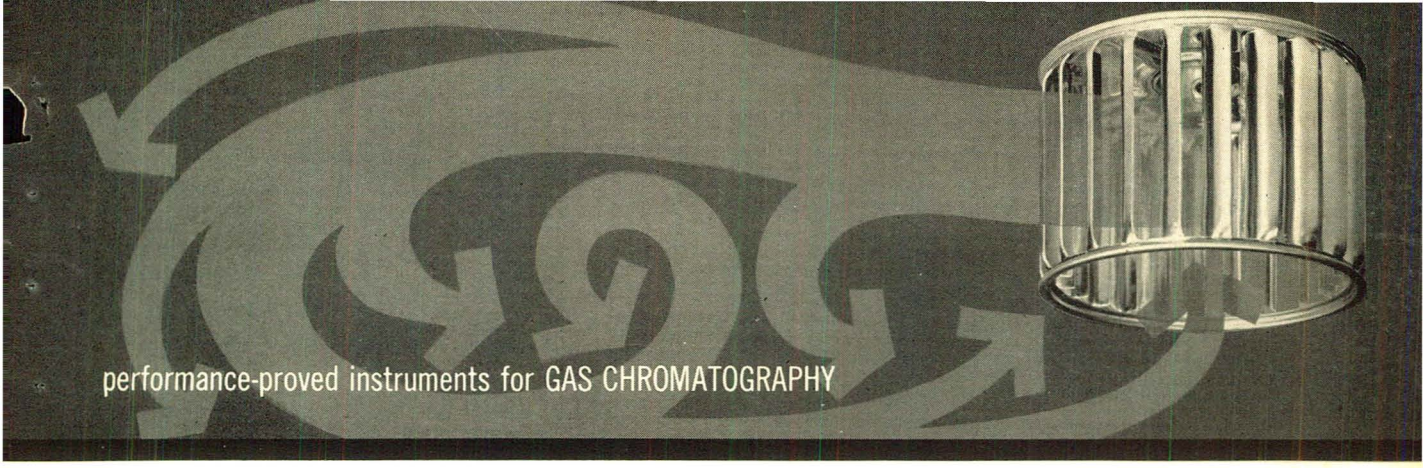
B12

JAMES G. BIDDLE CO.

Electrical Testing and Speed Measuring Instruments

PLYMOUTH MEETING, PENNSYLVANIA • Area Code 215/Mitchell 6-9200

Circle No. 27 on Readers' Service Card



TWO NEW PERKIN-ELMER® GAS CHROMATOGRAPHS— WITH DYNATHERMAL FEATURE— AS LOW AS $1500

Both have it: the new "dynathermal" concept of programmed-temperature control that circulates air *five times a second*, giving you faster heating and cooling of columns — elimination of temperature gradients — and precise, simple temperature programming.

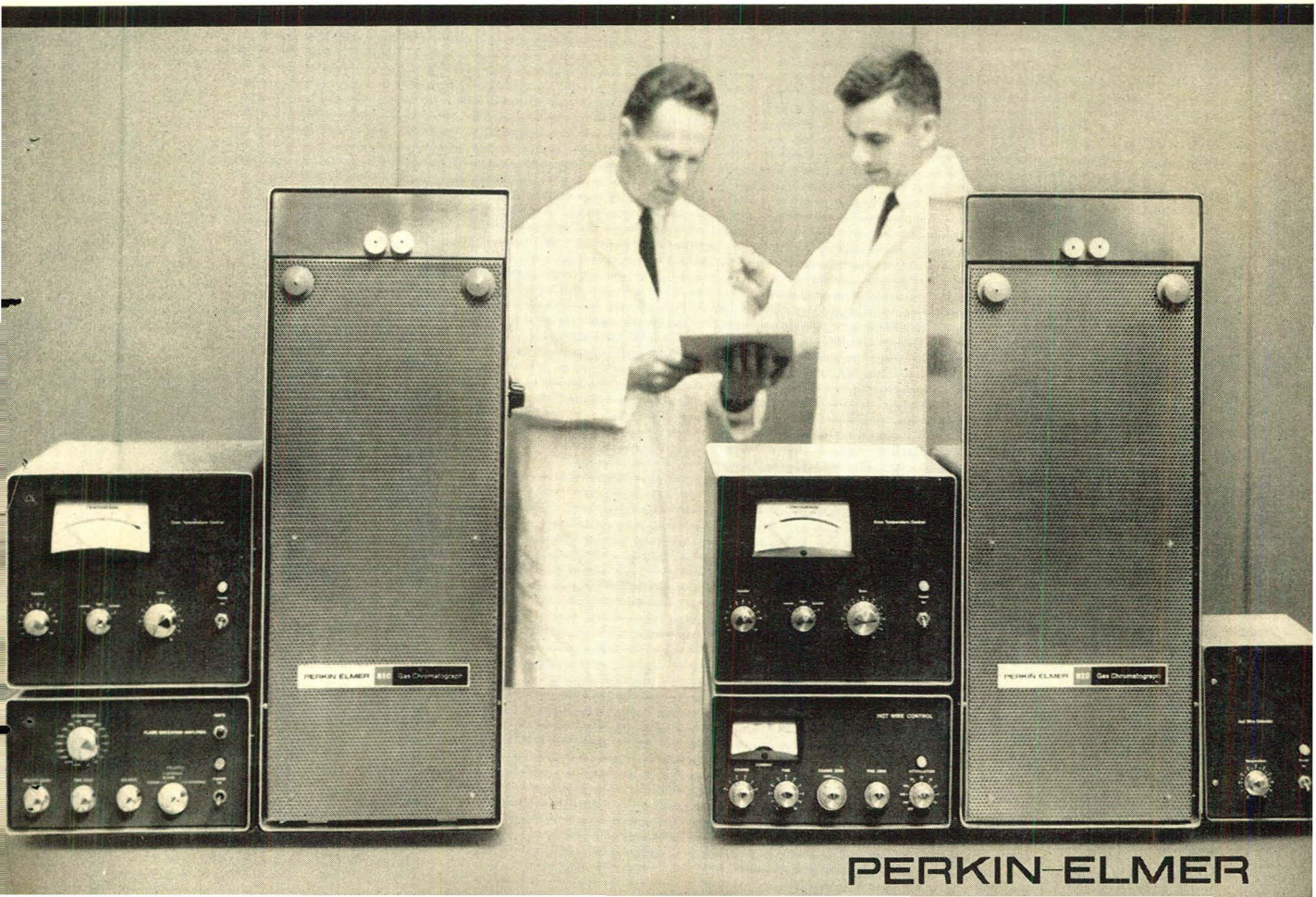
Both are dual-column instruments for baseline stability through automatic compensation of substrate bleeding in programmed analysis. Both have dual sample injectors to permit independent use of two different column materials when compensation is not needed. Both can perform temperature-programmed or isothermal analyses up to 350°C. And both cost far less than comparable instruments with similar capabilities.

Model 810: a differential flame detector instrument. Independent control of injection block and column oven temperatures. Uses packed and capillary columns. Costs $1,695.00. Delivery: now.

Model 820: equipped with a four-filament hot wire detector. Independent control of injection block, oven and detector temperatures. Operates with 1/8" packed columns up to 60 feet in length, or 1/4" packed columns up to 30 feet long. Provision for external sample collection. Price: $1,495.00. Delivery: now.

For details on these two low-cost instruments, and other gas chromatography products, write to Instrument Division, Perkin-Elmer Corporation, 751 Main Avenue, Norwalk, Connecticut.

Circle No. 130 on Readers' Service Card



A modern research instrument with built-in Koehler illumination for critical microscopic investigation

In less than one year since its introduction, the Nikon Series S has become one of the most talked about microscopes in the field. It has attracted wide and favorable attention for its mechanical ruggedness, its smoothly responsive controls, its seemingly unlimited versatility, and its almost incredible quality of optics.

The new Series S-Ke offers even more of special interest to the critical microscopist. Except for the base, the S-Ke employs the same construction as the Series S and accepts the same interchangeable eyepiece tubes and stages. The base is larger, and contains the light source and optics of the Koehler illuminator.

Koehler illumination is undoubtedly the most efficient known to optical microscopy, and is virtually prerequisite in photomicrography. Its principle advantage is that it makes the light source and microscope a compatible optical system. All available light is concentrated in the area under investigation. There is no glare or halo. Details, usually obscured by these conditions emerge with new clarity and definition.

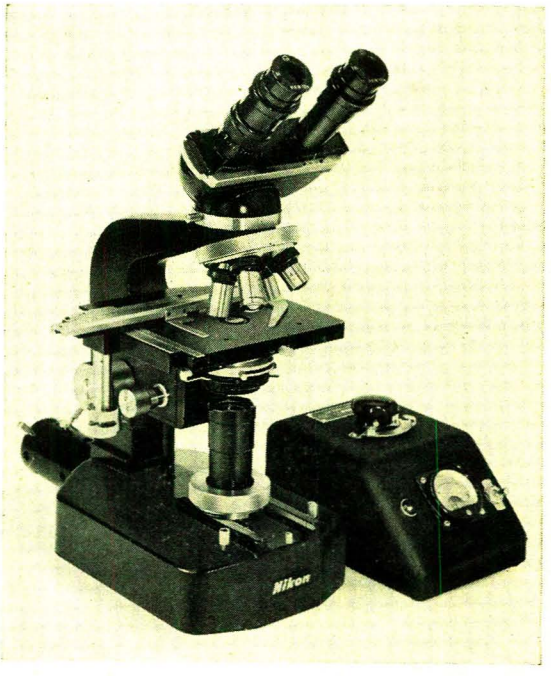
To attempt Koehler illumination with conventional mirror and external lamps is a difficult, time-consuming procedure. With the model S-Ke it is utterly simple and virtually automatic. A sliding, centerable optical system permits the user to enjoy its benefits over the entire magnification range of the microscope.

The S-Ke is supplied with a step-down transformer which provides the correct lamp voltage. This transformer has a built-in voltmeter and a variable intensity control with adjustable high- and low-position 'stops' so that any selected degree of brightness can be repeated.

Optional accessories: Interference-Phase, Phase-Contrast, and Polarizing attachments, Projection Head, Macro-Photo and Photomicrographic equipment.

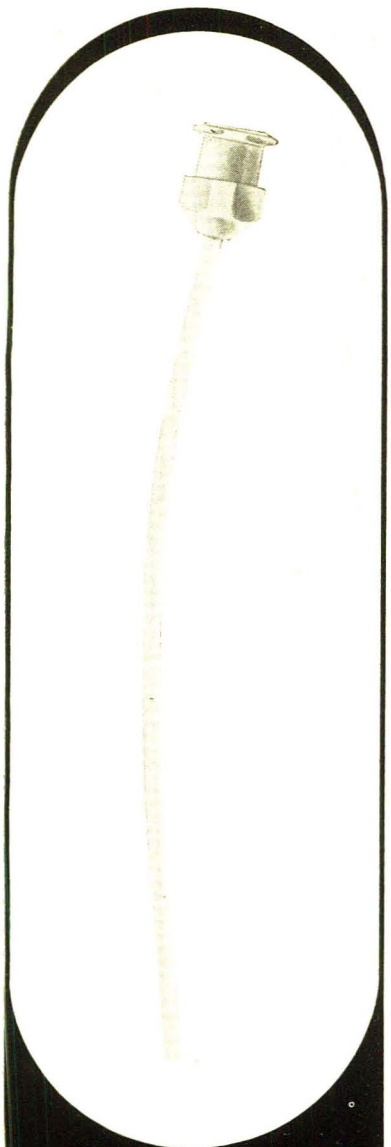
For complete details, write to Dept. AC-7.

Nikon Series S-Ke



NIKON INCORPORATED Instrument Division • 111 Fifth Avenue, New York 3, N. Y. • Subsidiary of Ehrenreich Photo-Optical Industries, Inc.

Circle No. 128 on Readers' Service Card



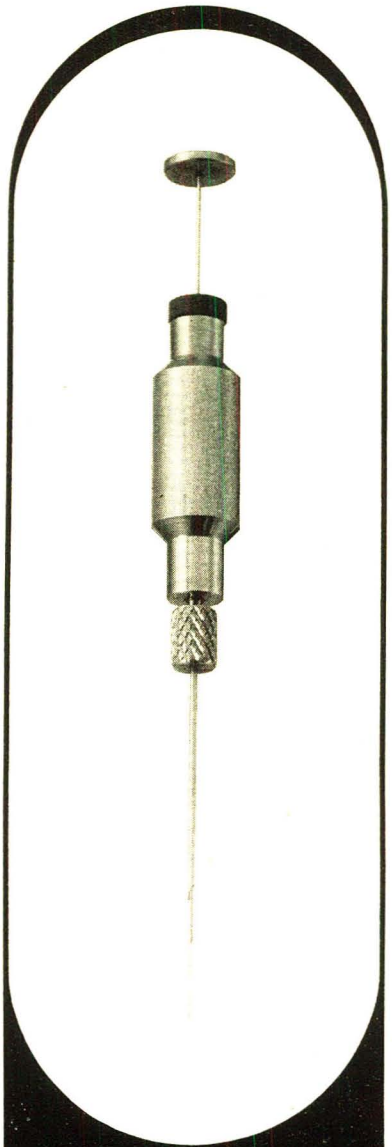
new teflon needle eliminates risk of contamination

You can eliminate risk of contamination or leakage when syringe pipetting high corrosive materials. Entirely inert Teflon tubing and Kel-F hub. Flexible, 8-22 gage, 1″- to 100′, leak tight to 100 psi. Write for prices.

Write for new Hamilton catalog and price list.

HAMILTON

HAMILTON COMPANY, INC.
P. O. Box 307B, Whittier, California
Circle No. 158 on Readers' Service Card



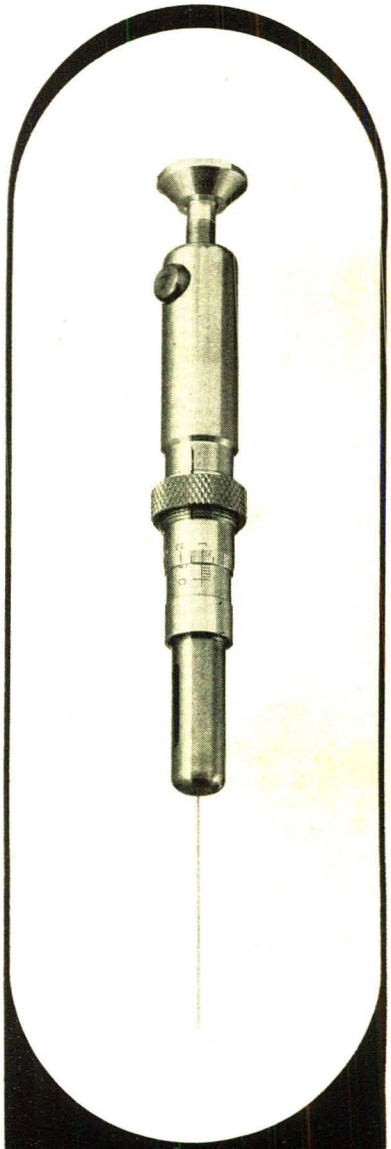
a new approach to solid sampling for chromatography

You simply place the dissolved or melted sample on the tongue of the plunger, withdraw into septum penetrating needle, insert, and depress. Easy to operate and clean. SS60 . . . $15.00 FOB.

Write for new Hamilton catalog and price list.

HAMILTON

HAMILTON COMPANY, INC.
P. O. Box 307B, Whittier, California
Circle No. 159 on Readers' Service Card



at push of button . . . reproducibility at a constant rate

Now you can deliver like quantities of similar liquids in like times . . . at the push of a button. Volume adjustable in one microliter units. Fast, accurate (±1%) easy to use. CR700 . . . $75.00—specify 1-20 ul or 10-200 ul.

Write for new Hamilton catalog and price list.

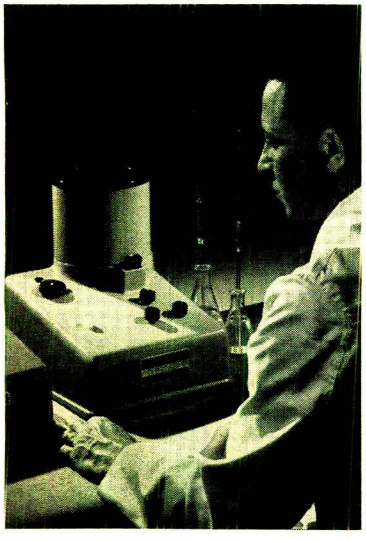
HAMILTON

HAMILTON COMPANY, INC.
P. O. Box 307B, Whittier, California
Circle No. 160 on Readers' Service Card

Chemical instrumentation by . . . COLEMAN

Coleman Flame Photometer speeds routine analysis of alkali metals

New speed and convenience in analysis of alkali metals using the simple, dependable Coleman Flame Photometer! Sodium, potassium, calcium, lithium, magnesium . . . up to 1000 analyses per day—completed by a single operator.

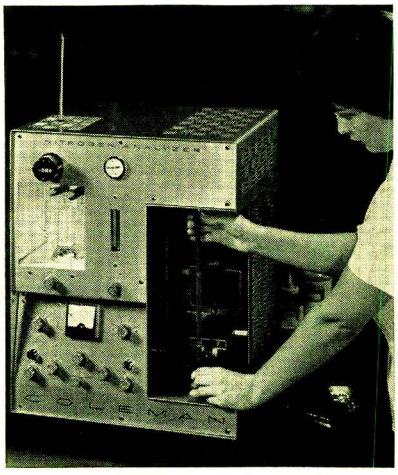


These rates are achieved with no loss of analytical accuracy—the Coleman Flame Photometer maintains routine accuracy within 1% constituent concentration for most analytical procedures.

Already dominating the field of clinical flame analysis, the instrument is daily proving its versatility in analysis of industrial materials—pharmaceuticals, fertilizer, soils, foods and many others.

The Coleman Flame Photometer needs no acetylene tanks, water connections, compressors, drains or special venting. It is as safe as an ordinary bunsen burner.

Write for bulletin AB-242 or ask your apparatus dealer for a demonstration.



Proven in automated nitrogen analysis

Now in use in hundreds of laboratories, the automated Coleman Nitrogen Analyzer is providing rapid and exacting results for an almost unlimited range of materials.

From foods to fertilizers, from plastics to petroleum derivatives, from biological materials to organic intermediates—the instrument is supplementing or replacing both the manual Dumas and the Kjeldahl methods.

Operation of the instrument is simple. The operator is required merely to weigh and install the sample, to actuate the instrument, and 8 minutes later to read and record nitrogen volume from a digital counter.

Thus, an analyst without extensive training in microchemistry can produce excellent results in both routine investigations and in research.

Find out how the Coleman Nitrogen Analyzer can benefit your laboratory — ask for Bulletin AB-258A and a demonstration.

Coleman Photofluorometer®

. . . the *working* tool for fluorescence analysis

The Coleman Photofluorometer is the practical tool for routine fluorescence analysis in the laboratory.

Simple and easy to use, it has proved its value over years of use in clinical and control laboratories having a large number of routine analyses.

Its sensitivity range covers all practical applications — quinines, quinoline, vitamins, porphyrins, steroids, metal complexes, etc. The instrument permits quantitative determination of fluorophors (quinine, for example) down to 3 parts in 10 billion.

The Photofluorometer achieves its sensitivity without photomultipliers or other elaborate, trouble-prone circuits. This forthright simplicity encompasses all aspects of the instrument's operation:

—samples insert directly into the instrument's optical system,

—readings are taken directly from the meter scale,

—a simple lens-and-aperture system prevents decay of sensitive substances by allowing exposure to irradiation only during the actual reading.

Priced at $480, the Coleman Photofluorometer provides an economical approach to routine fluorescence in the working laboratory.

Write for Bulletin AB-245A

COLEMAN INSTRUMENTS, INC., MAYWOOD, ILLINOIS

Circle No. 165 on Readers' Service Card

Circle No. 166 on Readers' Service Card

Circle No. 167 on Readers' Service Card

COLEMAN

Coleman pH Instrumentation

Three pH meters and complete selection of electrodes meet full range of laboratory pH measurement requirements

Low-cost Metrion pH Meter is a line-operated instrument featuring a basic simplicity of design and operation which make it ideal for general-purpose laboratory use. With measurement accuracy to 0.05 pH, the Metr*ion* provides a level of performance far out of proportion to its moderate cost.

Features:

- Stabilized against line voltage fluctuations over 95-125 volt range.
- Easy-to-read duplex scales cover 0-14 pH range.
- Calibration control provides compensation for temperature effect.
- Simplified operation—"push-to-read" pH control.

Cost—only $139.00.

Increased versatility, Metrion II pH Meter offers the same simplicity of design and operation as the basic Metr*ion*. It also features two additional circuits for increasing versatility of the instrument:

...a true temperature-compensating circuit with a control knob conveniently located on instrument's front panel.

...an output jack for use with an automatic titrator such as the Coleman Titr*ion*.

Addition of these two circuits makes the Metr*ion* II valuable for an increased variety of specialized laboratory applications with only a small price increase.

Cost—$160.00.

Fully-versatile Companion pH Meter is a zero-restoring instrument ideal for a broad range of laboratory applications. It provides pH measurement over the 0-14 pH range with a routine accuracy of 0.05 pH and reproducibility within 0.02 pH. The instrument also may be used for millivolt measurements over a 1400 mv span.

Features:

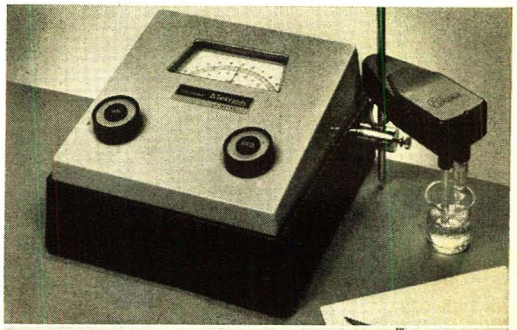
- Zero-restoring circuit for drift-free operation.
- May be used with recorder, automatic titrator, and automatic temperature compensator accessory.
- Simplified control system for easy operation.
- Manual Temperature Compensator control permits accurate measurement over 0-100° C. range.

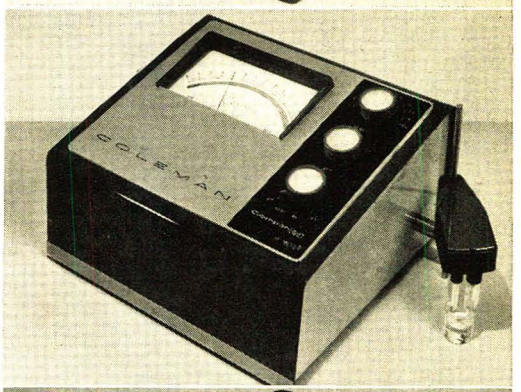
Cost—$300.00

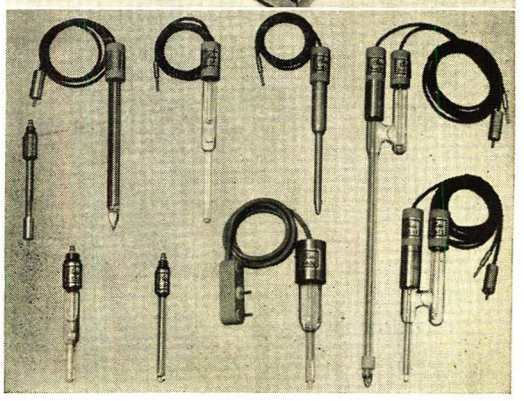
Complete selection of electrodes—Coleman electrodes cover virtually every practical application of laboratory pH measurement. They are usable with any Coleman pH meter or other instrument of modern manufacture.

- Glass electrodes, shielded against stray electrical fields, permit precise measurement over widely-varying conditions of temperature, viscosity, alkalinity.
- Reference electrodes are available in standard calomel or non-mercurous types.
- Metallic electrodes for electometric titrations.
- Special-purpose electrodes for unusual applications.

Coleman electrodes are priced about one-third less than the closest competitive designs.







Write for full details

COLEMAN INSTRUMENTS, INC., MAYWOOD, ILLINOIS

Circle No. 110 on Readers' Service Card

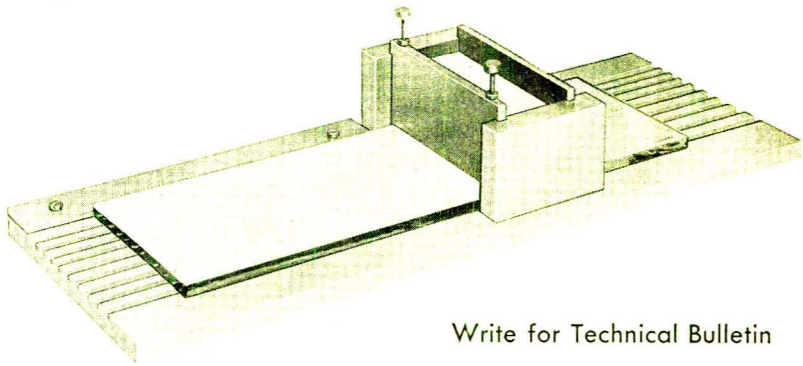
THIN LAYER CHROMATOGRAPHY APPARATUS

The KENSCO Apparatus is Simple to Use, Reliable, and Inexpensive.

Advantages of Thin-layer Chromatography

Simplicity of technique.
Rapid separations on a micro scale of compounds such as lipids, alkaloids, steroids, etc.
High sensitivity with sharper separations.
Applicable to a wide range of different compounds.
Corrosive spray agents may be safety applied.
Experiments with different solvent systems may serve as a guide for application to columns on a preparative scale.

Bibliography on request.



Write for Technical Bulletin

KENSINGTON SCIENTIFIC CORPORATION
1717 FIFTH STREET BERKELEY 10, CALIF.

Circle No. 109 on Readers' Service Card

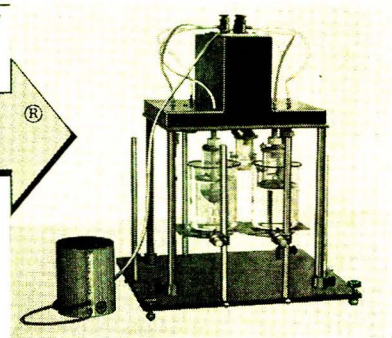
ROUTINE DIALYSIS
ANALYTICAL STUDIES
CONTINUOUS FLOW DIALYSIS
PREPARATIVE DIALYSIS
THIN-LAYER DIALYSIS
MICRO DIALYSIS
PRESSURE DIALYSIS
CRYODIALYSIS

Pat. No. 2,985,587

N.I.L.—HOCH
First Universal High-Precision Dialyzer

DIALYSTAT®

For the recovery of dialyzable salts, the removal or recovery of acids, and the separation of colloidal material from other solutes.



FEATURES

- Shearing motion agitates both sample and buffer to accelerate dialysis rate.
- Samples dialyzed against individual buffers or multiple samples against a single buffer.
- Portions of sample and buffer removable without disassembly of cell.
- Tap water or circulating cooler easily attached for constant temperature.
- Continuous dialysis carried out with temperature control and constant rates of flow of solutions and buffer.
- Rapid concentration of samples achieved by cryodialysis or heating.
- Cells may be autoclaved or chemically sterilized.
- Saves space, time, and drudgery.

APPLICATIONS OF THE DIALYSTAT ANALYTICAL CELL*

1. The measurement of small differences in size, shape, and charge of large molecular substances.
2. Makes possible the detection of interaction between proteins, or proteins and haptens, by escape rate measurement.
3. Microtechniques for work with volumes between 0.03 and 0.5 ml.
4. The detection of heterogeneity by dialysis.
5. The characterization of membranes by use of known mixtures.

NIL

National Instrument Laboratories, Inc.
12300 PARKLAWN DRIVE, ROCKVILLE, MARYLAND
IN METROPOLITAN WASHINGTON, D. C.
TELEPHONE: 933-1144

Bulletin 4-5000 for complete description

*Dialysis as an Analytical Tool, Hans Hoch and Ray C. Williams; Analytical Chemistry, Vol. 30, 1258-62, 1958 (copy obtainable on request from N.I.L.).

Circle No. 14 on Readers' Service Card

the EDITOR'S column

L.T. Hallett, Editor

THE ACCELERATING GROWTH of science and technology has created real problems in the transfer of scientific information. The President's Science Advisory Committee's Panel on Science Information has been studying this problem and has made some recommendations for improvement in the communication of science and engineering information. It is suggested that the scientific community must devote a larger share of its time and resources to the discriminating management of the technical record. To do otherwise will lead to fragmented and ineffective science and technology.

The first part of this study considers in some detail the nature of the information problem. Of special interest are the complications caused by mission-oriented research programs *vs.* the traditional disciplinary fields. For instance, the space program both generates and needs information related to physiology, chemistry, physics, etc. The switching of information in this case requires some duplication, even the original presentation often results in duplication.

In addition to recognizing and making some specific recommendations in regard to the responsibility of Federal Government Agencies, there are many suggestions made to the "technical community."

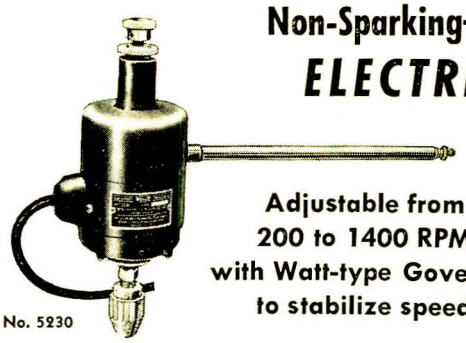
The technical community must instruct scientists and engineers in the techniques of handling information. Such instruction should be an integral part of the university science curriculum.

The committee's report greatly emphasizes the individual working scientist's share of the burden of the information transfer process. Beginning with the basic assumption that the handling of technical infor-

MAXIMUM SAFETY PROVIDED WITH THE WELCH

Non-Sparking—Speed Controlled

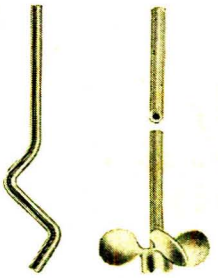
ELECTRIC STIRRER



No. 5230

Adjustable from 200 to 1400 RPM with Watt-type Governor to stabilize speed

Adjustable Chuck for stirring rods up to ¼-inch diameter



No. 5230M. No. 5230R.

An Ideal General Purpose Stirrer

INDUCTION TYPE MOTOR

No brushes or commutator

• QUIET OPERATION

No. 5230. ELECTRIC STIRRER. For 115 volts 50/60 cycles A.C. Each $58.50

No. 5230A. ELECTRIC STIRRER. With stepdown transformer, for 230 volts 50/60 cycles A.C. Each $64.50

STIRRING RODS

No. 5230G. GLASS STIRRING ROD. Double V form, for No. 5230 or No. 5230A Stirrer. Each $0.90

No. 5230M. MONEL STIRRING ROD. Double-V form, for No. 5230 or No. 5230A Stirrer. Each $2.50

No. 5230R. POLYETHYLENE STIRRING ROD. Propeller-blade form, for No. 5230 or No. 5230A Stirrer. Each $1.80

THE WELCH SCIENTIFIC COMPANY

ESTABLISHED 1880

1515 Sedgwick St., Dept. A-1, CHICAGO 10, ILL., U.S.A.

Manufacturers of Scientific Instruments and Laboratory Apparatus

hofman LABORATORIES, INC.

THE ONLY COMPLETE LINE IN CRYOGENIC EQUIPMENT

LIQUID NITROGEN/OXYGEN CONTAINERS 5 to 200 LITER CAPACITY

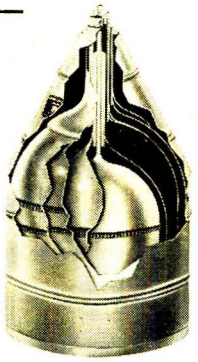
High Efficiency, designed for Storage and Transportation of Nitrogen, Oxygen, Argon and air.

STAINLESS STEEL DEWAR FLASKS

Especially designed for Dipping, Pouring and Utilization in Laboratories. Available in various depths and dimensions.

LIQUID HELIUM/HYDROGEN CONTAINERS FOUR WALL HIGH

Efficiency designed for storage and transportation of Liquid Helium, Hydrogen, and Neon. Available from 10 to 100 Liter capacities.



For further information on the above, ask for descriptive bulletins and price lists.

Hofman Laboratories, Inc. 225 Parkhurst Street Newark, N.J.

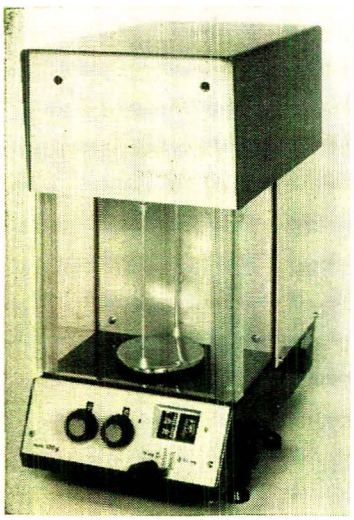
West Coast Facility

Paul Chemical Co. 6750 Caballero Blvd. Buena Park, Calif.

Circle No. 15 on Readers' Service Card

MECHANICAL TARING

greatest breakthrough in laboratory weighing since the single-pan balance!



Model 2623

With beaker on pan, all systems read ZERO. Now you proceed with the weighing.

The new Model 2623 analytical balance is another FIRST from SARTORIUS.

With this instrument, built-in weights are used for mechanical taring up to capacity—which is 100 grams. In other words, any vessel (beaker, flask, tube, etc.), or other supporting medium for the sample—even papers weighing only a few milligrams—can be tared to the fourth decimal place (0.1 mg). And the actual weighing of a sample proceeds from a scale and counter system which reads ZERO.

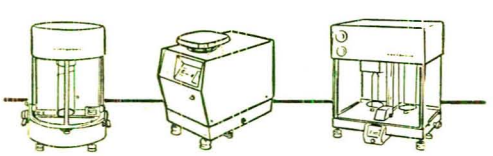
When weighing-out solutions or powders, the procedure can be reversed so that the balance is pre-loaded with any desired amount. Again, the weighing proceeds without regard for the container.

Calculations are eliminated, the possibility of reading errors is reduced and the entire procedure is completed in just seconds; if another vessel is needed, one can also readjust to a new tare value in seconds.

For users who really need taring facilities, this system is much faster and much simpler than any taring technique which involves a manual adjustment of weights. With the 2623, **you dial-in the tare—just as you dial-in the weight.**

For complete descriptive literature, please contact:

sartorius



BRINKMANN INSTRUMENTS, INC.
115 Cutter Mill Road, Great Neck, N. Y.
PHILADELPHIA · CLEVELAND · HOUSTON · MIAMI · MENLO PARK, CAL. · ST. LOUIS

Circle No. 106 on Readers' Service Card

mation is a worthy and integral part of science, it follows that the individual contributor must assist the professional documentalist. The following suggestions apply to authors of technical papers:

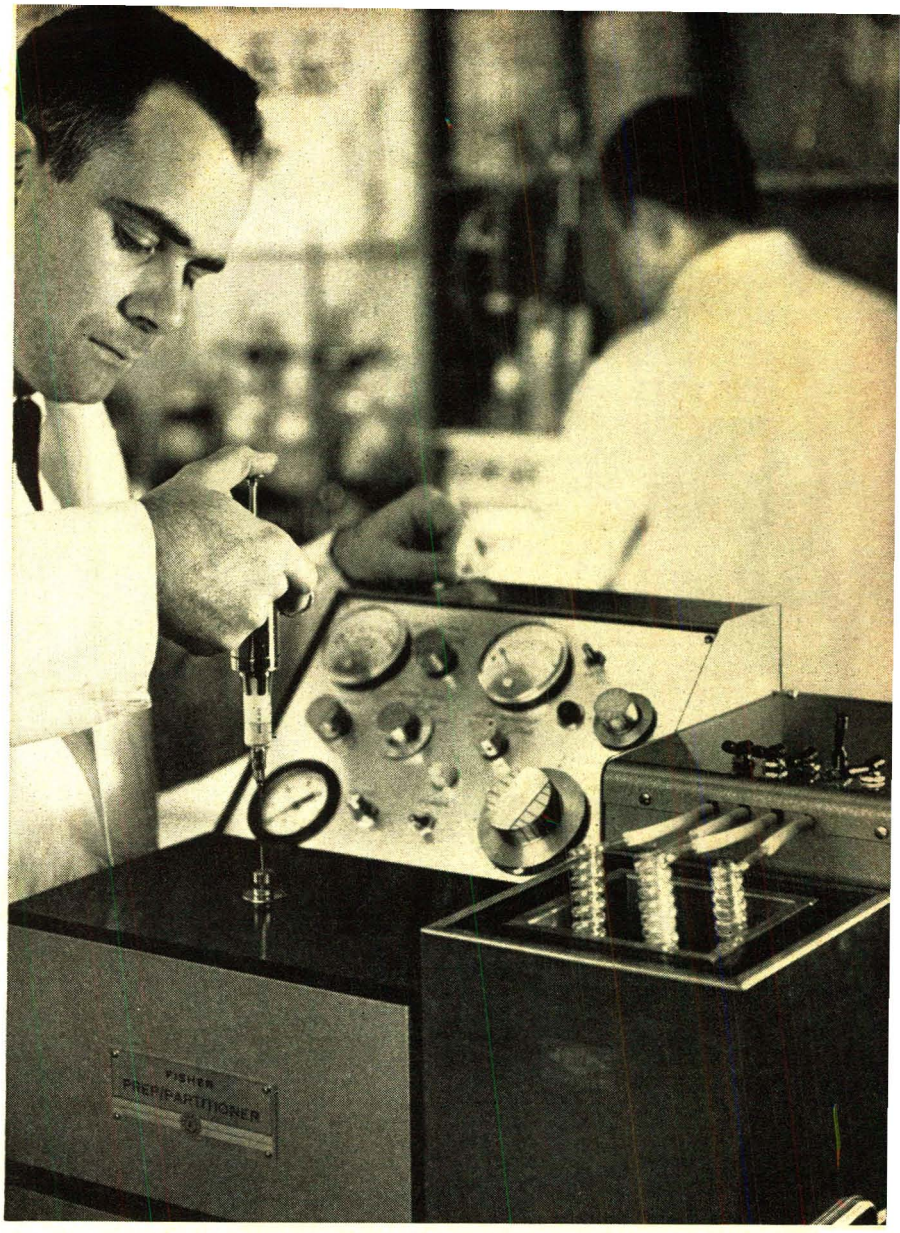
1. Title papers in a meaty and informative manner.
2. Index contributions with keywords taken from standard thesauri. Societies and editors are encouraged to establish such thesauri wherever practical.
3. Write informative abstracts.
4. Refrain from unnecessary publication.

The following recommendations are made to the technical community to ease the connection between the user of information with the information (not the document) that he needs:

1. Establish specialized information centers, preferably technical institutes, not technical libraries, wherever science and technology flourish. These centers should be staffed by working scientists who maintain close contact with their technical specialties.
2. Maintain central depositories for authors' manuscripts to simplify distribution. The committee urges technical societies to experiment with central depositories or some variant thereof, although recognizing the value of conventional journals.
3. Explore the use of automatic retrieval and mechanical information processing.
4. Study and consider methods of analyzing, indexing, and programming.
5. Encourage uniform and compatible procedures. The entire information system consisting of many subsystems should move toward uniformity in its practices of abstracting and indexing.

The 52-page report, "Science, Government, and Information," prepared by the President's Science Advisory Committee, is available from the Superintendent of Documents, U. S. Gov't Printing Office, Washington 25, D. C., for 25 cents.

Circle No. 44 on Readers' Service Card →



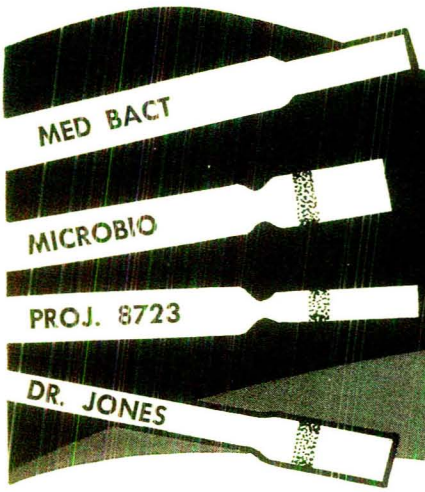
IF YOU CAN SEPARATE IT, YOU CAN COLLECT IT WITH THE FISHER PREP/PARTITIONER* Fisher's preparative-scale gas chromatograph can be run at 200°C, separates components boiling well above 250°C. Interchangeable sectional columns make it easy to vary chromatographic packing and column dimensions to separate the type of sample you have, faster and more efficiently than fractional distillation. Collection system isolates each component as it emerges—85 to 95% recovery with 2- to 3-ml components. Nitrogen carrier gas eliminates expense of gas reclaiming systems. Price: $2,750 and available under Fisher Financing Plan. **More facts** about the Prep/Partitioner? Get free Bulletin FS-239. Write today to Fisher Scientific Company, 100 Fisher Building, Pittsburgh 19, Pennsylvania. J-337

*Fisher Scientific Company Trademark

FISHER SCIENTIFIC

World's Largest Manufacturer-Distributor of Laboratory Appliances & Reagent Chemicals

Atlanta • Boston • Chicago • Fort Worth • Houston • New York • Philadelphia
Pittsburgh • St. Louis • Union, N. J. • Washington • Edmonton • Montreal • Toronto



"PERSONALIZED"

V.I.P. PIPETTES...

"personalized" with your Name, Dept. or Project

Now, at no extra cost you can have your V.I.P. non-corrosive, etch-proof, scratch-resistant Pipettes personalized. They'll be sure to return to you, your project or department every time!

Interested? Contact us!

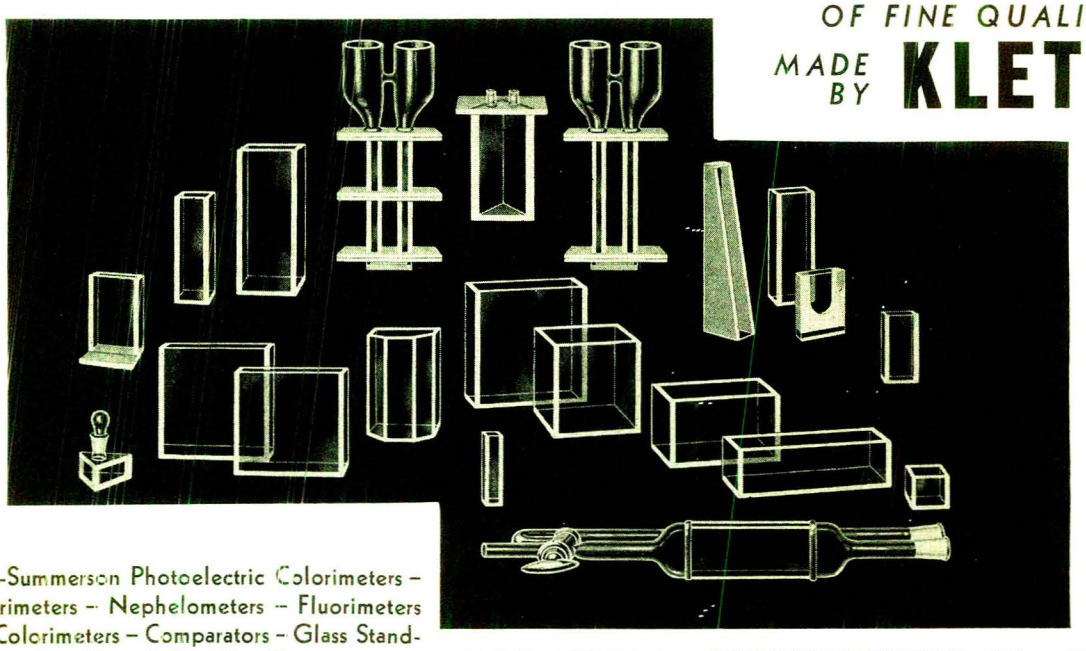
BELLCO GLASS INC.,
VINELAND, NEW JERSEY

We'll custom mark your pipettes to the identification that you designate. Markings are the same perma-brown material as description and graduations. Identification for the life of the pipette is ensured. Here's the deal . . . you order a minimum of 5 full cases of any graduated V.I.P. Pipette, regardless of size or stock number, and we will personalize them for you at no charge. Any combination of letters or numbers up to 12 spaces can be used. It's that simple!

Circle No. 26 on Readers' Service Card

GLASS ABSORPTION CELLS

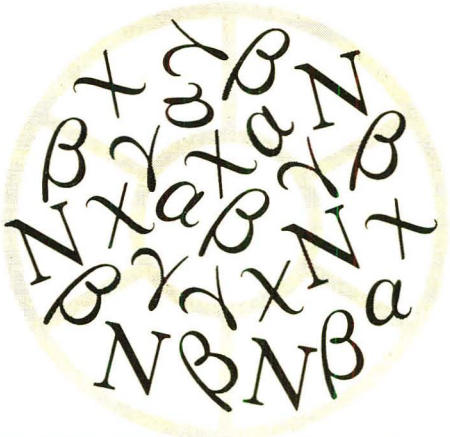
OF FINE QUALITY
MADE BY **KLETT**

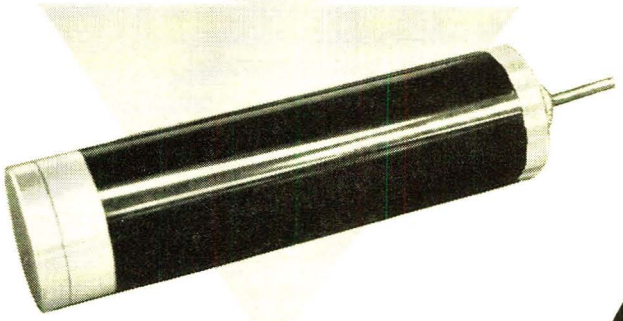


Klett-Summerson Photoelectric Colorimeters – Colorimeters – Nephelometers – Fluorimeters Bio-Colorimeters – Comparators – Glass Standards – Glass Cell – Klett Reagents

KLETT MANUFACTURING CO., INC.
179 EAST 87TH STREET
NEW YORK.....N. Y.

Circle No. 56 on Readers' Service Card





NUCLEAR INSTRUMENTATION by Norelco®

For Quantitative Spectrum Analysis of Radioactive Samples

Conceived, developed and introduced almost ten years ago — the flexibility and versatility of our instrumentation reflects the leadership, the technical ability and the experience that lies behind the production of all Norelco equipment.

The Automatic Counting Asembly, whose function is pictorially represented above, guarantees the user: *analysis of radioactive samples • unexcelled reproducibility • optimized counting geometry • proper sample distribution, which results in minimum background variation • and fully unattended operation with Digital Printout of sample number, count and time.*

Depend on Norelco quality — it is your assurance of instrumentation reliability.

PHILIPS ELECTRONIC INSTRUMENTS Norelco®

For detailed information in full line catalog write:

PHILIPS ELECTRONIC INSTRUMENTS

A Division of Philips Electronics and Pharmaceutical Industries Corp.

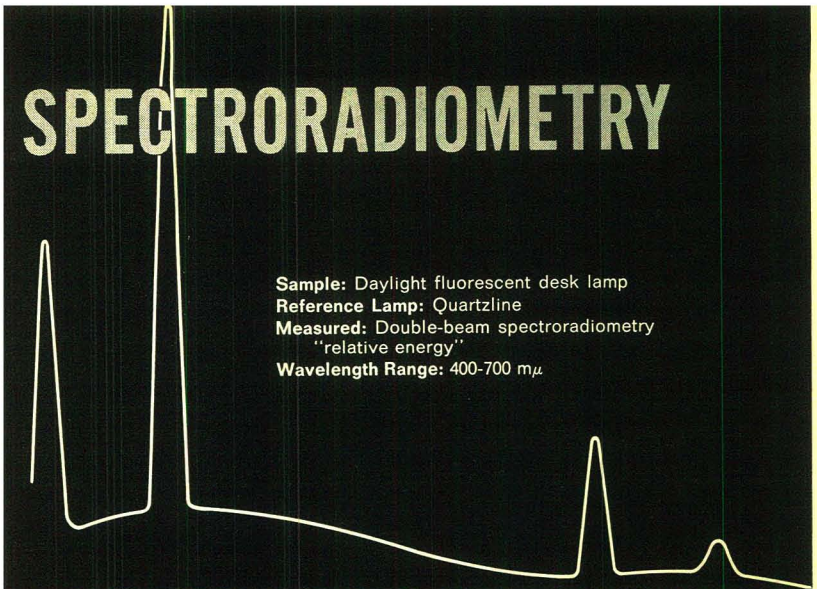
Dept. NI-33, 750 South Fulton Avenue, Mount Vernon, N. Y.

In Canada: Research & Control Instruments • Philips Electronics Ltd. • 116 Vanderhoof Avenue • Leaside, Toronto 17, Ontario

ELECTRON PROBE MICROANALYZERS · INDUSTRIAL RADIOGRAPHIC EQUIPMENT · PROCESS CONTROL INSTRUMENTATION
X-RAY SPECTROGRAPHS · ELECTRON MICROSCOPES · X-RAY DIFFRACTOMETERS · NUCLEAR INSTRUMENTATION

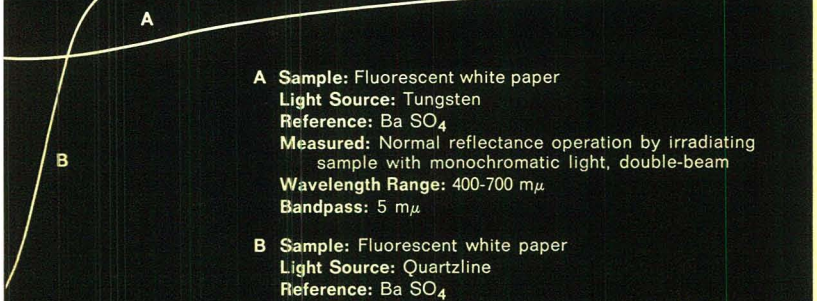
Circle No. 161 on Readers' Service Card

SPECTRORADIOMETRY



Sample: Daylight fluorescent desk lamp
Reference Lamp: Quartzline
Measured: Double-beam spectroradiometry "relative energy"
Wavelength Range: 400-700 mμ

SPECTROREFLECTOMETRY



A Sample: Fluorescent white paper
Light Source: Tungsten
Reference: Ba SO_4
Measured: Normal reflectance operation by irradiating sample with monochromatic light, double-beam
Wavelength Range: 400-700 mμ
Bandpass: 5 mμ

B Sample: Fluorescent white paper
Light Source: Quartzline
Reference: Ba SO_4
Measured: Direct-lighted sphere method, double-beam
Wavelength Range: 400-700 mμ
Bandpass: 5 mμ

ACCURATELY, QUICKLY

SAVE UP TO $5000 IN INSTRUMENT COSTS... save hours of time . . . while you easily measure reflecting-fluorescing samples with photometric accuracy of ±0.5% T. Maximum limit for stray light is 0.1%.

Curves and data above illustrate procedures used, and provide conclusive proof of the outstanding performance offered by the Bausch & Lomb Model 5 Relative Spectroradiometer/Spectroreflectometer . . . comparing with instruments costing up to $5000 more.

What is your problem? Double-beam comparison of spectral energy distribution of cathode ray tubes? Lamps? Arc lamps? Thermo-emission? Or is it direct-sphere measurement of reflection of fluorescing-reflectance samples, such as paper products, textiles, paints, or cosmetics? Regardless, you'll measure your samples accurately . . . faster, easier, at lower cost with the Bausch & Lomb Model 5.

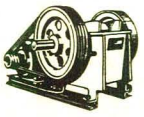
And, you'll get prompt delivery, including complete installation, check-out, and operating instructions by a factory-trained engineer.

Write for complete information. Please describe your application in detail. Address your inquiries to: Bausch & Lomb Incorporated, 81043 Bausch Street, Rochester 2, New York.

BAUSCH & LOMB

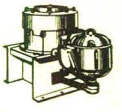
Circle No. 20 on Readers' Service Card

Laboratory Crushers and Grinders



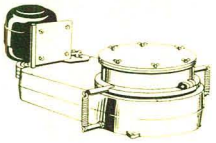
4"x 6" Massco Laboratory Jaw Crusher

Welded steel frame; manganese steel jaw and cheek plates; bronze bushed bearings; smooth jaws give better product and easier cleaning. Adjust for plate wear and product size by convenient hand wheel adjustment.



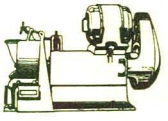
6" and 10" Massco Gy-Roll Reduction Crusher

Reduces ½" feed to as fine as 10 mesh in single pass. High capacity, low power consumption.



Gy-Rotary Laboratory Ball Mill

For wet or dry grinding; batch or continuous operation. The grinding chamber, 12" diameter by 3¼" deep, does not rotate, but travels in a circular path of small radius. The grinding balls bombard each other from all directions in small spheres or zones of activity.



Massco-McCool Pulverizers

Disc type grinder with a planetery movement. No gears. Will grind ¼" to 150 mesh in one pass.

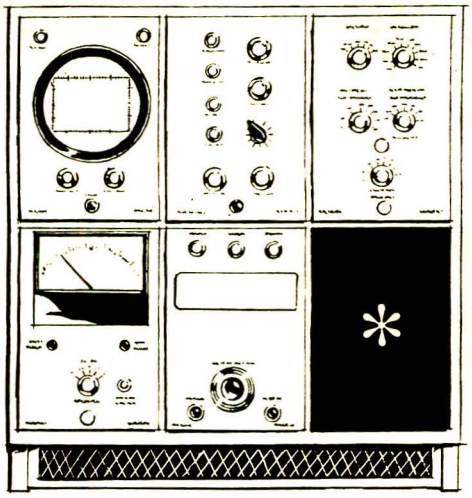
Marcy Pulp Density Scale

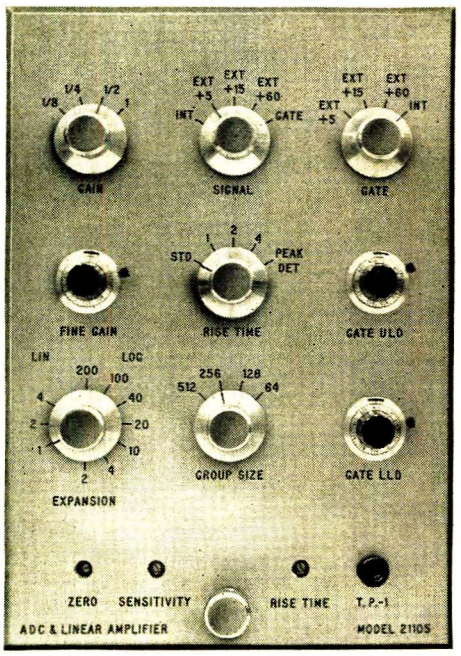
Gives direct reading of weight; specific gravity of liquids, pulps, and dry solids; percent solids in pulp. Very accurate. Easy to clean.

Dept. AC

MINE AND SMELTER SUPPLY CO.

3800 RACE STREET • DENVER, COLORADO
OFFICES AND AGENTS IN PRINCIPAL CITIES





* NEW YESTERDAY, TODAY, AND TOMORROW

Advances in research have made much equipment obsolete while still on the drawing boards. Or, worse still, shortly after it was purchased. This has not and can not happen to the RCL Multichannel Analyzer because it has extreme built-in flexibility and almost unlimited utility. For example, new input devices may be adapted for future experiments without modifying the Analyzer's ADC, thus keeping it new for years to come.

THESE "EXTRAS" ARE STANDARD ON THE RCL MULTICHANNEL ANALYZER. . . .
Logarithmic expansion of energy scale permits a full spectrum survey with excellent resolution. . . Direct compatibility with existing single and double delay line clipping amplifiers. . . . Built in single channel analyzer for coincidence and anticoincidence operation. . . . Exceptional stability for temperature and count rate variation. . . . All channels are useable with full scale linearity specification. . . . Direct control of input from experimental external gating circuitry without modification.

For Free Demonstration & Complete Specifications, Write;

RADIATION COUNTER LABORATORIES, INC. A SUBSIDIARY OF ALLIED RESEARCH ASSOCIATES, INC.

5121 West Grove Street, Skokie, Illinois, U.S.A., TWX: 9675150, Cable Address: RACOLAB / Phone YOrktown 6-8700

Circle No. 135 on Readers' Service Card

THIS NEW CHROMATOGRAPH
HAS GUARANTEED PERFORMANCE AT A NEW LOW PRICE

New Series 700 Gas Chromatograph with advanced Proportional Temperature Controller-Programmer

GUARANTEED

- **Linear Temp. Programming . . . continuously variable to 30°C/min.**
- **Electron Affinity Detector . . . quantitative to better than 1%.**
- **Servo-driven Proportional Control . . . to ± 0.02°C.**
- **Ionization Detectors . . . sensitive, linear, reproducible.**
- **Highly Stabilized Electronics . . . Series 700 Chromatographs stay calibrated.**
- **Nationwide Service . . . specialists available locally.**

Priced from $3,335 including; installation, operator training, and, a full 1-year warranty.

The new Jarrell-Ash 700 Series Chromatographs accommodate, in an interchangeable side-by-side arrangement, any two detectors, injectors and columns. Detectors available — Cross Section, Electron Affinity, Flame, Argon Diode. Injector systems — Capillary, Syringe, Gas Sampling, On Column. The instrument accepts a wide variety of columns from capillary to preparative in size. All analytical components are self-contained and are at your fingertips for quick, easy change-overs.

The 700 is performance proved in such applications as pesticides (DDT analyzed to 3% at the 1 ppm level, single injection) and steroids (urine pregnanediol analyzed at the nanogram level). The precision 700 will give comparable performance handling your own applications range, however varied.

For complete technical and applications data, ask for Bulletin 28-700.

Jarrell Ash

Dedicated to excellence in the research, development and manufacture of precision analytical instrumentation.

For further information . . . clip the coupon, attach to your company letterhead and mail

JARRELL-ASH COMPANY
26 Farwell Street, Newtonville 60, Mass.

Name _____

28-700

Circle No. 120 on Readers' Service Card

CARBON-14

A THIRD GROUP OF EIGHT NEW LABELLED COMPOUNDS

Radiochemical purities 97% to 100%. *Specific activity ranges shown in italics.*

Adenosine-8-C^{14} hydrate	*5-20 mc/mM*	
	$1050/500 μc	$140/50 μc
L-Arginine-(*guanido*-C^{14}) monohydrochloride	*5-15 mc/mM*	
	$380/500 μc	$52/50 μc
D-*threo*-Chloramphenicol (methylene-C^{14})	*2-10mc/mM*	
	$2100/500 μc	$300/50 μc
Erythritol-C^{14} (U)	*2-4 mc/mM*	
	$525/500 μc	$75/50 μc
D-Fructose-C^{14} (U) [high specific activity]	*50-80 mc/mM*	
	$335/500 μc	$45/50 μc
myo-Inositol-C^{14} (U)	*10-50 mc/mM*	
	$335/50 μc	$95/10 μc
Pregnenolone-4-C^{14}	*5-20 mc/mM*	
	$310/50 μc	$85/10 μc
Sodium DL-3-hydroxybutyrate-4-C^{14}	*2-10 mc/mM*	
	$360/500 μc	$50/50 μc

These new compounds do *not* appear in our recently published C-14 schedule. Ask for Radiochemical Bulletins listing these and many other newly available C-14, Tritium, P-32, S-35, and Cl-36 labelled compounds. Individual product schedules are also available.

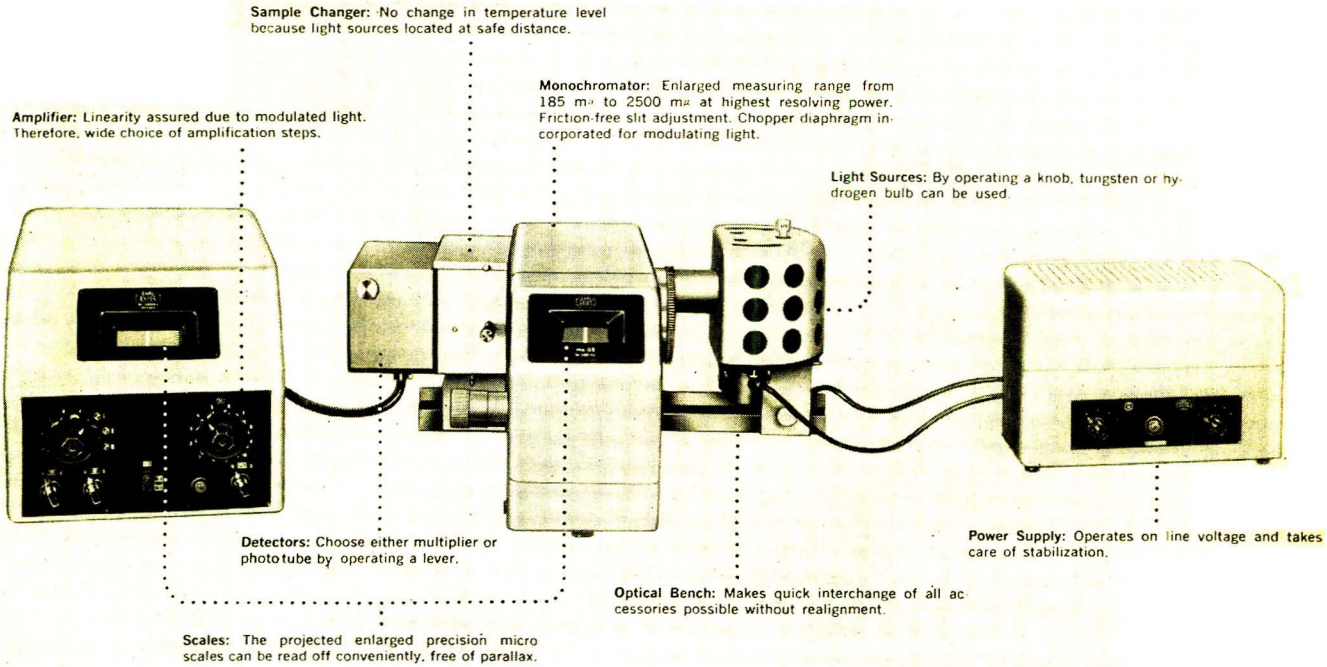
All prices F.O.B. destination. All shipments sent via prepaid Air Express. Requests for custom preparations are invited.

NUC: G-3-238

nuclear-chicago CORPORATION

351 Howard Avenue, Des Plaines, Illinois

Circle No. 129 on Readers' Service Card



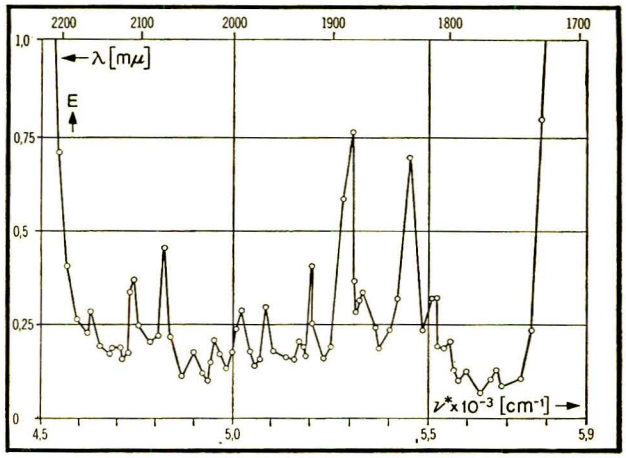
The Carl Zeiss Spectrophotometer PMQ II

The PMQ II is outstanding for rapid measurements of liquids, gases and solids at the highest resolving power of the spectrum. You can make a quick survey of a sample, find out where its absorption bands lie and determine its concentration precisely due to direct indication. The instrument operates on a.c. line voltage and is completely stabilized electronically. Modulation of the measuring light by built-in chopper diaphragm assures linearity of the amplification, constancy of zero point and the elimination of dark current. Sensitivity can be varied as follows:

0-10 (in steps of 0.1 optical density—calibrated)
10-100 (calibrated)
100 to approximately 3000

An adjustable damping device for varying the response time results in minimum fluctuations at highest amplification. This is especially useful for Flame Photometry. All important electrical circuits and tubes can be tested by a built-in checking device. Slit width can be set to 0.2 microns. Thanks to frictionless design of the Spectrophotometer PMQ II, no play is possible in slit and wavelength settings. Combined error of wavelength setting and reading, for instance at 250mμ, is ± 0.05mμ.

The PMQ II is extremely accurate and versatile. Accessories available are: servo motor to operate the 100 Point Adjustment Device, attachments for analysis of chromatograms, fluorescence and reflectance measurements, and for flame photometry. Write to us for further details or a demonstration of the Spectrophotometer PMQ II. **Complete service facilities available.**



CARL ZEISS
WEST GERMANY

The Symbol of World Famous Optics

Carl Zeiss, Inc., 444 Fifth Ave., New York 18, N. Y.

IN CANADA: CARL ZEISS CANADA LTD., 60 OVERLEA BLVD., TORONTO 17, ONTARIO

Circle No. 99 on Readers' Service Card

Pt for the lab

STANDARD LAB APPARATUS: *a complete line of quality ware*

SPECIAL LAB EQUIPMENT: *send us your specifications*

CHEMICALS: *over 40 salts, solutions, powders in stock*

Whatever your need for platinum, take advantage of BISHOP's long experience (since 1842) and complete facilities for the fabrication, refining and recovery of the platinum group metals.

And don't forget that your used lab ware and other platinum material has a high scrap value toward the purchase of new products.

Send for our catalog PLATINUM METALS PRODUCTS No. P-6.

BISHOP

J. BISHOP & CO. *platinum works*
MALVERN, PENNSYLVANIA
A JOHNSON MATTHEY ASSOCIATE

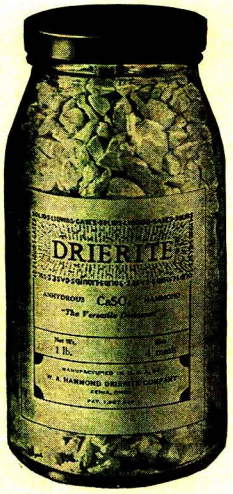
Circle No. 28 on Readers' Service Card

SOLIDS-LIQUIDS-GASES-SOLIDS-LIQUIDS-GASES-SOLIDS

DRIERITE®

"THE VERSATILE DESICCANT"

For Drying
SOLIDS - LIQUIDS - GASES



REGULAR DRIERITE

A low cost, all-purpose drying agent, DRIERITE is neutral in reaction, chemically stable, constant in volume, inert except toward water, insoluble in organic liquids and refrigerants, non-disintegrating, non-wetting, non-poisonous, non-corrosive, repeatedly regenerative, and non-channeling.

INDICATING DRIERITE

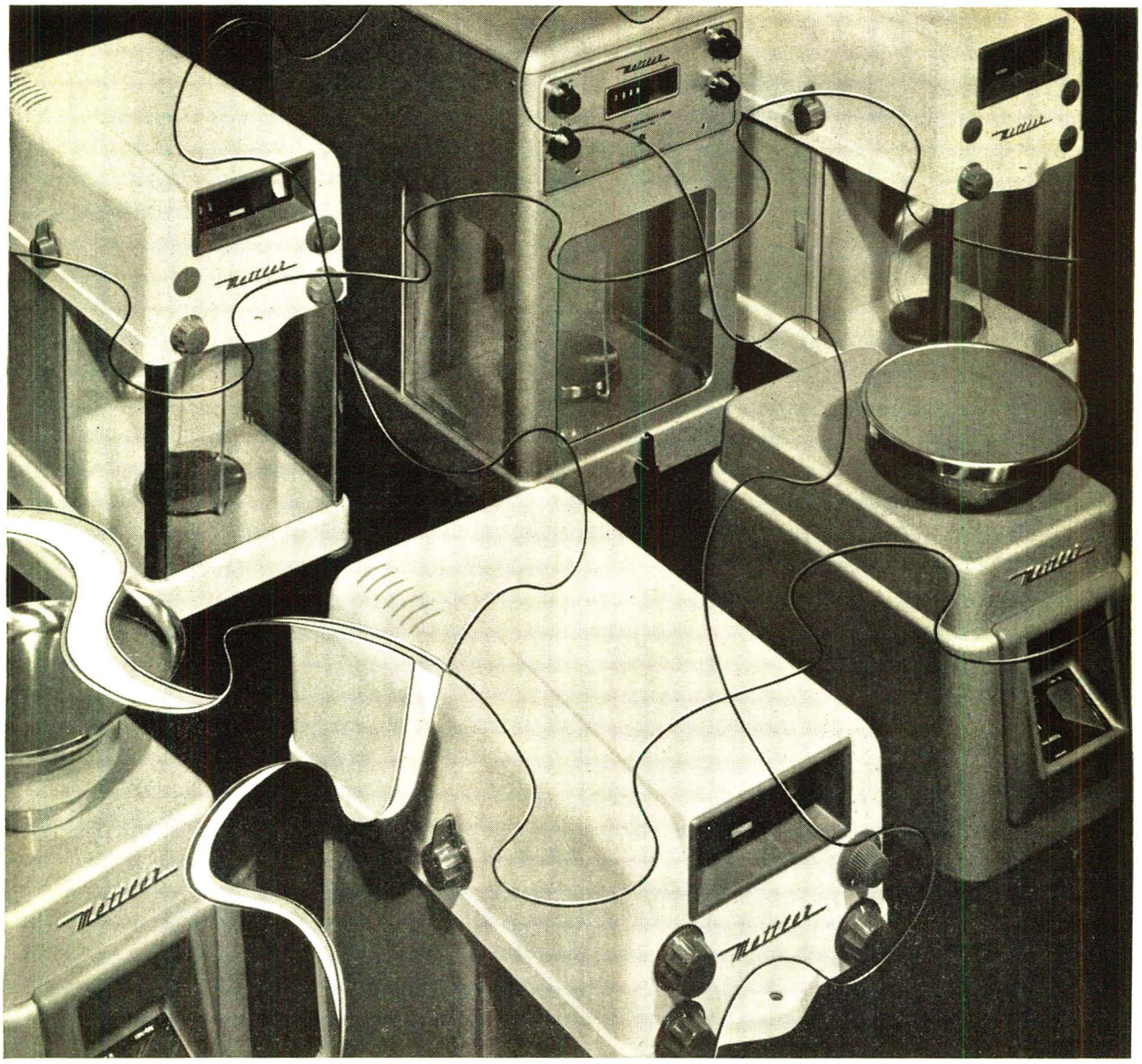
While possessing all of the properties of regular DRIERITE, INDICATING DRIERITE makes a clearly visible change from blue when dry to pink when exhausted.

Order directiy from your Laboratory Supply Dealer.

Write to us for our new 100-page book

W. A. HAMMOND DRIERITE COMPANY
120 Dayton Avenue, Xenia, Ohio

Circle No. 49 on Readers' Service Card



Mettler Balances from S/P

which one fits your needs?

From micro to macro, there's a Mettler Balance from S/P that's perfectly suited to your laboratory. These modern single pan balances are fast, accurate, convenient. With Mettler Balances, it takes less than 30 seconds to determine an unknown weight, and they're so simple to operate no special training is required.

Scientific Products has Mettler Balances in stock. For complete literature or a conclusive demonstration, ask your S/P Representative or write our General Offices (address below).

S/P scientific products

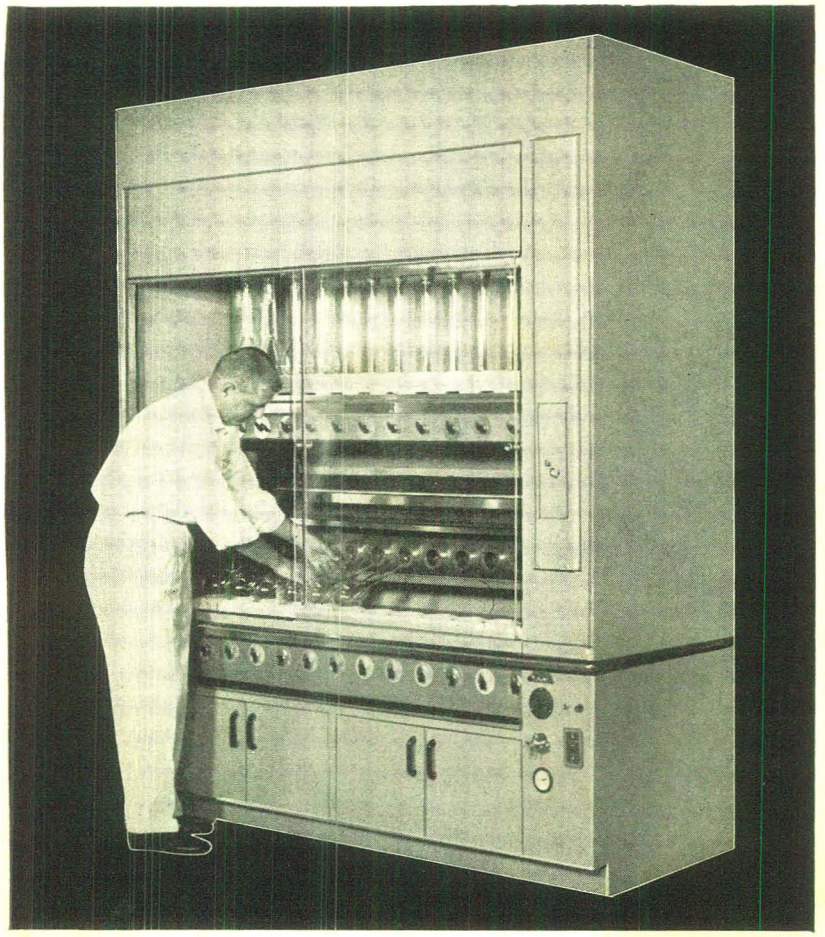
DIVISION OF AMERICAN HOSPITAL SUPPLY CORPORATION

GENERAL OFFICES: 1210 LEON PLACE, EVANSTON, ILLINOIS

Regional Offices: Atlanta · Boston · Charlotte · Chicago · Columbus · Dallas · Detroit · Kansas City
Los Angeles · Miami · Minneapolis · New York · San Francisco · Washington

Export Department—Flushing 58, L. I., New York. In Mexico: Hoffmann-Pinther & Bosworth, S. A.

Circle No. 83 on Readers' Service Card



LABCONCO HOODED KJELDAHLS SAVE UP TO 4 TONS OF AIR CONDITIONING CAPACITY

A 12-unit Kjeldahl produces up to 50,000 Btu's per hour. In air conditioned labs this heat loss could require as much as 4 tons of additional air conditioning capacity. Not so when you install a *hooded* Kjeldahl unit from Labconco. Heat and fumes are immediately exhausted to the outside —never affect the temperature of the lab.

Labconco hooded Kjeldahls are modern, streamline in appearance. The hood itself is made of formed metal, heavy resistant asbestos, and stainless steel hardware. The finish is baked enamel which can be painted in one of four standard colors or to your own specifications.

Labconco hooded Kjeldahls are available in 6- and 12-unit models, with or without sash, gas or electric heat, variable heat controls, timers, and thermo water controls. For a new 64-page product catalog describing the complete line of Kjeldahl apparatus and accessory items (as well as all other Labconco products), write Labconco, 8815 S. Prospect, Kansas City, Mo.

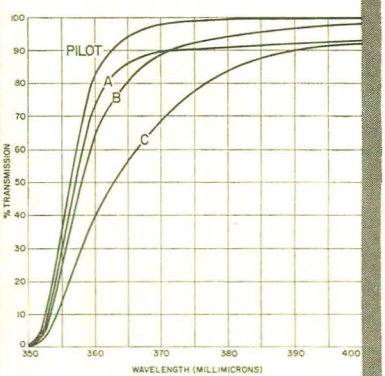
LAB CON CO

LABORATORY CONSTRUCTION COMPANY

Circle No. 61 on Readers' Service Card

HOW PURE IS YOUR PRESENT FLUOR?

If you're using Pilot Chemical's fluors you're using the purest — with maximum light output and high melting point. Recent tests, using Pilot PPO (2,5—Diphenyl-oxazole) and PPO from nine other commercial sources, proved Pilot's light transmission to be highest.*



Selected curves show the range of purities. (Measured on a Beckman DB Spectrophotometer, 1 cm. cell, 2% solution in spectro grade cyclohexane)

Why not test Pilot's PPO for yourself? Just send us your name and title and we'll send you a free sample. Pilot offers a large selection of scintillation grade fluors —here are a few:

- "ALPHA-NPO." 2-(1-Naphthyl)-5-phenyloxazole
- Anthracene.
- "BBO" 2, 5-Dibiphenylyloxazole
- "BOPOB." P-BIS [2-(5-P-Biphenylyloxazolyl)]-Benzene
- 9, 10-Diphenylanthracene
- P, P'-Diphenylstilbene
- "PBD" Phenylbiphenylyloxadiazole-1, 3, 4
- "POPOP" P-BIS [2-(5-Phenyloxazolyl)]-Benzene
- P-Quaterphenyl
- P-Terphenyl

Pilot manufactures both fluors and plastic scintillators as well as Liquifluor, a pre-mixed 25X concentrate of PPO and POPOP in specially purified Toluene. Write for help on special problems. Ask for Bulletin A-612.

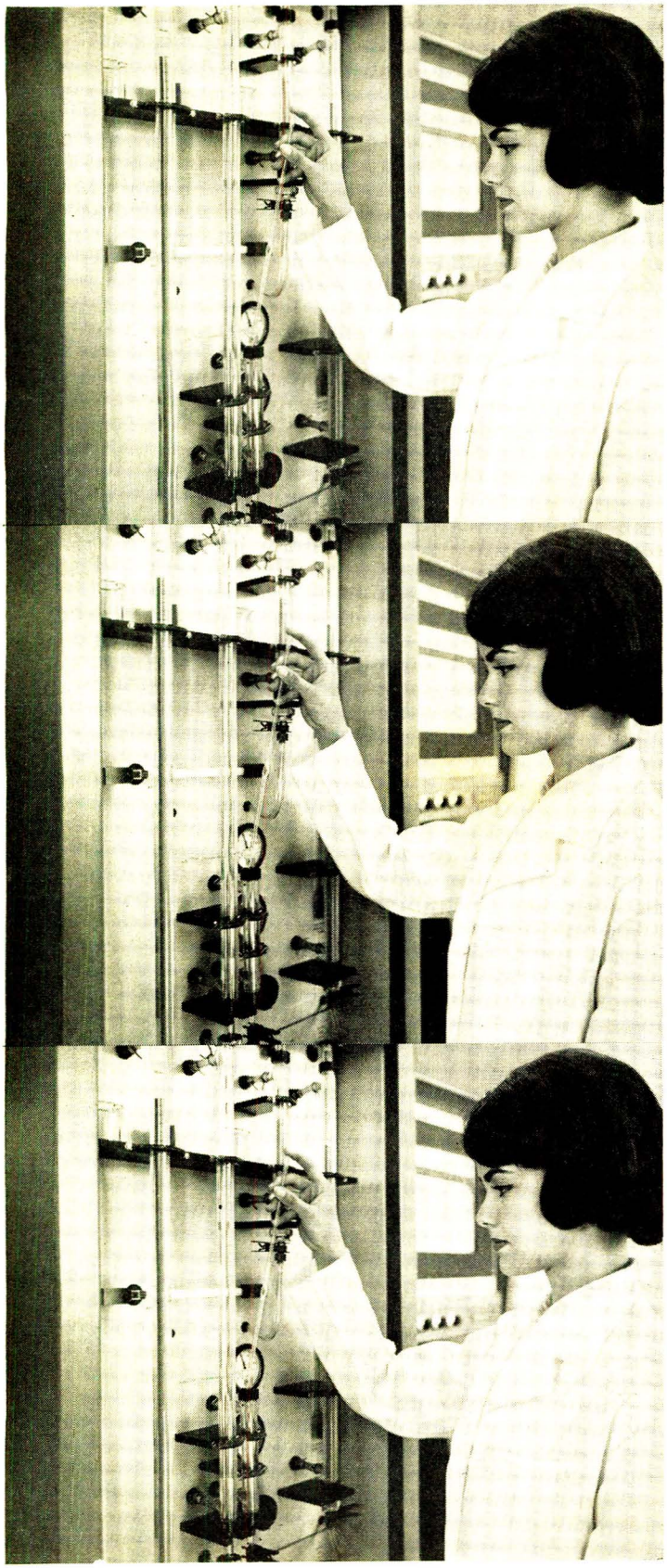
*Every batch of PPO from Pilot is quality controlled spectrophotometrically.

PILOT

CHEMICALS, INC.

36 PLEASANT ST., WATERTOWN 72, MASS.

Circle No. 78 on Readers' Service Card



NOW YOU CAN GET THREE COMPLETE AMINO ACID ANALYSES A DAY

(—and use smaller samples to do it!)

The Model 120B Amino Acid Analyzer with the new Accelerated Analysis procedure cuts the time for analyzing a protein hydrolyzate from 22 hours to 6½ hours. This new procedure means you can complete the first run by early afternoon, and get a second run programmed for automatic completion—all in the same working day. A third complete analysis is possible by coming in for two hours in the evening.

Equally good news—you now need less of your valuable sample. As little as 0.05 micromole (less than half the size formerly required with the Model 120B) gives the same accurate results.

Laboratories presently owning Beckman Amino Acid Analyzers (and some own as many as three) can employ the new Accelerated Analysis procedure with only minor changes.

If your work involves analyzing protein hydrolyzates, body fluids, tissue extracts, foods or pharmaceuticals, why not let the Beckman Analyzer take over the repetitive work for you. For more information, write for Data File 120-7.

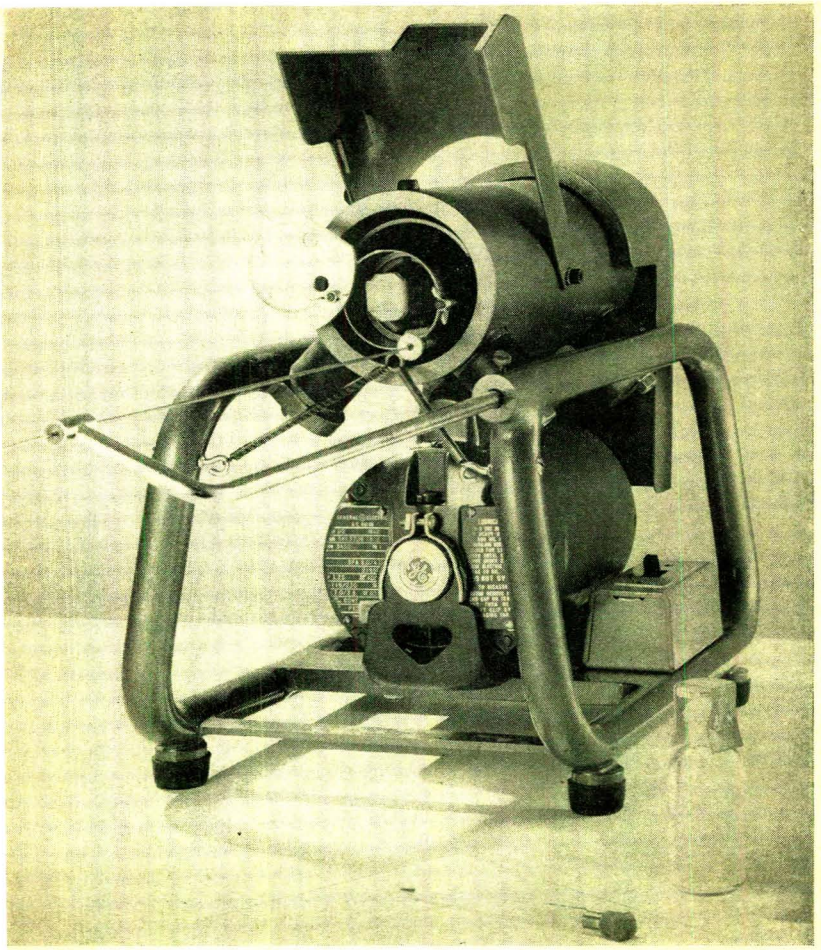
Beckman® INSTRUMENTS, INC.

SPINCO DIVISION

Palo Alto, California

International Subsidiaries: Geneva, Switzerland; Munich, Germany; Glenrothes, Scotland.

Circle No. 104 on Readers' Service Card



NOW FROM BRONWILL . . . THE RENOWNED BRAUN MODEL MSK, MECHANICAL CELL HOMOGENIZER

Offered for the first time in the U.S.A. . . . the outstanding Braun MSK cell homogenizer fully adapted for use in this country.

The superior Braun MSK prepares cell-free extracts for enzyme studies . . . homogenizes yeast, bacteria, tissue cultures or minced organs . . . pulverizes coarse particles (such as pigments or plastics) . . . and makes cell particles (for example yeast mitochondria) ready for study.

Biochemists, bacteriologists, cytologists or research scientists now have at their disposal this extremely efficient, highly effective and speedy tool for use with material either in the dry state or in suspension.

With yeast, 90% disruption of 10 grams is achieved after only 30 seconds at 4000 rpm . . . 99% after 60 seconds!

Bacterial cells show 70% to 90% breakdown after 1 or 2 minutes!

Intact yeast mitochondria are prepared in 20 to 30 seconds!

The remarkably short disruption time of the Braun MSK allows the processing of a series of batches, if necessary, in a relatively short period.

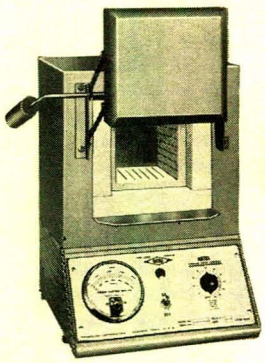
The Braun MSK features two-speed, elliptical shaking action. Cell walls are broken down by violent tumbling action of tiny glass beads. The sample may be cooled with CO_2 and kept below 5°C.

If the Braun MSK would be useful in your work, drop us a note and we'll send you all the details.

BRONWILL SCIENTIFIC
A DIVISION OF WILL SCIENTIFIC, INC.
218 N. GOODMAN ST., ROCHESTER 1, N. Y.

Circle No. 30 on Readers' Service Card

"lab-accepted standard of quality"



THERMOLYNE® type 1500 electric furnace

COMPACT — CONVENIENT — for general lab work and process control . . . Chamber size 4″ x 3¾″ x 4½″ or 4″ x 3¾″ x 9″ Welded steel construction . . . embedded heating elements.

COMPLETELY STEPLESS TEMPERATURE CONTROL

Select and hold any temperature from 350° F to maximum regardless of line voltage irregularities . . . One of the many features of this high quality THERMOLYNE furnace.

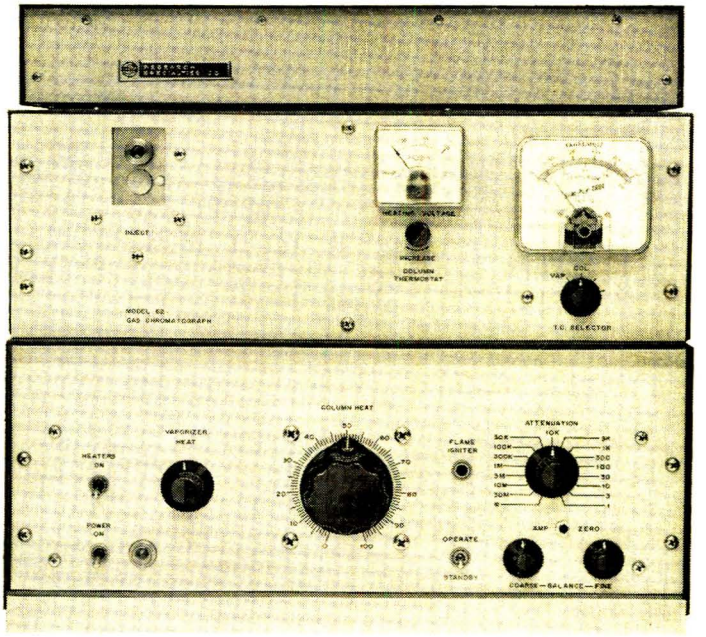
Designed for continuous operation up to 1850° F and intermittent operation to 2000° F . . . HIGH-TEMPERATURE models 2000° F and 2150° F . . . Attractive heat-resistant ENAMEL finish . . . Models for 115 and 230 volt current supplies.

PRICES $145.00 to $165.00

WRITE, WIRE OR PHONE FOR COMPLETE INFORMATION AND NAME OF NEAREST DEALER

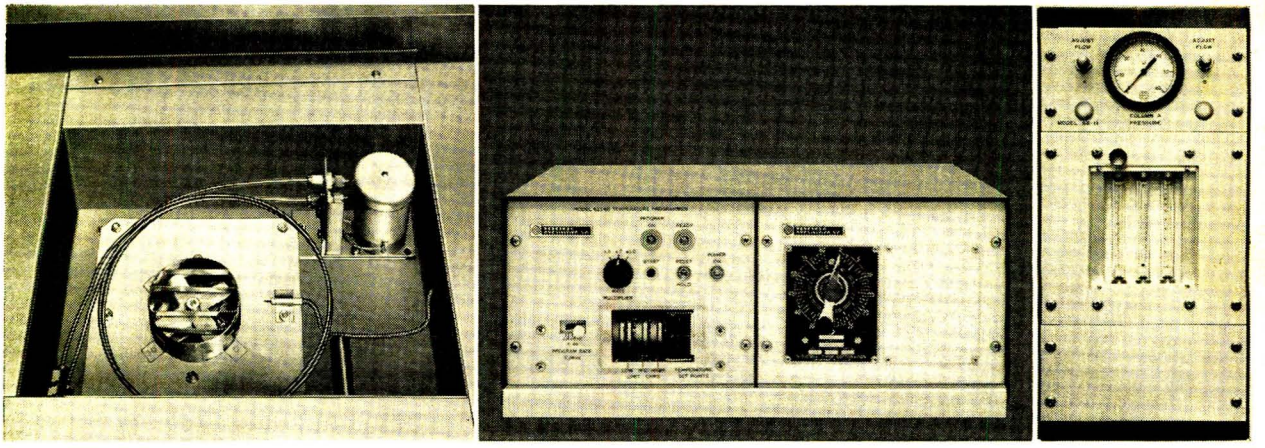
THERMOLYNE CORPORATION
Dept. 478, 2555 Kerper Blvd.
Dubuque, Iowa

Circle No. 88 on Readers' Service Card



Here's a brand new low-priced gas chromatograph that gives you

single or dual flame operation, automatic programming, and more!

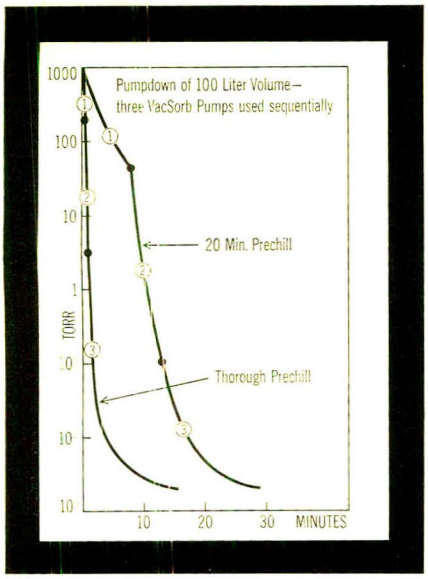


RSCo's new Model 62 is the only flame ionization gas chromatograph you can buy for $950. Add dual flame operation and automatic temperature programming and you have the most versatile, low-cost unit now available. The Model 62's wide range of accessories—separate detector ovens, sampling valves, input splitters, and flow meters—give it the versatility of a modular unit. □ Start with a basic model and add accessories as your needs expand. Good way to stretch a capital-expenditure budget? You bet. RSCo also makes the matchless 600 Series modular gas chromatography system. (It costs more, of course, but you can't buy a better one at any price.) Write us. We'd like to send you complete details.

RESEARCH SPECIALTIES CO.

200 SOUTH GARRARD BLVD. • RICHMOND, CALIFORNIA

Circle No. 145 on Readers' Service Card



quick, clean roughing with sorption pumps

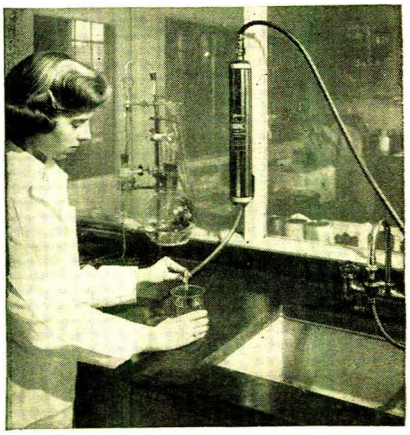
The fastest way to achieve *clean* roughing (down to 2 x 10^{-3} Torr) is with a sorption pump. In a few words, let's see what it is and how it works. ■ A sorption pump is simply a vacuum tight container filled with sorption material such as activated charcoal or molecular sieve. To get the pumping action, the sorbent is chilled by surrounding the pump with liquid nitrogen. Gas molecules in the system then come to rest on the surface of the sorbent (which is extremely large with respect to a given unit of weight) and are thereby removed from the system. The pump may be reused by bringing the material to room temperature, allowing the gases to be desorbed. ■ Sorption pumps are ideally suited to systems employing getter ion pumps, since the sorption pump quickly roughs the system to well beyond the starting pressure required for the ion pump. Example: Eight pounds of molecular sieve will pump a 100 liter volume to 10 microns in 3 minutes. Proper chilling is essential, as shown by the graph above. ■ In addition to their speed advantage, sorption pumps are clean. They contain no vapors or liquids; they will never be a source of contamination. They're also quiet and vibration free since they contain no moving parts. Sorption pumps are by all odds the cleanest way to rough a vacuum system. For a mass of facts and figures about Varian VacSorb® Pumps, write today.

VacSorb® is a registered trademark of Varian Associates.

VARIAN ASSOCIATES PALO ALTO, CALIF.
VACUUM PRODUCTS DIVISION
VARIAN A. G.: ZUG, SWITZERLAND

Circle No. 92 on Readers' Service Card

THROW-AWAY CARTRIDGE DE-IONIZER PRODUCES CHEMICALLY-PURE WATER RIGHT FROM THE TAP



INSTANT PURIFIED WATER

Open the tap or unclamp the tubing — you get chemically-pure water *at once.* Run only as much as you need — a few ounces or a bottle-full.

CHEMICALLY EQUIVALENT TO TRIPLE-DISTILLED

Note the purity of effluent shown in specifications below. De-ionized water is accepted by U S Pharmacopoeia as equivalent for all but injection solutions.

USED ONLY WHEN NEEDED

With this Cartridge De-Ionizer, your pure water is actually "on tap." You can come back for more at any time — it's always available. Flow rate is generous — 5 gph.

CONVENIENT — EASY TO INSTALL

You snap the Cartridge into the Wall Bracket, or clamp it into the Mounting Fixture. The resin changes color as exhausted — a clear line shows how much capacity remains. Write for Bulletin CD-161 giving full details.

RESEARCH MODEL	UNIVERSAL MODEL
Removes all ionizable solids including silica and CO_2. Average in effluent less than 0.5 ppm total solids.	Removes all ionizable solids, except silica and CO_2. Suitable for general pure water needs.
Capacity, 500 grains as $CaCO_3$.	**Capacity,** 1000 grains as $CaCO_3$.
Flow Rate, 5 gph max.	**Flow Rate,** 5 gph max.
Price, $12.50	**Price,** $9.75

WALL BRACKET with slip-on connection to water faucet.....$7.50
MOUNTING FIXTURE, clamp-in type for line-pressure use.....$12.00

Order from Your Laboratory Supply House

ILLCO-WAY

ILLINOIS WATER TREATMENT CO.
840 Cedar St., Rockford, Ill.

Circle No. 117 on Readers' Service Card

Visitor is shown arriving at the Pittsburgh airport with samples for magnetic resonance investigation. If the work cannot be completed in one day, he can use the airport terminal building's hotel facilities

LABORATORY OF THE MONTH

Analytical Instrument Applications Laboratory Includes World-Wide Facilities

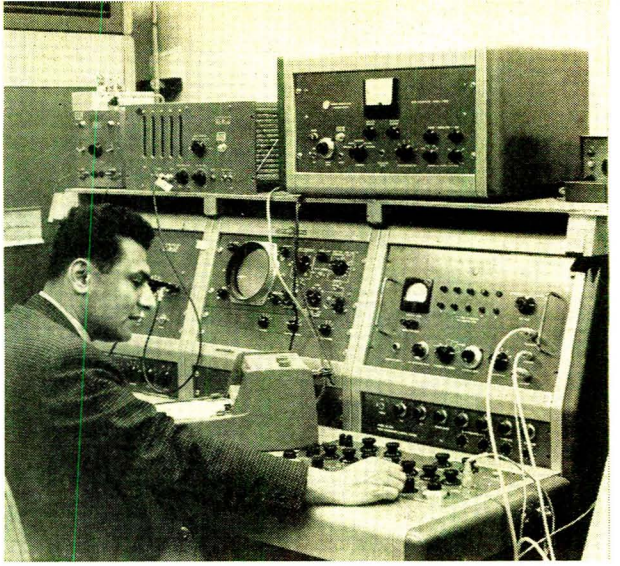
Varian Associates NMR/EPR Applications Laboratory and Service Center at the Greater Pittsburgh Airport Terminal Building at Pittsburgh, Pa. Reception lobby and offices are at right and laboratory is at left.

THE GREATER PITTSBURGH AIRPORT TERMINAL BUILDING, location of Varian's new Magnetic Resonance Applications Laboratory, provides convenient and rapid service to chemists in the eastern half of the United States. Served by airlines from most major cities, the terminal building location means a minimum of portal-to-portal time for scientists concerned with evaluating nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) methods. In most cases a day of work can be done on a commute basis. However, hotel and restaurant accommodations are available at the airport if more time is necessary.

Occupying approximately 1200 square feet of leased space, the Pittsburgh laboratory consists of an applications study area equipped with complete operating models of the company's spectrometers, a service shop, and administrative offices. This laboratory, operated by the Instrument Division of Varian Associates, is in addition to established facilities in Palo Alto, Calif., and Zurich, Switzerland.

Started in 1952 as a bold new approach to the problem of finding markets for complex and little-understood in-

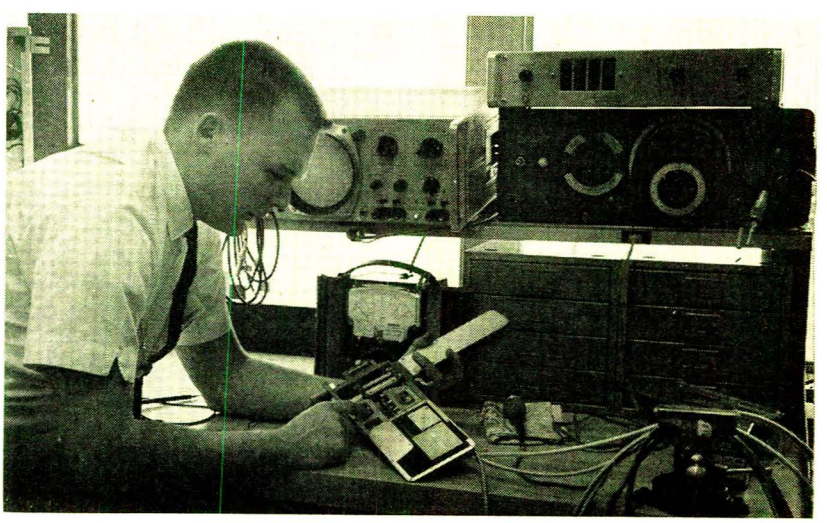
Pittsburgh applications laboratory chemist works with visiting scientist in collaborative effort to solve structure problem by combining chemical data with NMR spectroscopic study. An EPR spectrometer and an analytical spectrometer are also available if needed



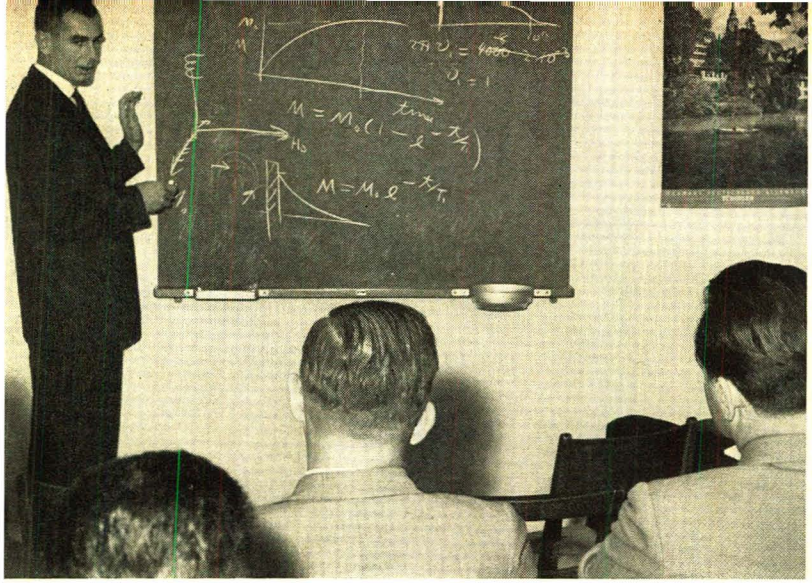
Complete research NMR spectrometer system operating at over 23,000 gauss is applied by Palo Alto laboratory NMR spectroscopist to determine structure of complex natural product submitted to laboratory for study. Air conditioner at left controls laboratory temperature to better than 0.1° C.

LABORATORY OF THE MONTH

Newly developed variable sample temperature controller for high resolution NMR spectrometer is discussed by scientist and development engineer



Service technician in the laboratory checks repaired spectrometer component at service bench prior to final check-out in the laboratory system



A company research physicist joins applications laboratory personnel during one of the annual NMR workshop courses. He is shown conducting a class on the theory of nuclear magnetic resonance

struments, the Palo Alto laboratory concentrated its early efforts on high resolution NMR, although Wide-line NMR and EPR techniques have recently enlarged its scope. Heavy emphasis has always been placed on the research nature of the work, particularly with regard to prompt publication of results in original and co-authored papers. Scientists from other organizations have been encouraged to make personal visits to the laboratory and thereby bring about a more rapid and far-reaching solution to their chemical problems through the collaboration of experts in the fields of chemistry and spectroscopy.

Another valuable function of the laboratory has been its contribution to the design of magnetic resonance spectrometers through the familiarity with the nature of the problems achieved by working on real and not hypothetical examples. Still another function is being added in the Pittsburgh laboratory where the availability of complete working instrument systems is utilized to provide test facilities for a Service and Repair Center serving Varian's instrument owner population in 37 eastern states.

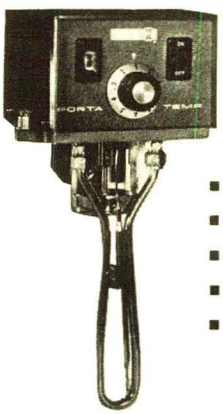
In recent years, increasing emphasis has been placed on the educational aspects of the Applications Laboratory capabilities through Varian's annual NMR-EPR workshops. In its seventh year at Palo Alto and third year in Zurich, the workshop will be kept in mind as a potential activity in Pittsburgh with the staff augmented by lecturers and laboratory instructors from the group of several chemists with special training in NMR and EPR spectroscopy employed in Palo Alto. Initially, the Pittsburgh laboratory will be staffed with a complement of one applications chemist, a service technican, and a service coordinator with additional staff planned as the need arises.

Current projects include studies of analytical applications of high resolution NMR, investigations with NMR instruments operating at high magnetic field strengths (23.5 kilogauss corresponding to a proton resonance frequency of 100 mc./sec.), production of a supplement to an extensive standard catalog of NMR spectra, applications of EPR to problems of biochemical and biological interest, and analyses of chemical and agricultural products for water and oil content. During its 11-year life span the applications laboratory group has seen high resolution NMR emerge from the status of a laboratory curiosity to take its place alongside other major analytical tools as a mature technique. To provide adequate facilities for the evaluation of these tools and to meet the educational demands posed by their existence are challenges which Varian believes can best be met by a world-wide laboratory facility with an imaginative, flexible program.

WILKENS-ANDERSON

INTRODUCES...

PORTA-TEMP



- COMPACT
- PORTABLE
- ACCURATE
- EASY TO USE
- ECONOMICAL

NEW LOW-COST, PORTABLE BATH HEATER AND CIRCULATOR

by PRECISION SCIENTIFIC CO.

Turns any convenient container into an accurate constant temperature water bath and circulating system. Maintains temperatures up to 90°C., even in uninsulated containers. Circulates up to 2 liters per minute. Uniformity of temperature controlled by hydraulic thermostat to within ±0.25°C. with sensitivity of ±0.125°C.

Constructed of cast aluminum and sheet steel with corrosion-resistant gray hammerloid finish. Has 1000 watt heater, electric stirring motor, hydraulic thermostat.

Price: $125.00
Available now from stock.

Request WACO Porta-Temp Bulletin for further information.

LABORATORY SUPPLIES AND EQUIPMENT
WILKENS-ANDERSON CO.
4525 W. DIVISION ST. CHICAGO 51, ILL.

Circle No. 98 on Readers' Service Card

CIC Standard Sampling Accessories shown with Crystal Polishing Kit

How CIC accessories can help you as a spectroscopist

Connecticut Instrument Company specializes in the development and manufacture of low-cost, dependable infrared sampling accessories generally available from stock. These mount in nearly all makes of infrared spectrophotometers.

A selection of CIC's standard sampling accessories include Cavity Cells — low-cost, ultrasonically machined from a single transmitting crystal — Precision Fixed Thickness Cells which can be disassembled and cleaned in the laboratory, Presslok Demountable Cells for mulls, and many others.

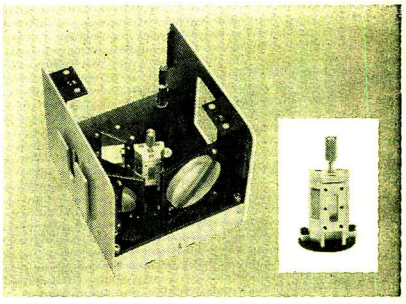
CIC's most recent efforts have been in the development of Commercial Attenuated Total Reflectance accessories. It maintains a firm lead in the development of this technique for analyzing solids, plastics, viscous liquids, films and the like. Among the list of ATR accessories available are the Standard and Micro sampling ATR attachments equipped with precision optics and Multiple Reflection accessories.

The Meaning of ATR To the Spectroscopist

ATR is a relatively new sample handling technique of tremendous value to the spectroscopist in that it permits analysis of solid and viscous liquid samples with little or no sample preparation.

By taking advantage of an optical phenomenon, a beam of reflected radiation can be made to interact with a sample in such a manner as to produce a well-defined absorption spectrum of such difficult samples as cured epoxies, hardened phenolics, rubber, leather, coatings on papers and films, skin tissue, food products; indeed, the list is seemingly limitless.

Samples, even opaque ones, are merely contacted to the reflecting crystal, and one or more reflections are made to produce the desired spectrum.



Multiple Reflection Accessory Mounted in MATR-1. **Inset:** detail of Multiple Reflection Accessory for Micro ATR Attachment.

Sample preparation may contribute heavily to the greatest portion of analytical difficulties, and since ATR simplifies preparation, one of ATR's main advantages is obvious.

Send for CIC's Complete Catalog

A complete catalog of CIC accessories and price list is yours for the asking. You'll find the catalog conveniently arranged for filing a wide variety of CIC literature, including the CIC Newsletter. If you are not receiving this Newsletter, ask to be placed on our mailing list. We think you'll enjoy its many interesting, informative articles on new products and new applications.

CIC

CONNECTICUT INSTRUMENT COMPANY

Division of BARNES ENGINEERING COMPANY

WILTON, CONNECTICUT • TELEPHONE (AREA CODE 203) 762-5545

Circle No. 112 on Readers' Service Card

HOW TO CURE MIXER-ITIS

Fed up with electric mixer repair bills? Give those worn-out mixers the boot and treat your lab to a new economy: the LIGHTNIN Mixer, Model L.

It weighs just eight pounds. But it's built to mix . . . and mix . . . and mix—for weeks at a time—without attention. You can use it for **years** without maintenance or adjustment. Hundreds of users do.

The 1/30-hp totally enclosed fan-cooled motor spins the shaft at a quiet, steady 1600 rpm; is safe with flammables. You can vary the mixing action by replacing the 2-inch propeller with different types.

Propeller and shaft come in 316 stainless steel or Monel. Your choice, too, of bronze tank clamp or ring-stand clamp. Order from your supply house, or write us. Specify LIGHTNIN Model L Mixer:

For 110v 60cy 1ph **$47.00**
For 220v 60cy 1ph **$51.00**

If you want the same dependability in a **variable-speed** mixer, send for Bulletin B112. It describes the complete line of heavy-duty LIGHTNIN Mixers and accessories for the laboratory. Write us, or check the reader service card.

Lightnin® Mixers

MIXING EQUIPMENT Co., Inc.

160-3 Mt. Read Blvd., Rochester 3, N.Y.

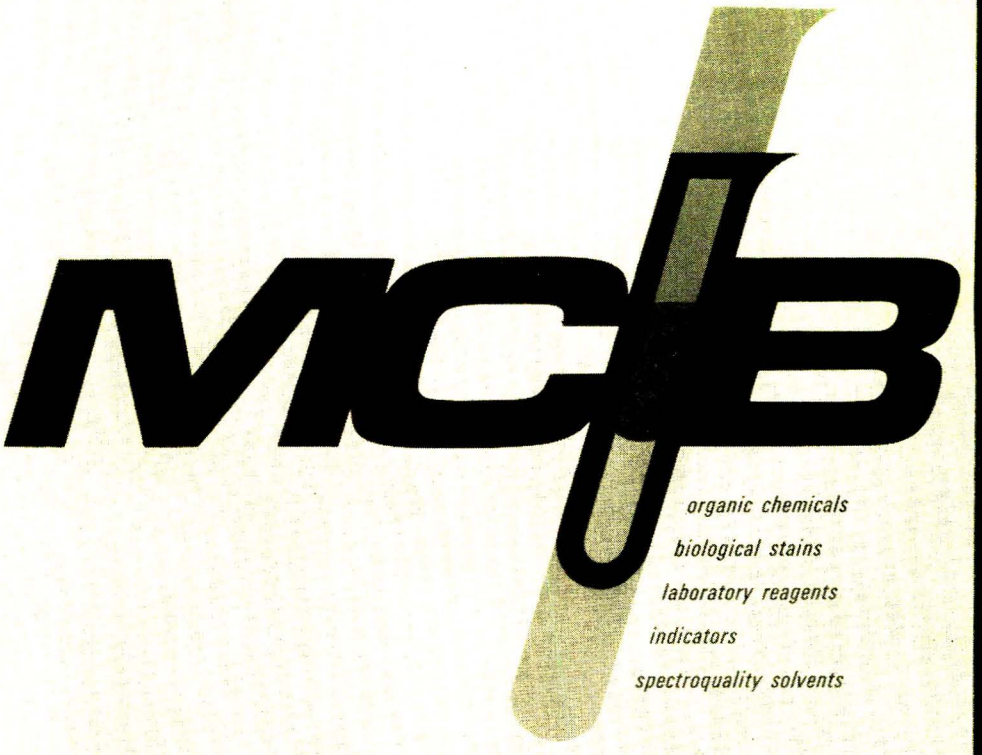
In Canada: Greey Mixing Equipment, Ltd., 100 Miranda Ave., Toronto 19, Ont.

In Europe: Lightnin Mixers, Ltd., Poynton, Cheshire, England

Circle No. 70 on Readers' Service Card

MATHESON COLEMAN & BELL
Laboratory Chemical Catalogue

NEW EDITION NOW READY



contents :

5,178 reasons why M C & B is the nation's fastest-growing producer of laboratory chemicals

It's Matheson Month — watch for your MC&B man!

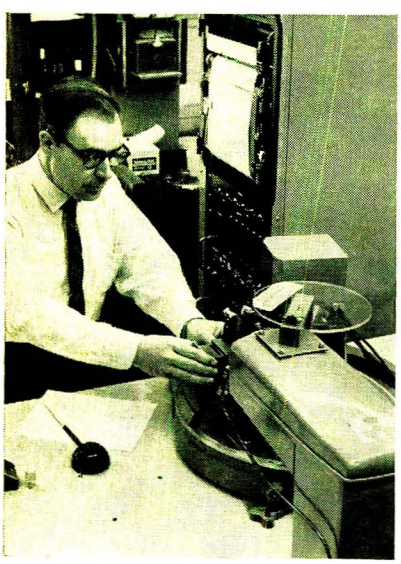
Matheson, Coleman & Bell
Division of The Matheson Company, Inc.
P. O. Box 85 East Rutherford, N. J.
☐ Please send the new MC&B Catalog
Name_____
Firm_____
Address_____
City_____ State_____

New PPB techniques exploit X-Ray emission, improve trace-element determination!

There's no real question of the feasibility of doing PPB techniques with x-ray emission. For petroleum, pharmaceuticals, metallurgy or other process industries — General Electric XRD equipment delivers analyses **in the parts-per-billion range** — with precision and consistent reproducibility. The petroleum application cited here (see chart) demonstrates a repeatability in the range of 5 to 50 PPB, for copper, iron, nickel and vanadium. Still another chemical processor uses XRD equipment for analyses of lighter elements — Al through Ti — over a range from ten to a few hundred PPM.

General Electric supplies XRD with widely diverse applications to perform PPB studies with flexibility and minimum detectability ¶ High wattage characteristics with up to 100-ma sample excitation give minimum percentage quantities ¶ Choice of six tube targets offers selective excitation ¶ Thin x-ray tube window (.010" Be) provides long wave length output for light element analyses ¶ Twin counter tubes with ultra-thin windows for widest spectral range efficiency ¶ Samples up to 2½" square or 3" diameter and 1½" thick can be conveniently presented ¶ *And*, all these advantages can be obtained on programmed equipment.

For further details on applications, and methods already proven in use, write Room UU-74, X-Ray Department, General Electric Co., Milwaukee 1, Wisconsin.



CONCENTRATION RANGES AND REPEATABILITY OF METHOD

Element	Concn. range (PPM)	Standard Deviations*
Copper	0.003-0.03	±0.003
	0.03 -0.1	±0.011
Iron	0.04 -0.4	±0.033
	0.4 -5.0	±0.51
Nickel	0.01 -0.1	±0.005
	0.1 -0.5	±0.011
Vanadium	0.01 -0.1	±0.006
	0.1 -0.5	±0.010

*Based on differences between the two values in respective duplicate determinations on 10 samples in each concentration range.

For the high range, relative accuracy at Pure Oil Company in determining the amount present varies approximately 2%—in the lowest range up to 50%.

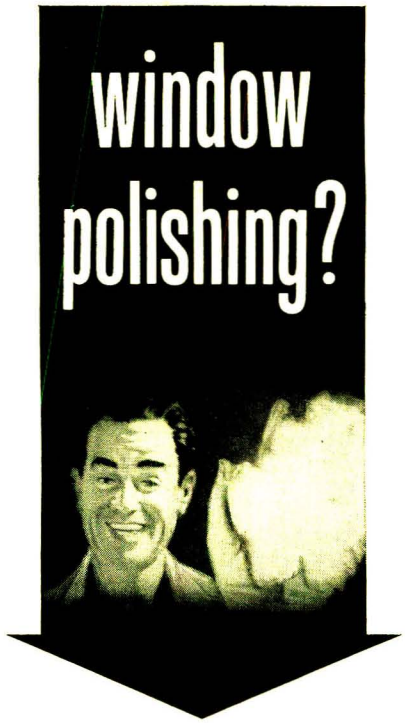
General Electric XRD equipment at Pure Oil Company Research Center (Crystal Lake, Ill.) analyzes refinery feedstocks for trace-metal concentrations from 0.003 to 5.0 PPM.

Progress Is Our Most Important Product

GENERAL ELECTRIC

Circle No. 46 on Readers' Service Card

window polishing?



Be independent. Polish your own NaCl and KBr windows with this complete kit. Recondition fogged or scratched windows flat to less than 5 fringes of Hg green line easily, quickly. Compact outfit — 6" x 7" x 11" — contains roughing, polishing and curved smoothing laps, optical flat, rouge, alcohol and sponge in a handsome wood case. All specially made for you by RIIC — the foremost firm in the accessory field.

PK-01 Polishing Kit

Another top quality product from

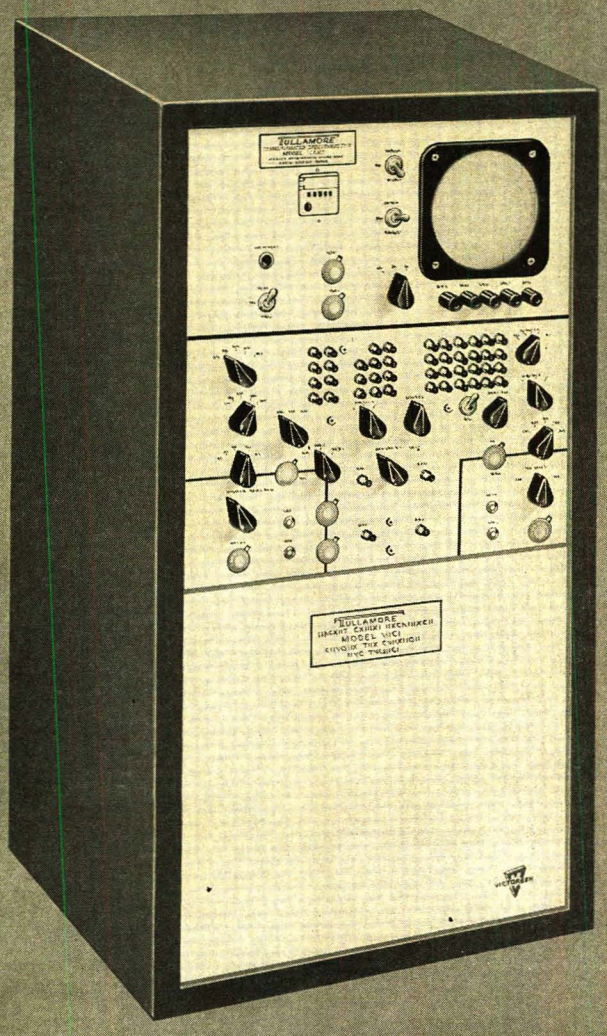
LIMIT

RESEARCH CORPORATION

Box 852, Darien, Conn.
Phone (203) 655-3991

Circle No. 122 on Readers' Service Card

Circle No. 93 on Readers' Service Card →



10,000 CHANNELS

$34,950*

VICTOREEN 10,000 CHANNEL REAL-TIME TOTALIZING MULTIPARAMETER ANALYZER

FEATURES

Two inputs, including preamplifiers, amplifiers and positive 10V/100V inputs—4 input capability in X-dimension provided by accessory mixer.

Linearity over 98% of full scale: Integral linearity better than 0.4%; differential linearity better than 2%.

Counting rate—negligible distortion over a wide range, including 50,000 pps.

Coincidence/anti-coincidence gating.

Ferrite core memory with parallel BCD logic.

10^5 Memory storage capacity (10^6 optional*).

Memory subgrouping with add/subtract logic.

Preset live or clock time with recycle programming.

Remote control of all major analyzer functions.

Visual digital neon indicating pushbuttons provide address and data presentation, and manual memory access.

Live or static 5″ CRT display—linear and/or optional log. X-Y contour map or single spectrum presentation is switch selected.

Compatible with Victoreen's wide range of readout accessories.

***Basic Model MP104-K . . . $34,950**

Deliveries to commence in late 1963. Price, FOB Chicago, Ill., subject to change without notice. Slightly higher overseas.

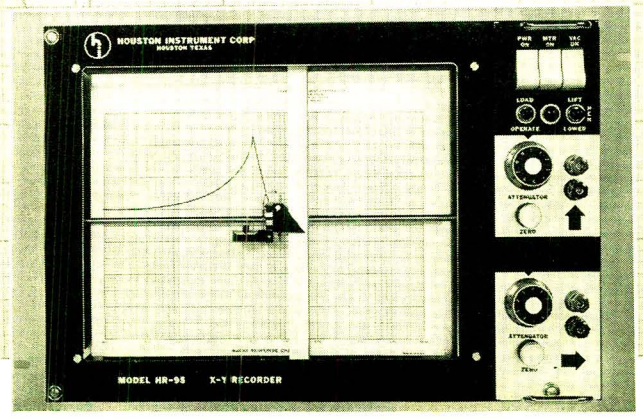
WORLD'S FIRST NUCLEAR COMPANY

VICTOREEN

THE VICTOREEN INSTRUMENT COMPANY
TULLAMORE DIVISION
5857 WEST 95th ST. • OAK LAWN, ILLINOIS
Victoreen European Office: P. O. Box 654, The Hague

VICTOREEN

8½" x 11" X-Y RECORDER



Model HR95-T0

$1250

Performance: 1 mv/in. basic sensitivity, 15 in/sec. pen speed, 0.25% overall accuracy, 600 in/sec² peak acceleration, 0.1% resetability.

Reliability: Special emphasis on a simple, straightforward design insures continued trouble-free performance. The HR-95 is fully warranted for one year.

Flexility: Plug-in control modules and compatibility with all standard converters and accessories, including the complete Houston Instrument line, assure the capability of the HR-95 to perform all recording functions.

Accessibility: Modular construction plus hinged recording surface permits complete access to all electrical and mechanical components in seconds.

Price: $1250 No time base
$1350 With time base

8 page brochure available upon request

houston instrument corporation
4950 Terminal Avenue/Bellaire 101, Texas
MOhawk 7-7403/Cable: HOINCO TWX 713-571-2063

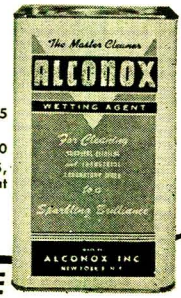
Circle No. 52 on Readers' Service Card

YOU'RE NEVER IN DOUBT WHEN IT'S "Alconox-Clean!"

In the laboratory or hospital, just "clean" isn't good enough. Make sure your glassware and equipment are "Alconox-Clean."

Proven *best* by test* for over 20 years!
**** for wetting power!***
**** for sequestering power!***
**** for emulsifying effect!***

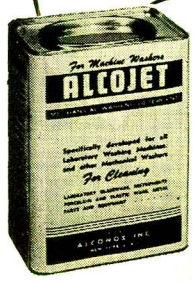
Use ALCONOX
For all equipment washed by hand
Box of 3 lbs.....$1.95
Case of 12 boxes — 3 lb. ea...$18.00
Available in drums of 25, 50, 100 and 300 lbs. at additional savings!
(Prices slightly higher West of the Rockies)



SAVE TIME AND MONEY! with ALCONOX

The World's Most Thorough Cleaner — Yet it costs up to 75% less!

Eliminates tedious scrubbing — Penetrates irregular and inaccessible surfaces — Removes dirt, grease, grit, blood, tissue, etc. with amazing ease — Completely soluble and rinsable — Gentle to the skin —



Use ALCOJET
For all equipment washed by machine
Box 5 lbs.....$3.00
Case of 6 boxes — 5 lbs. ea...$15.00
Available in drums of 25, 50, 100 and 300 lbs. at additional savings!
(Prices slightly higher West of the Rockies)

Clean Pipettes in one easy operation with ALCOTABS — for all pipette washers. Box of 100 Tablets.....$5.00

Order from your Supplier or ask him for samples and FREE Cleaning Guide.

ALCONOX, Inc.
853 Broadway, New York 3, N. Y.

Circle No. 153 on Readers' Service Card

NEW CHEMICALS

E. MERCK

(DARMSTADT, W. GERMANY)

...for thin-layer chromatography

New Silica Gel H and HF—exclusive adsorbents for T L C, both without $CaSO_4$ but with hydrated silicon dioxide binder (U.S. Pat. Pending)—are vastly superior to any other adsorbents without calcium sulphate binder because: (a) they really adhere to a plate as a solid layer, (b) they do not set until after they are spread and can be kept in suspension on the shelf, (c) they provide much faster development due to ideal particle size distribution (many others are too finely ground in order to get some adhesion), (d) only adsorbents without $CaSO_4$ which are practical for preparative techniques, (e) no interference from $CaSO_4$—especially recommended for the separation of phospholipids, inorganic compounds and hydrophilic substances, among others.

...for gas chromatography

1. Solid adsorbents for gas adsorption.
2. Inert solid carriers for gas partition.
3. Pure stationary phases.
4. Reference standards.

...for spectroscopy

Optically pure solvents and auxiliary agents for ultraviolet, infrared and nuclear magnetic resonance spectroscopy including deutero-chloroform, deuterium oxide, deutero-hydrochloric acid, deutero-sulphuric acid, hexadeuterobenzene, tetradeuteroacetic acid, deuterotrifluoroacetic acid, hexadeuteroacetone, hexadeuterodimethylsulphoxide, pentadeuteropyridine, etc.

All preparations described are available for immediate delivery from our stock. For further information and prices, please contact:

BRINKMANN

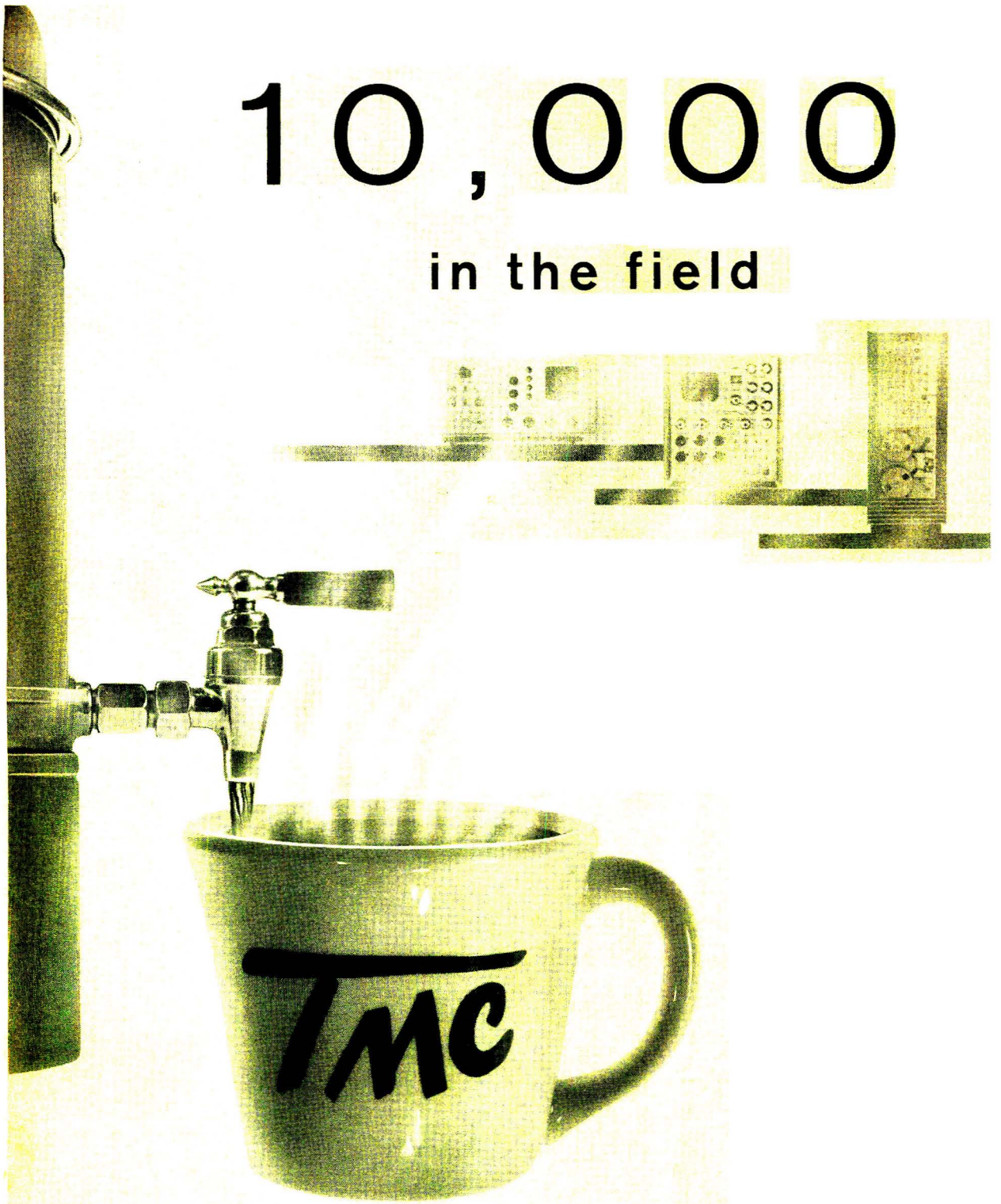
BRINKMANN INSTRUMENTS, INC., 115 CUTTER MILL ROAD, GREAT NECK, N.Y.

PHILADELPHIA • CLEVELAND • HOUSTON • MIAMI • MENLO PARK, CAL. • ST. LOUIS

Circle No. 152 on Readers' Service Card

10,000

in the field



TECHNICAL MEASUREMENT CORPORATION
441 Washington Ave., North Haven, Conn., CE 9-2501

DOMESTIC: Gardena, Calif.; San Mateo, Calif.; La Grange, Ill.; Silver Spring, Md.; Stoneham, Mass.; White Plains, N. Y.; Oak Ridge, Tenn.; Dallas, Texas.

CANADA: Allan Crawford Associates, Ltd., 4 Finch Avenue, W., Willowdale, Ontario, Canada
EUROPE: Technical Measurement Corporation, GmbH, Mainzer Landstrasse 51, Frankfurt/Main, Germany
JAPAN: Nichimen Company, Ltd., Muromachi, Nihonbashi, Chuo-Ku, Central P.O. Box #1136, Tokyo, Japan

Circle No. 144 on Readers' Service Card

by Ralph H. Müller

Applications of the Hall Effect

NEW MATERIALS, new instrumental techniques, and new concepts all contribute to the advancement of science and technology which, for some time, has been proceeding at an exponential rate. Occasionally, two or all three of those essential factors conspire to produce something extraordinary. An example which we wish to discuss, has done just that, and, in addition, has brought an eighty-four year old phenomenon to new and unexpected applications.

In 1879, E. H. Hall at Johns Hopkins, discussed the effect which bears his name. When current is flowing in a magnetic field, an electromotive force is generated which is at right angles both to the magnetic field and to the current, and is proportional to the product of the intensity of the current, the magnetic field, and the sine of the angle between the directions of these quantities. These are small but readily demonstrable effects, but with the advent of improved semiconductors, new interest from both the theoretical and experimental points of view in the Hall effect arose.

During the Los Angeles Meeting, we had an excellent opportunity to get caught up on some recent developments in this field. We made one of our frequent visits to Beckman Instruments, Inc., where we received the customary red carpet treatment. This is no measure of our importance, it's just the way they do things out there. Through the courtesy of Brice James and the research and engineering staffs, we learned the results of some two years of intensive research and development in Hall effect phenomena and the many useful devices and instruments which have emerged from these studies.

It is not appropriate here to go into the detailed physics of the Hall effect but better, perhaps, to outline these developments which have resulted in pre-eminently useful devices and instruments.

Of the many materials which could be used, indium antimonide and indium arsenide are the materials most commonly used in commercial Hall generators. Indium antimonide with its high carrier mobility, is superior to all other materials for power transfer efficiency, but has a high temperature dependence. Indium arsenide has a lower carrier mobility, but a much lower temperature dependence.

One of the most important developments has been the "thin film" Hall generator which owes its high sensitivity to the drastic reduction of the thickness parameter. This is achieved by Beckman by vacuum deposits of the semiconductor in films only a few microns thick. An additional improvement for high permeability consists in depositing a thin film on a ferrite slab and covering the film with another ferrite piece resulting in an effective air gap in the magnetic field some 15 times smaller than conventional Hall generators.

The advent of "thin film" Hall generators at once made voltage drive of a Hall generator possible. Heretofore, the generator has traditionally been regarded as a current controlled element. One of the most important results of voltage drive is the improvement of temperature coefficients which can be as high as fivefold.

Some typical Hall generators made by Beckman's Helipot Division and designated as Hallefex Voltage Generators include the Model 350, which is $^3/_8$" x $^1/_2$" x 0.025" with an indium antimonide film for maximum sensitivity. Model 351 is the same size but has an indium arsenide element for optimum performance over a wide range. Models 335 (indium antimonide) and 336 (indium arsenide) measure only $^1/_4$" x $^1/_4$" x 0.040" and have an effective air gap of less than 0.002".

A few Hall effect applications may be mentioned here. For power measurements, if the control current through the strip is proportional to, and in phase with, the line voltage while the magnetizing current is in phase with the line current, the Hall voltage output is a DC term proportional to real power and an AC double frequency term proportional to volt-amperes.

In a DC to AC converter, the "chopping" signal can be applied to either the magnetic circuit or the Hall element, depending upon the desired frequency. For example, if the magnet is excited by a current: $i_2 = I \sin wt$. and the signal to be converted i_1 is applied to the Hall element, the output voltage will be $V = Ki_1i_2 = K'i_1 \sin wt$.

Function generators of wide variety can be made by rotating the Hall element in uniform or nonuniform magnetic fields. In the former, sin 0, cos 0, $\sin^2 0$ or $\cos^2 0$ can be generated. In the latter, exponential functions can be generated, such as: Ke^x, Ke^{xy}, and $K(1-e^x)$.

As a multiplier, if the current applied to the magnetizing coil is thought of as one signal and the element control current the second signal, the Hall voltage is proportional to the product. Note that one of these inputs is electrically isolated from the output.

A "clip-on" DC or AC ammeter is achieved by exciting the Hall element with a constant current source and placing it in the magnetic field caused by the movement of charged particles. With this, one can measure current in a conventional conductor as well as the flow of ionized gases or liquids.

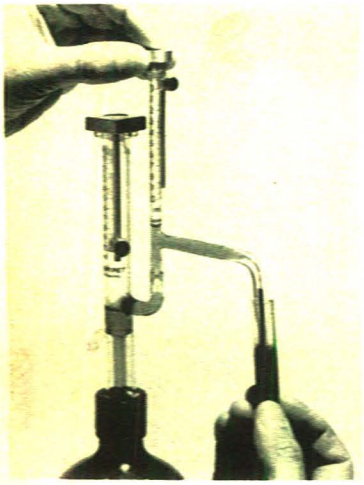
As a gaussmeter, control current to the Hall element is supplied from a constant current source and the Hall voltage is directly proportional to magnetic field strength. No relative motion between magnetic field and pickup element is required. The direction of the field can be determined by rotating the element until the maximum Hall voltage is obtained. Polarity of the field can be found because the Hall voltage changes sign with a 180° change in field direction.

Many other applications are possible and include modulation, mechanical positioning of systems to ±0.0004", resolvers, linear or rotary displacement transducers, gyrators, frequency multiplexing, field direction (compass), and wave analysis.

That there is more to come makes these superb developments all the more exciting. There are, of course, the related thermal and inverse effects of Nernst and von Ettinghausen and then, too, the Leduc and Corbino effects.

We are getting to that delightful stage where fundamental advances are completely dependent upon instrumentation and the latter is constantly improved or often revolutionized by new materials and new concepts.

AUTOMATIC DILUTOR ONLY $89.50?



That is all, and it buys you a more precise, much less troublesome automatic dilutor than those costing far more. **Labindustries'** all-pyrex Dilutor • instantly aspirates and dilutes with 1% accuracy simply by lifting and then pressing the plunger (0.1% reproducibility) • mounts directly on your diluent bottle, or ours, thus using no extra space • features a 100% visible, air-free system, allowing you to spot at a glance errors as small as .0005 ml.

Available in 1, 10, 20 and 50 ml. sizes, all quickly set for dilution ranges up to 1 : 50,000

Write us for full details and remember: **L/I** also offers you the best buy on *automatic dispensing pipets* (Repipets) and *Acquameters* for Karl Fischer reagent water determinations.

LABINDUSTRIES

1740 University Ave., Berkeley, California, Phone (415) 843-0220

Circle No. 59 on Readers' Service Card

PROPIPETTE

Safety Pipette Filler

holds liquids indefinitely

- Time Tested
- No moving parts
- Simple to operate

The new **PROPIPETTE** eliminates the dangerous practice of using the mouth to draw liquids into pipettes. It is simple to use and the operator soon becomes proficient so that liquids can be delivered quickly, precisely and safely. Measurement precision is extremely high (0.01cc). The instrument has three agate-ball valves which operate independently and the entire procedure can be done with only one hand.

Choice of black, red, green, yellow and blue..... **PRICE $7.60 each**
Available through laboratory dealers. *sent on approval*

All laboratory pipettes can be used with the PROPIPETTE — Safety Pipette Filler

Write for additional information

INSTRUMENTATION ASSOCIATES, INC.

Distributors of Laboratory and Scientific Specialties

17 West 60th Street **New York 23, N. Y.**

Circle No. 118 on Readers' Service Card

HELLER ELECTRONIC VARIABLE-SPEED AC CONTROLLER and Matching DC MOTOR

2T60 ELECTRONIC CONTROLLER with matching 1/50 H.P. DC MOTOR

$87

Complete, F.O.B., Las Vegas, Nevada

SPECIFICATIONS

• Thyraton tube operated controller gives stepless operation • Input: 110-120 V., 60 cy. single phase • Output: 0-120 V., 200 ma. DC to armature • 1/50 H.P. ball bearing, right angle, gear head, shunt wound, DC motor • Reversible • Armature shaft is extended • Armature speed 0 to 4000 R.P.M. • Motors in gear ratios: 6, 18, 30, 36, 60, 100, 300, 540, and 1120:1 in stock.

Other models to 3/4 H.P. motors available. Request data.

GERALD K. HELLER CO.

2673 South Western Street, Las Vegas, Nevada, P.O. Box 4426

Circle No. 51 on Readers Service Card

LABORATORY RECORDER

HIGH SENSITIVITY LOW COST $325.00

MODEL #22700 SERVO-GRAPHIC RECORDER

FEATURES:

- Pen travel 1 Second full scale.
- Accuracy 99% or better.
- Photoelectric Chopper for long life.
- Zener diode stabilized reference voltage.
- Adjustable paper speeds.
- Input suitable for high impedance sources.
- Adjustable range control.

RANGE: 0-10 MILLIVOLTS D.C.
0-100 MILLIVOLTS D.C.

The Servo-Graphic Recorder is an ideal laboratory instrument. Put it to work and save a valuable technician's time. O.E.M. users invited.

Write for literature

C. H. STOELTING CO.

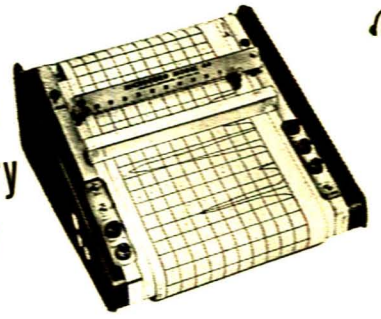
12" CHART SERVO RECORDERS
MULTI-CHANNEL HIGH FREQUENCY OSCILLOGRAPHS
POLYGRAPHS • KYMOGRAPHS • MANIPULATORS

424 NORTH HOMAN AVE., CHICAGO 24, ILL.

Circle No. 87 on Readers' Service Card

PHOTOVOLT CORPORATION

Super Sensitive Laboratory Recorder

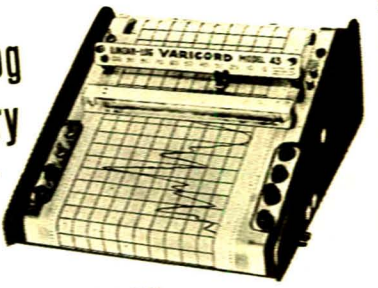


Microcord 44 **$890**

For gas chromatography, electro-balance service and other critical applications. ■ Ranges to ½ mV full scale. ■ Fast pen speed. ■ Highly accurate. ■ Speed-change switch. ■ Integrator connecter.

Write for Bulletin #1000

Linear/Log Laboratory Recorder



Varicord 43 **$885**

A versatile sensitive servo-recorder for general laboratory use. ■ Multi-range, potential and current recorder. ■ Choice of per cent transmission or absorbance indication in spectrophotometry. ■ For gas chromatography by conductivity or ionization. ■ True potentiometric input. ■ Less than 1 second pen speed – 10 millivolt full scale sensitivity. ■ Output connector for integrating and telemetering.

Write for Bulletin #1130

1115 BROADWAY ■ NEW YORK 10, N.Y.

Circle No. 163 on Readers' Service Card

NEW

RECORDING

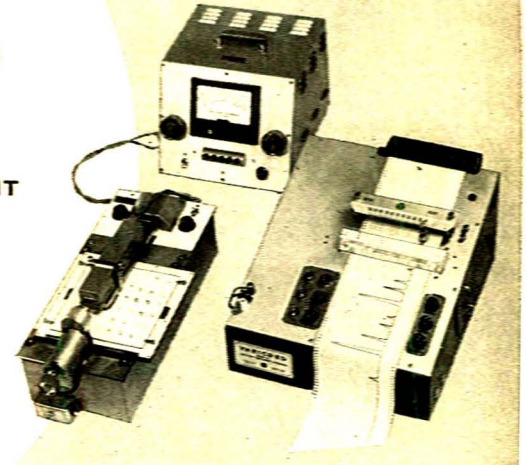
DENSITOMETER

for

THIN LAYER CHROMATOGRAMS

Direct, Manual or Fully Automatic Scanning of Plates by Visible or U.V. Absorbance, and by Fluorescence.

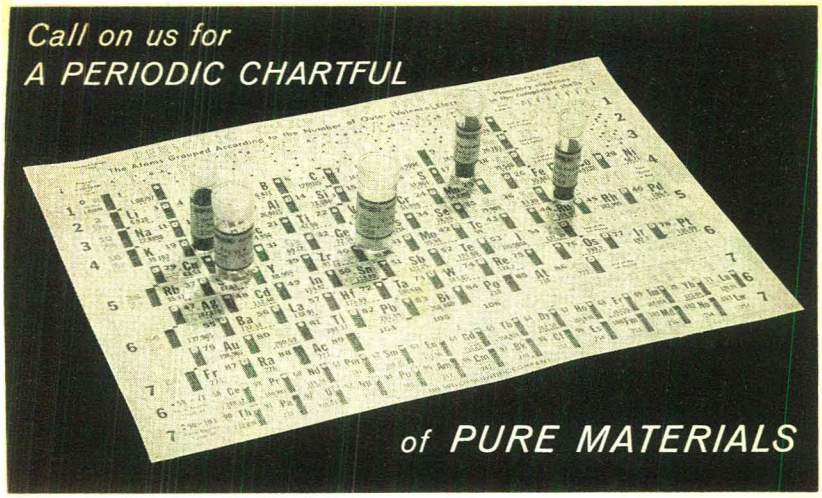
REPRODUCIBLE ■ ACCURATE ■ CONVENIENT



PHOTOVOLT CORPORATION

1115 BROADWAY • NEW YORK 10, N.Y.

Circle No. 164 on Readers' Service Card



with individual analysis certificates,

as well as
STANDARDS
SPECTROGRAPHIC PLATES
FILM
DEVELOPER
GRAPHITE ELECTRODES

SPEX INDUSTRIES, INC. • 3880 PARK AVENUE • METUCHEN, N. J.

Circle No. 85 on Readers' Service Card

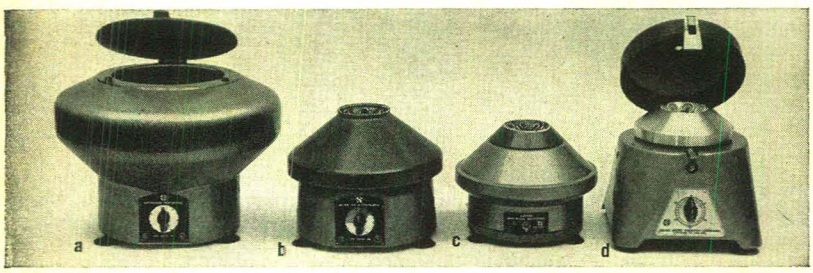


table model centrifuges to meet your analytical needs

From the most complete line of table model centrifuges . . . four Clay-Adams models designed for industrial and chemical laboratories . . . all are shock-mounted precision instruments engineered and manufactured to assure years of superior performance.

a-ADAMS SAFEGUARD CENTRIFUGE—ANGLE AND STANDARD HEADS: A multi-purpose, basic instrument for labs with heavy work loads . . . accommodates any one of four standard or four angle heads . . . useful for all common separations and special analytic procedures . . . holds tubes of 15 ml. or less and up to 50 ml. . . . dial rheostat control provides variable RPM and RCF range.

b-ADAMS SAFETY HEAD: For all commonly performed precipitate separations . . . adaptable for micro and semi-micro analyses . . . six-tube capacity (15 ml. or less) . . . angle head provides fast, efficient centrifugation . . . variable RPM and RCF . . . compact, light and portable.

c-ADAMS ANALYTICAL: For micro and semi-micro separations . . . accommodates six tubes (5 or 3 ml.) . . . also adaptable for 2 and 0.5 ml. tubes . . . angle-head efficiency . . . compact, portable, requires minimum table space . . . provides fixed 3,400 RPM speed.

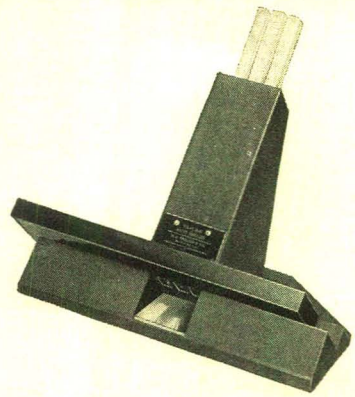
d-ADAMS MICRO-CHEMISTRY: For micro-analytic separations of organic and inorganic precipitates . . . eight-place angle head accommodates 1, 0.5, and 0.25 ml. glass or plastic tubes . . . provides high fixed speed (13,500 RPM–15,500 RCF) . . . high RCF assures separation of particles of similar specific gravities . . . complete, automatic stop in 60 seconds.

Available from your dealer

Clay-Adams
New York 10, N. Y.

Circle No. 33 on Readers' Service Card

PROVEN ACCURATE*
TAYLOR COMPARATORS GIVE QUICK, EASY WATER ANALYSIS



TAYLOR WATER ANALYZER
Also available: pH and Chlorine Comparators, Boiler Water Slide Comparator. Chromate Comparator for corrosion control.

You can maintain accurate, rigid control over important operations by making on-the-spot tests with Taylor sets in just minutes. No experience necessary. No fragile individual glass standards to handle.

* **The color standards in a Taylor Comparator — used for 21 years in the field — have been certified by an independent laboratory as true and still absolutely accurate. Copy of statement on request.**

Taylor color standards are unconditionally guaranteed non-fading. For Taylor sets or immediate replacement of supplies, see your dealer.

FREE HANDBOOK
1962 edition, 101 pages. Discusses importance of process control in chemicals, food, pharmaceutical, textile, paper, other industries. Illustrates and describes complete Taylor line.

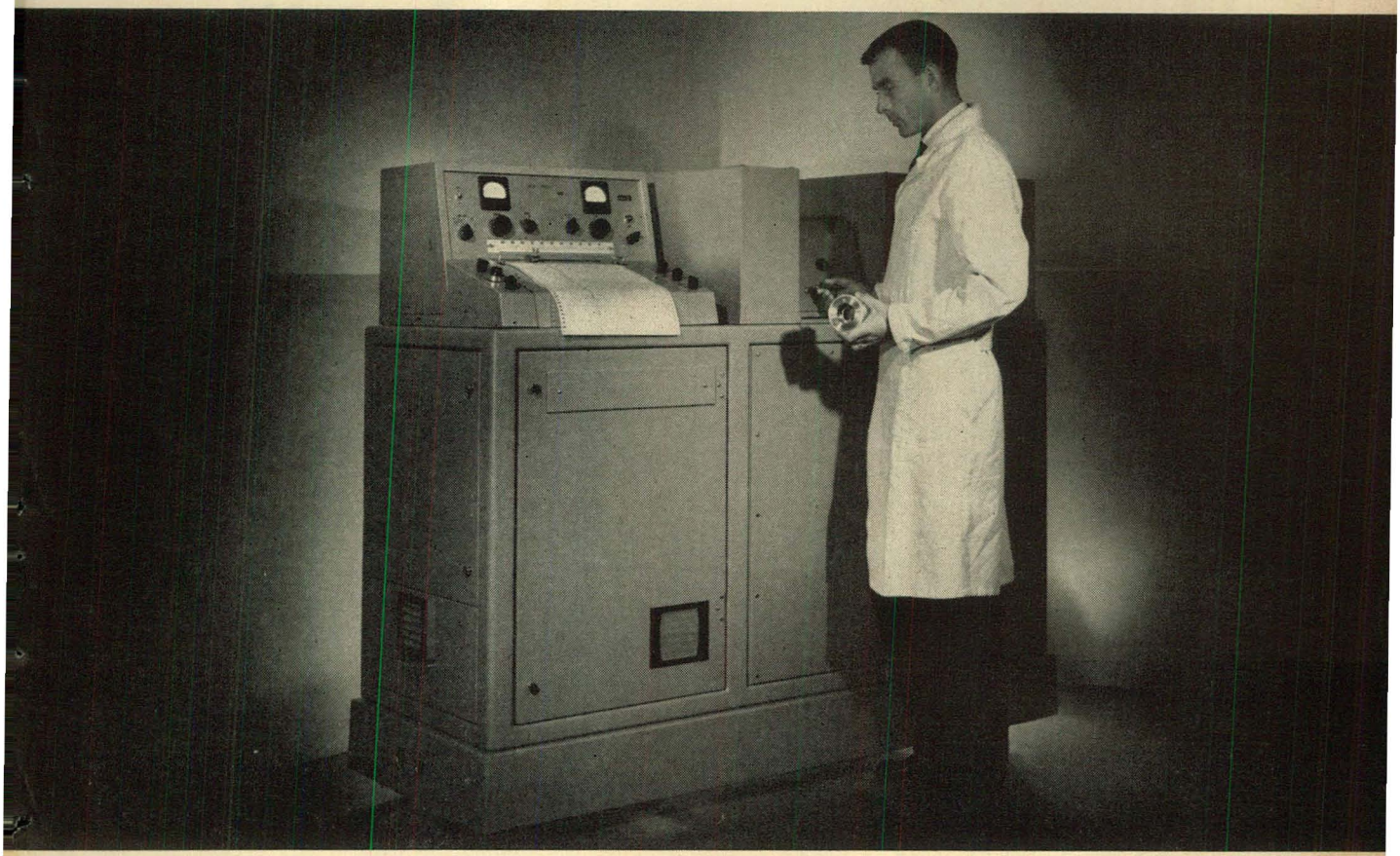
W. A. TAYLOR AND CO.
7306 YORK RD. • BALTIMORE-4, MD.

Circle No. 6 on Readers' Service Card

Circle No. 101 on Readers' Service Card →

New Cary-White Model 90 Infrared Spectrophotometer

OFFERS OUTSTANDING PERFORMANCE WHEN IT'S MOST IMPORTANT ...WHILE SCANNING!



Send for Data File A238-73.

Cary 'dynamic' specifications define Model 90 performance while scanning—not just in static operation. For instance a double-beam 18-minute scan can be run on the ratio-recording Model 90 with photometric accuracy of 0.2% on 0-100% T scale, or 0.1% on expanded scale, with resolution better than 1 cm^{-1} and S/N between 30/1 and 100/1. For longer scans resolution is up to 0.25 cm^{-1}.

Liquid helium or incandescent samples are handled with ease. Very high or low temperature materials can be scanned with accuracy because energy for the source is chopped only before it passes through sample and reference cells, thus radiation from the sample is not detected as transmitted energy. Large sample space (over 10 inches long) allows use of special equipment such as cryostats or furnaces.

Versatility for IR work—differential analysis and measurements of absolute intensity, or small absorbance differences at high absorbance—is provided by Model 90. Scan range: 4000 to 450 cm^{-1}. Strip chart recorder coupled with scan drive permits many cm^{-1} scale expansions, allows scan speed changes during operation without affecting display. Scan time is variable from 2 minutes to over 1000 hours.

APPLIED PHYSICS CORPORATION
2724 SOUTH PECK ROAD · MONROVIA, CALIFORNIA

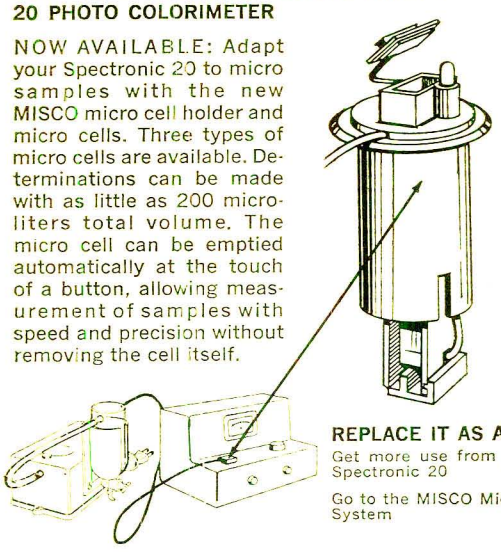
Cary
INSTRUMENTS

New! BY MISCO

MICRO CELL HOLDER AND MICRO CELLS

FOR THE BAUSCH & LOMB SPECTRONIC 20 PHOTO COLORIMETER

NOW AVAILABLE: Adapt your Spectronic 20 to micro samples with the new MISCO micro cell holder and micro cells. Three types of micro cells are available. Determinations can be made with as little as 200 microliters total volume. The micro cell can be emptied automatically at the touch of a button, allowing measurement of samples with speed and precision without removing the cell itself.



REPLACE IT AS A UNIT!

Get more use from your Spectronic 20

Go to the MISCO Micro System

MICROCHEMICAL SPECIALTIES CO.

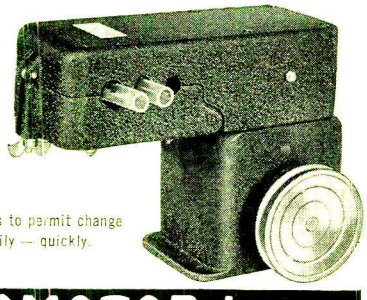
1825 EASTSHORE HIGHWAY BERKELEY 10, CALIFORNIA

Circle No 67 on Readers' Service Card

NOW

A LOW COST METERING PUMP FOR SULPHURIC ACID AND OTHER STRONG OXIDIZING AGENTS

Now a special formulation of Hypalon makes the dependable SIGMAMOTOR Pump applicable for metering sulphuric acid or other strong oxidizing agents. Liquid is forced through Hypalon tubing by wave-like action of steel fingers. Never contacts metal.

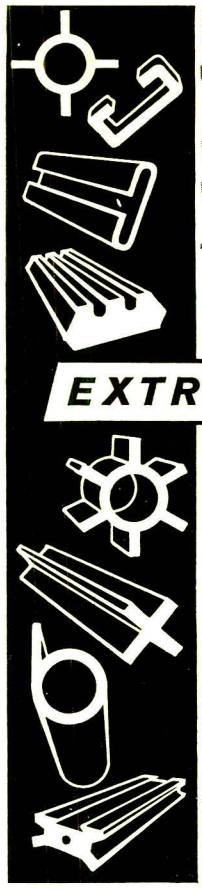


Model T6SH opens to permit change of tubing easily — quickly.

SIGMAMOTOR Inc.

47 NORTH MAIN STREET • MIDDLEPORT, NEW YORK

Circle No. 84 on Readers' Service Card



SAVE WITH SHAPES OF TEFLON*

EXTRUDED

BY PF

no machining

no molds

no wasted material

You get high quality Teflon parts at low cost by having PF extrude shapes to your design. PF extruded shapes are widely used in chemical and mechanical applications as fluid separators, feeding tubes, channels, seals, and for other uses where Teflon's unique properties offer big advantages.

PF Teflon shapes offer:

- complete chemical inertness — won't contaminate other materials
- widest service temperature range of any plastic: —450°F to +500°F
- lowest coefficient of friction of any solid material; best non-stick qualities
- very low permeability, easy cleaning

PF extrudes Teflon shapes to extremely close tolerances, cuts them to length, post forms to your requirements and performs any auxiliary machining steps. Simple or intricate shapes ranging from 2500 feet per pound to 6 feet per pound can be extruded. Often, part design can be modified to utilize these shapes for high quality, extremely accurate, lower cost parts.

Write, wire or phone for a quotation on your requirements.

PENNSYLVANIA FLUOROCARBON CO., INC. PF

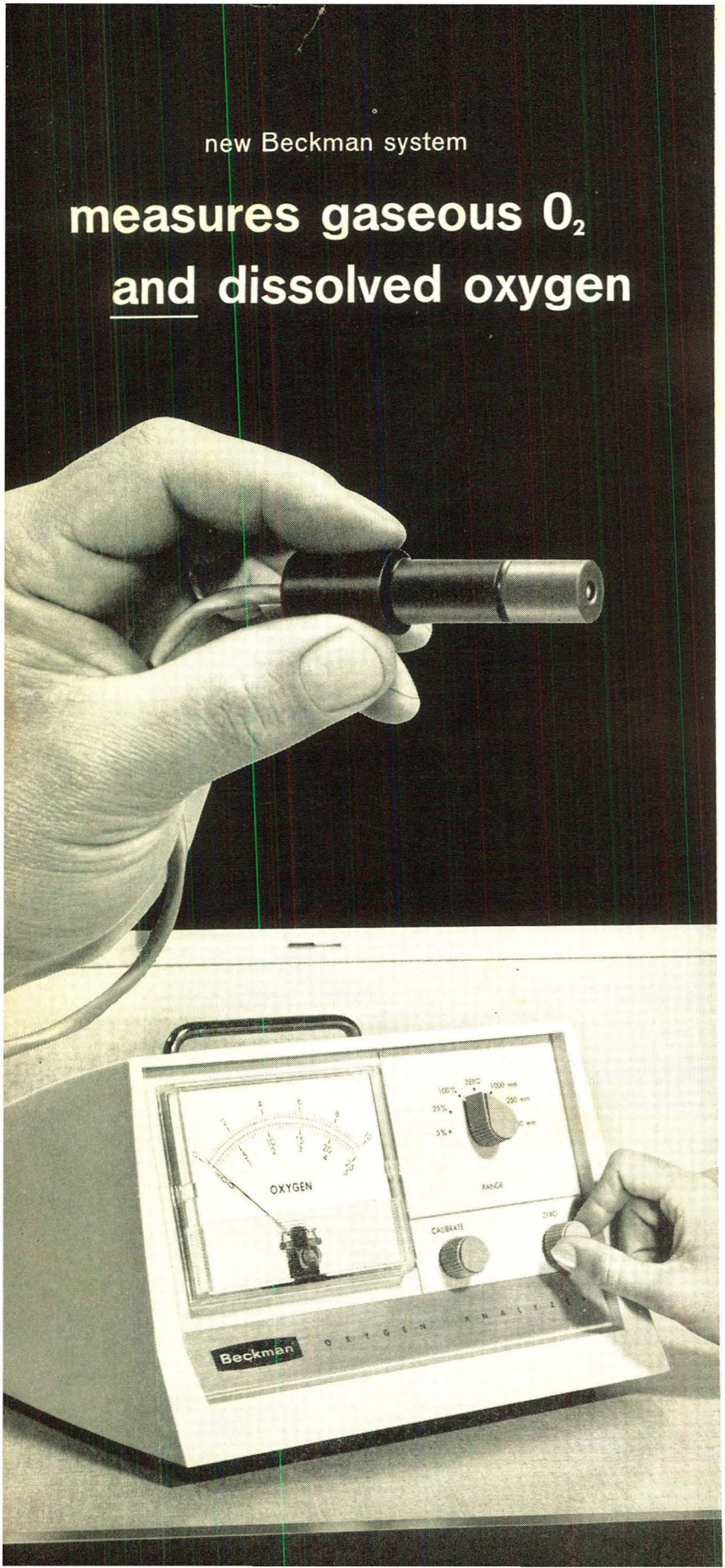
Holley St. & Madison Ave., Clifton Hts., Pa.
(215) MAdison 2-2300 TWX: 215-623-1577

*DuPont Reg. T. M.

Circle No. 75 on Readers' Service Card

new Beckman system

measures gaseous O_2 and dissolved oxygen



This is the concept developed by Beckman for critical oxygen analyses in the Project Mercury space capsules. Now Beckman offers a commercial version of this rugged, highly successful system for laboratory measurement of gaseous oxygen *or* of dissolved oxygen in aqueous or non-aqueous solutions.

The New Beckman Oxygen Sensor is the key to the system. Working on a patented polarographic principle*, a silver anode and a gold cathode are separated from the sample by an oxygen-permeable membrane. Thus, the membrane prevents sensor contamination, yet permits oxygen to diffuse to the sensor for fast determinations – 90% of response in less than ten seconds. A built-in thermistor compensates for temperature fluctuations. Readout is accomplished by one of two new Beckman devices:

Beckman Model 777 Oxygen Analyzer has a direct-reading meter plus recorder output, and translates sensor signal into convenient measurement units. Multiple ranges are expressed in per cent oxygen, mm. partial pressure, per cent air saturation, and parts per million dissolved oxygen. Features a line-operated, solid-state A.C. amplifier for drift-free performance. Especially designed for the modern laboratory, the Model 777 is attractively housed in a light-weight, corrosion-resistant, polypropylene case.

Beckman Oxygen Adapter allows the Beckman Model 76 Expanded Scale pH Meter to function as an oxygen analyzer. The Model 76 can then provide the same oxygen measurement ranges as the Model 777 with the same accuracy. The laboratory is thus equipped with a multi-purpose instrument readily convertible for either pH or oxygen measurements.

Your Beckman dealer has full particulars on these exciting new laboratory oxygen measuring devices. Remember too, that Beckman has comparable process oxygen equipment. Ask him, or write for data file LO-15-163.

Beckman® INSTRUMENTS, INC.

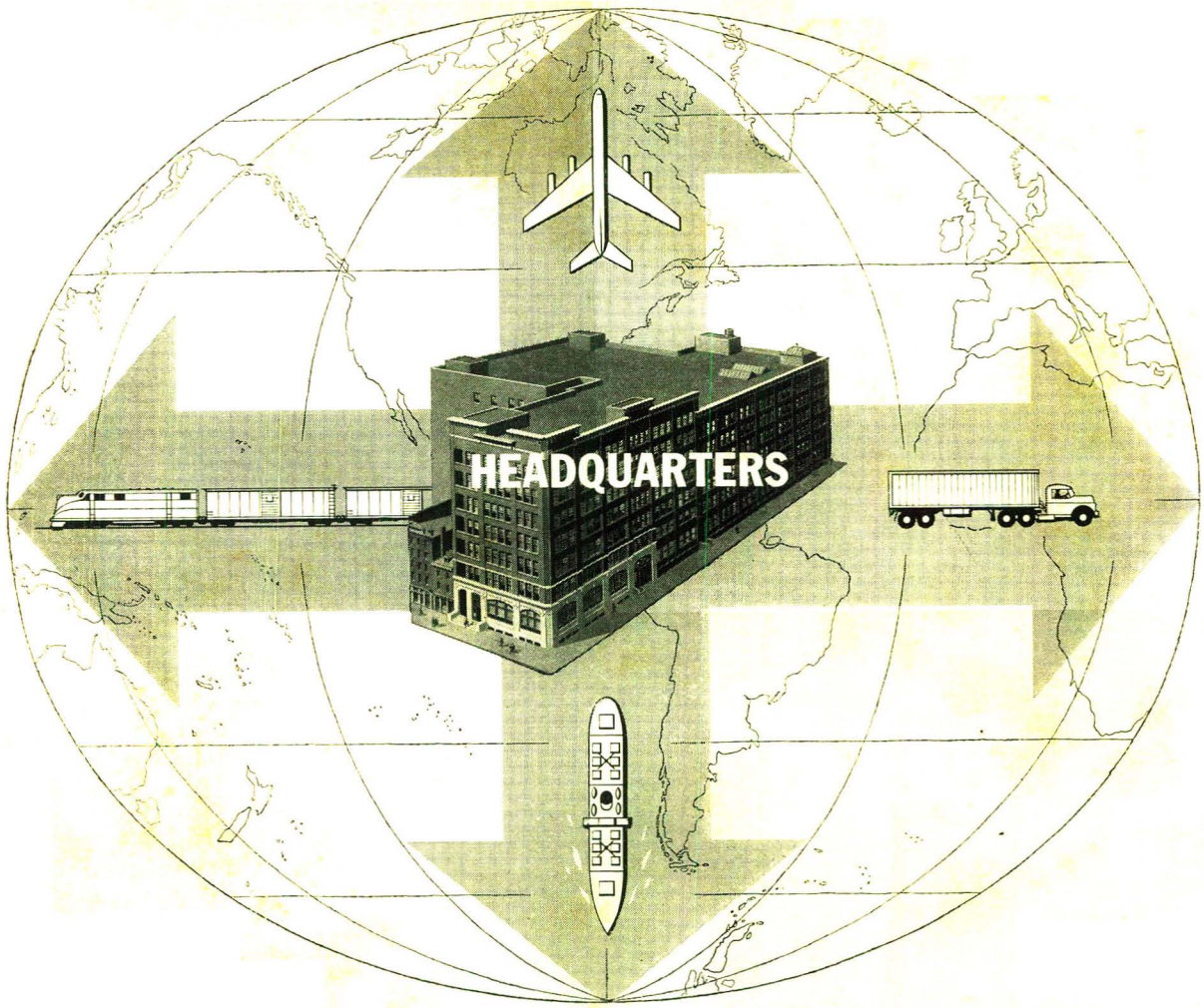
SCIENTIFIC AND PROCESS INSTRUMENTS DIVISION

Fullerton, California

International Subsidiaries:
Geneva, Switzerland; Munich, Germany; Glenrothes, Scotland

* U.S. PATENT NO. 2,913,386

Circle No. 105 on Readers' Service Card



You **SAVE** time and money when you order from *Thomas*

Shipments are made directly from our centrally located Philadelphia headquarters with unexcelled national rail, motor transport, seaport and international airport facilities.

Our streamlined order handling system results in more than 90% of orders being shipped either the day received or the day following.

The promptness and completeness of our shipments reduces waiting time of your laboratory personnel and minimizes expediting costs.

We carry the largest stocks and widest assortments of standard brands of Laboratory Apparatus available from any single source —mostly prepackaged for immediate shipment.

Stocks are carefully selected and continually inspected for quality and performance.

Packing is more than adequate to ensure safe delivery.

Accurate invoices and packing lists save you time and labor costs.

Copy of our general catalog sent to laboratory and purchasing personnel upon request

Thomas **ARTHUR H. THOMAS COMPANY**

Scientific Apparatus and Reagents

VINE STREET AT 3RD • P. O. BOX 779 • PHILADELPHIA 5, PA., U. S. A.

Circle No. 90 on Readers' Service Card

ANALYTICAL CHEMISTRY

EDITORIAL

July 1963, Vol. 35, No. 8
ANALYTICAL CHEMISTRY

Director of Publications, Applied Journals, ACS, Richard L. Kenyon
Director of Business Operations, Applied Journals, ACS, Joseph H. Kuney
Executive Assistant to the Director of Publications, Applied Journals, ACS, Rodney N. Hader
Assistant to the Director of Publications or Editorial Development, Applied Journals, ACS, William Q. Hull
Director of Editorial Research, Applied Journals, ACS, Robert F. Gould

Editor, LAWRENCE T. HALLETT

EDITORIAL HEADQUARTERS
Washington 6, D. C.
1155 Sixteenth St., N.W.
Phone: REpublic 7-3337 Teletype WA 23
Associate Editors: G. Gladys Gordon, Sue M. Solliday
Assistant Editor: Virginia E. Stewart
Editorial Assistants: Patricia Banko, Josephine Pechan
Editorial Reference: Barbara A. Gallagher
Production Staff-Washington
Joseph Jacobs (*Art Director*)
John V. Sinnett (*Art*)
Production Staff-Easton, Pa.
20th and Northampton Sts.
Associate Editor: Charlotte C. Sayre
Assistant Editor: Elizabeth R. Rufe

REGIONAL EDITORIAL BUREAUS

Eastern
Manager: Walter S. Fedor (New York)
NEW YORK 17, N. Y.
733 Third Ave.
PHILADELPHIA 3, Pa.
1725 Pennsylvania Blvd.
PITTSBURGH 30, Pa.
530 William Penn Place
Midcontinent and Western
Manager: Arthur Poulos (Chicago)
CHICAGO 3, Ill.
36 South Wabash Ave.
CLEVELAND 14, Ohio
1367 East Sixth St.
SAN FRANCISCO 4, Calif.
57 Post St.
LOS ANGELES 5, Calif.
422 South Western Ave.
HOUSTON 2, Tex.
1121 Walker St.
Washington
Southeastern
WASHINGTON 6, D. C.
1155 Sixteenth St., N.W.
European
FRANKFURT/MAIN, West Germany
32 Grosse Bockenheimerstrasse
LONDON, W. 1, England
77 South Audley St.

Contributing Editor: R. H. Müller
Advisory Board: R. N. Adams, G. H. Ayres, J. E. Barney II, E. C. Dunlop, J. C. Giddings, R. F. Goddu, P. B. Hamilton, H. V. Malmstadt, M. L. Moss, J. D. Neuss, W. H. Reinmuth, L. B. Rogers, Irving Shain, Sidney Siggia, J. K. Taylor

Advertising Management
REINHOLD PUBLISHING CORP.
(for Branch Offices, see page 127 A)

Meeting the Challenge of Curriculum Changes

WE HEAR MUCH DISCUSSION on curriculum changes in our academic institutions and how they will affect our traditional approach to teaching. These changes are triggered by the explosive increase in technological and theoretical knowledge and the increasing emphasis on the multidiscipline approach to problem solving. Certainly we cannot escape the fact that all professional training must undergo changes in emphasis and that some time honored courses will be eliminated with or without substitution of new ones. In line with this, analytical chemistry is going through a period of intense evaluation and criticism. Professor W. D. Cooke, head of analytical chemistry at Cornell University, has written and suggested a positive approach to strengthen analytical chemistry in our universities which you will find interesting.

"Many analytical chemists are concerned and alarmed by the discrepancy in the status of analytical chemistry in industry and academic circles. Although industrial recruiters compete feverishly for the few analytical Ph.D.'s, some of the better universities do not even offer graduate programs or courses in analytical chemistry. Some feel that the situation arises because research in analytical chemistry is thought to be of an 'applied' nature. Although this may be a factor, a great deal of the research carried out in analytical chemistry in academic institutions is of high quality and recognized as such.

This writer believes that a predominant factor is the questioning, by the department, of the role the analytical professor plays in the training of nonanalytical graduate students. 'Quant can be handled by a physical chemist, so why do we need an analytical man?'

Physical, organic, and inorganic divisions offer service courses of general usage to all graduate students. Each field then offers advanced courses, such as statistical mechanics and natural products, for its own majors. In contrast, beginning graduate courses in analytical have tended to aim at the specialist and have not contributed significantly to the programs of the nonanalytical student.

Today, an excellent opportunity exists for professors of analytical chemistry to present graduate courses of high general value. These courses might include ultraviolet, infrared, nuclear magnetic resonance, and mass spectrometric determination of structure, optical rotary dispersion, electron paramagnetic resonance, chromatographic separations, and perhaps a separate course in electronics and instrumentation. Such an offering would be of general interest to all students and would be very popular. Many of these subjects are well covered in other fields, particularly organic chemistry.

Advanced courses would then be aimed at those planning to specialize in analytical chemistry, and might cover such topics as electrochemical methods, emission spectroscopy, organic reagents, chemical methods, and other topics which are dear to the heart of the analytical chemist.

There is a great need for a course covering the first group of topics. If the analytical chemist accepts the opportunity and challenge, he will find the universities seeking him out; if he does not, his position in the university will further deteriorate."

Quantitative Measurement of Hydrogen Types by Integrated Nuclear Magnetic Resonance Intensities

J. L. JUNGNICKEL and J. W. FORBES
Shell Development Co., Emeryville, Calif.

▶The accuracy of integrated NMR intensities for determining hydrogen types has been demonstrated for a wide variety of chemically different types of hydrogen in organic compounds using the electronic integrator of the Varian A-60 analytical NMR spectrometer. Absorption bands for nonequivalent groups of protons in 26 carefully selected pure compounds were integrated to determine the apparent percentages of total hydrogen content. The relative standard deviation from theory for the means of three determinations on each compound was 0.3%. Accurate quantitative analysis is therefore possible. In addition, the effect of r.f. field strength on the integrals was studied. Maximum integral amplitude was obtained between 0.2 and 0.4 milligauss. At higher r.f. settings, selective saturation was noted.

HIGH RESOLUTION nuclear magnetic resonance (NMR) chemical shifts and spin-spin splittings have found widespread application for determining the chemical environment of magnetic nuclei (such as protons). NMR is therefore a valuable tool for identification of structures, especially those of organic compounds. Recently, it has become possible to integrate electronically the areas under NMR absorption bands. Since the area under an absorption band is (under proper operating conditions) strictly proportional to the number of nuclei contributing to the band, further applications are feasible. Thus, the number of hydrogen atoms of each type in a pure compound can be counted, making structure identification easier. Total hydrogen can be determined by comparison with samples of known hydrogen content, and quantitative analysis of mixtures of organic compounds becomes possible.

The peak height of the absorption mode, or v-mode, of the NMR signal under slow passage conditions is given by (*1*)

$$I_{max} = K \frac{\gamma H_1 T_2 N}{T[1 + (\gamma H_1)^2 T_1 T_2]} \quad (1)$$

where γ is the gyromagnetic ratio, H_1 is the driving r.f. magnetic field, N is the number of nuclei, T is the absolute temperature, T_1 is the spin-lattice relaxation time, and T_2 is the spin-spin relaxation time. Inasmuch as individual peak heights are affected by spin-spin couplings and also by variations of T_2, which varies inversely with line width, they are not a good measure of the number of nuclei.

The area under a peak, on the other hand, is given by the expression (*1*)

$$A_H = \int_{-\infty}^{+\infty} I dH = K' \frac{H_1 N}{T[1 + (\gamma H_1)^2 T_1 T_2]^{1/2}} \quad (2)$$

As the integral normally is obtained as a function of time rather than of magnetic field strength, this expression becomes

$$A_t = \int_{-\infty}^{+\infty} I dt = K'' \frac{H_1 N}{TR[1 + (\gamma H_1)^2 T_1 T_2]^{1/2}} \quad (3)$$

where R is the sweep rate dH/dt. This equation is valid only for slow passage conditions, where the magnetic field is swept so slowly that

$$\frac{T_1 R}{H_1} << \text{line width} \quad (4)$$

However, slow passage conditions would require a very long time to obtain the integral. Thus, for $T_1 = T_2 = 3$ seconds, a sweep rate of about 1 microgauss per second would be required (*2*). Sweeping through a line with a width of 0.1 milligauss at half height would require on the order of 1000 seconds (17 minutes) to include the wings of the peak. This is obviously impractical for a spectrum containing many such lines.

However, the behavior of the integral at fast sweep rate has been investigated. It has been shown (*2*) that for rapid passage T_1 should be replaced by the actual time during which transitions are permitted to take place. This time, τ, is the time spent traversing the resonance

$$\tau = \frac{\Delta H}{R} \quad (5)$$

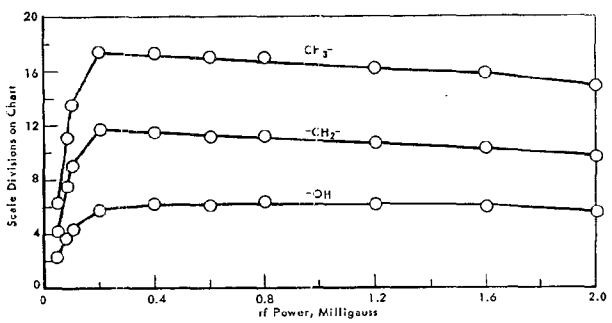


Figure 1. Effect of r.f. power on observed integrated band intensities for ethanol

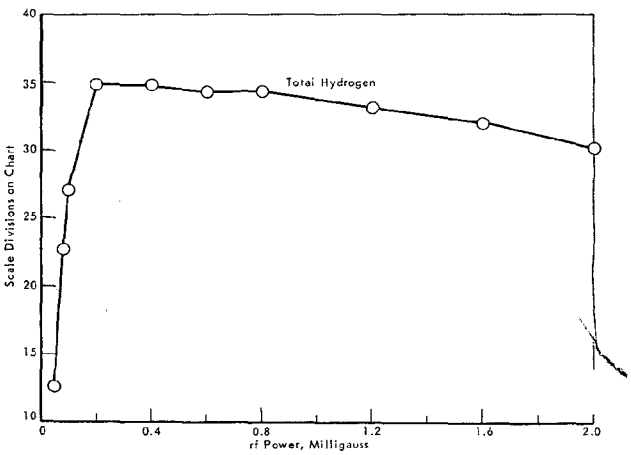


Figure 2. Effect of r.f. power on observed total integral for ethanol

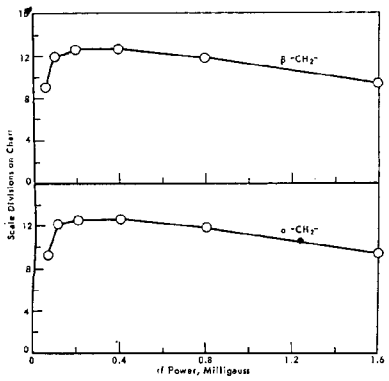


Figure 3. Effect of r.f. power on observed integrated band intensities for tetralin

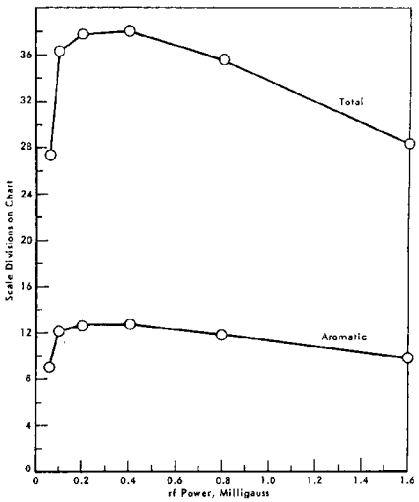


Figure 4. Effect of r.f. power on observed integrated band intensities for tetralin

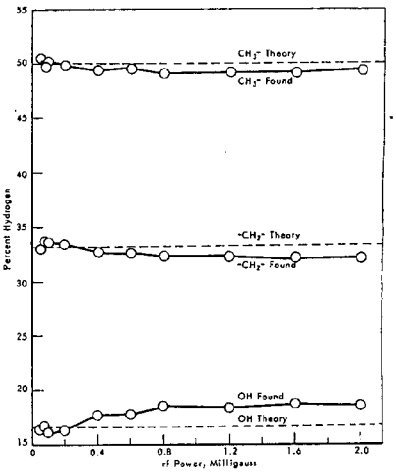


Figure 5. Effect of r.f. power on calculated per cent hydrogen of each type in ethanol

where ΔH is the line width. Now since

$$\Delta H = \frac{1}{\gamma T_2} \qquad (6)$$

it follows that T_1 in Equation 3 can be replaced by $1/R\gamma T_2$. This results in T_2 cancelling out and yields the equation

$$A_t = K'' \frac{H_1 N}{TR[1 + \gamma H_1^2/R]^{1/2}} \qquad (7)$$

For $\gamma H_1^2/R << 1$, this can be expanded to

$$A_t = K'' \frac{H_1 N}{TR} [1 - {}^1/_2\gamma H_1^2/R + \ldots] \qquad (8)$$

This equation is valid for the condition $\gamma R T_1 T_2 >> 1$ (fast sweep compared to relaxation times). Thus, the integrals of all lines obtained at fast sweep will be independent of relaxation times. Moreover, the measured areas will all be uniformly lower than the true areas by the term $1/2\gamma H_1^2/R$, as long as this is small.

The conditions for which Equation 8 is valid can be met with the Varian Model A-60 analytical NMR spectrometer, which incorporates an electronic integrator. In the course of routine analytical work in these laboratories using the A-60, numerous examples of apparent deviations from the theoretical relative amounts of hydrogen of various types in supposedly pure compounds were observed. It was not known whether these deviations were due to incorrect operating conditions or poor instrument performance or simply to impurities in the sample. Therefore, the accuracy of the A-60 integrator was checked by measuring the relative magnitudes of the integrals obtained for protons of different chemical shifts in selected compounds of established purity. The results of these measurements are given in this paper.

EXPERIMENTAL

All samples were run on a Varian Model A-60 analytical NMR spectrometer, Serial No. 143. The samples were dissolved in carbon tetrachloride, (sample concentration ca. 30% by volume) and tetramethylsilane was used as internal reference. The samples were not degassed. A sweep time of 50 seconds for a chart width of 500 c.p.s. (sweep rate, R = 10 c.p.s. per second) was used for all integrals. Unless otherwise stated, an r.f. power, H_1, of 0.1 milligauss (nominal dial setting) was used, although it developed during the course of the investigation that 0.2 milligauss probably would have been nearer to optimum. Only those types of hydrogen which produced bands well separated from other bands were calculated separately; all others were lumped together. In addition to integrated intensities, the chemical shifts of various types of hydrogen were

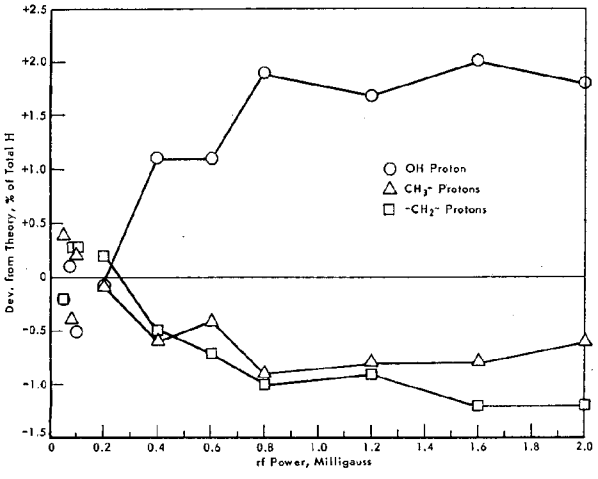


Figure 6. Effect of r.f. power on errors in per cent hydrogen of each type in ethanol

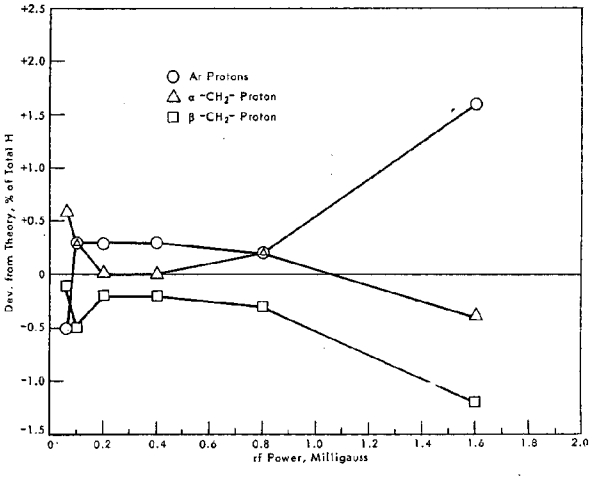
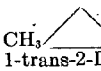
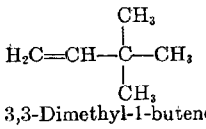
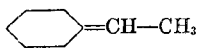
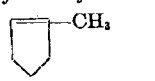
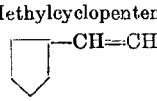
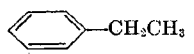
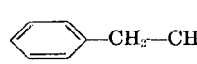
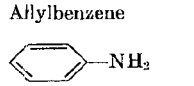
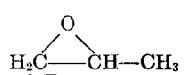
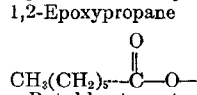
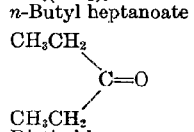


Figure 7. Effect of r.f. power on errors in per cent hydrogen of each type in tetralin

Table I. Results of Integration of Hydrogen NMR Spectra of Pure Compounds

Varian A-60 Serial 143
Sweep rate = 10 c.p.s./second
r.f. Field = 0.1 milligauss
Concn. ≃30% v. in CCl_4

Compound	Purity, %	Proton type	δ, p.p.m.	Per cent hydrogen Theory	Per cent hydrogen Found	Dev. from theory
 1-trans-2-Dimethylcyclopropane	99.77	$-CH_3$ Ring	1.03 0.25	60.0 40.0	59.9 40.1	−0.1 +0.1
 3,3-Dimethyl-1-butene	>99	$=CH-$ $=CH_2$ Alkyl	5.75 4.83 1.00	8.3 16.7 75.0	8.4 16.5 75.1	+0.1 −0.2 +0.1
$CH_3-CH=CH-CH_2-CH_2-CH_2-CH_3$ trans-2-Heptene	99.86	$=CH-$ Alkyl	5.3 0.9–1.9	14.3 85.7	14.2 85.8	−0.1 +0.1
 Ethylidenecyclohexane	99.86	$=CH-$ Alkyl	5.05 1.5–2.1	7.1 92.9	7.0 93.0	−0.1 +0.1
 1-Methylcyclopentene	99.9	$=CH-$ Alkyl	5.20 1.7–2.2	10.0 90.0	10.0 90.0	0.0 0.0
 Ethenylcyclopentane	99.9+	$=CH-$ $=CH_2$ Alkyl	5.66 4.83 1.5–2.4	8.3 16.7 75.0	8.3 16.7 75.0	0.0 0.0 0.0
 Ethylbenzene	99.8	Aromatic $Ar-CH_2-$ $-CH_3$	7.05 2.53 1.15	50.0 20.0 30.0	50.0 19.8 30.2	0.0 −0.2 +0.2
Tetralin	99.86	Aromatic $\alpha-CH_2-$ $\beta-CH_2-$	6.85 2.60 1.66	33.3 33.3 33.3	33.6 33.6 32.8	+0.3 +0.3 −0.5
 Allylbenzene	~95	Aromatic $=CH-$ $=CH_2$ $Ar-CH_2-C=$	7.05 5.8 5.0 3.25	50.0 10.0 20.0 20.0	52.2 9.4 19.2 19.2	+2.2 −0.6 −0.8 −0.8
 Aniline	99.9+	Aromatic $Ar-NH_2$	6.3–7.2 3.3	71.4 28.6	71.0 29.0	−0.4 +0.4
CH_3-CH_2OH Ethanol	99.94	$-OH$ $-CH_3$ $-CH_2-$	4.90 1.17 3.60	16.7 50.0 33.3	17.2 49.3 33.5	+0.5 −0.7 +0.2
$CH_3-CH_2-CH_2-CH_2OH$ *n*-Butanol	E.K. White Label	$-OH$ $O-CH_2-$ Alkyl	4.7 3.5 0.8–1.7	10.0 20.0 70.0	9.8 19.9 70.3	−0.2 −0.1 +0.3
$CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$ Di-*n*-propyl-ether	E.K. Anal. Distilled	$-CH_2-O$ $\beta-CH_2-$ CH_3-	3.30 1.50 0.90	28.6 28.6 42.8	28.8 30.0 41.2	+0.2 +1.4 −1.6
$CH_3-CH_2-CH_2-CH_2-O-CH_2-CH_2-CH_2-CH_3$ Di-*n*-butyl ether	E.K. Distilled Prob. 99+%	$O-CH_2-$ Alkyl	3.3 0.9–1.4	22.2 77.8	21.8 78.2	−0.4 +0.4
 1,2-Epoxypropane	E.K. White Label	$O-CH_2-$ Alkyl	2.2–2.8 1.22	50.0 50.0	49.8 50.2	−0.2 +0.2
 *n*-Butyl heptanoate	>99.5	$CO-O-CH_2-$ All other	4.00 0.9–2.2	9.1 90.9	9.1 90.9	0.0 0.0
 Diethyl ketone	E.K. Distilled	$CO-CH_2-$ $-CH_3$	2.35 1.0	40.0 60.0	39.9 60.1	−0.1 +0.1

(Continued)

Table I. *(Continued)*

Compound	Purity, %	Proton type	δ, p.p.m.	Per cent hydrogen Theory	Per cent hydrogen Found	Dev. from theory
$HC{\equiv}C{-}CH_2{-}CH_3$ 1-Butyne	>99	$\equiv C{-}CH_2{-}$	2.17	33.3	33.0	−0.3
		$\equiv CH$	1.78	16.7	16.7	0.0
		$-CH_3$	1.14	50.0	50.3	+0.3
Pyrrolidine	A.P.I. 99.85	$\alpha{-}CH_2{-}$	2.84	44.4	44.5	+0.1
		$\beta{-}CH_2{-}$ + NH	1.5–1.8	55.6	55.5	−0.1
$CH_3{-}CH(SH){-}CH_2{-}CH_3$ 2-Butanethiol	A.P.I. Std.	S—CH	2.83	10.0	10.0	0.0
		—SH, CH_3, CH_2CH_3	0.9–1.6	90.0	90.0	0.0
$CH_3{-}C(CH_3)_2{-}SH$ *tert*-Butyl mercaptan	99.92	—SH	1.69	10.0	9.9	−0.1
		Alkyl	1.40	90.0	90.1	+0.1
$CH_3{-}S{-}CH_2{-}CH_2{-}CH_3$ Methyl-*n*-propyl sulfide	99.97	$S{-}CH_2{-}$	2.4	20.0	19.4	−0.6
		$CH_3{-}S$	0.9–2.0	80.0	80.6	+0.6
		$-CH_2{-}CH_3$				
$CH_3{-}CH(Cl){-}CH_2{-}CH_3$ *sec*-Butyl chloride	E.K. Distilled	CH—Cl	3.9	11.1	11.3	+0.2
		$-CH_2{-}CCl$	1.5	55.6	56.7	+1.1
		$CH_3{-}CCl$				
		$CH_3{-}$	1.0	33.3	32.0	−1.3
$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}I$ 1-Iodooctane	E.K. White Label	$CH_2{-}I$	3.15	11.8	11.8	0.0
		Alkyl	1.30	88.2	88.2	0.0

measured and tabulated. These are expressed in terms of δ = p.p.m. from tetramethylsilane (internal reference).

RESULTS AND DISCUSSION

The compounds studied are listed in Table I, along with their purities, proton types, chemical shifts, and per cent hydrogen found experimentally. The compounds were selected to give a wide range of different types of nonequivalent proton groups. The proton resonance spectrum of each compound was integrated three times using identical instrumental conditions. An inspection of Table I shows that no anomalous proton intensities were detected—i.e., they all appear to be in the ratio of the number of protons in each group. The experimental scatter found for the compounds known to be 99% or better purity amounts to a relative standard deviation of 0.3% (from theory). This shows that the number of hydrogen atoms of each type in a pure compound can be counted with

Table II. Results of Integration of Ethanol Spectrum at Various r.f. Power Level

Varian A-60 Serial 143
Sweep rate = 10 c.p.s./second
Concn. ≃30% v. in CCl_4

r.f. Power, mG	Proton type	Per cent hydrogen found[a]	Dev. from theory	r.f. Power, mG	Proton type	Per cent hydrogen found[a]	Dev. from theory
0.05	CH_3—	50.4	+0.4	0.6	CH_3—	49.6	−0.4
	—CH_2—	33.1	−0.2		—CH_2—	32.6	−0.7
	—OH	16.5	−0.2		—OH	17.8	+1.1
0.08	CH_3—	49.6	−0.4	0.8	CH_3—	49.1	−0.9
	—CH_2—	33.6	+0.3		—CH_2—	32.3	−1.0
	—OH	16.8	+0.1		—OH	18.6	+1.9
0.1	CH_3—	50.2	+0.2	1.2	CH_3—	49.2	−0.8
	—CH_2—	33.6	+0.3		—CH_2—	32.4	−0.9
	—OH	16.2	−0.5		—OH	18.4	+1.7
0.2	CH_3—	49.9	−0.1	1.6	CH_3—	49.2	−0.8
	—CH_2—	33.5	+0.2		—CH_2—	32.1	−1.2
	—OH	16.6	−0.1		—OH	18.7	+2.0
0.4	CH_3—	49.4	−0.6	2.0	CH_3—	49.4	−0.6
	—CH_2—	32.8	−0.5		—CH_2—	32.1	−1.2
	—OH	17.8	+1.1		—OH	18.5	+1.8

[a] Theory = 50.0% in CH_3—, 33.3% in —CH_2—, and 16.7% in —OH.

Table III. Results of Integration of Tetralin at Various r.f. Power Levels

Varian A-60 Serial 143
Sweep rate = 10 c.p.s./second
Concn. ≃30% v. in CCl_4

r.f. Power, mG	Proton type	Per cent hydrogen found[a]	Dev. from theory
0.06	Ar	32.8	−0.5
	$\alpha{-}CH_2{-}$	33.9	+0.6
	$\beta{-}CH_2{-}$	33.2	−0.1
0.1	Ar	33.6	+0.3
	$\alpha{-}CH_2{-}$	33.6	+0.3
	$\beta{-}CH_2{-}$	32.8	−0.5
0.2	Ar	33.6	+0.3
	$\alpha{-}CH_2{-}$	33.3	0.0
	$\beta{-}CH_2{-}$	33.1	−0.2
0.4	Ar	33.6	+0.3
	$\alpha{-}CH_2{-}$	33.3	0.0
	$\beta{-}CH_2{-}$	33.1	−0.2
0.8	Ar	33.5	+0.2
	$\alpha{-}CH_2{-}$	33.5	+0.2
	$\beta{-}CH_2{-}$	33.0	−0.3
1.6	Ar	35.0	+1.7
	$\alpha{-}CH_2{-}$	32.9	−0.4
	$\beta{-}CH_2{-}$	32.1	−1.2

[a] Theory = 33.3% for each type.

good accuracy. However, as the compound purity is lowered to the 95% range, deviations from theory increase to an extent that accurate hydrogen counting would be difficult.

The spectra of two of the compounds, ethanol and tetralin, were integrated three times at each of several values of the r.f. field. This was done to see if selective saturation could be observed at high r.f. values and if so, to determine the optimum operating range of r.f. power. In Figures 1 and 2 the magnitude of the integral for each proton type and total hydrogen in ethanol is plotted against the different r.f. field settings. Similar plots for tetralin are shown in Figures 3 and 4. Inspection of these figures shows that maximum integral amplitude is obtained at r.f. settings of 0.2 and 0.4 milligauss and that the amplitude drops at higher values of r.f. power and even more rapidly at lower r.f. power. The probable explanation of drop-off at low r.f. power is nonlinearity of the automatic gain control incorporated in the A-60 circuitry. (The automatic gain control is intended to attenuate the signal proportionally as the r.f. power is raised.) The gradual drop-off at high r.f. power is probably due to the $-{}^1/_2\gamma H_1{}^2/R$ term of Equation 8.

Table II shows the per cent hydrogen found and the deviation from theory for each hydrogen type in ethanol, obtained from the integrals at each r.f. setting. Figure 5 is a plot of these data showing evidence of selective saturation as the r.f. field is increased. Figure 6 is a plot of the deviation from theory of each proton type against the r.f. setting. There is a definite trend in the curves, demonstrating selective saturation at r.f. settings greater than 0.2. The data for tetralin are indicated in Table III and shown in Figure 7. The results here are similar to those for ethanol except selective saturation does not occur until the r.f. field is increased above 0.8 milligauss.

CONCLUSIONS

It is concluded that apparent deviations from theory noted earlier were simply due to impurities in the samples under examination. Under optimum conditions of sample concentration, r.f. power, gain, and sweep rate, as employed in this paper, integrals should be accurate to within a few tenths of 1% of the total hydrogen content.

LITERATURE CITED

(1) Reilly, C. A., ANAL. CHEM. **30**, 839 (1958).
(2) Varian Associates, Instrument Division, Technical Information *Bulletin* **3**, No. 1 (1960).

RECEIVED for review February 14, 1963. Accepted April 8, 1963. Presented at 4th OCEANS, Pittsburgh, Pa., February 28–March 2, 1963.

The Physical Basis of Analytical Atomic Absorption Spectrometry

The Pertinence of the Beer-Lambert Law

KEIICHIRO FUWA and BERT L. VALLEE

Biophysics Research Laboratory of the Division of Medical Biology, Department of Medicine, Harvard Medical School, and the Peter Bent Brigham Hospital, Boston, Mass.

▶ **In this study the absorption of molecules in solution as expressed by the Beer-Lambert law has been used as a model for the investigation of atomic absorption. As predicted by this model, the sensitivity of measurement is a function of the length of the absorbing flame path and of the reflectivity of the surrounding cell surfaces. Employing absorption cells here described, the limit of detection of many elements has been lowered greatly. The limits of detection for zinc, cadmium, magnesium, copper, nickel, and cobalt have been found to vary from 0.4 to 16 p.p.b. The utilization of absorption cells for atomic absorption spectrometry should greatly enhance the usefulness of this analytic procedure.**

OVER THE COURSE of a very few years since its discovery by Walsh (*9*) atomic absorption spectrometry has achieved major prominence as an exquisite analytical method. Exceeding, however, the proceeds of the pioneering in this field up to the present, is the tremendous potential for further development. Knowledge of the physics underlying the phenomenon of atomic absorption has permitted the prediction that marked improvements in the sensitivity of detection of many elements will be forthcoming (*7*, *9*).

Although the principles which are common to molecular and atomic absorption spectrometry are readily apparent, the pertinence of this similarity to the further analytical exploitation of atomic absorption spectrometry has not been fully appreciated.

The investigation of various types of absorption cells, described in the present communication, demonstrates the pertinence of the Beer-Lambert law to atomic absorption spectrometry. The proportionality between the light entering a solution and to that absorbed as a result of the chemical and physical characteristics of its contents, to the concentration of the absorbing medium and the length of the absorbing path are so well known that they need not be dwelt upon further. The same principles were thought to apply both to atoms and molecules in gas or aerosol phases and hence to atomic absorption. This circumstance has led us to undertake a systematic investigation to define the optimal characteristics of absorption cells for use in this system. As a result of these studies the sensitivity of detection of many elements has been increased from 10- to 100-fold over those reported in the literature (*1–4*, *7*).

DESCRIPTION OF THE INSTRUMENT

Light Source. Hollow cathode discharge tubes for zinc and copper, WL-22607, magnesium WL-22604, cadmium WX4936, (Westinghouse Electric Corp.); nickel FL 155 and cobalt FL 157, (Hilger and Watts Ltd.) are used as light sources. Individual tubes are connected to a constant-current power supply with 800-d.c. volts compliance and operated at an appropriate current between 10 to 60 ma. The light from the hollow cathode lamp is collimated by a quartz lens of 12-cm. focal length placed 7 cm. from the tube window; it then passes through the absorption cell and is focused on the entrance slit of the spectrograph by another quartz lens of 15.5-cm. focal length placed 19.5 cm. from the slit. The distance between the two lenses is 113.4 cm. (Figure 1).

Absorption Cell. Absorption cells have been constructed of various

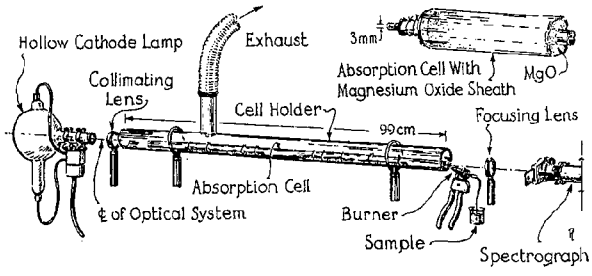


Figure 1. Absorption cell assembly for atomic absorption spectrometer and absorption cell

Cell covered with magnesium oxide sheath and 3-mm. exit orifice is shown in the insert

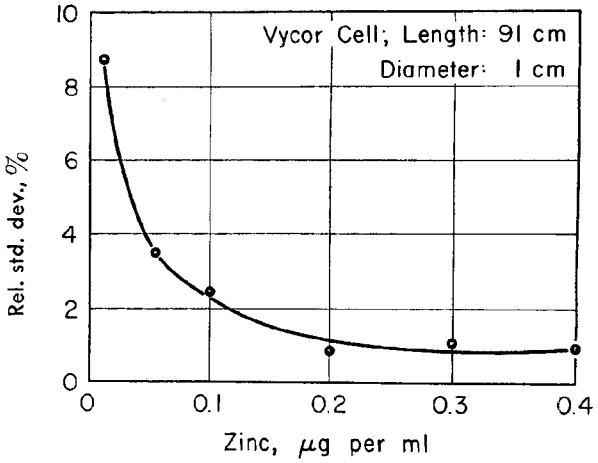


Figure 2. Repeatability of atomic absorption measurements with a Vycor cell; length 91 cm., diameter 1 cm.

Twelve measurements were performed at each concentration of zinc from 0.01 to 0.4 p.p.m.

kinds of combustion tubing: Vycor (inside diameters; 1, 1.65, and 2.6 cm.; length: from 23 to 91 cm.), asbestos (inside diameter: 1 cm.; length: 91 cm.), Alundum (inside diameter: 1.7 cm.; length 34.3 cm.); graphite (inside diameter: 1.7 cm.; length: 38.1 cm.) or Zirconia (inside diameter: 2.0 cm.; length: 76.2 cm.).

The absorption cell is held on a strip of asbestos shielding inside a length of borosilicate glass tubing, with an inside diameter of 4.8 cm. and an over-all length of 99 cm., placed horizontally between the two lenses. The open end of the cell is located near the focusing lens. The light from the source passes through the center of the absorption cell. A side arm of the outside glass tubing, 27 cm. from the end and close to the collimating lens, is connected to an exhaust system to protect the lenses from hot gases (Figure 1).

Burner. A Beckman atomizer burner (No. 4020) is used to spray the sample into the absorption cell. The fuel is a mixture of commercial hydrogen, at a pressure of 10 to 20 inches of water, and air, at a pressure of 15 pounds per square inch. The hydrogen pressure is adjusted for each type of absorption cell to obtain optimal flame length and maximal sensitivity. The flow rate of solution through the burner is approximately 1.5 ml. per minute. The burner is placed adjacent to the absorption cell near the focusing lens and is tilted at an angle of 15° to the optical axis to allow the flame to enter the tube without interfering with the light beam; the upper surface of the burner is filed off to prevent such interference (Figure 1).

Light Dispersing Element. Two spectrographs, one a Hilger E2 medium quartz instrument and the other a Bausch and Lomb, large Littrow spectrograph with exchangeable quartz and glass optics were adapted to serve as the light dispersing elements. For both spectrographs the entrance and exit slits were adjusted to a width of 0.4 mm.

Detectors. The following lines were employed to detect the respective elements: zinc 2138.56A., cadmium 2288.018A., magnesium 2852.129A., copper 3247.540A., cobalt 2424.930A., and nickel 2310.965A. Multiplier phototubes (RCA 1P28) were used as the detectors for the absorption measurements. The dynode voltages were identical for all stages, and were varied from 70 to 120 volts per stage.

The camera of the original spectrographs were replaced by facilities for mounting multiplier phototubes. An aluminum plate was coated with a photographic emulsion and was exposed to the hollow cathode light source. The plate was removed and developed, and the area of a particular absorbing line was excised precisely, and the rest of the plate was then blackened. After returning it to the original focal plane, the excised lines of the plate served as exit slits.

The mounting of multiplier phototubes was similar to that used previously for a multichannel flame photometer which has been described (*8*). The windows of the tubes used for the detection of zinc, cadmium, cobalt, and nickel were covered by a thin layer of sodium salicylate to increase the tube sensitivity at the low wavelengths for which they were employed.

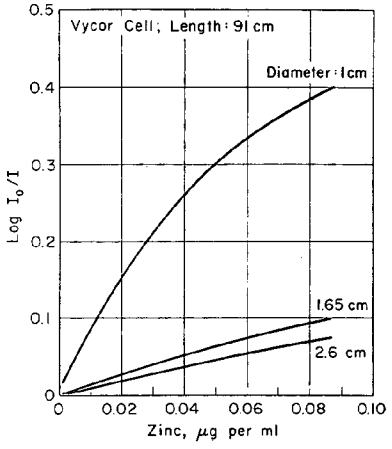


Figure 3. Effects of diameter of absorption cell on absorbance

Amplifiers. The instrument provides a high voltage power supply and amplifier for the multiplier phototube. They were arranged on a common chassis together with the hollow cathode lamp power supply.

The high voltage power supply provided a regulated voltage variable from 700 to 1200 volts d.c. for the multiplier phototube. The circuit consisted of a Y50HF rectifier followed by a voltage regulator. Output voltage was controlled by a total 1-megohm variable resistor, coarse and fine, on the control grid of a 12AX7 tube. The signal input to the amplifier was passed through an attenuator provided with precision resistors, so that the sensitivity of the amplifier might be varied by factors of 3 and 10 for each step of the attenuator switch. After passing through the attenuator the signal was sent to one side of a 12AU7 tube in a bridge circuit, which included a variable resistor to permit setting of the amplifier balance. Circuits for the high voltage power supply and amplifier were almost identical with those used in the multichannel emission flame spectrometer (*8*).

Meter. The output signal of the amplifier was indicated on a direct current microammeter with a range of 0 to 100 μa. This could be read easily to ±1 μa.

Standard Solutions. These were solutions of zinc, cadmium, magnesium, copper, cobalt, and nickel chlorides. Rods of zinc, cadmium, magnesium, and copper, cobalt sponge, and nickel oxide, spectrographically pure, (Johnson, Matthey and Co., London) were weighed out, and dissolved in 6*N* hydrochloric acid. The solutions contained 10,000 p.p.m. of metals. These concentrated stock solutions were diluted further with water purified by a mixed bed ion exchange resin column. The concentrations used covered a range from 0.0001 to 1.0 p.p.m. depending on the sensitivities of detection for individual metals.

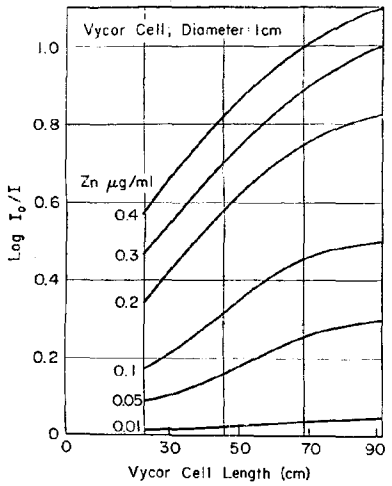


Figure 4. Effects of length of absorption cell on absorbance

EXPERIMENTAL

The air pressure to the burner is fixed at 15 lbs. per sq. inch and the hydrogen pressure adjusted until the microammeter gives a reading half that obtained before the flame is lit. After allowing the system to come to temperature equilibrium, the meter is zeroed by adjusting the dark current with the slit closed. Then, with the slit open, metal-free water is atomized through 8 cm. of polyethylene tubing attached to the burner capillary. During atomization, the meter is adjusted to an arbitrary light intensity, I_0, of 80 μa., by adjusting the voltage applied to the photomultiplier dynodes. A series of standard metal solutions is then atomized and the absorbed line intensity, I, is obtained for each.

RESULTS

The stability of the apparatus was tested by measuring the repeatability of a zinc solution (Figure 2). The relative standard deviation was less than 4% for all concentrations above 0.05 μg. per ml.

Using the zinc line at 2139A. the following characteristics of the absorption cell were examined:

A. Effect of Cell Diameter. The results with 91 cm. long Vycor cells having diameters of 2.6, 1.65, and 1.0 cm. are shown in Figure 3, which demonstrates that the smaller the diameter of the cell the higher the sensitivity. In all cases, sensitivity is lost at high concentrations, above 0.1 p.p.m. for a 1-cm. tube (Figure 1), above 1 to 2 p.p.m. for those of larger diameter (not shown). Sensitivity is not increased when the inside diameter is reduced below 1 cm.

B. Effect of Cell Length. This was examined with a Vycor cell having an inside diameter of 1 cm. which was found optimal (Figure 3). The results are shown in Figure 4. As the length of the cell is increased to about 70 cm., there is a corresponding linear increase in absorbance. On further increases of length, however, the rate of increase in absorbance diminishes until there is very little further change at a length of about 90 cm.

C. Reflection from the Inner Surface of the Tube. A rough-surfaced, asbestos cell (91 by 1.0 cm.) was prepared, and the absorbance in this cell is compared (Figure 5) to that of a Vycor cell of similar dimensions. At a given concentration of zinc the absorbance observed in a Vycor cell is about 10 times that observed with the asbestos cell.

D. Effect of a Magnesium Oxide Sheath. The Vycor cell employed in Figure 1 was surrounded by a layer of magnesium oxide powder, 5 mm. in thickness, to serve as an additional reflector from the outside of the cell. As seen in Figure 6, a 16% increase in response is obtained, when compared to that of the control Vycor cell.

E. Effect of Pressure. To test the effect or sensitivity of increasing the pressure within the cell, the exit of the Vycor cell used in D (*vide supra*) was modified by inserting an asbestos stopper containing another cell, 0.3 cm. in diameter, at the end of the cell employed in Figure 1. The results are also shown in Figure 6. At a zinc concentration of 0.1 p.p.m., a 30% increase in absorption was obtained.

Quantitative Determination of Cadmium, Magnesium, Copper, Cobalt, and Nickel. To construct working curves, measurements were also made using the following elements and lines: Zn 2139A., Cd 2288A., Mg 2852A., Cu 3248A., Co 2425A., and Ni 2311A. The results of these experiments, using a Vycor cell (91 by 1 cm.), are shown in Figure 7.

DISCUSSION

The analytical utilization of atomic absorption rests on the principle that the total absorption of light, expressed as log I_0/I, is directly proportional to the concentration and absorptivity of metal atoms in the flame. This has been well documented in flames of varying dimensions and characteristics (*5*, *7*). The absorption of light by a homogeneous species of molecules in solution is similarly dependent upon their absorptivity and concentration. In addition, however, the absorption of molecules in solution is directly dependent upon another variable, the path length. In solutions this relationship is expressed by the Beer-Lambert law which states that

$$\log I_0/I = a \cdot b \cdot c \qquad (1)$$

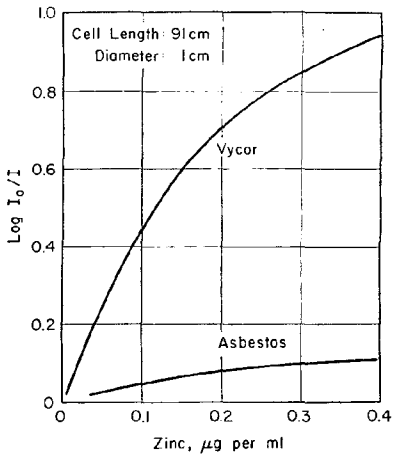


Figure 5. Effects of reflections from inner surface of Vycor and asbestos absorption cells on absorbance

Where a = absorptivity, b = the path length, and c = the concentration. It might be predicted, therefore, that atomic absorption would also be proportional to the path length of the flame. As shown by the present studies, when both absorptivity and concentration are held constant, the path length can be examined as the single variable of the experimental system. Increasing the path length of the flame was accomplished by recognizing that a flame is markedly lengthened when it is inserted into a suitable tubing. If the long axis of such a directed flame is employed as the absorption cell, its path length is increased as a function of the length of the tubing.

Using this system the predicted dependence of absorption on the path length of the flame is clearly borne out. As expected, however, the dynamic equilibrium of atoms in the flame cannot be maintained beyond certain limitations—e.g., the flame cannot be propagated infinitely. This is shown by the eventual failure to increase sensitivity as the path length is increased beyond 70 to 90 cm. (Figure 4). To define the precise limits of the contributions of the path length of absorbing flames to a modified Lambert's law for atomic absorption, it will be necessary to delineate the contributing physical factors which differentiate absorbing systems in liquid and gaseous phases from those in solution. Such studies are under way.

In molecular absorption spectrometry scattering of light from the surfaces of the absorption cell introduces significant errors of measurements. The absorbance varies as a function of wavelength, and under the conditions which usually prevail in practical absorption spectrometry, the light entering the absorption cell is not strictly monochromatic; the band width of the light beam entering the solution is a function both of the re-

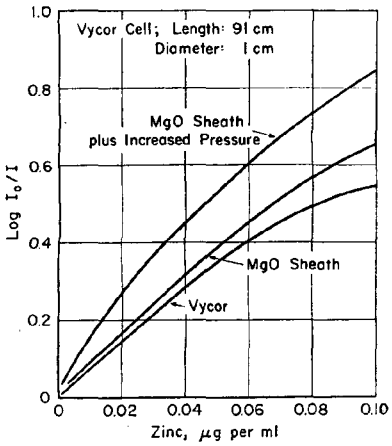


Figure 6. Effects of magnesium oxide sheath and increased pressure of absorption cells on absorbance

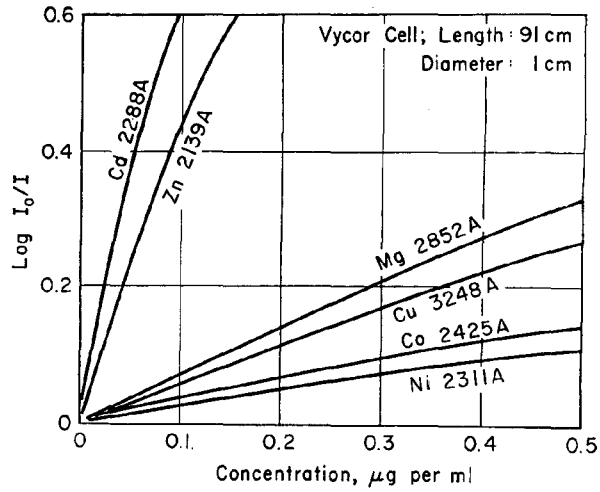


Figure 7. Typical calibration curves for cadmium, zinc, magnesium, copper, cobalt, and nickel as measured by atomic absorption

solving power of the dispersing element and of the entrance and exit slits of the spectrometer. Hence, there is background due to heterochromatic radiation. Light scattering will further contribute to this background absorption, as a fourth power of the wavelengths of the entering beam, and also as a function of the absorbance of the material under study.

In contrast, in atomic absorption spectrometry the intense radiation from the hollow cathode tube which enters the flame cell is strictly monochromatic since a specific electronic transition of the light source is selected for absorption in the gas or liquid-aerosol phase. Hence, this scattered monochromatic radiation, when reflected into the cell, will actually enhance absorption, while background will not be increased correspondingly.

The superiority of the Vycor over the asbestos cell demonstrated by these experiments may be accounted for on this basis. The effective path length is increased tenfold in the Vycor cell over the actual cell length. This is apparently due to a tenfold increase in circular reflections from the inner surface of the Vycor tubing over that obtained with the rough-surfaced, nonreflecting asbestos cell. The use of a magnesium oxide cover demonstrates that outside reflection may be employed similarly to enhance the effect. The loss in sensitivity observed with tubes having a diameter greater than 1 cm. may be attributed to a decrease in circular reflectivity of the larger cells.

It may be predicted from the Boyle-Charles law that the concentration of an absorbing species, b, will increase with increased vapor pressure in the absorption cell. The increased sensitivity resulting from constriction of the open end of the absorption cell bears out this anticipation experimentally.

The higher absolute sensitivity obtained by the use of the optimal conditions here defined permits the measurement of extremely small samples. This is of great importance when the size of the original sample and the concentration of the element under examination is limited, as is often the case with biological material. In this regard, the total consumption burner used in the present apparatus is greatly superior to those of the atomizer-chamber type where the volume of samples required is about 10 times greater.

The definition of the detection limit employed in Tables I and II is the concentration in micrograms per milliliter of metal which results in 1% absorption, or approximately one division of the needle deflection on the microammeter used for read-out.

The absolute amount of detectable metal, in grams, therefore, is the smallest quantity required to give a reading of 1% absorption. The values would vary according to the sample flow rate and the rate of response of the detection system. In the present system, 0.1 ml. of solution, which has a metal concentration equal to that defined above as the detection limit, constitutes the absolute amount of detectable metal.

Table I. Atomic Absorption Enhancement of Sensitivity for Zinc Analysis

	Log I_0/I = 0.1 μg./ml.	Detection limit, μg./ml.	Zn detectable, grams
1. Elongated burner[a]	7.5	0.3	3×10^{-7}
2. Beckman burner			
a. Vertical flame	8.2	0.3	3×10^{-8}
b. Horizontal flame	1.0	0.04	4×10^{-9}
c. Asbestos cell	0.3	0.01	1×10^{-9}
d. Vycor cell Diameter 2.6 cm.	0.16	0.006	6×10^{-10}
e. Vycor cell Diameter 1 cm.	0.016	0.0006	6×10^{-11}
f. Vycor cell Diameter 1 cm. MgO sheath	0.01	0.0004	4×10^{-11}
g. Vycor cell Diameter 1 cm. MgO sheath Higher Pressure	0.005	0.0002	2×10^{-11}

[a] Hilger-Watts Ltd., attachments No. H909 and H1090.

Table II. Atomic Absorption Detection Limits

Vycor cell, length 91 cm. Diameter 1 cm.

Elements	μg. per ml.
Cadmium	0.0004
Zinc	0.0006
Magnesium	0.005
Copper	0.007
Cobalt	0.013
Nickel	0.016

Apparatus currently available commercially is equipped with a chamber-atomizer that feeds into an elongated multiple Bunsen burner having a flame width of only about 10 cm. (5). Table I compares the sensitivity of the present arrangement (lines 2a to g) with that of a commercial instrument line 1 using the conditions defined to yield the highest sensitivity reported for both. For our studies a 91- × 1-

cm. Vycor tube covered with magnesium oxide powder, the exit of which is constricted, was employed. The lowest detection limit for zinc under these conditions is 10^{-11} gram, or 0.1 p.p.b.

In the early stages of our investigation of absorption cells a T-tube flame adaptor was placed over the burner, the flame being deflected in both directions. This system in our hands failed to yield any increase in sensitivity for the metals studied. Presumably this is due to the fact that only the upper part of the flame is deflected into the part of the tube which serves as the absorption cell. Thus there is a major disturbance of equilibrium of the flame due to the sudden change in the combustion brought on by the abrupt change in direction. Our negative results with this system are in accord with the conclusions of Robinson that such an "adapter could not be used for the measurement of the alkali metals or some of the transition metals" (*6*).

Table II shows the detection limits for six elements using a plain Vycor cell of 91 × 1 cm. Obviously, at these low concentrations corrections for simultaneous emission of the absorbing species are unnecessary. This is true particularly for elements such as zinc or cadmium which are excited with difficulty at these flame temperatures.

Although Vycor has been used in this work, the use of other materials for absorption cells is not precluded, of course. The only requirements for the cell material are that they have high temperature resistance, be chemically inert, and have a highly-reflecting surface. Other materials may well allow the use of higher flame temperatures. If the sensitivity requirements are not stringent, a nonreflective cell may be manufactured of materials like alundum or other ceramics, graphite, or asbestos. This might be an advantage since deposits on the surface are of no importance when reflectivity is not being exploited to enhance sensitivity.

The absorption cells may also be made to serve as a combustion tube, such that the organic matter with which the metals of interest may be combined may be burned while the sample is being atomized. In the process the metal atoms are liberated for analysis without prior ashing. Further studies of the physical factors affecting atomic absorption are in progress.

From these data it may safely be predicted that even greater sensitivity without interference may be anticipated with further development of absorption cell characteristics and the design of special burners for use in this system.

ACKNOWLEDGMENT

It is a real pleasure to acknowledge the valuable comments and advice of W. E. C. Wacker, both in the course of this work and in the preparation of the manuscript.

LITERATURE CITED

(1) Allan, J. E., *Analyst* **83**, 466 (1958).
(2) Allan, J. E., *Spectrochim. Acta* **17**, 459 (1961).
(3) David, D. J., *Analyst* **83**, 655 (1958).
(4) *Ibid.*, **85**, 779 (1960).
(5) Menzies, A. C., ANAL. CHEM. **32**, 898 (1960).
(6) Robinson, J. W., *Anal. Chim. Acta* **27**, 465 (1962).
(7) Russell, B. J., Shelton, J. P., Walsh, A., *Spectrochim. Acta* **8**, 317 (1957).
(8) Vallee, B. L., Margoshes, M., ANAL. CHEM. **28**, 175 (1956).
(9) Walsh, A., *Spectrochim. Acta* **7**, 108 (1955).

Work supported by the Howard Hughes Research Institute and a grant-in-aid from the Petroleum Research Fund of the American Chemical Society.

Application of Time of Flight Mass Spectrometry and Gas Chromatography to Reaction Studies

E. J. LEVY,[1] E. D. MILLER, and W. S. BEGGS

The Atlantic Refining Co., Philadelphia, Pa.

▷ A technique is described which permits the rapid qualitative and quantitative identification of the products from a complex chemical reaction. The system employed consists of a small scale reactor, a two-position indicating sample loop, a temperature programmed gas chromatographic unit, and a Bendix time of flight mass spectrometer. Identification of the gas chromatographic peaks is accomplished by mass spectrometry whereas the quantitative analysis is based on the chromatographic peak areas. The problems involved in operating the Bendix time of flight mass spectrometer under these conditions are discussed. Some results obtained in the catalytic cracking of nonane over silica alumina are presented as an example. The techniques described are applicable to any thermal, photochemical, or catalytic reaction, which can be carried out in a flow system.

THE WORK to be described represents an application of time of flight mass spectrometry and gas chromatography to the study of the changes in product distribution, as a function of cracking cycle time (*1*), during the cracking of *n*-nonane over a silica alumina catalyst. Cracking cycle time may be defined as the period that a catalyst is exposed to "feed" before it is regenerated. This paper will describe the experimental techniques and some of the initial results.

In the usual microcatalytic studies a hydrocarbon feed is allowed to pass over a catalyst for a given period of time—e.g., 15 minutes and then the products are collected and analyzed and the per cent conversion for the 15-minute period determined. The per cent conversion determined in this way is an integral conversion and represents the total conversion for the 15-minute period.

In the present investigation, the cracking period was divided into short intervals of approximately 28 seconds (corresponding to one slug of feed) and then the conversion and product distribution for each 28-second period was determined separately.

APPARATUS AND EXPERIMENTAL PROCEDURES

The equipment used in this investigation is shown schematically in Figure 1 and consists of: a Fisher introduction valve; a temperature-controlled reactor containing 5 grams of silica alumina catalyst; an indicating sampling system including a two-position, six-ported Aerograph valve, a sampling loop, and a Gow-Mac thermal conductivity cell; an F & M Model 500 gas chromatograph; and a Bendix Model-14 time of flight mass spectrometer.

[1] Present address, F & M Scientific Corp., Starr Rd. & Route 41, Avondale, Pa.

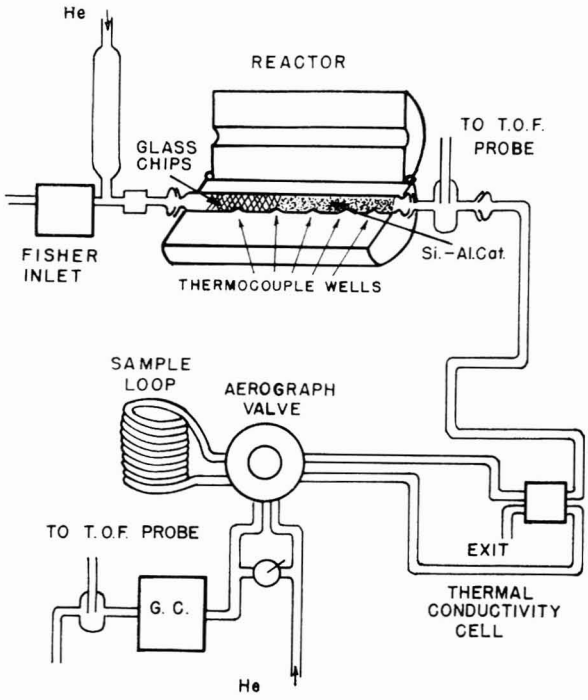


Figure 1. Schematic of equipment

In a typical run, a slug of 50 μl. (0.05 ml.) of *n*-nonane is introduced with a Fisher pipet through a Fisher introduction valve into a stream of preheated helium flowing at 30 ml. per minute and is carried over a catalyst bed maintained at 950° F. The *n*-nonane is partially cracked over the silica alumina catalyst and passes as a slug through the reference side of the thermal conductivity cell. In one position of the Aerograph valve the slug goes from the reference side of the thermal conductivity cell through the sample loop and out through the detector side of the thermal conductivity cell. As can be seen from Figure 2, with the valve in the position described, a positive and then a negative deflection was obtained from a recording potentiometer connected to the thermal conductivity cell. To transfer the product slug to the gas chromatography unit the above sequence is repeated, except that when the positive deflection from the reference side of the thermal conductivity cell returns to the base line the Aerograph valve is switched and the sample is carried to the gas chromatographic inlet line. As may be noted in Figure 2, no negative deflection was obtained indicating that the product slug was completely transferred to the gas chromatography unit.

The product slug was then separated by gas chromatography into some 35 peaks. The gas chromatographic column used for this separation was a 1/4-inch, 50-foot length of 20% silicone grease in series with a 4-foot section of 15% Carbowax 20M on 42–60 mesh Chromosorb W. The column temperature was maintained at 40° C. for the first 20 minutes and then programmed at the rate of 5.6° C. per minute up to 200° C. It was then held at 200° C. until all the gas chromatographic peaks emerged. The total running time for a chromatogram was approximately 90 minutes. Slugs 1, 2, 3, 4, 9, 14, 24, 34, and 44 were analyzed for each series before regeneration. Slug 45 would be equivalent to a slug 1 for a series using a catalyst after regeneration.

The catalytic cracking reactor shown diagrammatically in Figure 1, is followed by the first of two 9-micron glass leaks of the type shown in Figure 3. The first leak enables a portion of the entire product slug to be sampled by the time of flight mass spectrometer prior to separation by gas chromatography. This leak was of limited use in the present investigation because of the complexity of the product mixture. It did, however, prove helpful in studying the rate of catalyst regeneration by monitoring the concentration of oxygen remaining in an initial 5% oxygen and helium mixture after passage through the coked catalyst in the reactor at regeneration temperatures. This first leak and the second glass leak located at the exit of the gas chromatographic

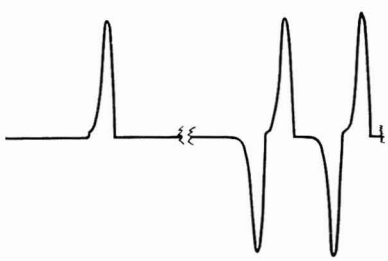


Figure 2. Sample trapping

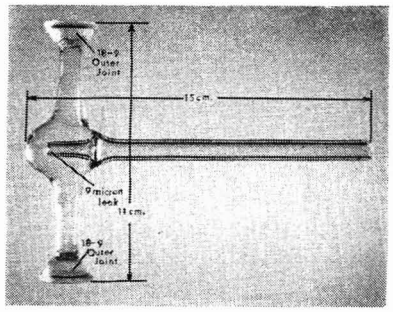


Figure 3. Photograph of glass leak

exit line were connected to the Bendix time of flight mass spectrometer by a vacuum manifold. This vacuum manifold enables the lines between the leaks and the spectrometer to be evacuated with an auxiliary vacuum pump before the valve to the spectrometer is opened. Once helium fills this line, little or no auxiliary pumping is required to maintain a pressure of 5×10^{-6} mm. in the spectrometer.

There are three modifications of the spectrometer that should be mentioned because they aided in obtaining usable mass spectra under the conditions of rapid variation of sample size over several orders of magnitude The first is a voltage selector switch which reproducibly changed the potential applied to the ion multiplier. It consisted of a high voltage rotary selector switch with neon bulbs connected in series between the selector positions. By turning the selector switch the gain of the ion multiplier can be changed rapidly and reproducibly to match the size of the sample being observed. The second modification is a total ionization switch which applied a −150-volt potential to the analog controller gate, thereby collecting the secondary electrons produced by ions at all masses present. This device is very convenient for determining the time delay between the maximum of the peak on the gas chromatographic thermal conductivity cell and the maximum intensity of the sample in the spectrometer. The ions produced by the helium carrier gas are gated out by setting the analog scanner at Mass 4. The third modification is an electrical connection between the scanner and the controller so that the scan generator for the scanner will also drive the controller and thereby record another complete mass spectrum separated by a small time interval as shown in Figure 4. The dual spectra permit detection of composition changes within a single gas chromatographic peak and help in making an accurate determination of the components contained with a single gas chromatographic peak.

ANALYSIS OF SPECTRA

The confidence that one can have in the reproducibility of the mass spectra under various conditions is shown in Tables I, II, and III. Hexene-1 was selected as the test compound because

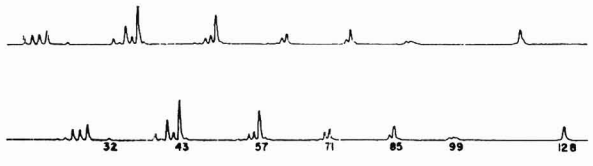


Figure 4. *n*-Nonane mass spectrum

Table I. Pattern Study of Hexene-1 through Inlet System

m/e	$\overline{M}$, %	σ	Range H-$\overline{M}$	Range $\overline{M}$-L	TA, %
84	46.7	2.88	2.7	4.1	75.3
69	30.9	1.37	1.0	2.0	69.2
56	100				
55	64.8	0.87	1.1	1.0	77.6
43	65.4	1.95	1.6	2.7	71.2
42	78.5	1.78	1.5	2.2	69.1
41	96.3	3.61	3.7	3.2	65.5
39	48.7	1.65	2.4	1.3	74.1
27	53.4	3.05	2.9	2.9	65.8

Table II. Pattern Study of Hexene-1 through Inlet System Plus Helium

m/e	$\overline{M}$, %	σ	Range H-M	Range M-L	TA, %
84	44.5	1 29	1.3	1.5	71.8
69	31.6	2.38	2.9	2.8	77.0
56	100.0				
55	65.1	4.47	5.1	4.2	69.9
43	66.8	3.96	4.6	3.9	71.2
42	78.4	1.55	1.0	2.3	67.4
41	97.1	3.98	4.1	3.6	66.4
39	48.0	0.90	0.9	1.1	79.7
27	54.6	0.32	0.3	0.3	64.8

it appeared to show a greater variability in pattern than the equivalent saturated hydrocarbon. In Table I, a pattern study is shown for hexene-1 introduced through a standard molecular leak in that system, and therefore maintained at relatively constant pressure. The first column lists the masses of major ions observed. The second column contains the mean values for the patterns based on m/e 56 = 100%. The third column lists the standard deviations for the patterns. The next two columns are the high and low range from the mean. The last column is the confidence that one can have that any pattern obtained will fall within the ranges defined. In Table II, the hexene-1 is introduced exactly as in Condition I, that is, through the standard molecular leak inlet system. But, in addition, a finite amount of helium is allowed to enter the spectrometer ionization region through the 9-micron glass leak from the gas chromatographic exit line. The data are treated in a similar fashion to that of Table I. The conditions in Table II are equivalent to the isolation of a gas chromatographic peak plus the additional pressure of the carrier gas such as contained in a valve system as described by Ebert (*2*). This experiment is designed to test the effects of additional helium on the hexene-1 pattern. The

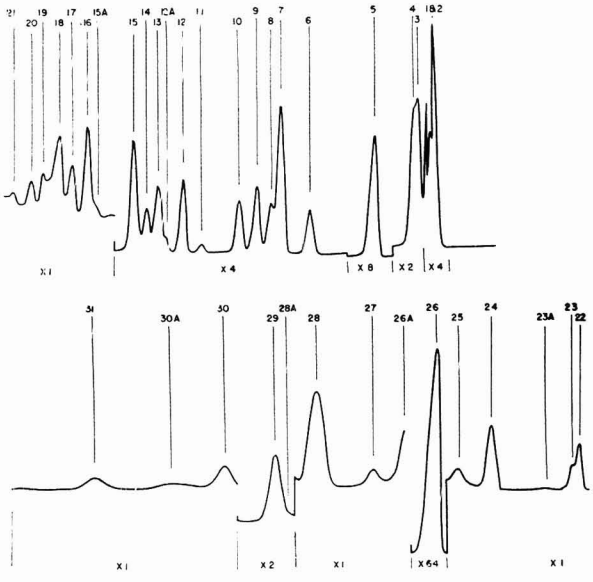


Figure 5. Gas chromatogram of cracked products

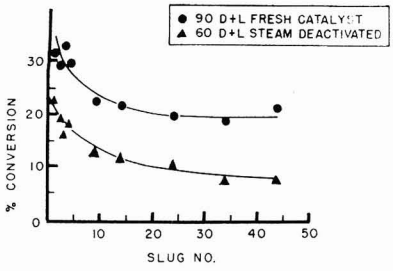


Figure 6. Per cent conversion vs. slug number

Table III. Pattern Study of Hexene-1 through Gas Chromatographic Leak

m/e	$\overline{M}$, %	σ	Range H-$\overline{M}$	Range $\overline{M}$-L	TA, %
84	42.9	1.30	1.8	1.2	73.7
69	27.4	1.28	1.2	1.8	74.5
56	100				
55	65.7	2.98	3.7	2.9	72.6
43	68.1	9.10	12.4	8.7	74.2
42	78.6	8.85	7.5	10.5	68.5
41	94.4	10.05	13.9	9.3	74.2
39	48.8	8.00	8.3	9.9	74.4
27	51.3	13.22	18.1	13.0	75.7

hexene-1 was maintained at relatively constant pressure during the run. In Table III, which represents actual running conditions, all the hexene-1 and the helium were introduced through the 9-micron leak from the gas chromatographic exit line in the standard procedure used throughout this work. While using the gas chromatographic exit line leak, the standard molecular leak inlet system is isolated from the spectrometer ionization region by closing the Veeco high vacuum valve. The data in Table III were treated in a fashion identical to that for Tables I and II.

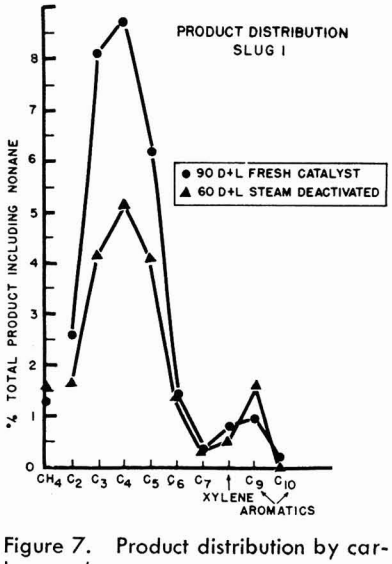


Figure 7. Product distribution by carbon number

Table IV. Identification of Gas Chromatographic Peaks and Product Distribution

Gas chrom. peak No.	Identification	Wt. %	Gas chrome peak No.	Identification	Wt. %
1	Hydrogen	2.4	17	3 Methyl pentane	0.165
2	Methane		18	*n*-Hexane	
3	Ethylene	0.920		3 Methyl pentene-2 trans	0.403
4	Ethane	0.895		3 Ethyl butene-1	
5	Propane	0.793	19	3 Methyl pentene-2 cis	0.128
	Propylene	3.172	20	Methyl cyclopentane	0.081
6	Isobutane	0.633	21	2 Methyl 1,3-pentadiene	0.041
7	1-Butene	2.148	22	Benzene	0.186
	Isobutylene			*n*-Heptane	
8	*n*-Butane	0.716	23	Heptanes	0.077
9	*trans*-Butene-2	0.964	24	Toluene	0.288
10	*cis*-Butene-2	0.663	25	Unidentified C_9?	0.045
11	3 Methyl butene-1	0.110	26	Nonane	78.395
12	Isopentane	1.060	26A	Xylene M + P	0.305
12A	Pentene-1	0.220	27	Xylene O	0.110
13	*n*-Pentane	1.069	28	Methylethylbenzene	0.801
14	Pentene-2	0.542	29	Trimethylbenzene	0.550
15	2 Methyl butene-2	1.409	30	Trimethylbenzene	0.178
15A	3 Methyl pentene-1	0.031	30A	C_{10} aromatics	0.083
16	2 Methyl pentane	0.277	31	C_{10} aromatics	0.124
	Cyclopentane				
	4 Methyl pentene-2				

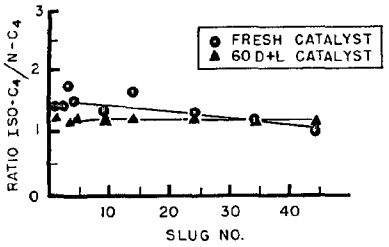


Figure 8. Iso-C_4/*n*-C_4 vs. slug number

From this study, it can be concluded that the conditions in Tables I and II produce mass spectral patterns with a range of ±5–10%, approximately 70% of the time. With the conditions shown in Table III, the variability in per cent pattern is considerably greater so that the spectra obtained have to be treated very cautiously. The repeated spectra as shown in Figure 4 helped considerably in establishing confidence in the patterns.

RESULTS AND DISCUSSION

A typical gas chromatogram obtained from the cracked products of *n*-nonane is shown in Figure 5. The identifications of the peaks in Figure 5 and the product distribution by weight per cent are shown in Table IV.

When per cent conversion was plotted against slug number as shown in Figure 6 an initial conversion of 32% was obtained with the fresh silica alumina (90 Atlantic D + L) catalyst and 23% with the steam deactivated catalyst (60 Atlantic D + L). The values dropped sharply after a few slugs and leveled off at 20% and 9%, respectively.

Product distributions by carbon number for an initial slug of *n*-nonane over a fresh and a steam-deactivated catalyst are shown in Figure 7. Analysis of succeeding slugs indicated that the product distribution by carbon number remained approximately constant as a function of slug number or cracking cycle time. As can be seen in Figure 8

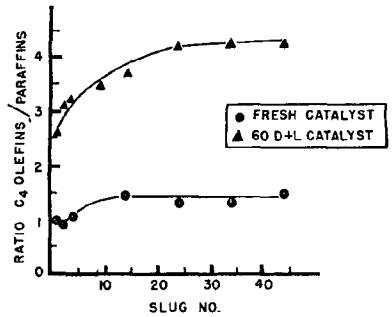


Figure 9. C_4 olefin/C_4 paraffin vs. slug number

when the ratios of iso-C_4 to *n*-C_4 are plotted against slug number there does not appear to be a significant change in ratio with slug number. When the ratios of C_4 olefin to C_4 paraffin are plotted against slug numbers (Figure 9), there does appear to be a significant increase in ratio with increase in slug number.

CONCLUSIONS

The general techniques described here can be applied to any reaction that can be carried out in a flow system. When applied to the study of the product distribution from the catalytic cracking of *n*-nonane over a silica alumina catalyst as a function of cycle time, it was found that the product distribution by carbon was relatively independent of cycle time, however, the hydrocarbon type within a carbon number changed as a function of cracking cycle time.

LITERATURE CITED

(1) Blanding, F. H., *Ind. Eng. Chem.* **45**, 1186 (1953).
(2) Ebert, A. A., Jr., ANAL. CHEM. **33**, 1865 (1961).

RECEIVED for review September 12, 1962. Accepted April 19, 1963. Presented at the 10th Annual Meeting, ASTM Committee E-14 on Mass Spectrometry, New Orleans, La., June 3–8, 1962.

Separation of Some Alkaloids, Steroids, and Synthetic Compounds by Thin-Layer Chromatography

B. P. KORZUN, LOUIS DORFMAN, and S. M. BRODY

Research Department, CIBA Pharmaceutical Co., Division of CIBA Corp., Summit, N. J.

▷ The unique advantages of thin-layer chromatography has led to the development of a preparative method. Preparative thin-layer chromatography has proved effective for separation of alkaloids, steroids, and synthetic compounds in amounts of 100 to 500 mg. Large glass plates, 10 by 15 inches, are coated with a layer of adsorbent 1 mm. thick and activated by heating. The sample mixture is applied as a streak across the bottom of the plate and developed with a solvent. After development, the bands are located by ultraviolet light or chemical reagent and scraped from the plate and each band eluted. A detailed account of the procedure, equipment, and examples of application is presented.

SINCE THIN-LAYER CHROMATOGRAPHY is successful with micro quantities, it was desirable to scale up to a preparative method capable of separating 100- to 500-mg. quantities. Attempts to use the adsorbents for thin-layer chromatography in packed columns were not successful. The resistance to flow through the column required considerable time to elute the substance from the column. A preparative method has been described for a horizontal column chromatography in a cellophane tube (*2*). Preparative thin-layer chromatography on regular 20 × 20 cm. plates was described (*5*). For complex mixtures the capacity was low. The scale-up is accomplished by using large plates 10 by 15 inches coated with an adsorbent 1 mm. thick. A plate this size is surfaced with approximately 55 grams of silica gel G or 120 grams of aluminum oxide G.

EXPERIMENTAL

Apparatus and Materials. The apparatus used to coat the plates with adsorbent is a slightly modified version of a design by Mutter and Hofstetter and described by Wollish (*7*). The applicator is enlarged to accommodate the 10- by 15-inch plates, and the adjusting screws are modified as shown in Figure 1. The width of the reservoir is slightly more than 10 inches to permit the plate to pass through. Aluminum is used to construct the applicator.

Storage Rack and Glass Plates. The storage rack to hold coated plates is an enlarged version of those commercially available. The glass plates are single-thickness, window-plate glass (10 by 15 inches) with beveled edges.

Chromatographic Chamber. Standard square jars 12 by 12 by 24 inches are used. The jars are lined with heavy filter paper on three sides to aid in rapid equilibration of the chamber with the solvent.

Adsorbent. Silica gel G and aluminum oxide G (Merck A.G., Darmstadt, Germany) are used.

Preparation of Coated Plates. A glass plate is placed under the reservoir of the applicator and the front gate is adjusted to 1 mm. above the plate by setting the adjusting screws with the aid of a thickness gauge. A slurry is prepared by adding 115 cc. of water to 55 grams of silica gel G or 110 cc. of water to 120 grams of aluminum oxide G and stirred carefully to eliminate lumps and to avoid entrapped air bubbles. The slurry is poured into the applicator reservoir, and the plate pushed through at a steady rate. The preparation of the slurry and coating of the plate should be done quickly because the slurry will start to set in a few minutes. The coated plates are placed on a level surface and allowed to set for 30 minutes and then inserted into the storage rack. The plates are placed in an oven without heating and allowed to set overnight (approximately 16 hours). This is necessary especially with silica

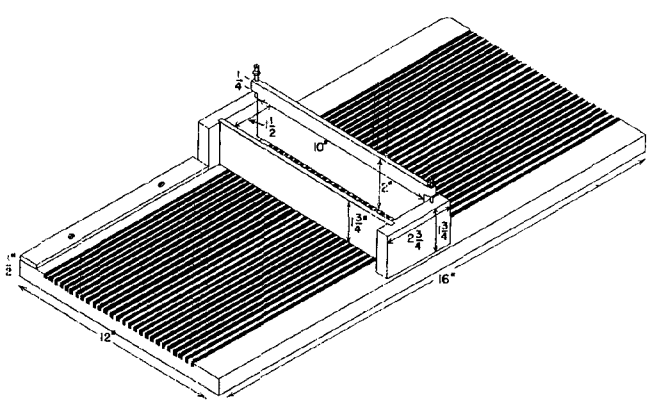


Figure 1. Applicator

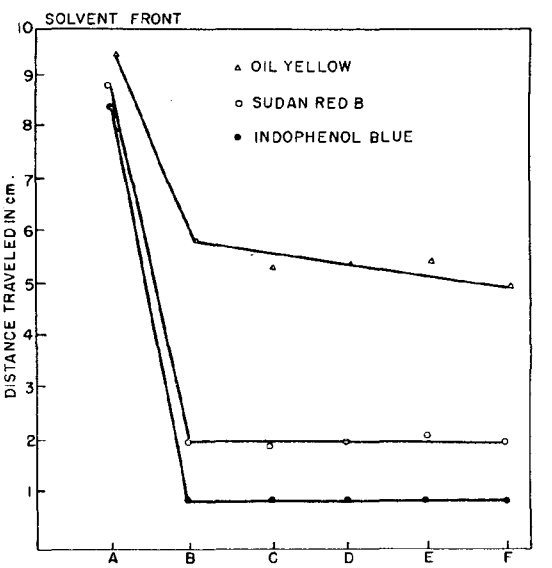


Figure 2. Adsorbent activity

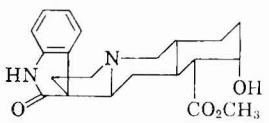
A—16 hours at room temperature
B—Activity II-III according to Stahl
C—Activated at 80° C. for 2 hours
D—C stored for 2 days over desiccant
E—C stored for 7 days over desiccant
F—Activated for 16 hours at 80° C.

gel G because if the water is allowed to evaporate too rapidly, cracking of the coat will develop. The oven is then radually heated to 80° C., and the adsorbent activated at this temperature for 2 to 4 hours. The plates are then stored in an air-tight cabinet containing a desiccant.

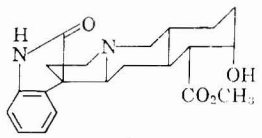
The activity of silica gel G is standardized by using a mixture of dyes which serve as the reference material. Three dyes are commonly used (*6*): *p* - dimethylamino - azobenzene (oil yellow), dihydroxy-azobenzene (sudan red B), and dimethyl-amino-phenyl-naphthoquinoneimine (indophenol blue). The dyes are developed with benzene, and the distance the solvent front travels is 10 cm. Figure 2 compares the distance traveled by the dyes for various conditions of activation and storage. The activity of aluminum oxide G is determined with the six dyes used for the Brockman activity test (*1*). Hĕrmánek (*3*) has determined the

Table I. Isolation of Oxindole Alkaloid Isomers

Adsorbent—silica gel G
Solvent—chloroform–ethyl acetate (5:95)
Development time—3 hours
Recovery—93.5%



B

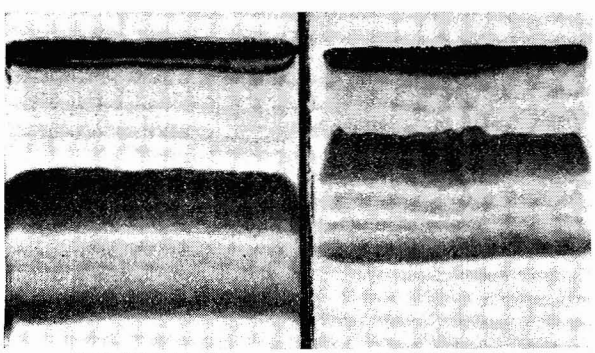


C

400-Mg. Sample Mixture

		R_f[a]
Band O origin	15 mg.	0.00
A	15	0.05
B	144	0.10—Pure B
B′	63	Mixture of B and C
C	105	0.20—Pure C
D	10	0.70
E front	22	0.95

[a] R_f value of isolated compound.



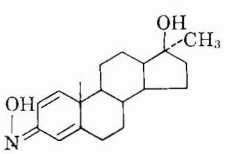
UNSATURATED JAR SATURATED JAR

Figure 3. Dye separation

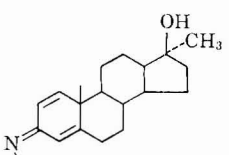
Dye mixture — 300 mg.

Table II. Isolation of 7α-Methyl-17β-hydroxy-1,4-androstadiene-3-one Oxime Isomers

Adsorbent—silica gel G
Solvent—chloroform–methanol (99:1) first development
Development time—3 hours
Solvent—chloroform ethyl acetate (7:3) second development
Development time 2.5 hours
Recovery—97%



A



B

400-mg. Sample mixture

	R_f[a]
Band 1—185.0 mg.	0.33—A
2— 77.0 mg.	Mixture of A and B
3—132.3 mg.	0.40—B

[a] R_f value of isolated compound.

R_f values of the dyes for activity II, III, IV, and V. Standardization of the adsorbent is necessary for consistent results.

Application of Sample. The sample mixture is applied to the plate with a 0.5-ml. pipet as a narrow band approximately 0.5 to 1 cm. wide and at a point 2.5 cm. from the end of the plate. The sample should be uniformly deposited across the width of the plate without disturbing the adsorbent. An apparatus (*4*) has been described which aids in applying the sample evenly.

PROCEDURE

Standard thin-layer chromatographic plates, 2 by 8 inches, are used as test plates for selecting solvents to effect the desired separation. The solvent selected is poured into the chamber over the filter paper liner in a sufficient amount to cover the bottom to a depth of about 1 cm. The chamber is covered and allowed to equilibrate for about an hour. The plates to be developed are placed in the chamber at an angle, and the solvent is allowed to ascend to about 2 to 4 cm. from the top. After developing, the plates are removed and air-dried. Occasionally, it is desirable to repeat the development to improve the separation.

An ultraviolet lamp is used to locate materials that fluoresce or quench ultraviolet light. For those compounds which cannot be detected under ultraviolet light a reagent must be used. The plate is protected with heavy paper, and a strip about 0.5 cm. wide along the edge or through the center is exposed and treated with an appropriate reagent. The bands revealed are marked and scraped off the plate, and the material is eluted from the adsorbent with an appropriate solvent and filtered through a fine sintered glass funnel.

Separation of Dyes. Figure 3 is an example of a separation of three dyes on silica gel G. To each plate 100 mg. of each dye was applied and both plates were developed with benzene. The need for equilibrating the chamber with solvent for the development of the plate can be readily seen if reproducible results are desired. The plate on the left was developed in a chamber without a paper liner to equilibrate the chamber, and time for development is 6 hours. The other plate is developed in a chamber with a paper liner saturated with benzene, and time for development is 3 hours. In the equilibrated chamber, the bands are more compact, especially the material that migrates to a higher R_f value. In addition, the R_f value is different.

Isolation of Alkaloid Isomers. A 400-mg. sample of a reaction product containing two oxindole alkaloid isomers is applied to a plate coated with silica gel G. The developing solvent is chloroform–ethyl acetate (5:95). At this concentration, overlapping of the bands occurs, and this section is removed and discarded. The isomers are completely separated when a 200-mg. sample is applied. The results of the isolation are given in Table I.

Isolation of 17α-methyl-17β-hydroxy - 1,4 - androstadiene - 3 - one oxime Isomers. A 400-mg. sample mixture is applied to a plate coated with silica gel G. The plate is first developed with chloroform-methanol (99:1), removed, and dried. The plate is then redeveloped with chloroform–ethyl acetate (7:3). The results of the isolation are given in Table II.

ACKNOWLEDGMENT

The authors thank F. F. Anderson for the construction of the apparatus used.

LITERATURE CITED

(1) Brockman, H., Schodder, H., *Ber.* **74**, 73 (1941).
(2) Dahn, H., Fuchs, H., *Helv. Chim. Acta* **45**, 261–70 (1962).
(3) Heřmánek, S., Schwartz, V., Cekan, Z., *Coll. Czech. Chem. Comm.* **26**, 3170–3 (1961).
(4) Mickibbins, S. W., Harris, J. F., Soeman, J. F., *J. Chromatog.* **5**, 207–16 (1961).
(5) Ritter, F. J., Meyer, G. M., *Nature* **193**, 941 (1962).
(6) Stahl, E., *Pharm. Rundschau* **1**, 2 (1959).
(7) Wollish, E. G., Schmall, Morto, Hawrylshyn, Mary, ANAL. CHEM. **33**, 1138–42 (1961).

RECEIVED for review November 19, 1962. Accepted April 22, 1963. Division of Analytical Chemistry, 142nd Meeting, ACS, Atlantic City, N. J., September 1962.

The Chromatographic Determination of Trace Amounts of Polynuclear Hydrocarbons in Petrolatum, Mineral Oil, and Coal Tar

WILLIAM LIJINSKY, IRVING DOMSKY, GLORIA MASON, HUSNI Y. RAMAHI, and TAHER SAFAVI

Division of Oncology, The Chicago Medical School, 2020 West Ogden Ave., Chicago 12, Ill.

▶ Methods of analyzing petrolatums, mineral oils, creosote, and coal tar for polynuclear hydrocarbons are discussed. Current methods involve absorption chromatography, solvent partition, and paper chromatography. These procedures are fairly quantitative but time consuming. Individual polynuclear hydrocarbons at a concentration of 40 p.p.m. or more have been determined in a 250-mg. creosote sample and those at a concentration of 0.01 p.p.m. or more in a 1-kg. petrolatum sample. Gas chromatography at moderate temperatures has been used for polynuclear hydrocarbon analysis. Using a column of SE-30 on glass beads, all of the common polynuclear hydrocarbons with boiling points up to that of benzo(g, h, i)perylene can be chromatographed in less than 1 hour at 200° C. The major polynuclear hydrocarbon constituents of petrolatum were observed in a chromatogram of a concentrate and those of coal tar in a dilute solution of the tar. Very small samples were required for gas chromatography (1 μg. of each hydrocarbon constituent).

SINCE PASSAGE of the 1958 Amendment to the Food, Drug, and Cosmetic Act of the U. S. A., with its specific reference to carcinogenic compounds, interest in the development of rapid analytical methods for the detection of such compounds has intensified. Attention has focused particularly on the polynuclear hydrocarbons, firstly because among this group of compounds is the largest number of known chemical carcinogens and, secondly, because of their ubiquitous occurrence, a consequence of the widespread use of coal, petroleum, and products derived from them.

Methods of detecting polynuclear hydrocarbons have improved as new analytical tools have been developed, since the pioneer work of Cook, Hewett, and Hieger led to the isolation of benzo(a)pyrene from coal tar in 1933 (*1*). Analysis of coal tar which once took months can now be completed in 7 to 10 days and, using gas chromatography, conceivably can be accomplished in 1 day. Parallel with improvements in resolution of mixtures of polynuclear hydrocarbons, the sensitivity of the analytical methods has been increased and the detection of 0.01 p.p.m. of a polynuclear hydrocarbon in a mixture is currently attainable, although only by rather lengthy procedures (*8*). A detectable limit of 0.5 p.p.m., on the other hand, can be realized with a 1-day procedure.

The essence of all of the analytical methods currently used is the concentration of the aromatic material in the mixture, with elimination of most nonaromatic compounds. This is achieved by adsorption chromatography or by partition between two suitable solvents. The aromatic concentrate thus prepared is resolved into its components by paper chromatography and the compounds are identified from their ultraviolet spectra and, if possible, their fluorescence emission spectra. In some cases, examination of the ultraviolet absorption spectrum of the aromatic concentrate is adequate for the identification of polynuclear hydrocarbons.

The use of gas liquid partition chromatography offers the prospect that paper chromatographic resolution of the aromatic concentrates can be dispensed with and the concentrate analyzed directly. Gas chromatography has already been used for analysis of lower boiling polynuclear hydrocarbons (*6, 13*) and for tars and heavy oils (*3-5*), in which high column temperatures were employed for detection of 4- and 5-fused-ring hydrocarbons, among which group almost all of the carcinogenic hydrocarbons are found. Unfortunately, at these high temperatures (approaching 400° C.) bleeding of many stationary phases drastically reduces the sensitivity. Gas chromatography of individual polynuclear hydrocarbons and synthetic mixtures at lower temperatures (230° to 260° C.) has been described (*2*), but here again large sample sizes were employed. Our concern has been to resolve complex mixtures of polynuclear hydrocarbons at moderate temperatures (180° to 210° C.) and with high sensitivity.

Improvements in the procedure leading possibly to quantitative determination of the components can be expected. Such improvements include temperature

programming and collection of fractions from the gas chromatograph for absorption or fluorescence spectrometric analysis; the latter would reduce the sensitivity of the procedure, which would be a serious disadvantage when, as with concentrates from petrolatums, waxes, etc., only minute quantities of sample are available.

EXPERIMENTAL

Procedure. The mineral oils and petrolatums (U.S.P. grade) were obtained commercially, as was the creosote. Medicinal coal tar was obtained from Gazzolo Drug and Chemical Co., Chicago. All hydrocarbon solvents were chromatographed (*9*) and distilled before use.

One-kilogram samples of petrolatum, dissolved in 1 liter of hot isooctane (2,2,4-trimethylpentane), were chromatographed on silica gel (grade 922, Davison Chemical Co.) as described in (*11*). After washing the column with hot isooctane the aromatic material was eluted with 1 liter of benzene. The residue after evaporation of the benzene was dissolved in 25 ml. of cyclohexane and partitioned with nitromethane (*11*). After distillation of nitromethane under reduced pressure, the residue was dissolved in a minimum volume of benzene and chromatographed on 15 × 50 cm. sheets of Whatman No. 1 filter paper (20 mg. of residue per sheet). The sample was applied with a micropipet to a line 10 cm. from the end of the sheet. Chromatography was carried out in a *N,N*-dimethylformamide–isooctane system (*8*). The fluorescent bands were cut out, eluted with benzene–ethanol (3:1) in a Soxhlet extractor, the solvent was evaporated under nitrogen, and the absorption spectrum taken from 250 to 450 mμ in isooctane. The fractions were rechromatographed until spectra corresponding to those of known polynuclear hydrocarbons were obtained. The identification was confirmed by the fluorescence emission spectra where possible. The concentration of each identified compound in the starting material was calculated from the absorption spectra.

The method used for analysis of mineral oil was essentially similar, except that 18 liters of mineral oil was mixed with an equal volume of hot isooctane and chromatographed on silica gel; the subsequent steps were the same as for petrolatum.

In the analysis of materials relatively rich in polynuclear hydrocarbons (as compared with waxes and mineral oils), such as coal tar and creosote, much smaller quantities of material could be used. To remove phenols and similar compounds, 100 to 500 mg. of tar or creosote was dissolved in 25 ml. of cyclohexane and shaken with 25 ml. of 90% methanol (*7*). The methanol extract was shaken with three 25-ml. portions of cyclohexane and the combined cyclohexane solutions were evaporated to dryness. The residue was dissolved in 25 ml. of cyclohexane and extracted with 25-ml. portions of nitromethane, as previously described. The residue, after evaporation of nitromethane, was diluted to 5 ml. with benzene and aliquots of the solution were chromatographed on paper to enable both major and minor components to be determined. Since the concentration of tricyclic and tetracyclic polynuclear hydrocarbons in coal tar and creosote is at least 10 times that of the pentacyclic hydrocarbons, it was sufficient to chromatograph 0.05 or 0.1 ml. of the benzene solution to determine the former compounds. For the determination of the pentacyclic compounds, 1 ml. or more of the benzene solution was chromatographed on a suitable number of sheets of paper (0.2 ml. on each 15 × 50 cm. sheet), and the four or five zones below and including that containing benz(a)anthracene were discarded, the compounds in these zones having been determined by chromatography of the small volume of benzene solution already described. The upper zones (numbering 6 or 7) were cut out, analogous ones from the several chromatograms were combined, and extracted with benzene–ethanol in a Soxhlet apparatus. The residues after evaporation of the solvent were rechromatographed on single sheets of paper in the dimethylformamide–isooctane system. Adequate separation of the components in this case required 12 to 20 hours development. Each fraction was examined spectrometrically as previously described.

All of these analyses required approximately 1 week (35 to 40 hours) to complete, the limiting factor being the time required to take the spectra, which again depended on the amount of dilution of the fractions necessary.

GAS CHROMATOGRAPHY. A Barber-Colman Model 20 instrument with a strontium-90 ionization detector, using argon as carrier gas, was used. Before applying this method to the analysis of unknown mixtures, it was necessary to establish the operating parameters for detection and separation of polynuclear hydrocarbons. A series of solutions of several polynuclear hydrocarbons in benzene, differing in concentration by factors of 10, was prepared. A standard sample size of 1 μl. was used and the lowest detectable concentration of each hydrocarbon was determined. The parameters varied were column temperature and argon pressure. The column was 8 ft. long, 1/4 inch in diameter, and was packed with glass beads 60–80 mesh coated with 0.25% of SE-30 Silicone (prepared by Chemical Research Services, Inc., Addison, Ill.).

The aromatic concentrate from the cyclohexane–nitromethane partition of the adsorbate from a petrolatum was dissolved in 0.1 or 0.5 ml. of benzene, and 1 μl. of this solution was used for gas chromatography. The results of this analysis applied to petrolatum sample 10 are given in Figure 1. Similarly, in Figure 2 are shown the chromatograms obtained from 5 μl. of the solution of the aromatic concentrate from coal tar.

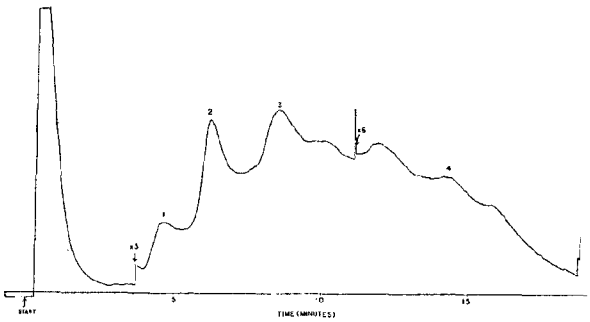


Figure 1. Chromatogram on SE-30 of silica gel adsorbate from 100 grams of Petrolatum 10, after cyclohexane–nitromethane partition; residue dissolved in 0.5 ml. of benzene, 1-μl. sample

1. Phenanthrene
2. Fluoranthene/pyrene
3. Methylpyrene (?)
4. Triphenylene (?)

RESULTS

The analysis of five samples of mineral oil revealed the absence of identifiable polynuclear hydrocarbons, even at a concentration of 1 part in 10^9. Similar analyses of hydrocarbon solvents led to the detection of some polynuclear hydrocarbons in most samples at this concentration (*9*).

The petrolatums analyzed by the procedure described all contained identifiable polynuclear hydrocarbons at concentrations of 1 part in 10^8 or higher. No carcinogenic compounds were detected. Of the 10 samples examined (Table I), there was a quantitative difference in polynuclear hydrocarbon content between the white petrolatums (samples 1, 2, and 3) and the amber petrolatums (samples 4 to 10). The total polynuclear hydrocarbon content of several petrolatum samples was of

the order of 10 p.p.m., whereas the highest value for any petroleum wax examined was approximately 1 p.p.m. (*14*).

The creosote and coal tar samples examined showed quantitative differences in polynuclear hydrocarbon content (Table II), although in general the same compounds were identified in both (two samples of different size are shown for each). The concentrations of tricyclic and tetracyclic hydrocarbons were higher in creosote than in coal tar, the reverse being true for the pentacyclic hydrocarbons. The variation in concentration given by analysis of two different aliquots of the same material is due to the greater difficulty in some cases of separating two particular components—e.g., benzo(j)fluoranthene and benzo(k)fluoranthene, anthracene and phenanthrene, benzo(a)pyrene and benzo(g, h, i)perylene. The results of the creosote analysis may be compared with the analysis of a similar sample by a much longer method, which has been reported previously (*12*).

Table I. Concentration of Polynuclear Hydrocarbons in Petrolatum (p.p.m.)

Sample	Benz(a)anthracene	Benzo(e)pyrene	Chrysene	Fluoranthene	Phenanthrene	Pyrene (incl. methylpyrene)	Triphenylene	Other
1	0	0	0.01	0	0	0.01	0	0
2	0	0	0	0.01	0	0.015	0	0
3	0	0	0	0.015	0	0.01	0	0
4	0.19	0.23	0.44	0	0	0	0.36	0.03 benzo(g, h, i)perylene
5	0.02	0	0.03	0.04	0.7	0.06	0.07	0
6	0.01	0.025	0.01	0.01	0	0.01	0.03	0
7	0	0.01	0.02	0.15	2.79	0.18	0.17	0
8	0.90	0	0.33	0.93	2.56	4.71	3.52	0.11 benzo(g, h, i)perylene 0.02 anthracene
9	0.03	0.01	0.04	0.08	0.59	0.31	0.15	0
10	0	0	0.04	0.59	6.70	2.32	4.83	0

Table II. Polynuclear Hydrocarbons in Creosote and Coal Tar

	Concentration in creosote (g./kg.)		Concentration given in (*12*) g./l.	Concentration in coal tar (g./kg.)	
	(1)	(2)		(1)	(2)
Anthracene	12.1	12.0	6.2	2.88	4.35
Benz(a)anthracene	2.77	2.94	2.75	6.24	6.98
Benzo(b)chrysene	0.03	0.06	...	0.93	0.80
Benzo(j)fluoranthene	0.29	0.29	...	0.63	0.45
Benzo(k)fluoranthene	0.30	0.11	...	1.08	1.07
Benzo(g, h, i)perylene	...	...	...	1.23	1.89
Benzo(a)pyrene	0.14	0.22	0.12	2.08	1.76
Benzo(e)pyrene	0.18	0.15	...	1.85	1.88
Carbazole	2.20	1.42	2.75	1.32	1.27
Chrysene	1.34	0.94	1.27	2.13	2.86
Dibenz(a, h)anthracene	...	...	...	0.30	0.23
Fluoranthene	24.8	22.2	7.8	17.7	17.8
Perylene	0.04	0.04	0.04	0.70	0.76
Phenanthrene	39.9	33.3	47.9	13.6	17.5
Pyrene	9.1	6.8	4.2	7.95	10.5

Table III. Gas Chromatography of Polynuclear Hydrocarbons on SE-30

Hydrocarbon	Sample wt., μg.	Retention time (min.) at 180° C.	200° C.	210° C.
Phenanthrene	0.01[a]	2	...	...
Fluoranthene	0.05[a]	3.2	...	...
Pyrene	0.02	3.7	2	...
4-Methylpyrene	1	5.5	3	...
1-Methylpyrene	1	5.7	3	...
3-Methylpyrene	1	6.0	3	...
Chrysene	0.2[a]	11.5	7	4.5
Benz(a)anthracene	0.1[a]	11.5	6.5	4.5
7,12-Dimethylbenz(a)-anthracene	0.5[a]	30	13	9
Triphenylene	1[a]	11	5.5	4
Benzo(a)pyrene	1[a]	38	16	12
Dibenz(a, h)anthracene	1[a]	...	40	26
Benzo(g, h, i)perylene	3[a]	...	44	28

[a] These were minimum quantities giving a good response with relative gain 30 and attenuation 1.

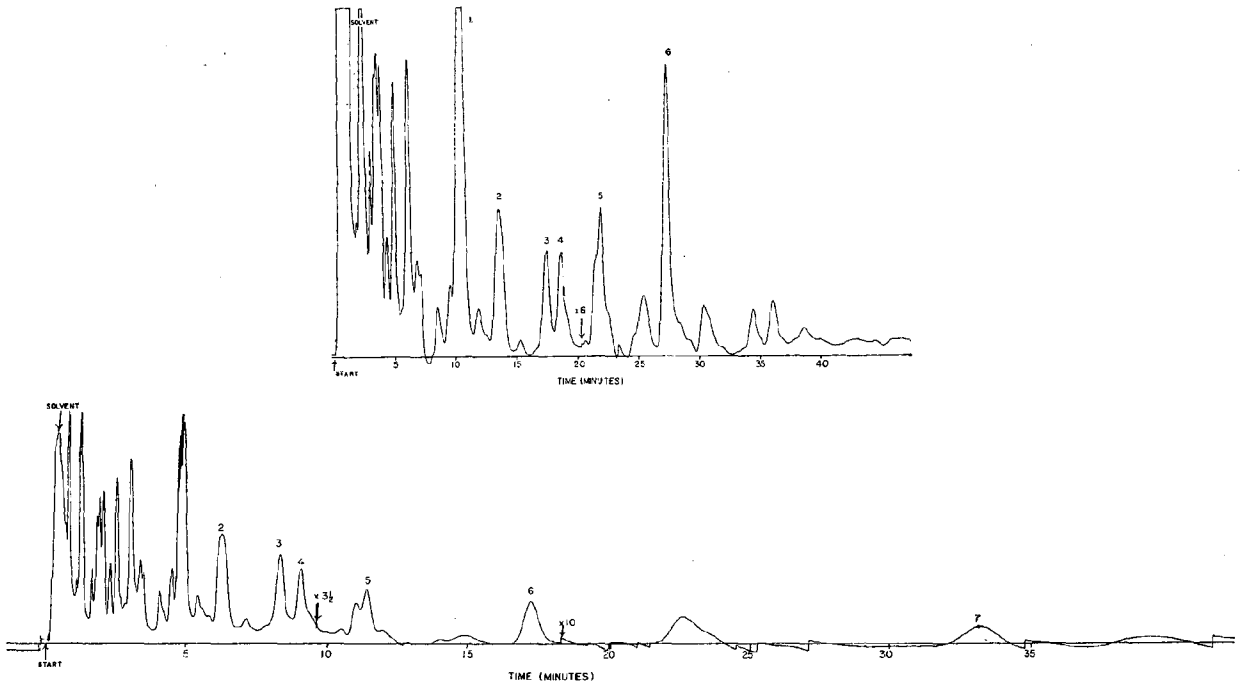
Operating parameters were: argon pressure 15 p.s.i. (32 ml./min.), detector voltage 1250, flash heater temperature 285° C., detector cell temperature 250° C., sample volume 1 μl.

By using gas liquid partition chromatography it was possible to separate and detect polynuclear hydrocarbons at moderate column temperature (Table III). The retention times given are relative and varied somewhat from one column to another. Even the high boiling point hydrocarbon dibenz(a, h)anthracene was easily detectable. The sensitivity of the system varied considerably between different compounds, being approximately 100 times greater for pyrene than for dibenz(a, h)anthracene. At the column temperature adequate for the detection of tricyclic and tetracyclic hydrocarbons (180° C.), most of the pentacyclic hydrocarbons were not detected. On the other hand, at 220° C., at which temperature benzo(a)pyrene and dibenz(a, h)anthracene were detectable, the retention times of phenanthrene, fluoranthene, and pyrene were so short as to make these compounds difficult to distinguish from the solvent. A mixture of pyrene, benz(a)anthracene, benzo(a)pyrene, and dibenz(a, h)anthracene was easily resolved. It proved possible to separate pyrene homologs from pyrene (although not from one another) and 7,12-dimethylbenz(a)anthracene from benz(a)anthracene in this system. Benzo(a)pyrene could be separated from benzo(g, h, i)perylene by gas chromatography, whereas their separation was difficult by paper chromatography, ultraviolet absorption spectrometry, and fluorescence spectrometry (*10*).

By submitting a concentrate prepared from petrolatum sample 10 to gas chromatography (Figure 1), several polynuclear hydrocarbons could be identified including fluoranthene and pyrene, phenanthrene, triphenylene, and methylpyrene.

The gas chromatogram of the coal tar sample (Figures 2*a* and *b*) showed that many of the polynuclear hydrocarbons detected by paper chromatography could be detected by gas chromatography.

It would seem desirable to collect the fractions from the gas chromatograph and to examine them spectrometrically. This has not yet been done because the low capacity of the column would make the collection of sufficient material difficult. Secondly, collection



Figures 2a and 2b. Chromatogram on SE-30 of coal tar, 250 mg. in 5 ml. of benzene, 5-μl. sample; 2a at 160° C., 2b at 180°C.

1. Phenanthrene/anthracene
2. Carbazole
3. Fluoranthene
4. Pyrene
5. 1-Methyl or 3-methylpyrene
6. Benz(a)anthracene/chrysene
7. Benzo(a)pyrene

of fractions would increase the sample size required and, therefore, greatly reduce the sensitivity of the procedure.

DISCUSSION

In the analysis of mixtures containing polynuclear hydrocarbons, the factors limiting the sensitivity of the method used (adsorption chromatography, cyclohexane–nitromethane partition, and paper chromatography) are: (*a*) the quantity of starting material to produce fractions containing 5 to 10 μg. of any polynuclear hydrocarbon (this being the minimum quantity required for accurate spectrophotometric determination) and (*b*) the time allotted to paper chromatography, this being dependent on the amount of background ultraviolet absorbing material present. Removal of background absorption is necessary to obtain spectra which can be compared with those of pure polynuclear hydrocarbons. A practical limit is set by the rapid increase in the number of paper chromatograms needed as the proportion of background absorbing material to polynuclear hydrocarbons increases. This limit has been, in our experience, 0.01 p.p.m. in waxes and petrolatums, and 0.0003 p.p.m. in mineral oils and solvents (*9*). The identification of polynuclear hydrocarbons is facilitated by the well defined and distinctive ultraviolet absorption spectra of most of these compounds; they also have high absorptivities, ranging up to 239,000 for dibenz(a, h)anthracene (*8*).

In this laboratory, the best paper chromatographic system for resolving mixtures of polynuclear hydrocarbons was *N,N*-dimethylformamide–isooctane on Whatman No. 1 paper, run by the descending technique. Some mixtures were difficult to resolve in this system. Benz(a)anthracene and chrysene could be resolved on partially acetylated paper, using toluene–methanol–water as the mobile phase (*8*). Pyrene and fluoranthene could be estimated in the single zone containing them using the 334-mμ absorption maximum of pyrene and the 286-mμ maximum of fluoranthene. Absorbance of the second compound at these wavelengths was low. Similarly, anthracene and phenanthrene could be estimated in a mixture of the two using the 375-mμ band of anthracene and the 294-mμ band of phenanthrene.

The results of analysis of the petrolatum samples shows that all contained essentially the same polynuclear hydrocarbons. As expected, the white petrolatums (samples 1 to 3) contained much smaller concentrations of polynuclear hydrocarbons than the amber petrolatums. This is probably a reflection of the more thorough refining of the white petrolatums. Although no known carcinogenic polynuclear hydrocarbons were detected in these materials, no conclusions can be drawn regarding their biological activity, since no biological testing of them has yet been carried out. One of the difficulties in such analyses is the differentiation of the hydrocarbons from their homologs. Differences in absorption spectrum between a polynuclear hydrocarbon and its homologs are often slight (the fluorescence emission spectra usually differ more), and gas chromatography might prove useful in separating a polynuclear hydrocarbon from its homologs.

The analysis of the coal tar and creosote samples revealed a higher concentration of the more volatile polynuclear hydrocarbons in the creosote and, conversely, a higher concentration of the less volatile (pentacyclic) hydrocarbons in the coal tar. These analyses, with a sensitivity approximating 10 p.p.m. of individual polynuclear hydrocarbons using 500 mg. or less of starting material, could be completed in about 1 week (40 hours), and could probably be applied to similar materials such as liquid smoke. Estimation of those polynuclear hydro-

carbons occurring at lower concentrations could be made using larger quantities of starting material, although this would increase the time of analysis considerably.

The results of the gas chromatographic investigation showed that most of the polynuclear hydrocarbons studied could be separated at column temperatures between 160° and 210° C. and argon pressure of 15 p.s.i., within 1 hour. Of special interest was the fact that it seemed possible to separate polynuclear hydrocarbons from their homologs by gas chromatography. This aspect of the subject is being explored further. Some compounds which were difficult to separate by other means [such as benzo(a)pyrene and benzo(g, h, i)perylene] could be separated by gas chromatography.

Since it was impossible to select a single column temperature at which separation of all polynuclear hydrocarbons would be optimal, temperature programming would be excellent for this purpose. This modification of the analytical procedure is now being investigated.

The sensitivity of the gas chromatographic method is superior to that of most other analytical methods for polynuclear hydrocarbons. Thus, since 5 μl. of the solution of coal tar (250 mg. in 5 ml.) contains 250 μg. of tar and this contains 0.5 μg. of benzo(a)pyrene, which is easily detected, the advantage over the spectrometric method is apparent.

Although not all of the polynuclear hydrocarbon components of commercial mixtures can be identified, it seems that the presence of known carcinogenic hydrocarbons in materials such as petrolatum above a level of 0.1 p.p.m. can probably be established using a gas chromatographic method.

ACKNOWLEDGMENT

The authors are grateful to Philippe Shubik for his interest and encouragement.

LITERATURE CITED

(1) Cook, J. W., Hewett, C. L., Hieger, I., *J. Chem. Soc.* **1933**, 396.
(2) Carugno, N., *Tabacco* **63**, 285 (1959); *C.A.* **54**, 5345a (1960).
(3) Dupire, F., *NCI Monogr. No. 9*, 183 (1962).
(4) Dupire, F., *Z. Anal. Chem.* **170**, 317 (1959).
(5) Dupire, F., Botquin, G., *Anal. Chim. Acta* **18**, 282 (1958).
(6) Hishta, C., Messerly, J. P., Reschke, R. F., Fredericks, D. H., Cooke, W. D., ANAL. CHEM. **32**, 880 (1960).
(7) Hoffmann, D., Wynder, E. L., *Ibid.*, **32**, 295 (1960).
(8) Lijinsky, W., *Ibid.*, **32**, 684 (1960).
(9) Lijinsky, W., Raha, C. R., *Toxicol. Appl. Pharmacol.* **3**, 469 (1961).
(10) Lijinsky, W., Raha, C. R., Chestnut, A., ANAL. CHEM. **33**, 1448 (1961).
(11) Lijinsky, W., Raha, C. R., Keeling, J., *Ibid.*, **33**, 810 (1961).
(12) Lijinsky, W., Saffiotti, U., Shubik, P., *J. Nat. Cancer Inst.* **18**, 687 (1957).
(13) Pinchin, F. J., Pritchard, E., *Chem. & Ind.* 1962, 1753.
(14) Shubik, P., *et al. Toxicol. Appl. Pharmacol.* **4**, Supplement (Nov. 1962).

RECEIVED for review May 28, 1962. Resubmitted February 18, 1963. Accepted April 22, 1963. In part, Division of Analytical Chemistry, 141st Meeting, ACS, Washington, D. C., March 1962. Work supported by grants C-5170 and CS-9212 from the National Institutes of Health, U. S. Public Health Service.

Detection and Identification of Mercaptans by Gas Liquid Chromatography

K. F. SPOREK and M. D. DANYI

Owens-Illinois Technical Center, Toledo 7, Ohio

▷ **Gas liquid chromatography is employed in conjunction with an iodine oxidation reaction, which converts mercaptans to disulfides, for separation, identification, and, if necessary, quantitative determination of mercaptans in admixtures with each other or with other substances. The procedure is particularly useful where the mercaptans cannot be isolated from the sample in a sufficiently pure form to be directly suitable for separation and identification by gas liquid chromatography. Thus the crude mercaptan sample is treated with iodine to form the corresponding disulfide; a second portion of the sample is then spiked with a known mercaptan and this is converted to a mixture of disulfides. In this way a series of disulfides can be formed from the original mercaptan with predictable retention times and relative abundances, thus providing an almost specific test for the unknown compound.**

THE DETECTION and identification of mercaptans are required in many instances when present either as major components or as traces. Because of the difficulties encountered with conventional methods of analysis, several attempts have been made recently to determine mercaptans, alkyl sulfides, and disulfides by gas chromatography. Adams and Koppe (*1*) tested kraft pulp digester blow gas and black liquor combustion products by a gas chromatographic procedure using Triton X-305 as the column filling. In their procedure, water interfered and had to be separated prior to the gas chromatographic analysis. Carson and Wong (*2*) tested Carbowax-1540, Reoplex 400, and Apiezon M for the separation of disulfides. Ryce and Bryce (*4*) used Celite coated with tricresyl phosphate on which they separated some of the lower mercaptans and dimethyl disulfide. Spencer, Baumann, and Johnson (*5*) used a column containing Johns-Manville firebrick C-22 coated with dinonyl phthalate; they obtained satisfactory separation of mercaptans used in several commercial odorants, which include methyl, ethyl, etc., thiols. More recently Farrugia and Jarreau (*3*) applied C-22 firebrick coated with di-*n*-butyl phthalate, tritolyl phosphate, and Silicone 200 as column filling. Their work involved separations of a series of thiols present in odorizing agents for odorless natural gases which also contained isopropyl alcohol as a cloud point suppressant. In all these procedures the only means of identification for individual mercaptans were the retention times under the specific conditions of the test. It was therefore assumed that an unknown substance would contain no substances other than thiols which would have identical retention times as the calibrating materials.

Because of the uncertainty of methods based on the identification by means of retention times alone, attempts were made in presently reported work to combine gas chromatography with a chemical reaction for the mercaptans to give a more specific test. As a result it was possible to convert mercaptans to a series of disulfides by a simple and fast oxidation with iodine in ether; this solvent was also used for extraction and concentration of thiols from aqueous and other samples. The so formed disulfides were separated and determined by gas liquid chromatography using silicone oil and silicone gum rubber coated firebrick as the fillings for the columns.

Table I. Retention Times of Mercaptans, Inert Solvents, and Disulfides

Retention time Min.	Sec.	Mercaptans	Inert solvents	Disulfides	Conditions of test
	24	MeSH			60° C., 20 p.s.i. Argon column: 4 ft. × 1/4 in. stainless steel tube filled with 20% Silicone gum rubber on Chromosorb P 60/80
	33	EtSH			
	37		Ether		
	56		Hexane		
	57	*t*-BuSH			
1	6	*n*-PrSH			
1	7		Chloroform		
1	35		Benzene		
1	38	*s*-BuSH			
1	45	iso-BuSH			
2	12	*n*-BuSH			
2	48			MeS_2Me	
5	28			MeS_2Et	
7	24		*m*-Xylene		
8	39			EtS_2Et	
8	51			MeS_2n-Pr	
10	43			MeS_2t-Bu	
12	24	*t*-Octyl SH			
90	00	*t*-Dodecyl SH			
	24		Ether		100° C., otherwise same as above
	37		Hexane, Chloroform		
	53		Benzene		
1	15			MeS_2Me	
2	03			MeS_2Et	
2	42		*m*-Xylene		
3	15			EtS_2Et	
3	27			MeS_2n-Pr	
3	48			MeS_2t-Bu	
4	33			MeS_2iso-Bu	
4	51			MeS_2s-Bu	
5	50			EtS_2n-Pr	
6	00			EtS_2t-Bu	
6	25			MeS_2n-Bu	
9	36			n-PrS_2n-Pr	
10	24			t-BuS_2t-Bu	
19	48			s-BuS_2s-Bu	
1	12		Hexane		150° C., 20 p.s.i. Argon column: 6-ft. × 1/4-in. stainless steel tube filled with 23% Silicone Oil 200 on Chromosorb P 60/80
2	18			MeS_2Me	
3	30			MeS_2Et	
5	12			EtS_2Et	
5	30			MeS_2n-Pr	
8	12			EtS_2n-Pr	
11	41			$MeS_2$3-Me-Bu	
12	30			n-PrS_2n-Pr	
17	20			$EtS_2$3-Me-Bu	
26	40			n-Pr$S_2$3-Me-Bu	
56	00			3-Me-Bu$S_2$3-Me-Bu	

Particular use was made of mixed disulfides formed by reacting the thiols present in the original sample with known added thiols. Further when mixtures of thiols were converted to the disulfides the latter were formed in definite proportions giving the highest quantity of a disulfide that usually contained the lower alkyl groups; this therefore provided a further means of identification for unknown thiols. It was possible to form mixed disulfides with optimum boiling points for use with the gas chromatographic procedures; consequently, a high boiling thiol could be combined with a low boiling thiol to give a relatively low boiling mixed disulfide.

These findings provided means for a nearly absolute test for mercaptans; when the original sample was tested in the gas chromatograph, a series of peaks due to thiols and other substances would be formed; then after conversion to disulfides, either pure or mixed, the original thiol peaks would disappear, nonthiol substances' peaks would remain and new peaks, due to the disulfides would appear. From the retention times of the thiols and the disulfides a reliable estimate could be made as to the identity of the original thiols. Further confirmation could be made by adding a known thiol to the original sample and thus forming mixed disulfides.

The oxidation of thiols to disulfides with iodine was rapid and quantitative as indicated by complete disappearance of thiol peaks from gas chromatograms after oxidation. The disulfides were easily soluble in ether and other organic solvents and owing to their relatively high boiling points and chemical stability were more convenient to handle than the original thiols.

In this work where the oxidation of thiols to the disulfides was carried out in acid solution, the highest amount of disulfides was that containing lower alkyl groups; this was contrary to findings of Carson and Wong (*2*) who used an alkaline oxidation. With their procedure, the oxidation of a mixture of methyl and propyl thiols resulted in the formation of a mixture containing 9.2% dimethyl, 38.5% methylpropyl, and 52.3% dipropyl disulfides. Although in our work no attempt was made to compare the alkaline and the acid oxidations, their different effects appear as a very interesting subject for future investigations.

Table II. Relative Abundances of Mixed Disulfides

Mercaptans used	Disulfides formed	Relative abundances as %[a]
MeSH	MeS_2Me	40.8
EtSH	MeS_2Et	49.0
	EtS_2Et	10.2
MeSH	MeS_2Me	49.1
n-PrSH	MeS_2n-Pr	42.7
	n-PrS_2n-Pr	8.2
MeSH	MeS_2Me	44.1
t-BuSH	MeS_2t-Bu	55.9
	t-BuS_2t-Bu	0.0
MeSH	MeS_2Me	57.7
s-BuSH	MeS_2s-Bu	37.1
	s-BuS_2s-Bu	5.2
MeSH	MeS_2Me	61.6
iso-BuSH	MeS_2iso-Bu	32.9
	iso-BuS_2iso-Bu	5.5
MeSH	MeS_2Me	64.3
n-BuSH	MeS_2n-Bu	35.0
	n-BuS_2n-Bu	0.7
EtSH	EtS_2Et	30.0
n-PrSH	EtS_2n-Pr	52.2
	n-PrS_2n-Pr	17.8
EtSH	EtS_2Et	16.8
t-BuSH	EtS_2t-Bu	83.2
	t-BuS_2t-Bu	0.0
MeSH	MeS_2Me	29.3
EtSH	MeS_2Et	31.4
n-PrSH	EtS_2Et + MeS_2n-Pr	25.9
	EtS_2n-Pr	9.9
	n-PrS_2n-Pr	3.5
n-PrSH	n-PrS_2n-Pr	35
3-Me-BuSH	n-Pr$S_2$3-Me-Bu	48
	3-Me-Bu$S_2$3-Me-Bu	17
MeSH	MeS_2Me	34
n-PrSH	MeS_2n-Pr	27
3-Me-BuSH	$MeS_2$3-Me-Bu + n-PrS_2n-Pr	27
	n-Pr$S_2$3-Me-Bu	6
	3-Me-Bu$S_2$3-Me-Bu	6
EtSH	EtS_2Et	29
n-PrSH	EtS_2n-Pr	28
3-Me-BuSH	n-PrS_2n-Pr	7
	$EtS_2$3-Me-Bu	21
	n-Pr$S_2$3-Me-Bu	10
	3-Me-Bu$S_2$3-Me-Bu	5

[a] Peak areas were measured with a disk integrator and % abundances are expressed as percentage areas normalized to 100%.

EXPERIMENTAL

Apparatus. The gas chromatograph apparatus employed in this work was a Research Specialties Co. instrument, Model 600, equipped with an ionization detector containing 10 mc. of strontium-90, using argon gas as the ionizing medium. Two column systems were used at various temperatures as indicated in the Tables.

Reagents. Methyl mercaptan, methanethiol, (MeSH), was obtained from Eastman Organic Chemicals, Rochester, N. Y., as were ethyl mercaptan, ethanethiol, (EtSH); *n*-butyl mercaptan, 1-butanethiol, (*n*-BuSH); and 3-methyl-1-butanethiol, (3-Me-BuSH).

n-Propyl mercaptan, propanethiol-1, (*n*-PrSH), 96.5%, was supplied by Phillips Petroleum Company, Bartlesville, Okla., as were *sec*-butyl mercaptan, butanethiol-2, (*s*-BuSH), 97.0%; isobutyl mercaptan, 2-methylpropanethiol-1, (iso-BuSH), 97.7%; *tert*-butyl mercaptan, 2-methylpropanethiol-2, (*t*-BuSH), 99.0%; *tert*-octyl mercaptan, (*t*-octyl SH), 95.5%; and *tert*-dodecyl mercaptan, (*t*-dodecyl SH), 97.0%. All above mercaptans were checked for purity by gas chromatography.

Procedure. The sample material suspected to contain mercaptans was extracted with ether, to the extract was added sufficient amount of iodine crystals to produce a dark brown solution, and the mixture was shaken for a few minutes. At this stage hydriodic acid usually separated in the form of brown oily liquid. The reaction mixture was then shaken with water, with a sodium thiosulfate solution, and again with water. The ether layer was dried with anhydrous sodium sulfate.

For calibration of the gas chromatograph equal volumes of 1% v./v. solutions of mercaptans in ether were used. The same solutions were then converted to disulfides, single or mixed, as described above.

Usually 1 μl. of a solution was injected providing about 10 μg. of the tested substance. The gas chromatograph was operated under conditions given in Table I with attenuation setting of $\times 50$.

On several occasions temperature programming was employed to speed up elution of high boiling disulfides; however, when no temperature programming facilities are available, the tested mercaptan may be reacted with MeSH to form a mixed disulfide with a substantially lower boiling point than that of the homo-disulfide.

DISCUSSION

The method was calibrated by a series of pure thiols which were converted by the iodine oxidation to identical and mixed disulfides. The retention times are shown in Table I and the relative abundances of disulfides in Table II.

The above values show that qualitative separation of all the tested disulfides was possible under the conditions used. The main value of the new technique however is its ability to provide nearly absolute identification of the mercaptan and detection of mercaptans when present with other gas chromatographic active substances. The values in Table II show that when starting with equal quantities of mercaptans, mixtures of disulfides are formed in which the proportions of individual disulfides follow definite abundance patterns.

Several tests were carried out to determine if any common organic solvents would interfere with the iodine reaction. The tested substances were dissolved in ether, treated with iodine, and the reaction mixtures were observed visually. No reaction was detected with common organic acids, alcohols, esters, ketones, chlorinated and aromatic hydrocarbons.

ACKNOWLEDGMENT

We thank the Phillips Petroleum Company, Bartlesville, Okla., for a gift of a number of mercaptans used in this work.

LITERATURE CITED

(1) Adams, D. F., Koppe, R. K., *Tappi* **42**, 601 (1962).
(2) Carson, J. F., Wong, F. F., *J. Org. Chem.* **24**, 175 (1959).
(3) Farrugia, V. J., Jarreau, C. L., ANAL. CHEM. **34**, 271 (1962).
(4) Ryce, S. A., Bryce, W. A., *Ibid.*, **29**, 925 (1957).
(5) Spencer, C. F., Baumann, F., Johnson, J. F., *Ibid.*, **30**, 1473 (1958).

RECEIVED for review December 20, 1962. Accepted April 10, 1963. Presented at Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1963.

A High Sensitivity Scanning Coulometer with Automatic Background Correction and Proportional Scan Rate

Titration of Plutonium and Other Redox Species

R. C. PROPST

Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, S. C.

▷ **The scanning coulometer is a new electroanalytical instrument for recording coulomb-potential curves of reversible processes under nearly equilibrium conditions. The circuit features a novel system for producing a scan rate that is an inverse function of the electrolysis current. Compensator networks provide automatic corrections for the continuous faradaic current and the charging of the electrical double layer. Application of the instrument is described to the direct determination of plutonium in irradiated nuclear fuel at the 2- to 5-μg. level with a precision of 2.1% ($n = 10$, $p = 0.95$).**

CONTROLLED - POTENTIAL COULOMETRY has been applied successfully in the nuclear energy industry for the precise determination of uranium, neptunium, and plutonium (*2, 4, 8, 11*). In the case of plutonium, however, the published procedures (*5, 9*) require a chemical separation step to isolate several hundred micrograms of plutonium from dissolved, irradiated fuel. The handling of solutions of irradiated fuel that contain such quantities of Pu requires elaborately shielded and remotely operated facilities (*3*), and the chemical separation of the plutonium leads to a loss of precision in the final determination. These disadvantages can be eliminated if only microgram quantities of plutonium are needed for coulometric titration and if chemical separations are unnecessary.

During studies to improve the precision of the controlled-potential coulometric method for the direct titration of microgram amounts of plutonium, it became apparent that a significant improvement in sensitivity might be obtained if an instrument were available that would be capable of recording coulomb potential curves during the titration of the sample. A coulogram (*10*) would portray the reactions that occur at the working electrode, and the quantity of electricity consumed in

the titration could then be measured at a potential that minimized the contributions of impurities.

Therefore a scanning coulometer was developed to titrate a redox species and to record simultaneously the coulogram for the titration. The coulometer scans the potential of the working electrode at a rate that is inversely proportional to the electrolysis current so that coulograms for reversible processes are recorded under nearly equilibrium conditions.

DESCRIPTION OF THE INSTRUMENT

A simplified block diagram of the instrument in the titrate mode with a titration cell attached is shown in Figure 1, and a schematic diagram is shown in Figure 2. The instrument is designed for use with a conventional 3-electrode cell. Titrations are initiated at the potential at which the working electrode and the ions at its surface are in equilibrium with the species in the bulk of the solution. Either oxidation or reduction titrations can be performed. During the titration, the rate of change of potential of the working electrode is controlled by a feedback circuit so that the product of the scan rate and the electrolysis current is a constant. In this instrument, the constant is 10^{-9} volt-ampere per second. Since a large portion of the total quantity of electricity consumed in the titration of 2 to 5 μg. of a substance is contributed by background processes, the resolution of the instrument has been improved by incorporating circuits that permit partial compensation of these effects. The compensation circuits are electrical analogs of the background processes discussed by Meites (*7*). The coulograms are plotted by an X-Y recorder.

Operational Modes. The instrument utilizes analog computer circuits and has four operational modes as determined by the position of the function switch: (*a*) balance, (*b*) standby, (*c*) titrate, and (*d*) integrator reset. Relays are utilized in the transposition from the standby to the titrate and integrator reset modes.

In the balance position, the amplifiers are connected to individual balance networks so that the operational condition of each amplifier can be readily determined and faulty units quickly located and replaced.

In the standby position, the instrument is connected as a null potentiometer, and the potential of the working electrode with respect to the reference electrode can be determined under essentially open-circuit conditions. Here the isolated electrode circuit is open, the working electrode is grounded, and the reference electrode is connected to the voltage-follower amplifier. The output from the voltage follower is compared with the voltage from the initial potential potentiometer in the potential-control amplifier, and the error signal is fed through the load compensator to the meter amplifier which functions as the balance indicator. Thus by adjusting the initial potential to give a zero reading on the electrolysis current meter, the working electrode is automatically adjusted to a potential which ensures that the titration will be initiated from the zero current or equilibrium condition. The equilibrium potential can be read from the initial potential dial.

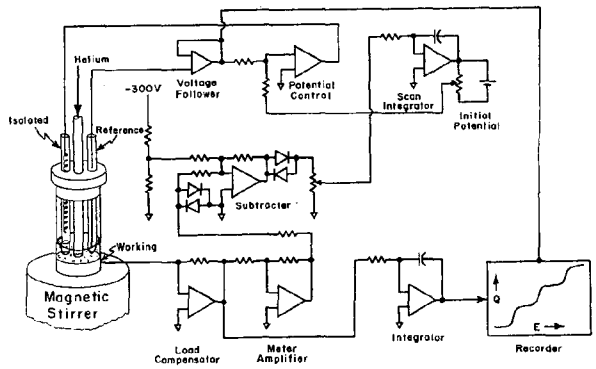


Figure 1. Block diagram of scanning coulometer

In the titrate position, the instrument functions as a conventional controlled-potential coulometer with the exception that the scan rate is a function of the electrolysis current as mentioned previously. A scan rate potentiometer is interposed between the subtracter and scan rate amplifier. This control permits the selection of any percentage of the maximum available scan rate; and with this control set at zero, the instrument functions as a low-capacity, controlled-potential coulometer. The direction of scan is controlled by the oxidize-reduce switch which determines the polarity of the voltage fed to the scan integrator. This switch is ganged with the current polarity switches of the electrolysis current meter and the integrator so that the proper polarity relationships are maintained. The current integrator has three ranges (10, 25, and 100 millicoulombs) to permit the titration of a range of sample sizes.

In the integrator reset position, the instrument remains in the titrate mode and the integrator is reset to zero. This mode is useful for starting titrations under conditions where the continuous faradaic current prohibits the initiation of the titration at zero current.

Scan Rate Circuit. The scan rate circuit is based on the logarithmic properties of solid state diodes. The voltage across a silicon diode is a logarithmic function of the diode current. Thus diodes can be utilized to compute the scan rate (dE/dt) from the relationship,

$$i\frac{dE}{dt} = k$$

where

i = electrolysis current, amperes

$\frac{dE}{dt}$ = scan rate, volts per second

k = constant, 10^{-9} $\frac{\text{volt-ampere}}{\text{second}}$

In the simplified circuit employed in this instrument, the relationship, $i\frac{dE}{dt} = k$, is only approximate because of loading effects on the circuits; however, the relationship is essentially linear in the range from 2 to 20 μa. which represents the range of current normally observed in titrations with this instrument. Above 40 μa., the scan rate is reduced to negligible proportions.

The scan rate circuit functions as follows: the voltage at the output of the meter amplifier which is proportional to the electrolysis current, i, is applied to a diode network through a dropping resistor. Assuming that the voltage developed across the diode is negligible compared to the voltage at the output of the meter amplifier, then the diode voltage is proportional to log i. The diode voltage is subtracted from a constant voltage in the subtracter amplifier to give a voltage at the output of the subtracter amplifier which is proportional to log k − log i. This voltage is applied to a resistor through a second diode network. Since the voltage developed across the resistor is small compared to the voltage across the diode, the current through the resistor and hence voltage across the resistor is proportional to the quantity k/i. The voltage across this resistor is applied to the scan integrator. Thus the output voltage of the scan integrator changes at the desired rate, $\frac{dE}{dt}$.

Compensator Circuits. The compensator circuits are electrical analogs of the continuous faradaic current and the charging of the electrical double layer, since these background processes make the major contribution to the background quantity of electricity for most titrations. These and other processes which contribute to the background quantity of electricity have been discussed by Meites and Moros (*7*). The circuits function by supplying currents to the integrator amplifier that reduce the charge on the integrator capacitor and hence reduce the integrated quantity of electricity.

The linear compensator corrects for background currents which are essentially constant over a range of potentials.

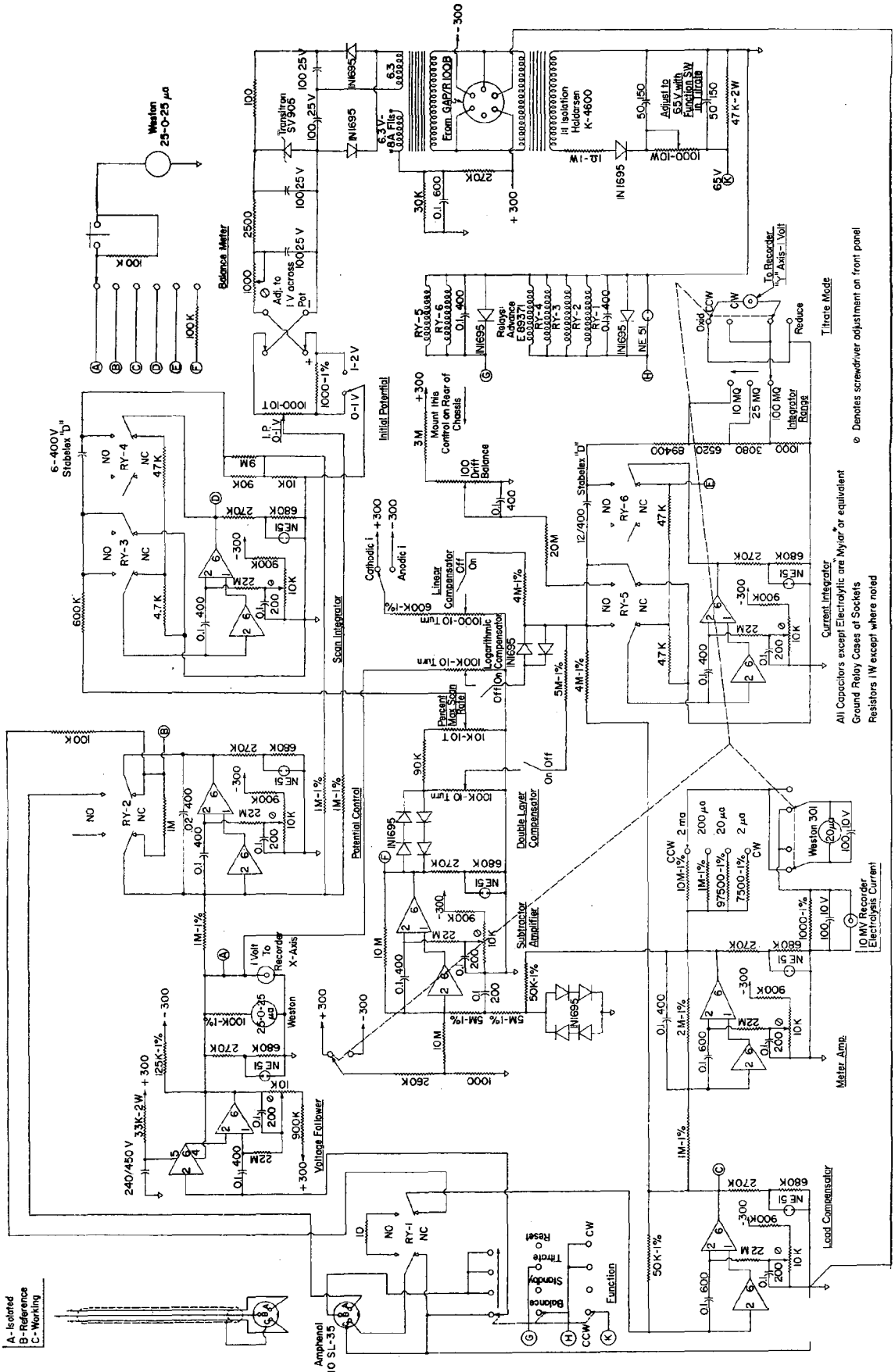


Figure 2. Circuit diagram of instrument

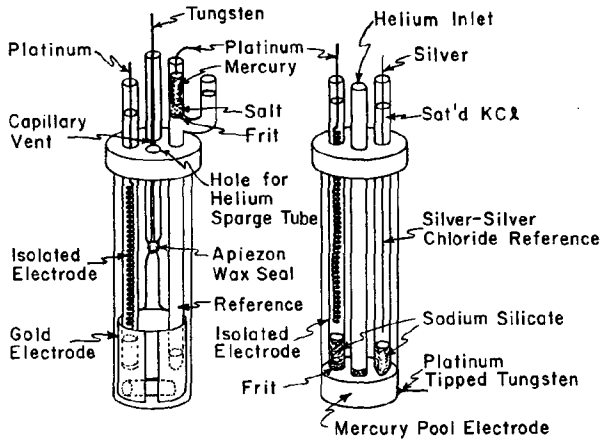


Figure 3. Titration cells for coulometric titrations

The range of this compensation is 0 to 10 μa.

The logarithmic compensation is based on the logarithmic properties of a diode. Since the continuous faradaic current varies as an exponential function of potential of the working electrode, the compensation current is derived from a diode network connected between the voltage follower and the summing point of the integrator amplifier. This simple circuit can be utilized to compensate in part for the continuous faradaic current in those cases where the titration covers a limited potential range, and where the voltage at the output of the follower amplifier is great enough to develop the required current. This condition is met in most titrations where some compensation for the continuous faradaic current is desirable. A potentiometer is incorporated into the circuit so that the maximum compensation current can be adjusted to the required value. Since the setting of the potentiometer must be determined by experiment, it is convenient to scan to the maximum potential of the titration, reduce the scan rate to zero, and adjust the potentiometer to minimize the charging rate of the integrator.

The double layer compensator is based on the fundamental relationship

$$i = C\frac{dE}{dt}$$

where

i = charging current
C = double layer capacity
$\frac{dE}{dt}$ = rate of change in potential across the double layer

Since the rate of change in potential across the double layer is the scan rate, the compensation current is derived by inserting a resistor between the summing point of the integrator amplifier and the resistor across which the voltage proportional to $\frac{dE}{dt}$ exists. This resistor is located in the output network of the subtracter amplifier as explained for the scan rate circuit. Since the integrator sees a current proportional to $\frac{dE}{dt}$, the magnitude of which is determined by the setting of the potentiometer (equivalent to C), the net result is the subtraction from the total charge on the integrator of a quantity of electricity which is equivalent to that required to charge the double layer. However, complete compensation cannot be obtained in those cases where the capacity of the double layer varies with potential.

Circuit Details. George A. Philbrick, Researches, Inc., operational amplifiers are utilized in this instrument. Limit lights in the output circuit of each amplifier indicate when the operational limits (±100 volts) of the amplifiers are exceeded.

An R-100B power supply manufactured by George A. Philbrick, Researches, Inc., Boston, Mass., furnishes the ±300 volts (regulated) to the amplifiers. Power for the relays is obtained from a conventional half-wave rectifier. A diode and condenser are connected across each relay circuit to suppress voltage transients. A Zener regulated supply provides voltage for the initial potential potentiometer, and a switch provides for any voltage between 0 to 1 and 1 to 2 volts Amplifier filament voltages are maintained at +30 volts with respect to ground to minimize hum pickup from this source.

A zero-center microammeter indicates the balance condition of the amplifiers. The meter is connected to the output terminal of the desired amplifier by a single pole, six-position switch. The electrolysis current meter serves as its own balance indicator, and the proper balance condition of the subtracter amplifier is indicated by equal deflections of the balance meter as the instrument is switched from the oxidize to the reduce modes. Balance adjustments must be made in the following order: scan integrator, voltage follower, potential control amplifier, load compensator, meter amplifier, subtracter amplifiers, and current integrator. The initial potential should be zero when the balance adjustments are made.

The computer circuits incorporated in this instrument have been described elsewhere (*1*, *6*). The choice of silicon diodes is not critical although high current types were not satisfactory for the logarithmic circuits. Of the various types of silicon diodes evaluated for use with this instrument, most gave a linear plot of log i *vs.* applied voltage over a range of currents from 10^{-8} to 10^{-3} ampere. (The current-voltage curves were readily obtained by means of a conventional controlled-potential coulometer.) The diodes are connected in series to increase the voltage characteristic when necessary.

A drift balance control for the current integrator eliminates drift in the amplifier due to leakage current. This control should be adjusted to minimize drift with the cathode lead open and the instrument in the titrate mode. Also the compensator controls should be off.

A Moseley Model 3S, X-Y recorder records the coulomb-potential curves. A separate jack is provided at the instrument for recording the electrolysis current and hence derivative titration curves if desired. A 10-mv. recorder is required for this purpose.

Calibration. The instrument is calibrated by connecting a mercury battery of known voltage and a 100 Kohm 0.1% precision resistor in series between the working electrode lead and ground. The leads for the reference and isolated electrodes are connected together to prevent overloading the amplifiers. The compensation controls must be off. The instrument is switched from standby to titrate and the time is noted for the recorder pen to cover a measured distance on the chart. The results are expressed in millicoulombs or microequivalents per chart division.

Titration Cells. The cells used for coulometric titrations at this laboratory are shown in Figure 3. Both types employ magnetic stirring. A helium sparge is utilized to eliminate dissolved gases. The reference electrode body is designed for versatility and ease of replacement. Sodium silicate solution in the tips of both the reference and isolated electrode bodies minimizes flow of the electrolyte into the titration cell. The gold electrode has an area of 19 square centimeters. Blanks equivalent to 2.5 millicoulombs over a 0.5-volt span are observed for the gold electrode in an electrolyte of 0.1M perchloric–0.01M sulfamic acid. The mercury pool electrode has twice the background of the gold electrode. The electrolyte must be freed from dissolved oxygen prior to the addition of mercury to obtain a low background with this electrode.

PROCEDURE

The following procedure is generally applicable for the titration of various redox species. Nine milliliters of electrolyte is pipetted into the cell (5.0 ml. in the case of the mercury pool electrode), the magnetic stirrer is started and helium is bubbled through the solu-

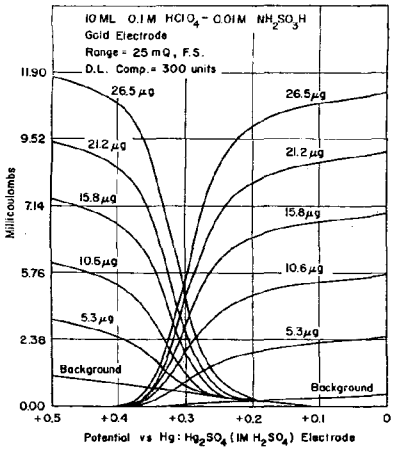


Figure 4. Titration curves for plutonium

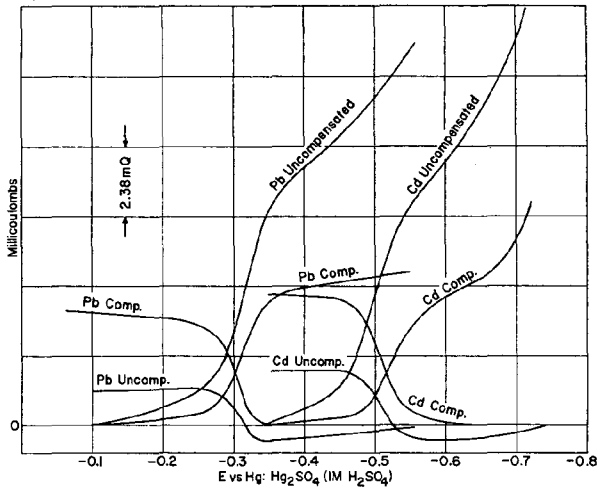


Figure 5. Coulograms of 3.6 μg. Pb and 2.4 μg. Cd in 0.1M $NaClO_4$–pH 5.2 mercury pool electrode

tion for 5 minutes. In the case of the mercury pool electrode, sufficient mercury is added to the cell at the end of 5 minutes to cover the platinum contact in the bottom of the cell to a depth of 2 to 3 mm., and the sparging is continued for an additional 5 minutes. A sample aliquot equivalent to 2 to 10 μg. is then added to the cell, and the sparging is continued for an additional 5 minutes.

The instrument is switched to the standby mode and the voltage and polarity of the working electrode with respect to the reference are noted from the voltmeter. The polarity of the initial potential is switched to agree with the meter, and the initial potential potentiometer is adjusted to give a null reading on the electrolysis current meter on the most sensitive (0 to 2 μa.) range. The oxidize-reduce switch is then set for the desired mode. At this point the recorder pen is adjusted to a convenient zero position on the Y-axis and its position on the X-axis is adjusted to agree with the initial potential as read from the potentiometer. The instrument is now switched to titrate, and the coulomb-potential curve is recorded.

Since the successful application of this instrument depends on a low electrolyte background, the background and working range of the electrolyte are determined before the addition of the sample. In some instances high background currents were traced to factors other than the electrolyte. Deionized water was necessary for the study since laboratory distilled water contained 70 p.p.b. dissolved copper which was readily detected. New gold electrodes were cleaned in cleaning solution, rinsed in distilled water, and stored in 1M nitric acid for 24 to 36 hours (with stirring) prior to use. This treatment produced a significant reduction in the background currents observed with these electrodes. Supporting electrolytes containing chloride ions should be avoided since high backgrounds are observed with the gold electrode when chloride ion is present in the cell. Sulfamic acid should be added with the electrolyte when the sample contains nitric acid to avoid the effects of nitrites.

RESULTS

The coulograms shown in Figures 4 and 5 are typical of the titration curves that can be recorded with this instrument.

Figure 4 shows the results obtained for the titration of plutonium(III–IV) in 0.1M perchloric–0.01M sulfamic acid electrolyte. The double layer compensator only was utilized in these titrations since the height of the background coulogram was unaffected by scan rate. A plot of the logarithm of the ratio of the per cent of plutonium reduced to the per cent oxidized *vs.* electrode potential was made for a titration at the 21.2-μg. level. Slopes of 0.0705 and 0.0630 volt for the reduction and oxidation scans, respectively, indicated that the titrations were made under nearly equilibrium conditions. The recoveries calculated from the quantity of electricity consumed at the potential corresponding to $E_{1/2} \pm 0.18$ volts were 100 ± 1%.

The instrument has been utilized for the direct titration of plutonium in solutions of irradiated nuclear fuel. The precision of the method ($n = 10$, $p = 0.95$) for the titration of 25-μl. aliquots containing 3.3 μg. of plutonium was 2.1%. A typical solution of irradiated nuclear fuel is 1.4M in uranium and 0.5 to 1.0M in nitric acid. The method is currently being evaluated for use with several types of fuel elements.

Exploratory titrations involving the deposition and dissolution of lead and cadmium at the mercury pool electrode are shown in Figure 5. In view of the magnitude of the background current in the perchlorate electrolyte, compensation was required to minimize distortion of the coulograms. Because it is difficult to compensate over a wide range of potentials, separate scans were made for each element. Double layer compensation was not required. The calculated contribution due to the electrical double layer based on a value of 10 μf. per square centimeter for mercury was 0.025 millicoulomb. For the titration of lead, the linear compensator was adjusted to minimize the effects of background currents at −0.1 volt and the logarithmic compensator was likewise adjusted at −0.55 volt. The logarithmic compensator only was utilized in the titration of cadmium, and this control was adjusted at −0.7 volt. The adjustment of these controls is not critical; however, care should be exercised to avoid over-compensation since this condition can also produce distortion in the coulograms.

The instrument combines the best features of polarography and coulometry and should find wide application in the field of analytical chemistry for the titration of microgram amounts of redox species. In sensitivity, the technique is comparable to square wave polarography and the classical stripping methods. In this laboratory, the technique is currently being utilized to study the electrochemical properties of elements at dilutions such that the diverse reactions experienced at high concentration are avoided.

LITERATURE CITED

(1) Booman, G. L., ANAL. CHEM. 29, 213 (1957).
(2) Booman, G. L., Holbrook, W. B., *Ibid.*, **31**, 10 (1959).

(3) Dykes, F. W., Fletcher, R. D., *et al.*, *Ibid.*, **28**, 1048 (1956).
(4) Farrar, L. G., Thomason, P. F., Kelley, M. T., *Ibid.*, **30**, 1511 (1958).
(5) Handshuh, J. W., U. S. At. Energy Comm., *Rept.* **HW-66441** (June 1960).
(6) Korn, G. A., Korn, T. M., "Electronic Analog Computers," McGraw-Hill, New York, 1952.
(7) Meites, L., Moros, S. A., ANAL. CHEM. **31**, 23 (1959).
(8) Scott, F. A., Peekema, R. M., U. S. At. Energy Comm., *Rept.* **HW-58491** (December 1958).
(9) Shults, W. D., U. S. At. Energy Comm., *Rept.* **ORNL-2776** (September 1959).
(10) Shults, W. D., U. S. At. Energy Comm., *Rept.* **ORNL-2921** (April 1960).
(11) Stromatt, R. W., ANAL. CHEM. **32**, 134 (1960).
RECEIVED for review January 8, 1963. Accepted April 17, 1963. The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

Electrolysis Cell for Continuous External Generation of Reagents in Reagent-Addition Analyzers

RICHARD B. KESLER

Engineering and Technology Section, The Institute of Paper Chemistry, Appleton, Wis.

▶ To extend application of the method of coulometry with externally generated reagents to use in reagent-addition analyzers, work was undertaken to design, build, and test an electrolysis cell for this specific purpose. The cell developed consumes generator-electrolyte solution at a rate of 3 ml. per minute or less, and is about 118 mm. high and 22 mm. in diameter and of single-piece construction. It is capable of continuously producing standard iodine solutions of about 0.08*N* concentration, and bromine solutions of about 0.2*N* concentration. Development of this cell permits economic use of the external generation technique for continuous applications through minimum consumption of chemicals, while simultaneously providing known reagent solutions in macro concentrations.

THE technique of coulometric titration with externally generated titrant was established by DeFord, Pitts, and Johns (*1*), who also developed a two-arm electrolysis cell for reagent generation. Later, in an extension of the original work, Pitts, DeFord, Martin, and Schmall (*4*) developed a second, single-arm electrolysis cell for generation of halogens. Head and Marsh (*2*) used a slightly modified model of the two-arm cell of DeFord, Pitts, and Johns.

While both of the electrolysis cells designed by DeFord, Pitts, and their associates are eminently suited for carrying out titrations in the laboratory on a batch basis, certain design features of each make them less suitable for use on a continuous basis. The two-arm cell requires a total flow of generator electrolyte solution of about 12 ml. per minute to sweep the electrolysis products out through the desired delivery tip. By increasing generator electrolyte concentration, lower liquid flow rates could probably be used while maintaining 100% current efficiency at the stated current level of 250 ma., but at these lower flow rates, gaseous electrolysis products collect around the cathode when generating halogens, resulting in increased resistance of the cell to both electrical current and fluid flow. The single-arm cell is, in many respects, a great improvement over the first, but obviously was not intended for continuous operation because the cathode chamber must be periodically refilled. This cell requires a generator electrolyte consumption in excess of 6 ml. per minute. Because the catholyte passes over the anode during cell operation, it is possible that its decreased hydrogen ion cencentration, caused by generation of hydroxyl ions at the cathode, may limit an otherwise higher current value obtainable for generation of some reagents at 100% current efficiency. Both cells are of multipiece construction.

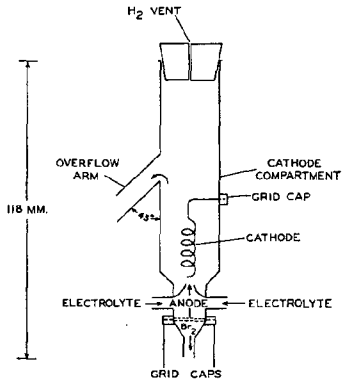


Figure 1. Electrolysis cell

While Pitts, DeFord, *et al.*, suggested that the external generation technique should find considerable application in continuous-flow analysis, no cell had been developed for this application. This paper reports the development of an electrolysis cell especially designed for continuous operation, as would be required, for instance, in a reagent-addition type of continuous-flow analyzer. The cell features single-piece, strong, compact construction; low generator-electrolyte consumption; and attainment of high current values for reagent generation at 100% current efficiency.

CELL DESIGN AND CONSTRUCTION

Figure 1 is a sketch of the cell. The anode, similar to that used by Pitts, DeFord, Martin, and Schmall, is made from ten 10-mm. diameter disks cut from 52-mesh platinum gauze, and two 10-mm. lengths of 20-gauge platinum wire. The disks are welded together by the flame-welding technique used by Pitts, DeFord, *et al.* The two 10-mm. lengths of 20-gauge platinum wire are each flattened at one end for about 2 mm. of their length, and are welded between the fifth and sixth disks at diametrically opposed points as close as possible to the periphery of the pad. These wires are for electrical connection to the anode.

The assembled anode pad is sealed inside a short length of borosilicate glass tubing, having an i.d. of about 10 mm., with the connecting leads sealed through the tubing wall. Just below the platinum anode, the glass tubing is sharply drawn down to an o.d. of 4 mm., and an 8-mm. length of 4-mm. tubing is joined to the constricted opening. About 4 mm. above the anode pad, two 8-mm. lengths of 4-mm. tubing are joined through the larger tubing at diametrically opposed points to provide a means of feeding electrolyte solution to the cell.

Immediately above these feed nipples, a tractrix-shaped structure of glass is sealed to the inner wall of the 10-mm. i.d. tubing and truncated to provide an orifice close to 3 mm. in diameter. This orifice leads to the cathode chamber, which is formed from an 85-mm. length of 22-mm. o.d. glass tubing drawn sharply down to about 10-mm. i.d. at one end and joined to the anode section as shown. About 35 mm. from the top of the cathode section, a 15-mm. length of 10-mm. glass tubing is sealed through the wall of the 22-mm. tubing at an angle of about 45° downward,

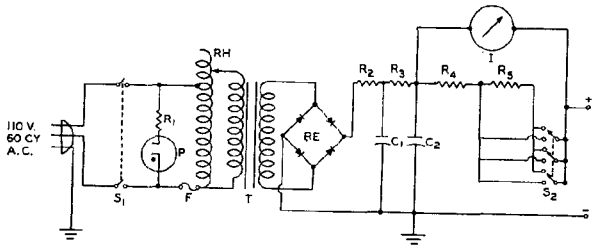


Figure 2. D.C. current supply with integrator

C_1, C_2. Filter condenser, electrolytic, 150 mfd., 150 volts
RH. Rheostat, 150 watts
RE. Rectifier stack, selenium, full wave, 1 ampere
R_1. Built-in resistor on pilot light assembly
R_2. Filter resistor, 2 ohms, 5 watts
R_3. Filter resistor, 10 ohms, 50 watts
R_5. Power resistor, 15 ohms, 200 watts
S_1. Toggle switch, double-pole, single-throw
S_2. Current range switch, triple-pole, double-throw, nonshorting
P. Neon pilot light
F. Fuse, 1.1-ampere, slow-blow
T. Isolation transformer, 32-volt tap on secondary
R_4, R_5. Power resistor, 15 ohms, 200 watts
I. Integrator

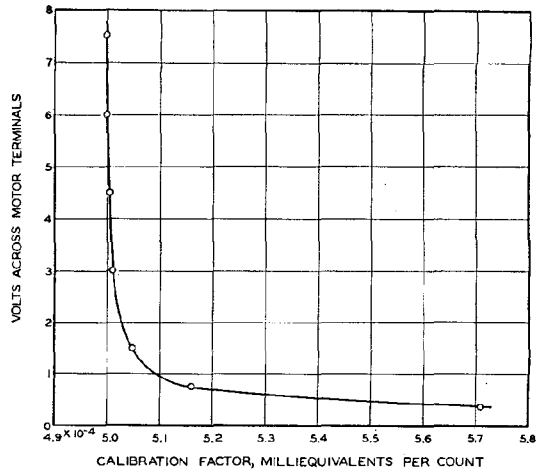


Figure 3. Calibration of integrator

to provide an overflow outlet from the cathode section.

The cathode is formed from a 130-mm. length of 20-gauge platinum wire, partially wound into a helix, with the other end sealed through the wall of the cathode chamber at a point opposite the overflow arm and several millimeters below the level of the overflow opening. This ensures its constant immersion in catholyte. The open top of the cathode chamber is closed with a vented polyethylene cap.

The protruding anode and cathode leads are soldered to grid caps, and the caps are fastened to the cell with a Khotinsky-type cement to secure a rigid, air-tight seal.

Two feed points for electrolyte solution are used to prevent any turbulent flow in the vicinity of the anode, preventing, in turn, anode reaction products from mixing with the liquid above it and possibly entering the cathode chamber. The truncated, tractrix-shaped structure leading into the cathode chamber ensures the escape of any gas bubbles from the anode compartment—for instance, when the cell is first filled through the feed nipples. The sharp constriction of the glass tubing immediately below the anode provides a holdup volume of about 0.5 cc.

CELL OPERATION

Although the cell is specifically designed for operation with metering pumps, fluid flow rates may be regulated by gravity flow. It is essential, however, that the generator electrolyte feed rate be maintained in slight excess of the rate at which the anolyte is drawn off through the nipple below the anode. This ensures a positive flow of fluid upward into the cathode section, thus preventing catholyte and anolyte from mixing. The excess fluid exits from the cell through the overflow arm in the cathode section.

The remainder of the generator electrolyte flows through the anode grid in a direction normal to its major plane, and constituents in the solution react at the electrode to produce the desired reagent, which is drawn off through the nipple below the anode.

Gaseous reaction products formed at the cathode escape through the vented polyethylene cap closing the top of the cathode section.

After an initial filling of the cell, occasionally some air will not be displaced from beneath the anode by liquid. Then, it is necessary to close off the overflow arm, the feed nipples, and the exit nipple by means of clamped rubber or plastic tubing and place the cell under vacuum from the top of the cathode chamber. This also serves to remove any tiny air pockets that may be lodged within the anode structure.

EXPERIMENTAL

Apparatus. CURRENT SOURCE. To supply d.c. current for the electrolysis cell, a line-operated, nonregulated source was used which incorporated a current integrator. Its circuit diagram is shown in Figure 2. The rheostat, *RH*, is used to adjust the d.c. output to the level desired. R_4 and R_5 are large power resistors with a temperature coefficient of $\pm 0.00002\%$. The windings are of Advance wire (43% Ni-57% Cu) on a Steatite L3 core. Switch S_2 has large silver contacts for negligible contact resistance and places either R_4 alone or R_4 and R_5 in series across the terminals of the integrator, *I*. The integrator is a low-inertia d.c. motor, of the type described by Parsons, Seaman, and Amick (*3*), which drives two hands on a dial face evenly divided into 100 divisions. The longer hand rotates 100 times faster than the shorter, and a full revolution of the slower hand results in 10,000 counts.

In this work, the integrator was used with only resistor R_4 across the motor terminals. The integrator was initially calibrated by means of a silver coulometer of the porous cup type recommended by Richards and Anderegg (*5*). Calibration was checked occasionally by a reference standard d.c. milliammeter and a timer.

Although the speed of rotation of the integrator motor is supposedly a linear function of the voltage drop across its terminals, this is not so until the drop approaches 3 volts, as shown by the calibration chart in Figure 3, and as discussed in more detail by Parsons, Seaman, and Amick.

PUMP. To feed generator electrolyte to the cell and to draw off the effluent through the anode, a multichannel peristaltic proportioning pump was used. This pump, manufactured by Technicon Controls, Inc., operates by driving rollers at constant speed over flexible tubes pressed flat against a plate. Various flow rates are obtained by selecting tubes of the proper i.d. and using them either singly or in various combinations to obtain the desired flow.

Tygon tubing was used to pump solution to the cell, and a specially resistant tubing supplied by the pump manufacturer and called Acidflex was used to pump the cell effluent. The Acidflex tubing was found to be practically inert to reaction with iodine and bromine under the experimental conditions.

REAGENTS. The solution used for generation of bromine was 1.5*M* in H_2SO_4 and 0.3*M* in KBr. That for iodine generation was 0.1*M* in H_3BO_3, 0.6*M* in Na_2SO_4, and 0.2*M* in KI. Both were placed under about 25-inch Hg vacuum for deaeration before use. Generated iodine solution was titrated with standard 0.1*N* $Na_2S_2O_3$ solution. Generated bromine solution was absorbed in various aliquots of standard 0.05 or 0.06*N* As_2O_3 solution. The amount of As_2O_3 used was calculated to provide an excess, which was subsequently titrated with standard 0.1*N* $KBrO_3$ solution, using the discolora-

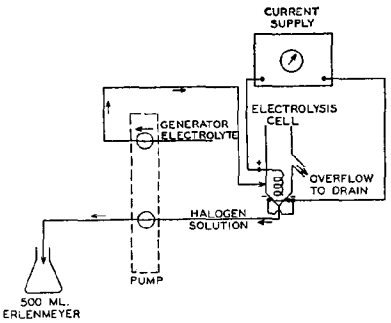


Figure 4. Experimental arrangement

tion of methyl orange indicator as a means of end point detection.

PROCEDURE. The efficiency of the cell for generation of iodine and bromine at various current levels and fluid flow rates was determined by generating a specific amount of halogen, as measured by the integrator, and comparing this with the amount found by titration.

The arrangement used is shown in Figure 4 in diagram form. Feed of generator electrolyte to the cell was maintained at a rate of flow close to 0.5 ml. per minute in excess of the effluent flow, by selection of the proper pump tubing. When generating iodine, the effluent solution was simply collected in a 500-ml. Erlenmeyer flask and titrated upon completion of the run. When generating bromine, the effluent was collected in the same flask by placing a delivery tip of 4-mm. glass tubing well below the surface of the As_2O_3 solution which was stirred by means of a magnetic stirrer. The initial total volume of the bromine absorbing solution was adjusted to 100 ml. and to a sulfuric acid concentration of 1.5*M*. Upon cessation of current flow to the cell, effluent solution was allowed to be pumped to the collecting vessel for 5 minutes to remove all generated halogen from the cell and pump lines.

RESULTS AND DISCUSSION

At two different flow rates of electrolyte solution through the anode, iodine was generated at increasingly higher current levels until the quantity of iodine found by titration differed significantly from that measured by calculation from the integrator reading. Titration results 0.5% below the calculated result were accepted as a significant departure from 100% current efficiency. In most cases, tiny gas bubbles, assumed to be oxygen, appeared on the anode when this difference in the two values arose. The appearance of oxygen, of course, indicates that a portion of the current is not being utilized for oxidation of iodide ions to iodine, but is being used for oxidation of the solvent. Usually, also, during the 5-minute flushing period following cessation of current flow, when gas bubbles had appeared on the anode, bits of solid iodine could be seen to drop from the anode structure and dissolve in the flowing electrolyte solution. The results for iodine generation are shown in Table I.

Table I. Generation of Iodine

Effluent flow rate, ml./min.	Duration of current flow, sec.	Counts on integrator	Milliequivalents of iodine				Approx. current, ma.	Approx. I_2 concn., equiv./liter
			Calcd.	Found	Diff.	Rel. error, %		
2.5	1987	2500	1.278	1.276	0.002	−0.16	60	0.015
	1014	3000	1.506	1.504	0.004	−0.13	140	0.035
	807	4000	2.000	1.999	0.001	−0.05	240	0.060
	589	4000	2.000	1.988	0.012	−0.61	325	0.082
3.0	600	3000	1.500	1.499	0.001	−0.07	240	0.050
	568	3500	1.750	1.743	0.007	−0.40	300	0.063
	573	4000	1.996	1.987	0.009	−0.45	335	0.070
	351	2500	1.248	1.244	0.004	−0.32	345	0.071
	388	3000	1.497	1.492	0.005	−0.33	375	0.077
	487	4000	1.996	1.987	0.009	−0.45	395	0.082
	686	6001	2.995	2.977	0.018	−0.60	425	0.087

Table II. Generation of Bromine

Effluent flow rate, ml./min.	Duration of current flow, sec.	Counts on integrator	Milliequivalents of bromine				Approx. current, ma.	Approx. Br_2 concn., equiv./liter
			Calcd.	Found	Diff.	Rel. error, %		
2.0	553	3500	1.750	1.750	0	0	305	0.095
	415	3000	1.497	1.500	0.003	+0.20	350	0.109
	1044	8500	4.242	4.238	0.004	−0.10	390	0.120
	885	8000	3.992	3.990	0.002	−0.05	435	0.135
	750	7500	3.743	3.739	0.004	−0.11	480	0.150
	664	7200	3.593	3.590	0.003	−0.08	530	0.165
	556	6500	3.244	3.245	0.001	+0.03	565	0.175
	556	7000	3.493	3.488	0.005	−0.14	607	0.189
	553	7300	3.643	3.628	0.015	−0.41	635	0.198
	498	6900	3.443	3.420	0.023	−0.67	666	0.208
3.0	1516	8000	4.000	4.000	0	0	255	0.053
	1040	7500	3.743	3.750	0.007	+0.19	345	0.072
	939	8500	4.242	4.235	0.007	−0.17	435	0.090
	503	5500	2.745	2.742	0.003	−0.11	525	0.109
	514	6501	3.244	3.240	0.004	−0.12	610	0.126
	604	8499	4.241	4.230	0.011	−0.26	675	0.140
	447	6501	3.244	3.232	0.011	−0.34	700	0.145
	602	9000	4.491	4.467	0.024	−0.53	720	0.149
	598	9000	4.491	4.455	0.036	−0.80	725	0.150
4.0	575	6000	2.994	3.000	0.006	+0.20	500	0.078
	511	6500	3.244	3.246	0.002	+0.06	610	0.095
	448	6700	3.343	3.340	0.003	−0.09	715	0.112
	437	7500	3.743	3.738	0.005	−0.13	825	0.129
	417	7601	3.793	3.787	0.006	−0.16	875	0.136
	399	7701	3.844	3.830	0.014	−0.36	930	0.144
	363	7400	3.700	3.675	0.025	−0.68	985	0.153

While higher generation currents can be used at 100% efficiency at higher rates of electrolyte flow through the anode pad, the resulting concentration of iodine in the anode effluent appears to reach a limiting value for the experimental conditions.

Table II shows similar data for generation of bromine at three rates of electrolyte flow through the anode. Again, it is shown that the concentration of halogen in the anode effluent reaches a limiting value for a given combination of generation current and anolyte flow rate, except at the 2.0-ml.-per-minute flow rate. The experiments at this flow rate were repeated with essentially the same results, but no factual explanation has been found for the production of more concentrated bromine solution.

Work nearly completed shows that the cell operates efficiently for continuous periods exceeding 6 days at the generation rates shown in this paper, and in industrial environments.

LITERATURE CITED

(1) DeFord, D. D., Pitts, J. N., Johns, C. J., ANAL. CHEM. **23**, 938 (1951).
(2) Head, W. F., Marsh, M. M., *J. Chem. Educ.* **38**, 361 (1961).
(3) Parsons, J. S., Seaman, W., Amick, R. M., ANAL. CHEM. 27, 1754 (1955).
(4) Pitts, J. N., DeFord, D. D., Martin, T. W., Schmall, E. A., *Ibid.*, **26**, 628 (1954).
(5) Richards, T. W., Anderegg, T. O., *J. Am. Chem. Soc.* **37**, 675 (1915).

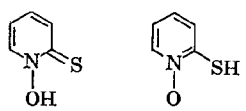
RECEIVED for review January 10, 1963. Accepted April 15, 1963.

Polarographic Analysis of a Series of Metal Ion 1-Hydroxypyridine-2-thione Systems

ALAN F. KRIVIS, EUGENE S. GAZDA, GEORGE R. SUPP, and MARTIN A. ROBINSON
Central Analytical Laboratories, Olin Mathieson Chemical Corp., New Haven, Conn.

▶ A polarographic study has been made of the copper-, zinc-, cadmium-, iron-, and nickel-1-hydroxypyridine-2-thione systems. In the copper, zinc, and cadmium cases, the polarograms showed separate waves for the complexed and uncomplexed organic moieties and for the complexed and uncomplexed metal ions. The ferrous system displayed the same differentiation and also showed the oxidation of Fe^{+2} to Fe^{+3} during the reaction. The nickel system gave a combined polarographic wave for both the complexed and uncomplexed metal ion which was shifted in potential from the wave for a simple nickel ion reduction.

THE COMPOUND 1-hydroxypyridine-2-thione (I) or 2-pyridinethiol-1-oxide (II) (*9*) and a number of its derivatives (*10*)



I II

have demonstrated bactericidal and fungicidal activities and, in particular, the metal derivatives have become commercially important (*7*). To aid in the production of these materials, analytical information, both qualitative and quantitative, was desired. Since polarographic data appeared to offer promise of fulfilling the necessary conditions simultaneously, a study of the polarographic behavior of the metal derivatives of I was undertaken.

The polarography of all of the individual metal ions used in the present study has been discussed in detail (*4*).

Polarographic studies of a wide variety of mercapto and heavy metal–mercapto systems have been made by Zuman and have been summarized very effectively (*2*). Three general classes of polarograms were obtained, depending on whether the waves for the complexed materials were separated from the mercapto and/or metal ion waves. Subclassifications also were established, based on whether the waves for the simple metal ions were more positive, coincident with, or more negative than the anodic waves for the mercapto compounds.

EXPERIMENTAL

Apparatus. A Sargent Model XXI Polarograph or a Metrohm Polarecord E-261R was used in conjunction with a thermostated H-cell (25° ± 0.1° C.) containing a saturated calomel reference electrode (*5*). The experiments using the Sargent Polarograph were made with damping equivalent to galvanometer performance and those with the Metrohm Polarecord were made with a damping setting of 5. The capillary used had a constant of 2.049 $mg.^{2/3} second^{1/6}$ at 25 cm. of Hg, open circuit in distilled water.

Chemicals. All inorganic chemicals were reagent grade and were used without further purification.

A 0.2*M* sodium acetate–0.02*M* acetic acid aqueous buffer stock solution was used for the entire study; the apparent pH after dilution with ethanol to give a 50% ethanol solution was 6.3, or where noted, 6.7. The pH was chosen to afford maximum stability of the organic moiety while still permitting solution of the metal ions.

The sodium salt of 1-hydroxypyridine-2-thione (NaPyr) (Olin Mathieson Chemical Corp.) was recrystallized from water and assayed 98.7%, based on a silver nitrate titration (*8*).

Gelatin (Fisher Scientific Co.) was used as a maximum suppressor and purified and equilibrated nitrogen was used to remove oxygen from the solutions.

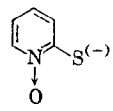
Procedure. Five (5) ml. of stock buffer solution were transferred to a 10-ml. volumetric flask and 0.1 ml. of 0.5% gelatin was added. The proper amount of metal salt dissolved in ethanol was added, followed by the requisite volume of NaPyr dissolved in ethanol. The solution was diluted to volume with ethanol, (to make a 50% ethanol solution), mixed thoroughly, and transferred to the H-cell. The final solutions contained ca. 0.5m*M* metal ion and a range of 0.1 to 3.0m*M* NaPyr. Equilibrated nitrogen was bubbled through the solution for 10 minutes and the polarogram was run. Ethanol was used to give at least partial solubility of the metal compounds formed.

Values of $E_{1/2}$ and i_d were determined graphically, using the average of the recorder traces.

The magnetic susceptibility data were obtained by the Gouy method using ferrous ammonium sulfate hexahydrate and nickel chloride hexahydrate as standards. Diamagnetic corrections were made for the ligands and anions so that the reported values are the moments attributable only to the metal ions.

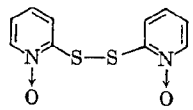
RESULTS AND DISCUSSION

The second pKa of 1-hydroxypyridine-2-thione has been found to be 4.67 ± 0.3 (*3*). Therefore, at the pH of the buffer used in the present study, the predominant species in solution should be the anion III.



III

Polarograms of III showed only a single anodic wave at −0.32 volt *vs.* S.C.E. with a diffusion current constant, *I*, of 1.2 over the concentration range 0.1 to 3.0m*M*. The most likely mechanism involved formation of a mercury complex.



IV

Polarograms of known disulfide (IV), under the same conditions, showed only one cathodic wave at −0.33 volt *vs.* S.C.E. with an *I* value of 2.2. Mixtures of III and IV, when polarographed, gave only one combined anodic-cathodic wave.

The various metallo-organic systems studied will be described under classifications based on the periodic groups.

Group IB—Cu. Table I shows the polarographic data obtained. Difficulties were experienced because of the poor solubility of the compound formed and the effect of the precipitate on the mercury indicating electrode and agar salt bridge.

Three waves were found which are listed as I, II, and III. Wave I corresponded to the cathodic reduction of Cu^{+2} to Cu amalgam, and wave II corresponded to the anodic reaction of

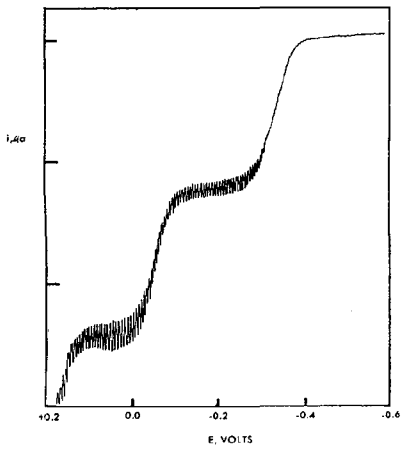


Figure 1. Anodic waves for the NiPyr system at a 4 Pyr : 1 Ni ratio

NaPyr. Wave III apparently was the reduction of Cu^{+2} which had been complexed by NaPyr; a cathodic shift of 0.5 volt from the simple copper reduction wave was produced. As the NaPyr concentration increased, wave I was lowered in height until, at the stoichiometric ratio of the compound formed (2NaPyr:1Cu), it disappeared entirely. Because of insolubility, the complexed copper wave also was lowered with increasing NaPyr concentration.

Group IIB—Zn, Cd. The data obtained for these two systems are listed in Tables II and III. In both cases, the complexes formed have been found to contain 2 Pyr:1 metal.

The zinc systems involved a total of four different polarographic waves. Wave II was the anodic wave for NaPyr; and wave III, the two-electron reduction of Zn^{+2} to Zn amalgam. At low ratios of NaPyr:Zn, two other waves were produced. Wave IV appeared to be the reduction of the Zn^{+2} which was complexed by the sulfur in NaPyr, while wave I was the anodic wave for the sulfur which appeared to be complexed by the Zn^{+2}. As can be seen, wave I appeared throughout the range, as did wave IV; bound zinc and sulfur would be expected at all times when both zinc and NaPyr are present in the mixture. Wave III was lowered in height with increasing NaPyr concentration and vanished at the stoichiometric ratio, while wave II initially appeared only at the 2:1 ratio and then increased with increasing NaPyr concentration. The slight lowering of waves I and IV primarily can be attributed to insolubility of the compound formed. At higher concentrations, precipitation of the compound was noticed.

Cadmium followed essentially the same pattern as zinc; four waves were found also, with the gradual disappearance of wave III and appearance of wave II after the stoichiometric amount of NaPyr had been added. No significant decrease in waves I and IV was found after an excess of NaPyr had been added probably because of the better solubility of the cadmium complex.

Group VIII—Fe, Ni. These systems behaved in a somewhat more complicated manner than the others reported.

The ferric compound with 1-hydroxypyridine-2-thione is prepared commercially by reacting ferrous ion with NaPyr to give $Fe(Pyr)_3$. Although NaPyr is a reducing agent rather than an oxidizing agent under most circumstances, the conversion of ferrous ion to ferric takes place upon mixing Fe^{+2} with NaPyr. The magnetic moment for the iron in the $Fe(Pyr)_3$ compound has been found to be 6.18 Bohr Magnetons. These data indicate the presence of the ferric state in the complex. The actual mechanism for the

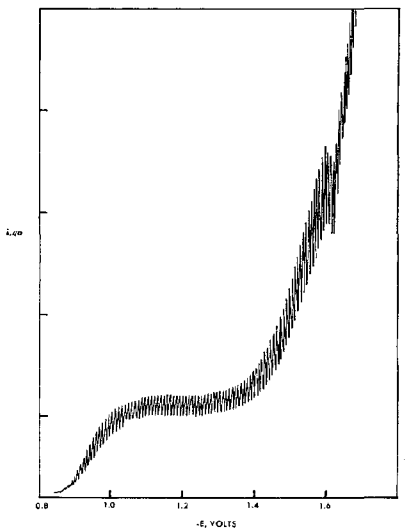


Figure 2. Cathodic waves for the NiPyr system at a 4 Pyr:1 Ni ratio

Table I. Polarographic Values[a] for Copper–NaPyr[b] Mixtures at pH 6.3

Mole ratio NaPyr:Cu^{+2}	Wave I $-E_{1/2}$, volt	Wave I i, μa.	Wave II[c] $-E_{1/2}$, volt	Wave II[c] i, μa.	Wave III $-E_{1/2}$, volt	Wave III i, μa.
0:1	0.02	2.35	...	...	...	...
0.5:1	0.03	1.54	...	...	0.58	0.20
1:1	0.03	1.08	...	...	0.58	0.14
2:1	...	...	...	...	0.59	0.09
3:1	...	...	0.32	0.94	...	...
4:1	...	...	0.32	2.17	...	...

[a] *vs.* S.C.E.
[b] NaPyr = sodium salt of 1-hydroxypyridine-2-thione.
[c] Anodic wave.

Table II. Polarographic Values[a] for Zinc–NaPyr[b] Mixtures at pH 6.7

Mole ratio NaPyr:Zn^{+2}	Wave I[c] $-E_{1/2}$, volt	Wave I[c] i, μa.	Wave II[c] $-E_{1/2}$, volt	Wave II[c] i, μa.	Wave III[d] $-E_{1/2}$, volt	Wave III[d] i, μa.	Wave IV[d] $-E_{1/2}$, volt	Wave IV[d] i, μa.
0.0:1	...	...	...	...	1.03	1.83	...	...
0.1:1	0.135	0.18	...	...	1.01	1.68	1.2?	?
0.4:1	0.13	0.36	...	...	1.015	1.38	1.23	0.3
0.6:1	0.15	0.63	...	...	1.01	1.44	1.24	0.42
1.3:1	0.15	1.35	...	...	1.01	0.84	1.23	0.96
1.9:1	0.15	1.77	...	...	1.01	0.24	1.22	1.41
2.5:1	0.14	1.74	0.31	0.42	...	...	1.22	2.04
3.2:1	0.145	1.56	0.33	0.99	...	...	1.27	1.59
3.8:1	0.125	1.11	0.32	1.89	...	...	1.27	1.14
4.4:1	0.135	0.75	0.32	2.61	...	...	1.25	0.87

[a] *vs.* S.C.E.
[b] NaPyr = sodium salt of 1-hydroxypyridine-2-thione.
[c] Anodic wave.
[d] Cathodic wave.

Table III. Polarographic Values[a] for Cadmium–NaPyr[b] Mixtures at pH 6.3

Mole ratio NaPyr:Cd^{+2}	Wave I[c] $-E_{1/2}$, volt	Wave I[c] i, μa.	Wave II[c] $-E_{1/2}$, volt	Wave II[c] i, μa.	Wave III[d] $-E_{1/2}$, volt	Wave III[d] i, μa.	Wave IV[d] $-E_{1/2}$, volt	Wave IV[d] i, μa.
0:1	...	...	...	...	0.60	2.06	...	...
0.5:1	0.14	0.34	...	...	0.60	1.40	0.74	0.43
1:1	0.14	0.74	...	...	0.60	0.92	0.76	0.80
2:1	0.16	0.30	...	...	0.60	0.15	0.73	0.45
3:1	0.15	0.44	0.30	0.62	...	...	0.77	0.50
4:1	0.14	0.65	0.31	1.57	...	...	0.79	0.92

[a] *vs.* S.C.E.
[b] NaPyr = sodium salt of 1-hydroxypyridine-2-thione.
[c] Anodic wave.
[d] Cathodic wave.

Table IV. Polarographic Values[a] for Ferrous–NaPyr[b] Mixtures at pH 6.3

Mole ratio NaPyr: Fe^{+2}	Wave I[c] $-E_{1/2}$, volt	Wave I[c] i, μa.	Wave II[c] $-E_{1/2}$, volt	Wave II[c] i, μa.	Wave III[d] $-E_{1/2}$, volt	Wave III[d] i, μa.	Wave IV[d] $-E_{1/2}$, volt	Wave IV[d] i, μa.	Wave V[d] $-E_{1/2}$, volt	Wave V[d] i, μa.
0:1	...	...	...	...	...	...	...	...	1.34	1.1
0.5:1	0.16	0.36	...	...	...	...	1.18	0.79	1.35	0.7
1:1	0.18	0.73	...	...	0.90	0.05	1.18	0.92	...	...
2:1	0.19	0.87	...	...	0.92	0.13	1.17	0.30	...	...
3:1	0.21	0.60	...	...	0.95	0.23	...	...	...	...
4:1	...	...	0.31	0.97	...	...	...	...	...	...

[a] *vs.* S.C.E.
[b] NaPyr = sodium salt of 1-hydroxypyridine-2-thione.
[c] Anodic wave.
[d] Cathodic wave.

Table V. Polarographic Values[a] for Nickel–NaPyr[b] Mixtures at pH 6.3

Mole ratio NaPyr: Ni^{+2}	Wave I[c] $-E_{1/2}$, volt	Wave I[c] i, μa.	Wave II[c] $-E_{1/2}$, volt	Wave II[c] i, μa.	Wave III[d] $-E_{1/2}$, volt	Wave III[d] i, μa.	Wave IV[d] $-E_{1/2}$, volt	Wave IV[d] i, μa.
0:1	...	...	...	...	1.08	1.9	...	...
0.5:1	0.08	0.51	...	...	0.88	2.4	1.44	2.7
1:1	0.09	1.25	...	...	0.89	2.6	1.49	4.4
2:1	0.06	2.1	...	...	0.90	3.0	1.48	4.8
3:1	0.05	1.9	0.31	0.6	0.94	2.8	1.47	4.2
4:1	0.04	2.0	0.30	1.9	0.92	1.5	1.46	3.9

[a] *vs.* S.C.E.
[b] NaPyr = sodium salt of 1-hydroxypyridine-2-thione.
[c] Anodic wave.
[d] Cathodic wave.

conversion of the Fe^{+2} to Fe^{+3} is presently under investigation.

To obtain valid analytical data, the polarographic solutions were prepared by mixing Fe^{+2} with NaPyr as is done in the synthesis of the compound. Therefore, in the present discussion, the systems are being called Fe^{+2}–NaPyr systems although it should be understood that oxidation of the added Fe^{+2} to Fe^{+3} takes place.

Polarograms of the Fe^{+2}–NaPyr systems appeared to show the conversion of Fe^{+2} to Fe^{+3} (Table IV). The reduction of simple Fe^{+3} gave two waves corresponding to the one-electron reduction of Fe^{+3} to Fe^{+2} (−0.23 volt) and the two-electron reduction of Fe^{+2} to Fe^{0} (−1.34 volt) while reduction of simple Fe^{+2} gave only the latter wave. The Fe^{+2}–NaPyr systems studied produced a total of five different waves. Wave V corresponded to the Fe^{+2} reduction and wave II, to the oxidation of NaPyr. Waves I, III, and IV apparently involved the complexed species. Wave I appeared to be the anodic wave for complexed NaPyr and wave IV, the cathodic wave for complexed Fe^{+2}. The shift to more positive potentials followed the behavior found with the nickel systems described below. Wave III appeared to be the reduction of complexed Fe^{+3}. At low NaPyr:Fe^{+2} ratios, the complexed and free Fe^{+2} waves appeared. As the concentration of NaPyr was increased, free Fe^{+2} (wave V) disappeared, and an Fe^{+3} wave (III) appeared. At the stoichiometric ratio, only the anodic complexed NaPyr wave and the complexed Fe^{+3} wave were present. Because of the insolubility of the ferric salt formed, only the anodic wave for NaPyr was found in the presence of excess NaPyr.

The nickel in the $Ni(Pyr)_2$ compound had a magnetic moment of 0.34 Bohr Magnetons which is equivalent to a zero moment and indicated a square coplanar configuration for the compound. The nickel ion, therefore, had been changed from an octahedral aquo species to a square coplanar one.

Polarograms of the nickel system in the presence of 0.005% gelatin still displayed a maximum in the nickel wave. Therefore, another series containing 0.01% gelatin was run in an attempt to eliminate the maximum. However, no significant change in the data was obtained except for the appearance of a small post wave on wave III.

Although the Ni^{+2} systems gave four polarographic waves (Table V), the current values deviated from the previous patterns. Wave I, the anodic wave for the complexed sulfur, increased with increasing NaPyr concentration and wave II, the anodic NaPyr wave, appeared after the stoichiometric amount of NaPyr had been added (2NaPyr:1Ni). However, wave III, the reduction of Ni^{+2}, showed both a shift toward more positive potentials and an increase in current with increasing NaPyr concentration. Shifts to more positive potentials for the irreversible reduction of complexed Ni^{+2} have been found previously (*4*, *6*), but no reports of current increases for the metal wave alone could be located. In the present case, the current increased until the stoichiometric ratio was exceeded and then it decreased. The wave, however, did not disappear after formation of the compound, as was found in all the other systems studied. Wave IV qualitatively followed the same current trends. However, it was found that wave IV was not a diffusion-controlled process, while the other waves were. The limiting current of wave IV did not vary linearly with the square root of the mercury height and, furthermore, the current had a temperature coefficient of 12% per ° C. over the range 14° to 24° C. and 4% per ° C. over the range 24° to 49° C. Therefore, it appears that wave III was a combined wave for complexed and uncomplexed nickel such as Zuman found for certain metallo-mercapto systems (*2*). The increase in current of wave III can be attributed to a change in the nickel from an octahedral to a square coplanar species. Wave IV was probably a kinetic/catalytic wave similar to those found with protein sulfhydryl materials (*1*). The shape and character of wave IV are in agreement with the assumption of catalytic hydrogen evolution.

LITERATURE CITED

(1) Brdicka, R., *Collection Czech. Chem. Commun.* **5**, 148 (1933).
(2) Brezina, M., Zuman, P., "Polarography in Medicine, Biochemistry, and Pharmacy," revised English ed., Interscience, New York, 1958.
(3) Jones, R. A., Katritzky, A. R., *J. Chem. Soc.* **1960**, 2937.
(4) Kolthoff, I. M., Lingane, J. J., "Polarography," 2nd ed., Interscience, New York, 1952.
(5) Komyathy, J. C., Malloy, F., Elving P. J., ANAL. CHEM. **24**, 431 (1952).
(6) Krivis, A. F., Supp, G. R., unpublished data, Olin Mathieson Chemical Corporation, 1961.
(7) Pansy, F. E., Stander, H., Koerber, W. L., Donovick, R., *Proc. Soc. Expl. Biol. Med.* **82**, 122 (1953).
(8) Ryland, L. B., Tamele, M. W., IND. ENG. CHEM., ANAL. ED. **8**, 16 (1936).
(9) Shaw, E., Bernstein, J., Losee, K., Lott, W., *J. Am. Chem. Soc.* **72**, 4362 (1950).
(10) U. S. Patents: 2,686,786; 2,734,903; 2,742,393; 2,742,476; 2,745,826; 2,678,116; 2,809,971; 2,826,585; 2,826,586; 2,922,790; 2,922,791; 2,922,792; 2,922,793; 2,940,978.

RECEIVED for review January 10, 1963. Accepted April 25, 1963.

The Dead-Stop Titration of Indium

L. S. MARTENS[1] and HERSCHEL FRYE

Department of Chemistry, University of the Pacific, Stockton 4, Calif.

▶ The familiar dead-stop titration method has been applied to the determination of indium by hexacyanoferrate(II) with good results. Mole ratios of five indium(III) to four hexacyanoferrate(II) were obtained, in agreement with ratios previously reported.

THE concept fundamental to the familiar "dead-stop" titration method was originated by Salomon (*8*) and developed by Foulk and Bawden (*5*), who coined the name. Among a number of successful applications are those to zinc by Swinehart (*9*) and to gallium by Fetter and Swinehart (*4*). The simple apparatus used by these workers is essentially that used in the indium determination.

The method itself is uncomplicated because the analyst need not know either the potential applied across the identical platinum electrodes or the current flowing at any time. The end point is indicated by a considerable change in current, which is apparent as an upswing of the galvanometer needle. The galvanometer used in the present work had a sensitivity of 1×10^{-6} ampere per mm., resulting in a particularly rugged apparatus.

Theory of the method has been presented by Foulk and Bawden (*5*), Reilley, Cooke, and Furman (*7*), Bradbury (*1*), Gaugin and Charlot (*6*), and more recently by Delahay (*3*).

EXPERIMENTAL

Standard solutions of indium(III) and hexacyanoferrate(II) were prepared. The indium solution was prepared by dissolving Fisher Scientific reagent grade indium metal (assay 99.99%) in 6*N* reagent grade hydrochloric or nitric acid and diluting to volume. Baker and Adamson reagent grade potassium ferrocyanide was pulverized and dried to constant weight at 100° C. The anhydrous salt was then weighed and dissolved in doubly distilled water; 2 grams per liter of reagent grade sodium carbonate (Baker and Adamson) was added to stabilize the solution, which was then diluted to volume with water.

Present address, Oakland City College, Oakland, Calif.

Table I. Titrations

Potential, mv.	Concn.,[a] mole/liter	Temp., ° C.	Sweeping gas	Mole ratio
200	0.001	27	N_2	1:1.237
400	0.001	27	N_2	1:1.238
400	0.01	25	O_2	1:1.259
300	0.001	27	None	1:1.245
300	0.01	70	None	1:1.254
400	0.01	27	None	1:1.237
500	0.001	71	None	1:1.248

[a] Concentration refers to both indium(III) and hexacyanoferrate(II).

Volumes of the standard indium(III) solution were dispersed from a calibrated buret into the titration vessel, the mechanical stirrer was started, and current readings were taken within 1 minute after each addition of hexacyanoferrate(II) solution; the latter solution was also added by means of a 10-ml. precision buret. No supporting electrolyte, in the polarographic sense, was used. After a sufficient number of readings had been taken to establish the shape of the curve, additional titrations were carried out recording only the volume of the titrant at which the upswing of the galvanometer needle was noted.

DISCUSSION

Table I summarizes the results of a number of the titrations. Typical conditions are listed, together with the calculated corresponding mole ratios of indium and hexacyanoferrate(II); these latter data were obtained from the molarities of the reagents prepared as indicated above.

From these data, taken over a wide variety of conditions and excluding the determination made with oxygen as the sweeping gas, the average mole ratio was calculated as 1 to 1.243. Standard deviation was ±4.9. More carefully controlled conditions substantially increase the precision. Solutions of indium(III) containing up to 2% by weight of ammonium sulfate and 6*N* sulfuric acid showed no improvement in end point characteristics.

At the potentials used in these determinations, the reduction of indium(III) is irreversible, whereas that of hexacyanoferrate(III) to hexacyanoferrate(II) is reversible. Doubtless the solutions of hexacyanoferrate(II) contain a little hexacyanoferrate(III), and current will flow when the hexacyanoferrate(II) is in excess. The sharpness of the end point is dependent on the continued low concentration of hexacyanoferrate(II) because of the low solubility of the indium hexacyanoferrate(II). As soon as the concentration of indium(III) has been reduced sufficiently, current will flow because hexacyanoferrate(II) is being oxidized at the anode and hexacyanoferrate(III) is being reduced at the cathode.

From the data in Table I and those based on many similar titrations, the authors conclude that under appropriate, controlled conditions, indium may be determined by "dead-stop" hexacyanoferrate(II) titration. The mole ratios indicated above are very close to five indium(III) to four hexacyanoferrate(II), in agreement with Bray and Kirschman (*2*).

The authors also checked the method for the determination of zinc, with good results. In their experience, a higher potential must be maintained in the indium titration than in that of either zinc or gallium.

LITERATURE CITED

(1) Bradbury, J. H., *Trans. Faraday Soc.* **49**, 304 (1953).
(2) Bray, U. B., Kirschman, H. D., *J. Am. Chem. Soc.* **49**, 2739 (1927).
(3) Delahay, P., "New Instrumental Methods in Electrochemistry," pp. 258–64, Interscience, New York, 1954.
(4) Fetter, N. R., Swinehart, D. F., ANAL. CHEM. **28**, 122 (1956).
(5) Foulk, C. W., Bawden, A. T., *J. Am. Chem. Soc.* **48**, 2045 (1926).
(6) Gaugin, R., Charlot, G., *Anal. Chim. Acta* **8**, 65 (1953).
(7) Reilley, C. N., Cooke, W. D., Furman, N. H., ANAL. CHEM. **23**, 1226 (1951).
(8) Salomon, E., *Z. Physik. Chem.* **24**, 55 (1897).
(9) Swinehart, D. F., ANAL. CHEM. **23**, 380 (1951).

RECEIVED for review October 22, 1962. Accepted April 25, 1963.

Determination of Trinitrotoluene in Warhead Exudates by Linear Sweep Polarography

GERALD C. WHITNACK

Chemistry Division, Research Department, U. S. Naval Ordnance Test Station, China Lake, Calif.

▶ A reliable, linear sweep polarographic method of analysis has been developed for the rapid determination of trinitrotoluene (TNT) in milligram samples of warhead exudates. The method is based on the presence of only microgram amounts of TNT in a 25% acetone and 75% 0.1*M* lithium chloride solution, and depends upon the measurement of the wave produced by the TNT at −0.66 volt vs. a Hg pool in this solution. 2,4-Dinitrotoluene, cyclotetramethylenetetranitramine (HMX), and cyclotrimethylenetrinitramine (RDX) in concentrations up to a 50-50 mixture with 2-, 4-, 6-TNT do not interfere with the method, while the isomers 2-, 3-, 4- and 2-, 4-, 5-TNT, in concentrations in the 10^{-5} to 10^{-6} grams per ml. range used in the method do not appear to affect the measurement of the 2-, 4-, 6-TNT wave at −0.66 volt. The use of an X-Y recorder with a linear sweep polarograph allows the determination of TNT to be made within a few minutes.

A RAPID and reliable method of analysis was needed for the amount of trinitrotoluene (TNT) in milligram samples of warhead exudates and explosive mixtures which might range from a few tenths of a per cent of TNT to as much as 50%.

Infrared spectrophotometric methods have been used successfully to analyze TNT isomeric mixtures (*7–9*); however, interference from many substances found in the exudates of warheads prohibits the use of these methods.

Titrimetric, colorimetric, and solvent extraction techniques (*2*, *4*) are time consuming, require large samples, and the solutions have to be treated very carefully.

Polarographic methods have been successfully applied to the rapid analysis of small samples of explosive compositions containing TNT and cyclotrimethylenetrinitramine (RDX) (*1*, *3*, *4–6*), and since explosives such as RDX, cyclotetramethylenenitramine (HMX), and dinitrotoluene (DNT) might be present in exudates from warheads, a linear sweep polarographic method of analysis for TNT in such mixtures was investigated.

The purpose of this report is to present and discuss the polarographic method of analysis that was finally developed, and its application to the analysis of some warhead exudates.

EXPERIMENTAL

Apparatus and Materials. A linear-sweep cathode ray Polarotrace, manufactured by Southern Instruments, Ltd., in England, was used throughout this work.

Acetone solutions of trinitrotoluene, 2,4-dinitrotoluene, RDX, and HMX were prepared in the 10^{-5} gram per ml. range and aliquots of these standard solutions were added to a supporting electrolyte and reduced.

The supporting electrolyte used in this work was aqueous 0.1*M* LiCl, with enough acetone added to make the final solution 25% acetone and 75% 0.1*M* LiCl by volume. Thus, 2.5 ml. of acetone were added to a 10-ml. volumetric flask and diluted to volume with the 0.1*M* LiCl solution.

The dropping mercury electrode had a drop time of 7 seconds in distilled water and m = 7.7 mg. per drop. Borosilicate glass polarographic cells, furnished with the Polarotrace, and provided with side arms for the anodic connection and for bubbling with nitrogen, were used in all work. About 2 ml. of the acetone–lithium chloride solution were placed in the cell, the solution was then purged with pure nitrogen for about 3 minutes and reduced with nitrogen flowing over the solution. The pure nitrogen was passed through a 75% water–25% acetone solution before entering the polarographic cell solution. All polarographic measurements were made at 25° ± 0.10° C. Redistilled Hg, C.P., was used as the anode and all current peak potentials and heights are referred to an Hg pool.

A Moseley Model 2-A X-Y recorder was used to record some of the data. This method of plotting the polarograms produced greater accuracy in measurement, a gain in sensitivity and resolution, and an improved method of obtaining a permanent record of data then either plotting by eye or taking a picture of the cathode-ray polarograms. The X and Y ranges of the recorder were set to record a polarogram that measured twice the number of divisions seen on the scope. A standard $8^1/_2$- × 11-inch graph paper of 10 × 10 to the $^1/_2$ inch was used for recording the data. This size paper was then easy to file in standard loose-leaf notebooks.

Procedure. A 5- to 10-mg. sample of the exudate is added to 2.5 ml. of C.P. acetone in a 10-ml. volumetric flask. The exudate is dissolved in the acetone with gentle shaking of the flask. The contents of the flask are then diluted to volume with the 0.1*M* LiCl solution and a 2-ml. aliquot of the mixed solution is placed in a borosilicate glass polarographic cell. After flushing nitrogen through the solution for 3 minutes, the polarogram is recorded with the start potential dial of the Polarotrace set at −0.40 volt and the scale factor dial of the instrument adjusted correctly for the concentration on TNT in the solution. A scale factor setting on the Polarotrace of 2.5 on direct current is best for solutions of TNT that are about 5×10^{-6} gram per ml.

The concentration of TNT is obtained by a standard addition technique, using a 10^{-5} gram per ml. of TNT solution as the standard solution. After the wave height on the original sample is obtained, a known concentration of the TNT standard solution is added to the solution in the cell and the wave height for TNT is again recorded. The calculation of TNT in the original sample is then determined from the two wave heights. Additions of 0.01 to 0.10 ml. of the TNT standard solution are used to minimize volume effects.

RESULTS AND DISCUSSION

The data in all figures and tables were obtained in a 25% acetone–75% 0.1*M* LiCl solution.

The supporting electrolyte used by Lewis (0.05*M* Na_2NO_3–0.05*M* borax) was tried in early experiments, but abandoned in favor of the neutral solution of lithium chloride. The first peak current (i_p) for TNT in the LiCl solution occurred at −0.66 volt, and was sharper than the i_p of −0.55 volt that was found for TNT in the buffer solution of Lewis. In addition, the first TNT wave in the buffer solution slowly decreased in height, while in the LiCl solution the first TNT wave height (i_h) remained the same for several hours. Acetate buffers and HCl solutions were also tried but gave no better TNT waves.

Table I shows the i_p and i_h values for solutions of TNT and DNT. The values for TNT observed at −0.83 and −1.03 volts, respectively, are obtained as a double wave. Single waves are produced at −0.66 volt

and −1.47 volts. The wave at −0.66 volt is approximately 2.5 times larger than the waves at −0.83 volt and 1.47 volts, respectively, and 5 times larger than the wave at −1.03 volts. The wave at −1.03 volts is ½ that of either the wave at −0.83 volt or that at −1.47 volts. A linear relationship of i_h values *vs.* concentration of TNT was found for the wave at −0.66 volt over a tenfold range in TNT concentration (10^{-5} to 10^{-6} gram per ml.).

A 5.08×10^{-5} gram per ml. solution of 2,4-DNT produced two waves with i_p values of −0.86 volt and −1.33 volts, respectively. The first wave height is about 2 times larger than the second wave.

The first wave for TNT (−0.66 volt) is not affected by 2,4-DNT in concentrations up to a 50-50 mixture. It is also very likely that larger amounts of DNT will not affect the TNT results, as good separation of DNT and TNT i_p values is obtained in the LiCl–acetone solution.

Since RDX is found in some exudates, this explosive was examined by the linear sweep technique. The results are given in Table II. None of the i_p values for RDX are near the −0.66-volt wave of TNT, and with up to 50-50 mixtures of RDX and TNT there was no effect of RDX on the i_h value of the first TNT wave. It should also be possible to measure the most negative RDX wave (−1.83 or −1.60 volts), as neither TNT nor DNT give waves at such negative voltage. The derivative current of the Polarotrace appeared best for measurement of this RDX wave (Table II).

RDX sometimes contains small amounts of HMX as an impurity, and if RDX is used in the warhead explosive composition it is possible that very small amounts of HMX may also be present in the warhead exudates. HMX solutions were studied polarographically and the results are given in Table II. Thus, no interference from HMX on the TNT wave at −0.66 volt was observed. A few mixtures of HMX and RDX were studied and the data are presented in Table III. The RDX wave about −0.90 volt might be used to analyze for RDX in the presence of HMX and the HMX content then calculated by subtracting the RDX wave height equivalent from the total wave (HMX + RDX) at −1.1 volts.

In this work, the method of standard addition was used exclusively in analysis of the sample warhead exudates for TNT as these exudates may contain other constituents that alone or combined might affect the i_h value of the TNT wave. The use of standard addition makes the effect of the constituents on the TNT wave negligible.

Table I. Trinitrotoluene and Dinitrotoluene in 25% Acetone–75% Lithium Chloride (0.1 M)

(TNT = 4.44×10^{-5} gram per ml.; DNT = 5.08×10^{-5} gram per ml.)

Explosive	i_p, Volts	i_h, Divisions	Scale factor	Start potential, volts
TNT	−0.66	27.0	10	−0.40
TNT	−0.83	11.0	10	−0.65
TNT	−1.03	6.0	10	−0.65
TNT	−1.47	11.0	10	−1.20
DNT	−0.86	21.0	10	−0.60
DNT	−1.33	13.0	10	−1.10

Table II. RDX and HMX in 25% Acetone–75% Lithium Chloride (0.1 M)

(RDX = 5.00×10^{-5} gram per ml.; HMX = 5.08×10^{-5} gram per ml.)

Explosive	i_p, Volts	i_h, Divisions	Scale factor	Start potential, volts
RDX	−0.90	45.0	1.5	−0.70
RDX	−1.15	10.0	1.5	−0.70
RDX	−1.43	24.0	1.5	−1.10
RDX	−1.83	19.0	10.0	−1.45
RDX	−1.60[a]	10.5	0.10	−1.35
HMX	−1.06	18.5	2.5	−0.80
HMX	−1.80	28.0	4.0	−1.45
HMX	−1.63	13.0	0.04	−1.45

[a] Derivative current.

A standard graph for TNT could be prepared, and used satisfactorily if one knew the general composition of a particular warhead exudate or explosive mixture would not change. Although two measurements per sample are needed in the standard addition technique of the linear sweep polarographic method, the results are obtained very rapidly.

Five different samples of warhead exudates were analyzed for TNT content by the proposed method. The results (Table IV) showed the TNT amount in this particular type of exudate varied from about 0.10% to as high as 37%.

Since the viscous nature of the samples gives some doubt of their homogeneity, only tests of reproducibility of the analysis on duplicate samples from three runs were made. The data indicated the method was precise to ±5% of the amount of TNT present.

RDX, 2,4-DNT, and HMX in concentrations up to the amount of TNT present appeared to have little or no effect on the TNT determination, and by using the standard addition technique the effects of other constituents found in exudates from most warheads are negligible. If constituents are present that produce a wave within ±100 mv. of −0.66 volt, they may have to be removed from solution before the TNT wave can be accurately measured. However, the Polarotrace will resolve some traces whose i_p values are within ±50 mv. of each other with the derivative circuit.

Some typical camera and X-Y plots of TNT, DNT, RDX, and HMX solutions are shown in Figures 1–3. In Figure 1, the four waves obtained with TNT solutions are shown. Figure 2 illustrates the first wave obtained for TNT (−0.66 volt) in a sample of exudate and shows the increase of peak current at this voltage upon addition of a standard TNT solution. Figure 3 shows the X-Y recordings for the same solution. The divisions of current obtained with the X-Y traces are twice those found with the camera

Table III. RDX and HMX in Admixture in 25% Acetone–75% Lithium Chloride (0.1 M)

(RDX = 2.5×10^{-5} gram per ml.; HMX = 2.6×10^{-5} gram per ml.)

i_p, Volts	i_h, Divisions	Scale factor	Current
−0.92	20.0	2.5	Direct
−1.07	9.0	2.5	Direct
−0.84	32.0	0.025	Derivative
−0.98	10.0	0.025	Derivative

Table IV. Analysis of Some War Head Exudates

Sample No.	Sample Grams	Wave height Divisions	Wave height Scale factor	TNT found, per cent
4	5.0×10^{-4}	13.0	2.5	14.4
8	3.3×10^{-3}	21.0	40.0	37.3
10	3.0×10^{-3}	23.0	2.5	3.0
12	5.2×10^{-3}	36.0	10.0	9.0
16	1.2×10^{-3}	10.0	0.25	0.1

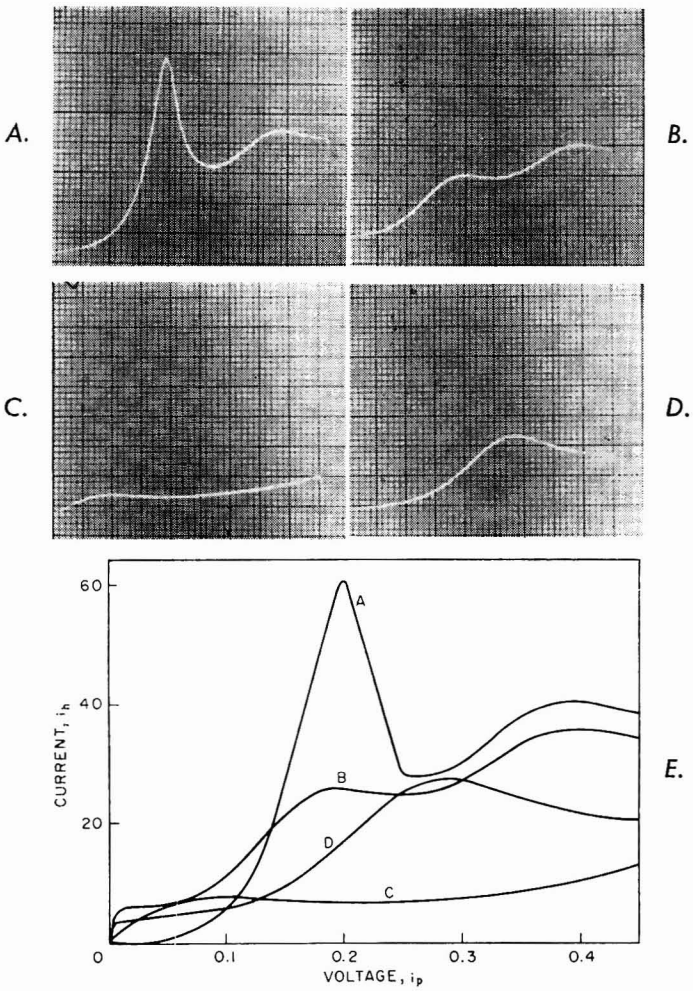


Figure 1. Land camera and X-Y recorder traces of TNT in 25% acetone–75% 0.1M LiCl

(TNT = 4.44 × 10^{-6} gram per ml.)
A. S.P. = −0.45 volt
S.F. = 10
B. S.P. = −0.65 volt
S.F. = 10
C. S.P. = −1.45 volt
S.F. = 10
D. S.P. = −1.20 volt
S.F. = 10

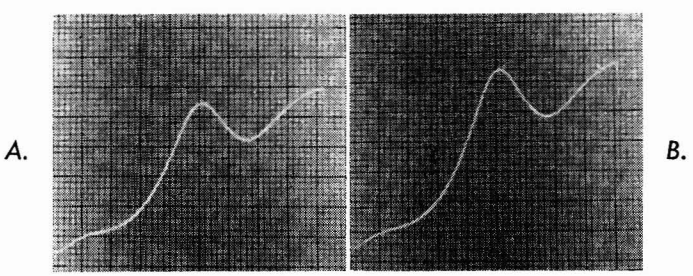


Figure 2. Land camera traces of TNT as found in sample of exudate

(2mg. sample in 25% Acetone–75% 0.1M LiCl)
Sample, S.P. = −0.40 volt, S.F. = 2.5
Sample plus 4.44 × 10^{-6} gram per ml. of TNT

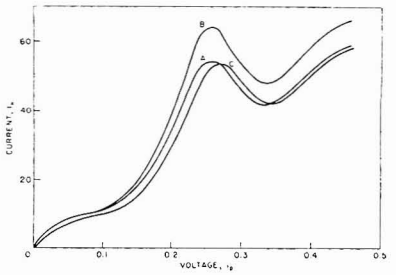


Figure 3. X-Y recorder traces of TNT as found in sample of exudate

(2-mg. sample in 25% acetone–75% 0.1M LiCl)
A. Sample, S. P. = −0.40 volt, S. F. = 2.5
B. Sample plus 4.44 × 10^{-6} gram per ml. of TNT
C. Sample (X-axis of recorder drifted slightly)

oscilloscope traces. The X-Y traces are obtained immediately, while readings from the scope must be taken either by eye or camera before one can determine the TNT content.

A mixture of TNT and RDX (5.0 × 10^{-5} gram per ml. of each) in solution was investigated on the Polarotrace. The height of the first TNT wave is not affected by an equivalent concentration of RDX in the LiCl solution. The wave for the RDX at the most negative potential may be used to determine the RDX content in the presence of TNT. In this work, no study of an analysis for RDX was made. However, if derivative current is used, a sharp-peaked wave is obtained for RDX at −1.6 volts, but concentrations of RDX in solution have to be 10 times or larger for equivalent wave heights.

A mixture of HMX and RDX (5.0 × 10^{-5} gram per ml. of each) in solution was also reduced. There is approximately a 150-mv. spread between the first waves of these two explosives in the LiCl solution. Thus, the first wave of RDX might be used for its determination in a mixture with HMX. A wave was also observed at −1.43 volts with RDX solutions. This wave did not appear with solutions of HMX.

A mixture of TNT and DNT was prepared in the LiCl solution, and as seen in Table I, no wave for DNT is found at −0.66 volt and no effect from DNT on the height of this TNT wave was observed.

A solution containing TNT, DNT, and RDX was reduced. The concentrations were TNT = 4.44 × 10^{-5}, DNT = 2.54 × 10^{-5}, and RDX = 5.00 × 10^{-5}, gram per ml. The height of the TNT wave at −0.66 volt is not affected by the presence of the other explosives. The height of the TNT was measured after 4 hours and no change was observed. The acetone–

LiCl solution of TNT appears to be very stable. The height of the RDX derivative wave at −1.60 volts also appeared to be unaffected in solutions containing these four explosives.

In developing the method, the alpha 2,4,6 was expected to be the predominant form of TNT found in the exudates and only this form was used in the standard TNT solution and in mixtures with the other explosives. The melting point of the 2,4,6-TNT used in this study was 81° to 82° C.

Since small amounts of the beta 2,3,4 and gamma 2,4,5 forms of TNT might also be present in the exudates, solutions of these explosives were prepared in the LiCl–acetone solution and reduced. In the 10^{-5} to 10^{-6} gram per ml. concentration range, no waves were observed for either the beta or gamma form of TNT at −0.66 volt. Both of these forms did produce peak currents at more positive potentials and more negative potentials than the −0.66-volt peak used to determine the TNT in this method. The melting points of the beta and gamma TNT used in this investigation were 103° to 104° C. and 109° to 111° C., respectively.

The observed differences in wave heights and peak potentials of these isomers of TNT may allow one to determine them in admixture by a polarographic procedure. Further study of mixtures of the TNT isomers is in progress.

In conventional polarography, maxima suppressors are sometimes necessary in quantitative work. However, with the linear sweep polarographic method maxima suppressors are seldom needed and were not necessary in this work.

ACKNOWLEDGMENT

The author expresses his thanks to Charles W. Falterman of the Propulsion Development Dept. for the samples of exudates and explosives used in these studies.

LITERATURE CITED

(1) Dennis, S. F., Powell, A. S., Astle, M. J., *J. Am. Chem. Soc.* **71**, 1484 (1949).
(2) Halfter, G., Winkler, H., *Die Chemie* **57**, 17/18, 124 (1944).
(3) Hetman, J., "Trace Techniques," using the K-1000 Cathode Ray Polarograph, Vol. 1, P. 43, Southern Instruments Ltd., Camberley, Surrey, England, (1949).
(4) Lewis, D. T., *Analyst* **79**, 644–8 (1954).
(5) Page, J. E., *Quart. Rev. (London)* **6**, 262 (1952).
(6) Pearson, J., *Trans. Faraday Soc.* **44**, 683 (1948).
(7) Pristera, Frank, Fredericks, W. E., *Technical Rept.* No. **2485** (1958), Samuel Feltman Ammunition Laboratories, Picatinny Arsenal, Dover, N. J.
(8) Pristera, Frank, Fredericks, W. E., *Technical Rept.* No. **2546** (1958), *Ibid.*
(9) Pristera, Frank, Halik, Michael, *Technical Rept.* No. **2221** (1955), *Ibid.*

RECEIVED for review October 8, 1962. Accepted April 23, 1963.

Potentiometric Titration of Acids in an *N,N*-Dimethyl Fatty Amide

CHARLES A. REYNOLDS, JAMES LITTLE, and MERLE PATTENGILL

Department of Chemistry, University of Kansas, Lawrence, Kan.

▶ **Potentiometric titrations of a variety of acids and acid mixtures ranging in strength from mineral acids to phenols have been performed using a commercially available mixture of *N,N*-dimethyl fatty amides as a solvent. A conventional glass indicating electrode was used with a saturated calomel reference electrode modified by replacing the saturated potassium chloride solution with a saturated aqueous solution of lithium chloride. The solvent gave reproducible titration curves which, in all but a very few cases, had flat buffer regions. This fact, coupled with its large potential range, makes the solvent especially suitable for differentiating titrations.**

IN RECENT years, a wide variety of substances have been used as solvents for the titration of acids. Thus far, however, each solvent tried has presented at least one definite drawback, either in scope and applicability, or in mechanics. A brief survey of some of the more popular solvents illustrates this point.

Basic solvents such as ethylenediamine (*4*, *9*) and *n*-butylamine (*6*) have been used in the determination of weak and very weak acids for several years. However, the leveling effect these solvents exert makes differentiation between mineral and carboxylic acids impossible. In addition, these solvents possess very small potential ranges (*11*) which severely limit the size of the potentiometric break which can be obtained, and they are very prone to carbon dioxide absorption. Ethylenediamine is so strong in this latter respect that it has been recommended as a quantitative carbon dioxide absorbent (*10*).

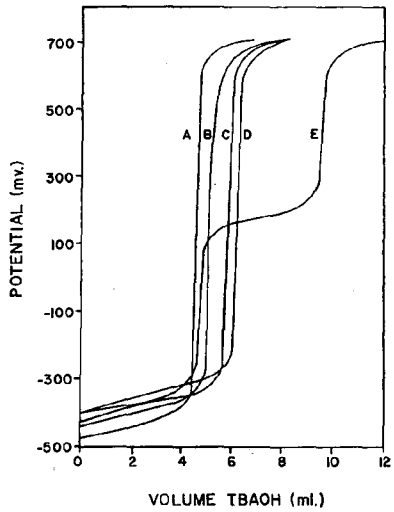


Figure 1. Titration of mineral and sulfonic acids

A. Perchloric acid
B. *p*-Toluene sulfonic acid
C. Hydrochloric acid
D. Nitric acid
E. Sulfuric acid

Acetone (*8*) and acetonitrile (*12*) have been disqualified for the titration of mineral acids and mineral acid mixtures because of strong acid-solvent reactions (*3*). Further, the titration curves of carboxylic acids and phenols in these solvents usually have steep buffer regions, making differentiating titrations difficult.

Although pyridine (*2*) can be used for the titration of mineral, as well as weak acids, steep buffer regions are obtained with many carboxylic acids and phenols. In addition, its highly offensive odor makes provisions for the removal of its vapor necessary.

Dimethylformamide (DMF) (*4*) and methyl isobutyl ketone (*1*) have been reported to be of only limited use for the titration of mineral acids or their mixtures because of strong acid-solvent reaction (*3*). DMF's instability in excess base (*4*), its high volatility, and its high

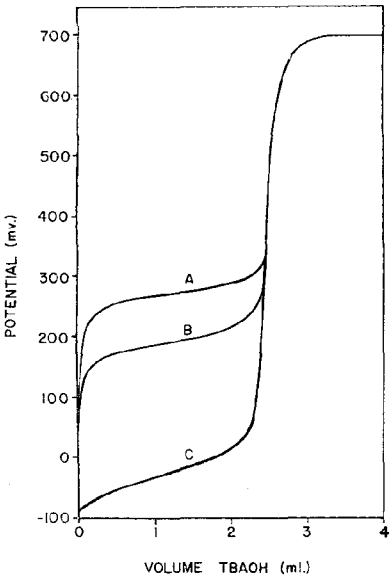


Figure 2. Titration of carboxylic acids
A. Stearic acid
B. Benzoic acid
C. Salicylic acid

cost offer further disadvantages to its use.

Methyl and ethyl alcohols are useful in the determination of relatively strong acids, but are too acidic to give good results when used as solvents for weak acids (*5*). Tertiary butyl alcohol (*7*) has recently been shown to be feasible for the titration of a wide range of acids and to give titration curves with flat buffer regions. However, to obtain reproducible results in this solvent, it is necessary to use a relatively complicated, three-phase salt bridge.

The purpose of this research has been to present a solvent which avoids most of the above-mentioned disadvantages, while offering a simple, efficient means for the titration of a wide range of acids and acid mixtures.

EXPERIMENTAL

Reagents. All acids used were of reagent grade purity. The titrant used was tetra-*n*-butylammonium hydroxide (TBAOH) in a benzene–isopropyl alcohol–water solvent and was prepared by dilution of 1.0*M* aqueous TBAOH with a mixture of reagent grade benzene and isopropyl alcohol. The aqueous TBAOH was polarographic grade and was obtained from Southwestern Analytical Chemicals. The solvent used, Hallcomid M-12, was obtained from the C. P. Hall Co. of Illinois and consisted of approximately 95% *N,N*-dimethyllauramide, 3% *N,N*-dimethylmyristamide, and 2% *N,N*-dimethylcapramide. As obtained from the manufacturer, the Hallcomid M-12 contained a titratable acid impurity. This impurity, however, was easily removed by passage of the solvent through a basic alumina column. After passage through the column, acid blanks were less than 0.01 meq. of acid per 25 ml. of solvent.

Apparatus. A conventional glass indicating electrode and a saturated calomel reference electrode modified by replacing the saturated potassium chloride solution with saturated aqueous lithium chloride were used for all titrations. The modification in the calomel electrode was necessary because potassium chloride is only slightly soluble in Hallcomid M-12. Potential measurements were made with a Leeds & Northrup pH meter (catalog number 7664).

Procedure. The titration procedure, very similar to one suggested by Deal and Wyld (*4*), consisted of dissolving the sample in 25 ml. of the solvent and titrating under a nitrogen blanket in lipless beakers fitted with Teflon covers.

In all cases, the titrant was standardized against primary standard benzoic acid in 25 ml. of Hallcomid. Although a number of different titrant

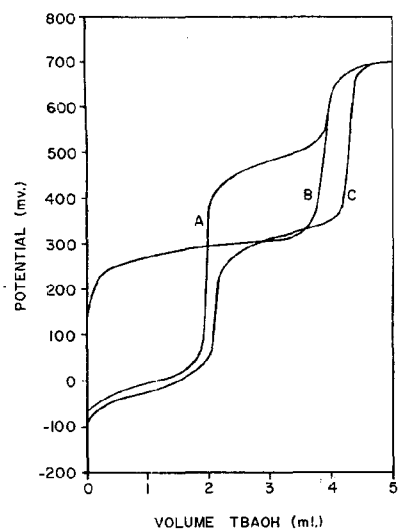


Figure 3. Titration of dicarboxylic acids
A. Malonic acid
B. Pimelic acid
C. Oxalic acid

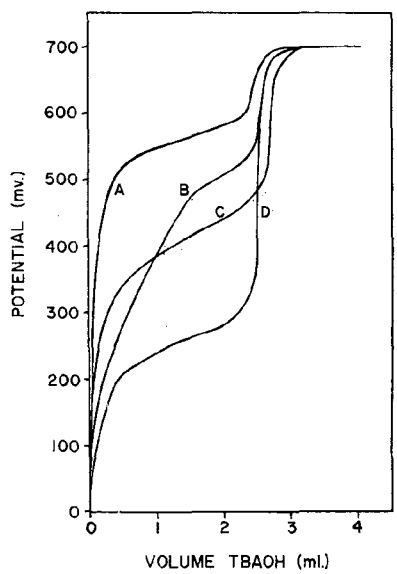


Figure 4. Titration of ortho substituted phenols
A Phenol
B. Catechol
C. o-Bromophenol
D. o-Nitrophenol

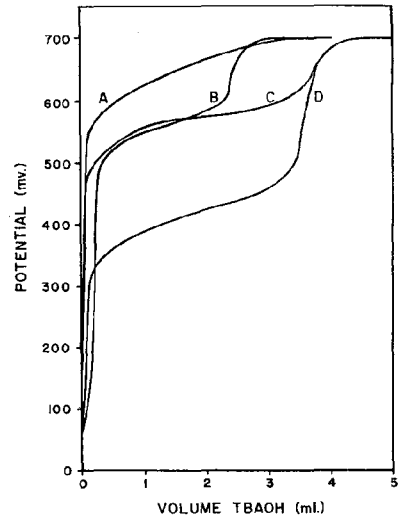


Figure 5. Titration of meta substituted phenols
A. Resorcinol
B. Phenol
C. *m*-Cresol
D. *m*-Chlorophenol

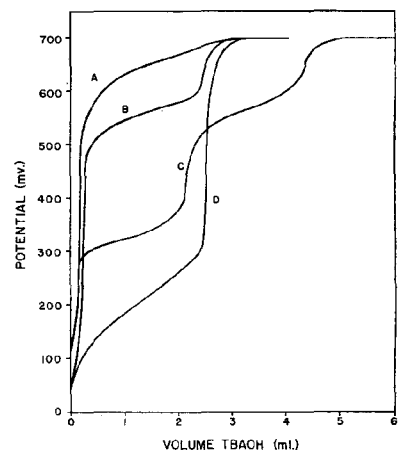


Figure 6. Titration of para substituted phenols
A. Hydroquinone
B. Phenol
C. *p*-Hydroxybenzoic acid
D. *p*-Nitrophenol

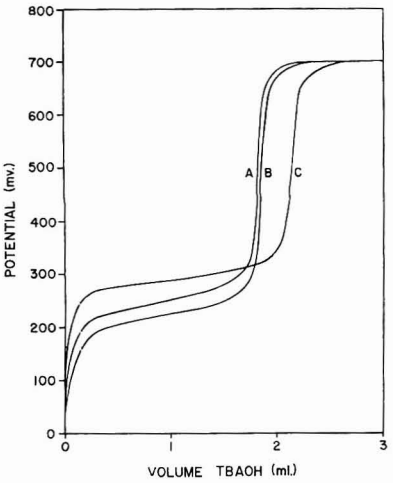


Figure 7. Titration of alkyl substituted thiophenols

A. 4-*t*-Butylthiophenol
B. Thiophenol
C. 4-*t*-Butyl-O-thiocresol

concentrations were employed during this work, all of the figures were obtained using 0.05*M* TBAOH.

RESULTS AND DISCUSSION

Figure 1 shows the titration curves obtained for four typical mineral acids and a sulfonic acid. Although the titrant was only 0.0461*M*, large, sharp potential breaks were obtained in all cases. All the acids were apparently stable in the solvent, for when the titration time was lengthened to over an hour, no significant differences were noted in the curves obtained. The apparent order of acidity for the mineral acids was $HCl_4 > H_2SO_4 > HCl > HNO_3$.

Figure 2 shows the titration of three carboxylic acids. In this solvent stearic acid appears to be nearly as strong as benzoic acid.

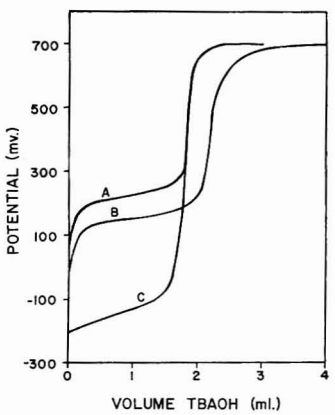


Figure 8. Titration of chloro substituted thiophenols

A. Thiophenol
B. *p*-Chlorothiophenol
C. Pentachlorothiophenol

In Figure 3, the titrations of three typical dicarboxylic acids are shown. Two definite breaks, corresponding to each acidic hydrogen, were obtained for oxalic and malonic acids, while only one break, corresponding to total acidity was observed for pimelic acid.

Figures 4, 5, and 6 show the titrations of phenol and various ortho, meta, and para substituted phenols. In all cases except resorcinol and hydroquinone, definite potential breaks were obtained. The unusually steep buffer region of catechol is most probably the consequence of intermolecular association between molecules of the acid.

Titrations of thiophenol, alkyl substituted, and chloro substituted thiophenols are shown in Figures 7 and 8. As would be expected, the substitution of alkyl groups reduces the size of the break, while substitution of chloro groups increases it. The magnitude of

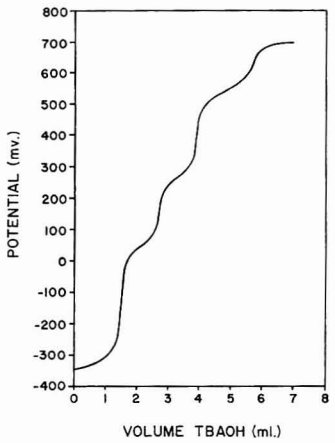


Figure 9. Titration of a mixture of perchloric acid, salicylic acid, thiophenol, and phenol

the break for thiophenol in Hallcomid M-12 is almost identical with that obtained in butylamine (*6*).

Figure 9 shows the titration of a four-component mixture containing a mineral acid, a carboxylic acid, a thiophenol, and a phenol.

Although no quantitative data are presented as such, frequent checks were made throughout the course of this research by titrating carefully weighed samples of pure acids. In all cases, a relative error of 0.5% or better was obtained. In addition, the glass-calomel electrode system in this solvent always gave potential readings that were reproducible within 2 millivolts.

Hallcomid M-12 offers many possibilities as a solvent for acid-base titrimetry. As shown above, nearly all types of acids and many acid mixtures can be titrated in it, using a simple procedure and electrode system. Figures 10 and 11 show the effect of varying

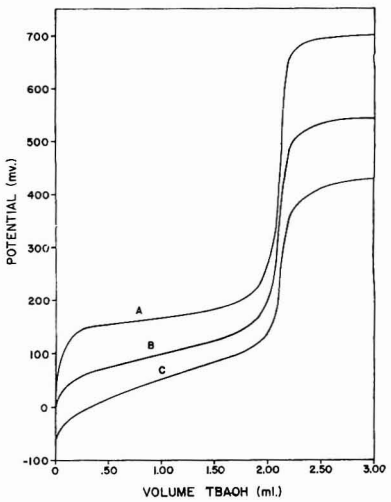


Figure 10. Effect of water on the titration of benzoic acid

A. 0.07% H_2O
B. 3.8% H_2O
C. 7.4% H_2O

amounts of water on the titration of two typical acids. As is evident, good, distinct breaks can be obtained even in the presence of a considerable amount of water. The solvent's high polarity and compatability with a wide range of organic solvents, both polar and nonpolar, make it superior to many substances such as alcohols and amines as a solvent for all kinds of acids. Although some inorganic salts appear to be insoluble in Hallcomid M-12, most of these could be put into Hallcomid solution by first dissolving them in a minimum quantity of water. These advantages coupled with the Hallcomid's stability, its relatively inoffensive odor, its low cost (~$6.70 per gallon) and its low vapor pressure make it easy and pleasant to use. No attempt was made to use this solvent with an automatic titrater; however, the rapid attainment

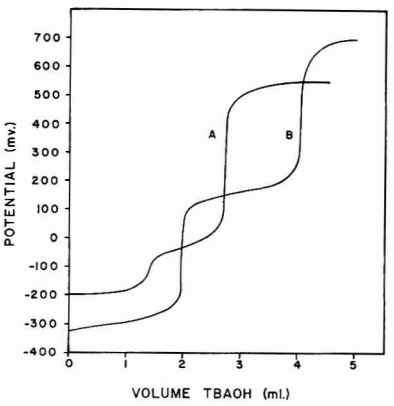


Figure 11. Effect of water on the titration of sulfuric acid

A. 3.8% H_2O
B. 0.0% H_2O

of equilibrium observed in all titrations indicated that such an application could easily be made.

LITERATURE CITED

(1) Bruss, D. B., Wyld, G. E. A., ANAL. CHEM. 29, 232 (1957).
(2) Cundiff, R. H., Markunas, P. C., *Ibid.*, 28, 792 (1956).
(3) *Ibid.*, 30, 1447 (1958).
(4) Deal, V. Z., Wyld, G. E. A., *Ibid.*, 27, 47 (1955).
(5) Fritz, J. S., Hammond, G. S., "Quantitative Organic Analysis," p. 44, Wiley, New York, 1957.
(6) Fritz, J. S., Lisicki, N. M., ANAL. CHEM. 23, 589 (1951).
(7) Fritz, J. S., Marple, L. W., *Ibid.*, 34, 921 (1962).
(8) Fritz, J. S., Yamamura, S. S., *Ibid.*, 29, 1079 (1957).
(9) Moss, M. L., Elliot, J. H., Hall, J. T., *Ibid.*, 20, 784 (1948).
(10) Swick, R. W., Buchanan, D. L., Nakao, A., *Ibid.*, 24, 2000 (1952).
(11) van der Heijde, H. B., *Dahmen*, E. A. F. M., *Anal. Chim. Acta* 16, 378 (1957).
(12) Yamamura, S. S., Ph.D. thesis, Iowa State College, Ames, Iowa, 1957.

RECEIVED for review November 16, 1962. Accepted April 12, 1963.

Determination of Hexafluorophosphate by Amperometric Titration with Tetraphenylarsonium Chloride

HAROLD E. AFFSPRUNG and VERNON S. ARCHER

Department of Chemistry, The University of Oklahoma, Norman, Okla.

▶ A method for the amperometric titration of hexafluorophosphate ion with tetraphenylarsonium chloride is described. The indicating ion is the tetraphenylarsonium ion, and the necessary supporting polarographic data on the arsonium ion are included. The method was tested by titrating solutions of potassium hexafluorophosphate and comparing the results with those obtained with the Nitron (4,5-dihydro-1,-4 - diphenyl - 3,5 - phenylimino -1,2,4 triazole) precipitation method. Agreement was good and no interference from fluoride ion was found.

IN A STUDY of hexafluorophosphoric acid and its salts, Lange and Müller (*3*) first reported that Nitron (4,5-dihydro-1,4-diphenyl-3,5-phenylimino-1,2,4-triazole) was a suitable reagent for the gravimetric determination of the hexafluorophosphate anion. Since that time no other reagent has been proposed for the latter's determination and, while Nitron is adequate as a reagent, it is not stable in solution. In addition, there is usually a significant amount coprecipitated as the acetate along with the hexafluorophosphate salt to make the determination uncertain. Tetraphenylarsonium chloride solutions are stable and insoluble precipitates with the hexafluorophosphate ion are formed. It would appear therefore that a suitable determination using this onium ion might be developed for the fluoride complex. Also, a new reagent for this complex is needed to provide a method for confirming the Nitron procedure. In previous studies (*6*), an excess of indifferent electrolyte was necessary for the quantitative precipitation of tetraphenylarsonium salts. Consequently, a method where contamination with coprecipitated salts would not cause difficulty would appear to be the most suitable. For these reasons an amperometric titration for the hexafluorophosphate ion was developed utilizing the reaction:

$$(C_6H_5)_4As^+ + PF_6^- = (C_6H_5)_4 AsPF_6$$

Hexafluorophosphate ion cannot be oxidized or reduced readily at the mercury drop so that development of the method required an investigation of the reduction of the tetraphenylarsonium ion.

Tetraphenylarsonium chloride has been used for quite a variety of determinations. Willard and Smith (*6*) introduced the reagent in potentiometric titrations where it was added in excess and back-titrated. Kolthoff and Johnson (*2*) used the reagent for amperometric titrations where the substance being titrated was reduced, while in the titration reported here the reagent is the indicating ion. Menis, Ball, and Manning (*4*) have also studied an amperometric titration with tetraphenylarsonium chloride, applying it to the determination of mercury by precipitating the chloride complex. Shinagawa, Matsuo, and Nakashima (*5*) have made some investigations on the polarographic behavior of tetraphenylarsonium ion, the results of which appear to be in essential agreement with the polarographic data here.

This report gives a procedure for the amperometric titration of the hexafluorophosphate ion using tetraphenylarsonium chloride as the titrant. Also, the necessary investigation of the polarographic behavior of the tetraphenylarsonium ion is included. As is shown, the method is good and the results agree well with those of the Nitron determination of this fluoride complex.

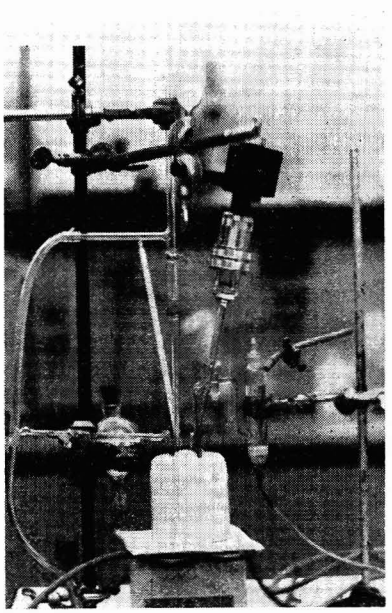


Figure 1. Amperometric titration setup for fluoride-containing solutions

EXPERIMENTAL

Apparatus. The polarograms were made with a Sargent Model XXI recording polarograph using an H-type cell, one arm of which contained a saturated calomel electrode connected to the dropping cell by an agar bridge and sintered glass disk. The cell was thermostated at 20° ± 0.2° C. The drop time was regulated in all cases to approximately 1 drop per 5 seconds.

The amperometric titrations were carried out in a cell made from empty polyethylene bottles. Figure 1 shows the titration apparatus assembled and ready for use. A magnetic stirrer and a stream of nitrogen gas were used to mix the solution and free it from oxygen after each addition of titrant. Since small volumes of reagent were added the amount of oxygen in each addition was very small and did not add to the time required to make a reading of the current. A Manostat microburet which delivered 10 ± 0.002 ml. was used for the titrations. The buret, nitrogen delivery tube, and dropping and reference electrodes are visible in Figure 1.

The titration vessel consisted of the lower portion of a polyethylene bottle of approximately 250-ml. capacity and

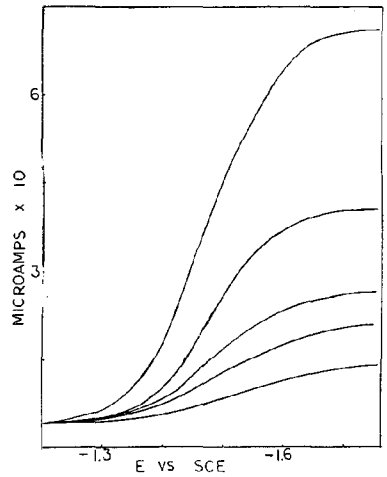


Figure 2. Polarographic reduction curves of tetraphenylarsonium chloride

Supporting electrolyte was 1N KCl, containing 0.1% Triton X-100. Concentration varied from approximately $10^{-5}M$ to $2 \times 10^{-4}M$

is not visible. The outer polyethylene cover was used to retain the nitrogen atmosphere while the current readings were being made. The two windows in the cover were made by pressing polyethylene vial caps into holes cut into the outer bottle. The tops were removed from the vial caps and replaced with glass microscope slide covers. These windows allowed the drop time to be controlled and also allowed the removal of any drops of titrant which adhered to the buret tip.

Since all of the solutions might contain fluoride ions, the contact of the solutions with glass was kept to a minimum. As most of the titrations were carried out in basic media, the fluoride ion did not attack the glass capillary of the dropping electrode to such an extent that it was noticeably damaged. In one case the dropping electrode was apparently stopped up with precipitate and this difficulty was removed by simply breaking off about 1 centimeter of the capillary tube.

All volumetric ware was calibrated.

Reagents. Standard solutions of tetraphenylarsonium chloride were prepared by weighing an approximate amount of the salt and standardizing by titration with potassium triiodide according to the method of Willard and Smith (*6*). These solutions were used for both the amperometric and the polarographic studies.

Solutions of potassium hexafluorophosphate were prepared from the salt donated by the Ozark-Mahoning Co., Tulsa, Okla. The salt was recrystallized from water after boiling for approximately 1 hour in potassium hydroxide at a pH near 11. A small amount of a reddish brown precipitate which formed during the boiling was discarded. The solution was neutralized with dilute hydrochloric acid and the volume was reduced. After cooling, a white precipitate appeared which was filtered and washed with cold water and alcohol. This material was dried in vacuo at 50° C. for 24 hours and then at 105° C. before preparation of the solutions. Ammonium hexafluorophosphate and the double salt with ammonium fluoride were also obtained from Ozark-Mahoning and were used without purification.

Rohm and Haas Triton X-100 and gelatin were used as maximum suppressors. All of the remaining reagents were of analytical reagent quality.

Procedure. For the amperometric titrations of potassium hexafluorophosphate a 10-ml. aliquot of a solution of approximately $0.02M$ was taken and added to 10 to 20 ml. of a buffer of ammonium hydroxide and ammonium chloride; the whole was then diluted to 55 ml., this final volume being used because of the cell dimensions. The final pH of the solution was approximately 9 in all cases. Nitrogen was bubbled through the solution until no apparent current from oxygen could be detected. Before the end point the reagent was added in 0.5-ml. increments; after the end point the increment was reduced to 0.1 ml. to avoid inconveniently high diffusion currents. Nitrogen was bubbled through the solution after each increment of titrant to stir as well as sweep out any oxygen added with the reagent. The current was then measured at -1.7 volts *vs.* the saturated calomel electrode (S.C.E.) Each solution contained 0.004% gelatin, added just after the end point was reached. This addition was made late in the titration to lessen the chances of forming a colloidal-size suspension of the precipitate which apparently can be reduced at the drop. All of the values of the current were corrected for dilution.

The determination of the hexafluorophosphate ion was checked by comparing analytical results obtained from a Nitron precipitation of the complex with those from the titration. The procedure for the Nitron determination was essentially that of Lange and Müller (*3*), the only modification made was introduced into the washing procedure. Nitron acetate is decomposed upon heating while the hexafluorophosphate salt is stable. The yellow decomposition product of Nitron acetate is soluble in benzene, while the acetate and the hexafluorophosphate salt are not soluble in this solvent. Consequently, the precipitate was washed with benzene saturated with Nitron hexafluorophosphate after each heating period to remove the decomposed Nitron acetate. This cycle of heating and washing was continued until a constant weight was obtained and no further discoloration of the precipitate occurred upon heating.

RESULTS AND DISCUSSION

A study of the conditions needed for a polarographic analysis of the tetraphenylarsonium ion was undertaken and a series of polarograms was obtained with potassium chloride as the supporting electrolyte. Such a set of reduction curves is shown in Figure 2. The curves are irreversible and the half-wave potential decreases as the concentration increases until a minimum value of -1.43 volts *vs.* the S.C.E. is reached. A large maximum in the half wave is observed in acid and neutral solution and at least 0.1% Triton X-100 is necessary to remove it when the concentration is as great as $0.0001M$. Gelatin is ineffective as a maximum suppressor compared to Triton X-100 in neutral and acid medium. However, gelatin is adequate in basic solutions, and the maximum could be suppressed with a gelatin percentage of 0.004% up to concentrations of about $0.0001M$ when the solution had a pH of approximately 9.

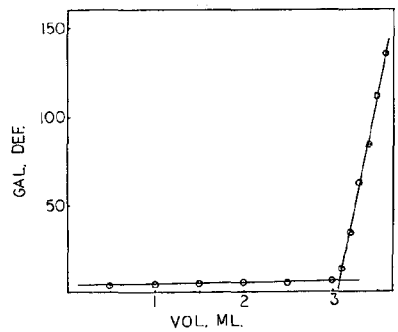


Figure 3. Titration curve of potassium hexafluorophosphate with tetraphenylarsonium chloride

Over the concentration range $0.00001M$ to $0.0002M$ the diffusion currents are quite reproducible. The values of the currents did not seem to be affected by a change in pH or greatly affected by a change in the supporting electrolyte. Although the polarographic curve is irreversible, it appears to obey the condition of Delahay (*1*) that the diffusion current is proportional to concentration and an equation of the Ilkovič type is satisfied. Straight line plots of diffusion current *vs.* concentration were obtained for a variety of supporting electrolytes: potassium chloride, sodium chloride, and potassium sulfate; buffer solutions of ammonium chloride and ammonium hydroxide were among those used. Since the half-wave potential varies with concentration, the diffusion current was always measured at a set potential of -1.7 volts. The curve is flattened at this potential and the residual current was extrapolated to this value to estimate the diffusion current. The slope of the current *vs.* concentration curve was 3400 μa. per liter mole.

As a result of the studies on the polarographic reduction of the tetraphenylarsonium ion the amperometric titrations of the hexafluorophosphate ion were made at a set potential of -1.7 volts *vs.* the S.C.E. Figure 3 shows a typical titration curve and, as may be seen, the break is quite sharp leading to a

Table I. Amperometric Titrations of Hexafluorophosphate with Tetraphenylarsonium Chloride

Sample No.[a]	Vol. $(C_6H_5)_4AsCl$ 0.06593M	Wt. of PF_6^- found, grams	PF_6^- in KPF_6, %
1	3.055	0.02920	79.31
2	3.040	0.02906	78.92
3	3.080	0.02944	79.96
4	3.100	0.02963	80.47
5	3.040	0.02906	78.92
6	3.100	0.02963	80.47
7	3.090	0.02954	80.22
8	3.060	0.02925	79.44
9[b]	3.065	0.02930	79.57
10[b]	3.075	0.02939	79.83
11[b]	3.060	0.02925	79.44

[a] Each solution contained 0.03682 g. of KPF_6.
[b] Each solution contained 0.171 g. of KF.
Average, 79.69% PF_6^-. Standard deviation, ±0.55.

Table II. Gravimetric Determination of Hexafluorophosphate with Nitron

Wt. KPF_6, g.	Wt. of Nitron: HPF_6, g.	Wt. PF_6^- found, g.	PF_6^- in KPF_6, %
0.3682	0.9252	0.2926	79.48
0.3682	0.9242	0.2923	79.39
0.3682	0.9237	0.2922	79.35
0.3682	0.9210	0.2913	79.12
		Av.	79.34

small error in estimating the volume of titrant.

The titration results of a series of determinations made on a solution of the potassium hexafluorophosphate salt are given in Table I. The theoretical percentage of hexafluorophosphate ion in the salt is 78.76, and all of the values obtained on the solution were a little above this value. As a comparison Table II contains the results of an analysis of the same solution using the gravimetric Nitron procedure. Since the salt is not a primary standard, the values obtained with both methods agree very well with the theoretical value. A comparison of the Nitron data with the results of the amperometric titration method shows that the two methods agree within the limits of the error of the determinations.

All of the titrations whose results are reported in Table I were carried out in ammonium hydroxide–ammonium chloride buffer solutions with a pH approximately 9. The buffer served as the supporting electrolyte and also helped to flocculate the precipitate. It is necessary that the precipitate settle, except for large particles, before a current reading is taken since particles of colloidal size appear to be reduced at the drop and can lead to large spurious values of the current before the end point is reached. Table I also contains three determinations where an excess of fluoride ion was added before the titration was made. The results show that no interference from fluoride ion occurs in the determination up to a tenfold molar excess of this ion.

Analytical data on titrations of solutions of ammonium hexafluorophosphate are given in Table III. These data show that successful titrations can be made in near neutral solutions containing a considerable excess of various electrolytes. The concentrations of hexafluorophosphate, which were determined, ranged from 0.0014M to 0.01M and the pH varied from about 6 to 8. In these titrations potassium sulfate was used as the supporting electrolyte and, with the excess ammonium ion, was usually, but not always, effective in coagulating the precipitate. In the slightly acid solution, the results were not so reproducible as in basic solution, and for this reason the investigation of the precision of the method using potassium hexafluorophosphate was made in basic solution as described above.

From the data presented here, as well as other qualitative data, it is possible to say that hexafluorophosphate ion may be determined with tetraphenylarsonium chloride in concentrations as dilute as 0.001M without difficulty. Also, many ions may be present without interfering, for example, sulfate, chloride, hydroxide, fluoride, phosphate, and monofluorophosphate do not interfere even when present in tenfold excess. Ions which precipitate with tetraphenylarsonium ion will interfere. However, ions such as perchlorate, perrhenate, and permanganate that do precipitate are not apt to occur in solutions of the hexafluorophosphate ion. Also, any substance which is reduced at the mercury drop by the applied potential will interfere in the sense that the precision will be decreased by a large background diffusion current.

Finally it should be said that the Nitron determination of the fluoride complex has been confirmed and a new reagent is furnished for the hexafluorophosphate ion in the presence of many electrolytes.

Table III. Amperometric Titrations of Ammonium Hexafluorophosphate with Tetraphenylarsonium Chloride

(−1.7 volts *vs.* S.C.E. K_2SO_4 0.05M was used as supporting electrolyte and each solution contained 0.003% Triton X-100)

Substance	Concn. found, m./l.		
NH_4PF_6	pH = 6		
0.01M	0.010	0.011	0.011
$NH_4PF_6 \cdot NH_4F$	pH = 6		
0.0014	0.0014		
0.0020	0.0021		
0.0042	0.0044		
0.0070	0.0071		
0.010	0.0088	0.009	
NH_4PF_6	pH = 8	pH = 7	
0.01M + 0.0048M KF	0.0085		
0.01M + 0.0096M KF	0.0085	0.0080	

LITERATURE CITED

(1) Delahay, P., Strassner, J. E., *J Am. Chem. Soc.* **73**, 5219 (1951).
(2) Kolthoff, I. M., Johnson, R. A., *J. Electrochem. Soc.* **98**, 231 (1951).
(3) Lange, W., Müller, E., *Ber.* **63**, 1058 (1930).
(4) Menis, O., Ball, R. G., Manning, D. L., ANAL. CHEM. **29**, 245 (1957).
(5) Shinagawa, M., Matsuo, H., Nakashima, F., *Kogyo Kagaku Zasshi* **60**, 1409 (1957); *C.A.* **51**, 17564*e* (1957).
(6) Willard, H. A., Smith, G. M., IND. ENG. CHEM., ANAL. ED. **11**, 186 (1939).

RECEIVED for review December 31, 1962. Accepted April 26, 1963. Work supported by The National Science Foundation. Presented in part at the Southwest Regional Meeting of the American Chemical Society, Oklahoma City, Okla., December 1960.

Polarographic and Coulometric Determination of Technetium

G. B. S. SALARIA, CHARLES L. RULFS, and PHILIP J. ELVING
The University of Michigan, Ann Arbor, Mich.

▶ Since technetium in any oxidation state can be readily converted to Tc(VII), the selective determination of the latter will allow technetium to be determined in most types of samples in which it may be expected to occur. The polarographic and coulometric determination of Tc(VII) have consequently been investigated. Measurement of Tc(VII) wave I at pH 2 generally results in optimum selectivity and sensitivity, with the measurement of wave I or II at pH 13 being used if interfering polarographic waves occur at pH 2, or for equally cogent reasons. Measurement of catalytic wave III at pH 13 affords maximum sensitivity for the estimation of technetium at very low concentration levels. Technetium can also be accurately determined by controlled potential electrolysis and coulometric measurement. The feasibility of determining technetium polarographically in complex mixtures is indicated by the opportunity of using different waves at radically different pH values; the wave used would be determined by the location of the polarographic waves given by other sample components. Technetium can be readily determined in the presence of rhenium at pH 2; technetium and rhenium in admixture can be simultaneously determined by polarography in 2*M* hydrochloric acid.

THE COMPLEX PATTERN of polarographic behavior exhibited by technetium has been discussed in a systematic study (*5*) of the reduction of pertechnetate ion and succeeding oxidation states over the pH range of −0.60 to 13.3. The polarography of technetium has also been investigated by Colton *et al.* (*1*), Magee, Scott, and Wilson (*3*), and Miller, Kelley, and Thomason (*4*). Little, however, has been reported on the polarographic determination of technetium, especially in the presence of rhenium, and on possible sources of error. Miller *et al.* (*4*) reported that technetium in concentrations as low as 0.2 p.p.m. can be determined in pH 7 phosphate buffer. After the present paper had been submitted for publication, a paper by Terry and Zittel (*6*) was called to our attention.

The present investigation has established that the first polarographic wave, corresponding to a 4*e* reduction, obtained from pertechnetate solutions at pH 2 and the first and second waves obtained at pH 13, corresponding to 3*e* and 1*e* reduction, respectively, can form the basis for the quantitative determination of technetium. The third wave observed at pH 13, which is apparently catalytic in nature, can be used for qualitative assessment of very small amounts of technetium. The first wave at pH 2 can be used to determine technetium in the presence of rhenium, which can itself also be determined (polarographically) together with technetium in 2*M* hydrochloric acid solution. Since technetium in any oxidation state can be readily converted to Tc(VII), the determination of Tc(VII) is sufficient to cover most situations in which technetium is to be determined.

EXPERIMENTAL

Chemicals. A solution of ammonium pertechnetate in water (pH 4) containing 46.75 mg. of Tc^{99} per ml. and 3×10^{-6} mc. of Tc-95m per gram of Tc^{99} was obtained from the Oak Ridge National Laboratory; coulometric studies of this solution substantiate the stated concentration (*5*). Technetium stock solution I was prepared by diluting 10 ml. of the pertechnetate solution in a 250-ml. volumetric flask; 10 ml. of solution I was further diluted to 100 ml. to give stock solution II.

Nitrogen (oil-pumped) was used without further purification for purging solutions of oxygen. All other chemicals used were of C.P. grade. The supporting electrolytes generally used were 0.5*M* KCl with HCl added to pH 2 and 0.25*M* K_2SO_4 with KOH added to pH 13.

Apparatus. A Fisher Elecdropode and a Leeds and Northrup Electro-Chemograph Model E were used for polarographic measurement. pH was measured with a Leeds and Northrup No. 7664 pH meter.

The dropping mercury electrode essentially consisted of a capillary (Corning marine barometer, 8 cm. long) connected to a mercury reservoir with Tygon tubing. The capillary constants (at a corrected height of 42.4 cm. of mercury) at potentials at which the limiting currents were measured, were m = 3.47 mg. per second and t = 2.27 seconds at pH 2, and 3.46 and 2.24 for wave I and 3.45 and 2.01 for wave II at pH 13. Polarographic measurements were made in an H-cell thermostatically controlled at 25.0° ± 0.1° C., one leg of which contained a saturated calomel electrode, S.C.E. All reported potentials are therefore *vs.* S.C.E. at 25° C.

A thin window Geiger counter (Nuclear Chicago Model 151A) and a flow transfer type scintillation well counter (Atomic Instrument Model 162) were used to measure the β-activity of technetium samples.

Chemical Reduction Procedure. Five milliliters of stock solution II, mixed with an equal volume of 2*M* hydrochloric acid, was shaken with an excess of mercury for 4 to 5 hours and left overnight. The clear solution was decanted; the mercury was thoroughly washed with distilled water and treated with ammonia and hydrogen peroxide to dissolve technetium. The ammonium pertechnetate solution thus obtained was evaporated under an infrared lamp onto an aluminum planchet, whose β-activity was counted. The results were compared with those for a known sample of technetium (Table I).

Analogous experiments were performed by shaking 0.945*M* Tc(VII) solutions (0.05 or 1.2*M* HCl, or 1*M* H_2SO_4) with mercury. The solution was then diluted to a known volume;

Table I. Chemical Reduction of Pertechnetate[a] by Mercury

No.	$[H^+]$ *M*	Contact time, min.	Tc recovery,[b] %
1	1	(4–5 hours; left overnight)	0.0511
2	1	(4–5 hours; left overnight)	0.0552
3	1	10	0.0012
4	0.1	10	0.0011
5	1[c]	10	0.0013
6	0.1	10[d]	0.0009
7	0.1	20[d]	0.0010
8	0.1	30[d]	0.0011

[a] Tc(VII) concn. = 0.189m*M*.
[b] Percentage of total Tc present recovered from mercury.
[c] Present as H_2SO_4; HCl was used in the other experiments.
[d] Time of contact with dropping-mercury electrode.

Table II. Coulometric Determination of the Faradaic *n* Value for Technetium(VII) in Acidic Solution

No.	pH[a]	Acid	Potential applied, volts	*n*	Solution change
1	−0.3	1*M* H_2SO_4	+0.12	3.05	brown ppt.
2	−0.3	1*M* H_2SO_4	−0.05	4.09	black ppt.
3	0.8	HCl + KCl	−0.03	3.05	brown ppt.
4	1.1 (1.3)	HCl + KCl	−0.30	3.81	green soln.
5	2.0 (7)	HCl + KCl	−0.16	3.08	brown ppt.
6[b]	1.0	HCl + KCl	−0.3	3.92	green soln.
7[b]	1.1	HCl + KCl	−0.3	3.94	green soln.
8[b]	1.75	HCl + KCl	−0.3	3.05	brown ppt.
9[b,c]	1.75	HCl + KCl	−0.5	3.74	green soln.

[a] Numbers in parentheses indicate the pH at the end of electrolysis.
[b] Acid was added during these runs to keep the pH constant.
[c] 9.35 mg. Tc was present in this run; 18.7 mg. was present in all others.

aliquots, after deoxygenation with nitrogen, were examined polarographically.

Polarographic Procedure. Polarographic test solutions were usually prepared by diluting an aliquot of stock solution II to 50 ml. in a volumetric flask with the desired supporting electrolyte to give a solution of the desired Tc concentration. The pH of this solution was measured; about 15 ml. was transferred to the H-cell, deoxygenated with nitrogen for 10 to 15 minutes, and then polarographed over the desired potential range. Triton X-100 (concentration 0.0013%) was added in a few cases to suppress maxima. $E_{1/2}$ and i_d were determined graphically, utilizing the average of the recorder trace; in the case of the Elecdropode, the maximum deflections were used.

Coulometric Procedure. For coulometric and macroscale electrolysis at controlled potential, 50 ml. of buffer solution was added to the coulometer cell containing a large mercury pool cathode, deoxygenated for about 10 minutes, and electrolyzed at a potential several tenths of a volt more negative than that at which the electrolysis was to be run, until the current fell to its minimum value, generally 1 to 2 ma. (Any hydrogen peroxide produced during the gas purging would be destroyed during the electrolysis.)

A known volume of Tc stock solution I was separately deoxygenated and then added to the coulometric cell; the coulometer was connected (the hydrogen-oxygen coulometer was presaturated with the gases); and the solution was electrolyzed at the desired potential as nitrogen was continuously passed through it. Initial currents of 35 to 40 ma. fell to 1 to 2 ma. at the conclusion of a run. In runs 6 to 9 of Table II hydrochloric acid was added from a buret to maintain the pH constant during the run. The volume of hydrogen-oxygen evolved was plotted against time to establish the optimum stopping point. From the curve thus obtained, the volume of the gas evolved during electrolytic reduction was determined and corrected for the residual volume due to the background electrolysis, temperature, pressure, and vapor pressure.

RESULTS AND DISCUSSION

Sources of Error. Two sources of error observed during the present investigation are of general interest in connection with the chemistry of technetium as well as its polarography.

Fifteen milliliters of pertechnetate solution [0.189m*M* Tc(VII); 0.5*M* KCl + HCl to pH 1.00] in the polarographic cell at 25° C. was purged with nitrogen for 10 minutes. The nitrogen and entrained $HTcO_4$ escaping from the cell were led into a tube containing ammonia solution, whose β-activity was equivalent to 0.84% of that of the Tc in the test solution, as calculated from a standard sample similarly counted. The loss would naturally be greater with longer bubbling or from solutions of higher acid concentration; it would be minimized by presaturating the nitrogen in an appropriately thermostatted bubbler containing an identical solution. In any event, it seems advisable that all effluent gases from acid media containing Tc(VII) be trapped in alkali.

The direct chemical reduction of Tc(VII) by hydrochloric acid more dilute than 2*M* is very slow at room temperature. However, in the presence of mercury some chemical reduction does occur even with more dilute acid. In all cases a minute fraction of the technetium (perhaps 0.001% of the total present) appears as a grey film (Tc metal ?) on the surface of mercury during the time required to run a polarogram.

Actually, the formation of the grey film at the surface of mercury drops was noticed. Since the solutions in experiments 1 to 5 (Table I) were shaken with a large excess of mercury, the low values of Tc recovered suggest that a thin film suffices to retard further reduction. Experiments 6 to 8 show that during the time normally required for the polarographic examination of a pertechnetate solution, the extent of chemical reduction of Tc(VII) by mercury will be negligible.

The polarographic behavior of pertechnetate solutions in hydrochloric or sulfuric acid, which had been shaken with mercury, was quite informative. In 2.4*M* HCl, only the second of the two waves obtained for a Tc(VII) solution was observed, indicating that Tc(VII) is reduced almost quantitatively to Tc(IV) or (III). Evidently, there is some reduction to still lower states since 20 to 47% decreases in the height of wave II are found. In 0.1*M* HCl or 2*M* H_2SO_4, both Tc(VII) waves appear but wave I is reduced by 87 and 59%, respectively.

Coulometry and Coulometric Analysis. The reproducibility of wave I diffusion currents in acidic media is not always satisfactory (*5*), because of the tendency for a stepwise separation of the (VII)–(IV) and (IV)–(III) stages, which tends to be more prominent at higher acidities, and in sulfuric (as compared to hydrochloric) acid solution.

It is possible to obtain an *n*-value of 3 by carefully electrolyzing just at the $E_{1/2}$ of wave I (cf. runs 1, 3, and 5, Table II); this is readily done in sulfuric acid media. Continued electrolysis on the resulting brown TcO_2 suspension at a more negative potential does not result in further reduction. However, initial electrolysis of Tc(VII) at a more negative potential does give an *n* of 4; the resulting black suspension is apparently Tc_2O_3. It is also possible to obtain an *n* of 3 in hydrochloric acid solution, resulting in a brown TcO_2 suspension, but one need only have the initial potential just on the plateau of the wave to obtain an *n* of 4 and a green solution (run 4), which still exhibits polarographic wave II.

Further investigation has shown that it is possible to obtain an *n* of 4 within 2%, if the coulometry in hydrochloric acid solution is made at −0.30 *vs.* S.C.E.—i.e., on the plateau of the wave—and the pH is maintained constant within 0.1 unit by adding acid.

Near pH 1.75 the stepwise separation of the (VII)–(IV) and (IV)–(III) stages becomes more prominent (cf. runs 8 and 9) and an *n* of 3 can be obtained by electrolyzing on the plateau of the first wave. However, initial electrolysis of pertechnetate at more negative potential does give an *n* of 4.

Determination of Technetium. Review of the polarographic behavior of solutions of pertechnetate ion (*5*) indicated that successful analytical procedures would most likely be developed from the wave patterns observed at pH 2 and 13.

The chemical reduction of pertechnetate by mercury in the presence of hydrochloric or sulfuric acid makes it difficult to obtain reliable and reproducible data for the first reduction

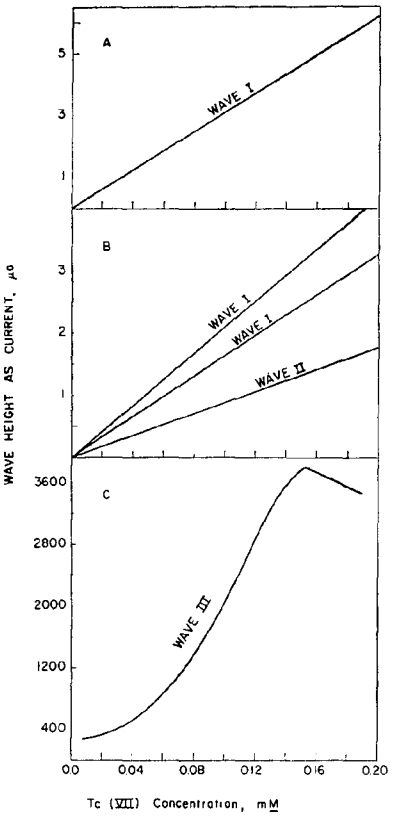


Figure 1. Variation of wave height with pertechnetate concentration

A. Measured at pH 2 with Electro-Chemograph
B. Measured at pH 13 with Electro-Chemograph (lower two curves) and Elecdropode (upper curve)
C. Measured at pH 13 with Elecdropode

wave of Tc(VII) in solutions more acidic than pH 1. On the other hand, the pH range of 3 to 5 involves a change in the nature of the electrochemical reduction from a $4e$ to a $3e$ process. In view of these difficulties, pertechnetate solutions of pH 2.0 were studied in the attempt to devise a procedure for estimating even very small amounts of technetium on the basis of diffusion current.

At pH 2, Tc(VII) gives three diffusion-controlled polarographic waves with half-wave potentials of −0.14, −0.91, and −1.12 volts. The magnitude of wave II (runs 1 to 4, Table III) is about 1.5 times that of wave I, evidently corresponding to a $6e$ reduction of Tc(III), which might involve the formation of a technetohydride, conceivably TcH_3. In runs 5 to 7, the magnitude of wave II is about the same as that of wave I and may involve the formation of TcH. Attempted coulometry at a potential appropriate to wave II results in electrolysis beyond an n equivalent to seven, while the pH of the unbuffered solution rises continuously. Such behavior could result from cyclic process involving technetohydrides.

At pH 2, the value of the diffusion current constant in the range of 0.01 to 0.2mM Tc(VII) (Table III; Figure 1) is fairly constant at 11.9 ± 0.1 for wave I, suggesting that technetium in concentrations as low as 0.01mM can be estimated with an accuracy of ±0.8%. Waves II and III do not show any constancy in diffusion current constant, except in the low concentration range of 0.01 to 0.04mM Tc(VII), although their variation with drop-time (mercury height) shows that they are diffusion-controlled (*5*).

At pH 13, Tc(VII) also gives three waves of $E_{1/2}$, −0.81, −1.02, and −1.60 volts. However, only wave I, which corresponds to a $3e$ reduction process, is diffusion-controlled. Wave II is adsorption-controlled and apparently involves further reduction to Tc(III). Wave II is followed by a large catalytic hydrogen discharge wave, which is probably due to the lowering of the high hydrogen overvoltage of mercury by the deposit of a thin film of technetium metal. The appearance of the dropping mercury electrode is similar to that of mercury shaken with acidic pertechnetate solution. Chemical extraction of the film gives a solution showing β-activity.

At pH 13, the diffusion current constant is constant at 6.32 ±0.13 for wave I (Table IV; Figure 1) and at 3.50 ± 0.03 for wave II. Both waves provide a means for accurately estimating very low technetium concentrations. Although it is possible to record wave III for low technetium concentrations, the large and variable values of i_l/C suggest that the wave is catalytic.

Determination of Technetium in Presence of Rhenium. Polarography of a pH 2 solution, which was 0.01 to 0.189mM in Tc(VII) and 0.1 to 2mM in Re(VII), gave a first wave corresponding to the $4e$ reduction of pertechnetate at $E_{1/2}$ of −0.16 to −0.20 volt, which was 0.01 to 0.04 volt more negative than observed for solutions containing only Tc(VII) (Table VI). The magnitude of the diffusion current was in agreement with the reduction of Tc(VII) to (III). Measurements made on wave I gave a mean diffusion current constant of 11.2 ± 0.3 for an accuracy of 3%, compared to 11.7 observed for Tc alone. Since perrhenate solutions do not show any polarographic wave at pH 2, wave I can be used to estimate quantitatively pertechnetate in the presence of perrhenate even when

Table III. Variation of Current with Technetium Concentration at pH 2[a]

No.	Tc concn., mM	Wave I i_d μa.	Wave I i_d/C	Wave I I[b]	Wave II i_d μa.	Wave II i_d/C	Wave III i_d μa.	Wave III i_d/C	Waves II and III i_d/C
1	0.0095	0.30	31.6	12.0	0.53	55.8	0.15	15.8	71.6
2	0.0189	0.59	31.2	11.9	1.05	55.6	0.30	15.9	71.5
3	0.0378	1.17	31.0	11.8	2.11	55.8	0.60	15.9	71.7
4	0.0756	2.33	30.8	11.7	3.66	48.4	0.72	9.53	57.9
5	0.1133	3.54	31.2	11.9	4.31	38.0	1.34	11.8	49.8
6	0.1511	4.71	31.2	11.9	5.57	36.9	1.94	12.8	49.7
7	0.1889	5.88	31.1	11.8	6.60	34.9	2.76	14.6	49.5
			Mean	11.86					
			Std. dev.	±0.098					

[a] Background electrolyte: 0.5M KCl + HCl; temp.: 25° C. Data obtained with Electro-Chemograph.
[b] $I = i_d/Cm^{2/3}t^{1/6}$.

Table IV. Variation of Current with Technetium Concentration at pH 13[a]

No.	Tc concn., mM	Wave I i_d μa.	Wave I i_d/C	Wave I I[d]	Wave II i_l μa.	Wave II i_l/C	Wave II I[d]	Wave III[b] i_l μa.	Wave III[b] i_l/C
1	0.0095	0.160	16.9	6.44				2.67	282
2	0.0189	0.320	16.9	6.47	0.170	8.99	3.51	8.66	458
3	0.0378	0.620	16.4	6.27	0.340	8.99	3.51	61.2	1619
4	0.0756	1.23	16.3	6.22	0.690	9.13	3.56		
5	0.1133	1.86	16.4	6.27	1.02	9.01	3.51		
6	0.1511	2.54	16.8	6.42	1.35	8.93	3.48		
7	0.1889	3.03	16.0	6.13	1.67	8.84	3.45		
8[c]	1.889	32.8	17.4	6.64	4.50	2.38	0.93		
			Mean	6.317			3.503		
			Std. dev.	±0.127			±0.034		

[a] Background electrolyte: 0.25M K_2SO_4 + KOH; temp.: 25° C. Data obtained with Electro-Chemograph.
[b] It was not possible to record catalytic wave III for Nos. 4 to 8 because of the high values of the limiting current.
[c] Values for this run were omitted in calculation of mean and standard deviation.
[d] $I = i_d/Cm^{2/3}t^{1/6}$.

Table V. Variation of Current with Technetium Concentration at pH 13[a]

No.	Tc concn., mM	Wave I i_d μa.	Wave I i_d/C	Wave I I[d]	Wave II[b] i_l μa.	Wave II[b] i_l/C	Wave III i_l μa.	Wave III i_l/C
1	0.0095	0.200	21.1	8.04			2.43	255.8
2	0.0189	0.400	21.2	8.09			7.11	376.2
3	0.0378	0.810	21.4	8.19			18.4	486.8
4	0.0756	1.61	21.3	8.14			94.9	1256.
5	0.1133	2.41	21.3	8.13			282.	2488.
6	0.1511	3.21	21.2	8.12			570.	3773.
7	0.1889	3.92	20.8	7.93			654.	3462.
8	1.889	48.2	25.5	9.75[c]	10.40	5.50	877.	464.2
			Mean	8.091				
			Std. dev.	±0.085				

[a] Background electrolyte: 0.25M K_2SO_4 + KOH; temp.: 25° C. Data obtained with Fisher Elecdropode.
[b] Because of its ill-defined shape, it was not possible to evaluate wave II for Nos. 1 to 7.
[c] This value was omitted in calculation of mean and standard deviation.
[d] $I = i_d/Cm^{2/3}t^{1/6}$.

Table VI. Concentration-Current Relations for Solutions Containing Both Technetium and Rhenium[a]

Run	Tc[b] concn., mM	Re[b] concn., mM	Wave I i_d μa.	Wave I i_d/C	Wave I I[c]	Wave II i_d μa.	Wave II i_d/C	Wave II I[c]	Wave III i_l μa.
1	0.0095	0.100	0.288	30.3	11.6	0.97	102	40.1	0.36
2	0.0095	0.200	0.282	29.7	11.4	0.97	102	40.1	1.09
3	0.0095	2.00	0.286	30.1	11.5	0.99	104	40.9	2.09
4	0.1889	0.100	5.45	28.9	11.1	5.55	29.4	11.3	2.22
5	0.1889	0.200	5.35	28.3	10.9	5.55	29.4	11.3	4.44
6	0.1889	2.00	5.35	28.3	10.9				94.
				Mean	11.23				
				Std. dev.	±0.307				

[a] Background electrolyte: pH 2, 0.5M KCl + HCl. Temp.: 25° C. Data obtained with Fisher Elecdropode.
[b] NH_4TcO_4 and $KReO_4$ were used.
[c] $I = i_d/Cm^{2/3}t^{1/6}$.

the Tc(VII) is present in very low concentration—e.g., 0.01mM.

Although wave II appears at an $E_{1/2}$ of −0.84 to −0.93 volt compared to −0.93 volt observed for pertechnetate alone, the variation in the magnitude of the limiting currents does not permit any reliable generalization to be made. The magnitude of the limiting current for this wave (runs 1 to 3, Table VI) is approximately 1.5 times that for technetium alone. In runs 4 and 5, the value of the limiting current (I = 11.3) is approximately the same as for technetium alone (*5*). With higher concentrations of rhenium (run 6), wave II merges with wave I.

$E_{1/2}$ of wave III is near to that observed for the perrhenate wave alone. The current of the composite wave for a mixture does not provide any feasible analytical tool, since the wave height is apparently influenced by other factors, such as mutual oxidation and reduction of the two species, catalytic reduction, etc.

The polarographic determination of rhenium in the presence of technetium was investigated, based on the fact that an Re(VII) solution, which is 2M in HCl, gives a well defined wave with an $E_{1/2}$ of −0.42 volt, whereas Tc wave I appears at −0.005 volt. Polarography of a solution, which was 0.189mM in Tc(VII) and 2.0mM in Re(VII) and contained 0.5M KCl + 2M HCl as background electrolyte, gave only a wave at −0.426 volt with a diffusion current of 25.8 μa., which is much less than the 38.2 μa. observed for Re(VII) alone. The disappearance of the Tc(VII) wave I may be due to a chemical reduction by Hg in acidic solution of Tc(VII) to lower oxidation levels (*5*), but not to Tc° in this case, which are partially reoxidized with consumption of some Re(VII) until an equilibrium obtains with most of the Tc in the (III) state. Most of the redox couples involved are irreversible in character. This is supported by the fact that when solutions 0.189mM in Tc(VII), 2mM in Re(VII), and 2M in HCl are shaken with metallic mercury, Tc(VII) is not partially reduced chemically to metal as it is when Re(VII) is absent.

On the other hand, two well defined waves are observed for solutions 0.189mM in Tc and only 0.1mM in Re (0.5M KCl + 2M HCl as background electrolyte). The first wave ($E_{1/2}$ = −0.005 volt) is due to technetium; the magnitude of its diffusion current supports the 4*e* reduction (*5*) of Tc(VII) to (III) and indicates that the pertechnetate is not chemically reduced by mercury and hydrochloric acid with this ratio of perrhenate present. The second wave ($E_{1/2}$ = −0.425 volt) represents the reduction of Re(VII) to (IV) (*2*). If the Re(VII) concentration in the polarographic test solution is kept low enough, these waves could provide a method for the estimation of pertechnetate and perrhenate when present together.

Evaluation of Analytical Applicability. The polarographic determination of technetium, based on the measurement of wave I at pH 2, generally provides for optimum selectivity and sensitivity. If measurement at pH 2 offers difficulty because of interfering polarographic waves or equally cogent reasons, technetium can be determined by measurement of wave I or II at pH 13; measurement of wave III at pH 13 affords maximum sensitivity for the estimation of technetium at very low concentration levels.

The flexibility afforded by the opportunity of using different Tc(VII) reduction waves at two radically different pH values indicates the feasibility of determining technetium polarographically in complex mixtures, where the choice of the analytical wave would be dictated by the location of the polarographic waves given by the other components of the sample.

Technetium can also be accurately determined by controlled-potential electrolysis and coulometric measurement; use of an electronic current integrating device rather than a hydrogen-oxygen gas coulometer would yield results of high precision and sensitivity.

ACKNOWLEDGMENT

One of the authors (G.B.S.S.) thanks the National Academy of Sciences for an appointment supported by the International Cooperation Administration under the Visiting Research Scientist Program.

LITERATURE CITED

(1) Colton, R., Dalziel, J., Griffith, W. P., Wilkinson, G., *J. Chem. Soc.* **1960**, 71.
(2) Lingane, J. J., *J. Am. Chem. Soc.* **64**, 1001 (1942).
(3) Magee, R. J., Scott, I. A. P., Wilson, C. L., *Talanta* **2**, 376 (1959).
(4) Miller, H. H., Kelley, M. T., Thomason, P. F., "Advances in Polarography," I. S. Longmuir, ed., **Vol. 2**, pp. 716–26, Pergamon Press, London, 1960.
(5) Salaria, G. B. S., Rulfs, C. L., Elving, P. J., *J. Chem. Soc.* **1963**, 2479.
(6) Terry, A. A., Zittel, H. E., ANAL. CHEM. **35**, 614 (1963).

RECEIVED for review January 21, 1963. Accepted April 22, 1963.

Liquid-Liquid Extraction of Pertechnetate Ion with Methyltricaprylammonium Chloride

G. B. S. SALARIA, CHARLES L. RULFS, and PHILIP J. ELVING
The University of Michigan, Ann Arbor, Mich.

▶ **Liquid-liquid extraction with a chloroform solution of methyltricaprylammonium chloride results in the quantitative isolation of pertechnetate ion from aqueous media, ranging from 4*M* sulfuric acid or 9*M* hydrochloric acid to pH 13. The specificity of the separation is indicated by the report that a similar type of extraction results in a highly selective separation of perrhenate from ions of most other elements. The formation of a 1:1 pertechnetate–organic cation adduct appears to be requisite for the extraction at any pH; an excess of the organic reagent is only necessary where extraneous anions can compete with the pertechnetate ion. The competition of chloride ion in the liquid-liquid anion exchange system involved has been studied.**

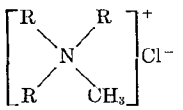
THE EXTRACTION of technetium(VII) from aqueous acidic, neutral, and alkaline solution by a wide variety of organic compounds, including alcohols, ketones, ethers, esters, amines, and organo-phosphorus or nitro compounds dissolved in nonpolar solvents has been reported (*1*). It has also been pointed out that a basic oxygen or nitrogen atom in the organic molecule is desirable in effecting partition and that extraction is often more efficient from acidic than from neutral or alkaline aqueous phases. The extraction mechanism with amines dissolved in inert solvents has been described as an anion exchange (*2*).

Churchward [see (*3*)] suggested the use of a quaternary amine to extract selectively small amounts of rhenium from basic solutions. His coworkers (*3*) found that methyltricaprylammonium chloride (MTC) is a highly selective reagent for the analytical isolation of trace amounts of rhenium(VII). Consequently, it was considered worthwhile to examine MTC as a possible means for separating the pertechnetate ion.

EXPERIMENTAL

Chemicals. A solution of ammonium pertechnetate in water (pH 4) containing 46.75 mg. of Tc^{99} per ml. was obtained from the Oak Ridge National Laboratory; this concentration was substantiated by coulometric measurement (*4, 5*). Technetium stock solution I was prepared by diluting 10 ml. of this solution to 250 ml.; 10 ml. of solution I was diluted to 100 ml. for stock solution II.

A sample of "Aliquat 336," essentially methyltricaprylammonium chloride, was kindly supplied by the Chemical Division of General Mills, Inc., Kankakee, Ill. It has the general formula



where R is a mixture of C_8 and C_{10} carbon chains, with the C_8 predominating. This material has an average molecular weight of 442, on which basis solutions of approximate molarity in chloroform were prepared. In some experiments the chloroform solutions of MTC were acid-washed before being used; the results were essentially identical with those for unwashed extractant solutions. All other reagents were of Mallinckrodt or J. T. Baker analytical reagent grade quality. Nitrogen (oil-pumped) was used without further purification for purging polarographic solutions.

Apparatus. A Fisher Elecdropode was used for polarographic measurements, which were made in a thermostatted H-cell *vs.* a saturated calomel reference electrode, S.C.E. A Leeds & Northrup pH meter was used. Negative values of pH were not measured and only represent a formalized device for incorporating the results obtained in 1 to 9*M* acid.

A thin window Geiger tube and Nuclear-Chicago scaler, Model-151A, were used to measure the β-activity of technetium samples.

Extraction Procedure. The test solution was usually prepared by diluting 5 ml. of stock solution II to 50 ml. in a volumetric flask with the desired acid or base to give a 0.189m*M* Tc solution. The pH of this solution was measured; an aliquot was transferred to a 50-ml. separatory funnel and vigorously shaken with an equal volume of 8% MTC solution in chloroform; after separation of the two layers, the chloroform layer was drawn off. The pH of the aqueous layer was measured; the latter was again extracted with an equal volume of the reagent and the organic layer was separated. One milliliter of the residual aqueous phase and 1 ml. of each extract were transferred to stainless steel planchets; any free acid was neutralized with ammonia; the resulting mixtures were dried under an infrared lamp and counted.

The distribution ratio in the present study was defined as

$$D = \frac{\text{activity in the organic layer}}{\text{activity in the aqueous layer}}$$

Close temperature control does not appear to be critical during the extractions, which were conducted at ambient room temperatures (about 24° ± 2° C.).

Polarographic Procedure. Ten milliliters of the pertechnetate solution in 2*M* HCl was shaken with an equal volume of MTC solution in chloroform. The aqueous layer was separated from the organic layer and, after adjustment to pH 2.0, diluted to 25 ml. in a volumetric flask. About 15 ml. was transferred to the polarographic cell, deoxygenated by nitrogen purging for 10 to 15 minutes, and then polarographed over the desired potential range. From the height of the technetium(VII)/(III) wave, $E_{1/2}$ at −0.18 volt (*4, 5*), the amount of technetium left unextracted in the aqueous layer was determined.

RESULTS AND DISCUSSION

Radiometric assay for (Tc^{99}) pertechnetate ion indicates that over 99% of the technetium can be extracted by a two-stage process using equal volumes of (0.15*M*) solution of MTC in chloroform throughout the pH range of −0.95 to 13.05 (Table I). Chloroform alone is essentially incapable of extracting pertechnetate ion; the resulting per cent extracted of 0.02 to 0.09 can be considered as being due to the solubility of water in chloroform.

The use of 8% (0.15*M*) extractant and the specification of the pH before extraction was consistent with prior work on this system (*2*). Actually, much lower concentrations of reagent (in general, comparable with the pertechnetate concentration) are satisfactory. In extraction from unbuffered media, the pH after equilibration has naturally more significance. However, since the efficiency of the extraction is not significantly pH-dependent for the system under study, the latter point is not too important. The large changes of pH noted for the 0.15*M* reagent (Table II) are not obtained in the case of the less than 1m*M* reagent concentration actually needed in the present study.

Table I. Liquid-Liquid Extraction of Tc(VII) with Chloroform Solutions of Methyltricaprylammonium Chloride

Solution composition[a]	Initial pH[b]	Tc extracted,[c] %	D[d]
H_2SO_4	(4M)	I 97	31
		II 99	91
H_2SO_4	(2M)	I 99	67
		II 97	34
H_2SO_4	(1M)	I 98	47
		II 98	51
H_2SO_4	(0.5M)	I 99	76
		II 96	25
H_2SO_4	1.0	I 97	32
		II 94	15
H_2SO_4	2.02	I 95	19
		II 95	18
H_2SO_4	4.10	I 88	7.2
H_2SO_4	6.40	I 92	11
HCl	(9M)	I 98	39
		II 97	36
HCl	(6M)	I 98	42
		II 99	175
HCl	(4M)	I 98	44
		II 99	91
HCl	(2M)	I 98	44
		II 99	91
HCl	0.85	I 97	32
		II 98	55
HCl	2.0	I 93	13
		II 98	43
HCl	3.40	I 92	12
HCl	5.50	I 93	14
HCl	7.0	I 92	11
		II 90	9.1
KOH	9.05	I 95	19
KOH	11.0	I 95	
KOH	13.1	I 98	58

[a] Original aqueous solution was 0.189mM in pertechnetate and contained acid or base indicated; chloroform extractant solution was 0.15M in MTC.

[b] Liquid-liquid extraction with 0.15 MTC solution in $CHCl_3$ involves large change in pH of pertechnetate solution after equilibration for pH range of 6 to 11 (Table II).

[c] Roman numbers refer to successive extractions of aqueous layer. Equal volumes of aqueous and organic phase were used in each extraction in this table. Pertechnetate content of phase used in calculation is based on radiometric assay for Tc^{99}.

[d] Distribution ratio, D, is defined as (activity in organic layer)/(activity in aqueous layer). These data were calculated from % E values expressed to four significant figures.

Table II. Change in pH on Extraction of Aqueous Tc(VII) Solution with $CHCl_3$ Solution of Methyltricaprylammonium Chloride[a]

pH before extraction	pH after extraction
2.00	2.15
3.40	3.20
4.10	3.60
5.50	3.60
6.40	3.65
9.50	3.70
11.0	4.90
13.1	13.0

[a] Aqueous solution originally 0.189mM in Tc(VII); chloroform solution 0.15M in MTC.

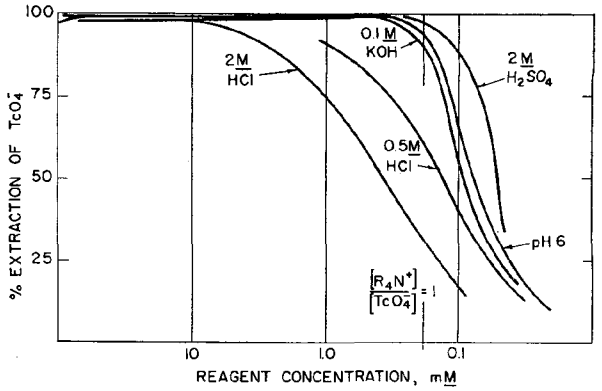


Figure 1. Liquid-liquid extraction of Tc(VII) from several aqueous media with various concentrations of MTC in chloroform

Volumes of aqueous and organic phases are equal

In another set of experiments, the concentration of technetium was kept fixed and the concentration of MTC was varied to find the average number of extractant molecules, n, associated with the extracted metallic species. The results are shown in Figure 1, where the extraction data for pertechnetate ion at pH −0.6 (H_2SO_4), 6.4, and 13.05 (KOH) are consistent with $n = 1$. In all of these media, 90 to 98% extraction obtains with but one MTC per TcO_4^- ion present.

The fact that the extraction of pertechnetate ion from 2M HCl with MTC (Figure 1) requires a tenfold excess of reagent for nearly complete extraction must be due to a less favorable competition between pertechnetate ion and chloride ion for the cation of the reagent.

To ascertain that MTC in the presence of 2M HCl does not act as a reducing agent, the aqueous extract after extracting pertechnetate from 2M HCl was diluted to a known volume, the pH adjusted to 2, and the solution scanned polarographically. The most positive polarographic wave (*4, 5*) corresponding to the 4-electron reduction of Tc(VII) to (III) appeared; its height due to unextracted pertechnetate was in agreement with the results of the radiometric determination (Table III), confirming the validity of the radiometric measurements and the nonreducing action of the reagent. In connection with the further study of the chloride effect in this system, some additional polarographic checks were made after extraction from 0.5M acid.

Evidently, (a) a 1:1 compound exists, (b) both the reagent and the MTC-pertechnetate adduct distribute predominantly into the chloroform layer, (c) $HTcO_4$ does not extract significantly, and (d) reduction of Tc(VII) is not important. Considering only the major aspects of the chloride competition in the heterogeneous system as a whole,

Table III. Comparison of Radiochemical and Polarographic Measurements of Residual Tc(VIII) in Aqueous Layer after Extraction[a]

Reagent concn., mM	% Extraction measured by β-activity	% Extraction measured by Polarography
0.384	39.5	40.2
0.768	70.9	67.5
1.92	85.2	85.5
0.192	52.2	51.2
0.384	70.1	70.2
0.768	86.9	86.7

[a] Aqueous solution was originally 0.189mM in Tc(VII), and 2M in HCl (Nos. 1 to 3) and 0.5M in HCl (Nos. 4 to 6).

$$TcO_4^- + [R_4N^+Cl^-]_0 \rightleftharpoons [R_4N^+TcO_4^-]_0 + Cl^-, \quad (1)$$

and,

$$K_e = \frac{[R_4N^+TcO_4^-]_0(Cl^-)}{(TcO_4^-)[R_4N^+Cl^-]_0} \quad (2)$$

Defining D as,

$$D = \frac{[R_4N^+TcO_4^-]_0}{(TcO_4^-)} \quad (3)$$

then,

$$K_e = D \times \frac{(Cl^-)}{[R_4N^+Cl^-]_0} \quad (4)$$

or

$$D = K_e \times \frac{[R_4N^+TcO_4^-]_0}{(Cl^-)} \quad (5)$$

With low concentrations of MTC, of course, appropriate correction must be made on the "free" MTC concentration for the portion bound to extracted pertechnetate.

Values of K_e calculated from the present data for 2M HCl and from 0.1 to 8M MTC concentrations range from (7.2 to 7.8) × 10^3. For 0.5M HCl and MTC concentrations of 0.08- to 0.8mM,

the calculated values of K_s range from (4.8 to 6.1) $\times 10^3$. Consequently, a K_s of (6.5 $\pm$ 1) $\times 10^3$ is indicated, and the conception of the mechanism involved appears to be essentially valid. A more refined treatment is not warranted until a reagent of 100% purity is available.

Attempts were also made to use MTC as an extractant for Tc(III) or Tc(IV). Only 2.4% of the technetium could be extracted from the green colored solution of Tc(III) which was obtained by coulometric reduction of a Tc(VII) solution, 0.1*M* in HCl and 0.5*M* in KCl, at −0.03 volt *vs.* S.C.E. Since a polarographic run on the Tc(III) solution used showed the presence of about 3% of Tc(VII), it may be concluded that it is not possible to extract Tc(III) with the quaternary ammonium salt. No significant extraction was found for Tc(IV) obtained by the reduction of pertechnetate with ascorbic acid.

The prior work on perrhenate with MTC (*3*) indicates the general utility and great selectivity of this extraction in isolating Re—and therefore also Tc—from most other elements. Chromium, cobalt, rhenium, and vanadium are among the few elements which might coextract with technetium. Unlike technetium, however, the distribution in some of these systems is strongly pH-dependent; hence, resolution from technetium may still be feasible by control of pH in the aqueous phase.

Perrhenate can be recovered from the quaternary ammonium salt extract by stripping the latter with 2.5*M* perchloric acid in three stages (*3*); over 90% is recovered in the first stripping solution. An attempt was made to separate pertechnetate and perrhenate from 2*M* HCl solutions with MTC extraction, which involved measuring the amount of Tc in both aqueous and organic layers by the radiometric method and the unextracted Re in the aqueous layer polarographically. Rhenium follows technetium so closely that their separation from each other is not possible from the indicated medium. This separation might be feasible, however, using sulfuric or perchloric acid media.

ACKNOWLEDGMENT

One of the authors (G.B.S.S.) thanks the National Academy of Sciences (U. S. A.) for an appointment supported by the International Cooperation Administration under the Visiting Research Scientist Program.

LITERATURE CITED

(1) Boyd, G. E., Larson, Q. V., *J. Phys. Chem.* 64, 988 (1960).
(2) Moore, Fletcher L., "Liquid-liquid Extraction with High-Molecular Weight Amines," NAS-NS 3101, Office of Technical Services, Washington, 1960.
(3) Peterson, H. E., MacDuff, J. S., Hovey, M. W., *Report* 5889, United States Department of Interior, Bureau of Mines, 1961.
(4) Salaria, G. B. S., Rulfs, C. L., Elving, P. J., ANAL. CHEM. 35, 979 (1963).
(5) Salaria, G. B. S., Rulfs, C. L., Elving, P. J., *J. Chem. Soc.* 2479 (1963).

RECEIVED for review February 8, 1963. Accepted April 10, 1963.

A Scheme for the Separation of Platinum, Palladium, Rhodium, and Iridium by Solvent Extraction

G. H. FAYE and W. R. INMAN

Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada

▶ A new scheme is described for the fractionation of solutions containing microgram or milligram quantities of platinum, palladium, rhodium, and iridium by solvent extraction procedures. The iodide complexes of platinum and palladium are extracted with tributyl phosphate, and thereby separated from rhodium and iridium. Modifications and extensions of existing methods are used for the separation of palladium from platinum and for the separation of iridium from rhodium. The addition of phosphoric acid improves the precision of the stannous chloride–hydrobromic acid method for the spectrophotometric determination of iridium.

THE METHODS THAT have been developed in these laboratories for the determination of the platinum metals (*11*, *12*) have involved the use of an anion exchange procedure (*9*) for the separation of platinum, palladium, and rhodium in sample solutions obtained subsequent to fire assay. This method is tedious, time consuming, and involves the use of large quantities of perchloric and hydrochloric acids; in addition, it does not readily permit the isolation of iridium from a solution of mixed platinum metals. Therefore, an alternative method was sought that would overcome these problems.

Various solvent extraction methods for fractionating certain binary mixtures and for separating pairs of the platinum group metals have been proposed (*4–6*, *16*), but, until recently, the literature did not reveal a solvent extraction scheme that will permit the fractionation of a solution containing platinum, palladium, rhodium, and iridium by simple batch-wise operations. After the work described in this paper had been completed, Sen Gupta and Beamish (*15*) described a solvent extraction scheme in which micro amounts of platinum, palladium, rhodium, and iridium are separated by a combination of the methods of Yoe and Kirkland (*18*), and of Tertipis and Beamish (*16*).

The present paper describes an alternative solvent extraction procedure for the isolation of the individual platinum metals from solutions containing microgram or milligram amounts of platinum, palladium, rhodium, and iridium. Platinum and palladium are separated simultaneously from rhodium and iridium by extraction of their iodide complexes with tributyl phosphate. Palladium is then separated from platinum with *p*-nitrosodimethylaniline by the method of Yoe and Kirkland (*18*), and iridium is separated from rhodium with tributyl phosphate by a modification of the method of Wilson and Jacobs (*17*).

EXPERIMENTAL

Reagents and Solutions. Equilibrated Tri-*n*-butyl Phosphate (TBP). This was prepared by shaking the purified grade of TBP (Fisher Scientific Co.) with an equal volume of 6*N* hydrochloric acid in a separatory funnel for approximately 1 minute.

Standard Platinum and Palladium Solutions. These were prepared separately by dissolving an accurately-weighed quantity of Johnson, Matthey and Co., Inc., Specpure platinum or palladium sponge in aqua regia, evaporating the solution to dryness several times with hydrochloric acid, then dissolving the residue and diluting to a known volume with 1*N* hydrochloric acid.

Standard Rhodium Solution. This was prepared by dissolving Johnson and Matthey Specpure ammonium chlororhodite in a known volume of 1*N* hydrochloric acid. The solution was standardized gravimetrically with thiobarbituric acid (*10*).

Standard Iridium Solution. This was prepared by dissolving Johnson and Matthey Specpure ammonium chloroiridate in a known volume of 1*N* hydrochloric acid. The solution was standardized gravimetrically with 2-mercaptobenzothiazole (*3*).

More dilute solutions of the above metals were prepared by diluting aliquots of the concentrated solutions to known volumes with 1*N* hydrochloric acid.

Recommended Procedure. (a) Separation of Platinum and Palladium from Rhodium and Iridium. Evaporate the sample solution, containing a mixture of the platinum metals as their chloro-complexes, to incipient dryness in the presence of a few milligrams of sodium chloride. Dissolve the salts in 10 ml. of 6*N* hydrochloric acid and transfer the resulting solution to a 60-ml. separatory funnel by washing with an additional 10-ml. portion of 6*N* hydrochloric acid. Shake the sample solution with 5 ml. of an aqueous 4% (w./v.) solution of sodium iodide and allow the mixture to stand for approximately 10 minutes. Extract the platinum and palladium iodide complexes with two separate 15-ml. portions of a 15% solution of TBP in hexane. Withdraw the aqueous phase, wash it with 10 ml. of hexane in a separate funnel, and then reserve it for the separation of rhodium and iridium as in Procedure (c).

Combine the TBP–hexane extracts and strip the mixture of platinum and palladium by shaking it with three separate 10-ml. portions of concentrated nitric acid for approximately 30 seconds each. Place the nitric acid stripping solution in a separatory funnel, dilute with an equal volume of water, and shake with 10 ml. of hexane to wash out as much TBP as possible.

If the sample solution is expected to contain 50 μg. or less of palladium, transfer it to a beaker and treat as in Procedure (b) for the separation and/or the determination of palladium. When the sample solution is expected to contain more than 50 μg. of palladium, dilute it to a known volume and remove a suitable aliquot for the separate determination of palladium. In the latter case, place both the aliquot and the remainder of the solution in separate beakers and treat as in Procedure (b).

(b) Separation and Determination of Palladium and Platinum. The following procedure is based largely on the work of Yoe and Kirkland (*18*), but because it differs in certain aspects from their procedure, it is presented in detail here.

Treat the platinum–palladium solution obtained in (a) with a few milligrams of sodium chloride and evaporate to incipient dryness. To convert platinum and palladium to their chloro complexes, add 2 to 3 ml. of 12*N* hydrochloric acid, evaporate the solution just to dryness, then repeat these operations twice. Add 2 ml. of sodium acetate–hydrochloric acid buffer solution (*14*) and approximately 10 ml. of water to the residue in the beaker. Warm the mixture gently for a few minutes and, with a rubber policeman, carefully loosen any sticky salt deposits that may be adhering to the bottom of the beaker. Cool the solution to room temperature in a cold water bath.

When palladium is to be determined (in the whole sample solution or aliquot thereof), add 1 ml. of a 0.5% alcoholic solution of *p*-nitrosodimethylaniline, 15 ml. of 95% ethyl alcohol, and dilute the solution to 50 ml. with water. Measure the absorbance of the solution at 525 mμ according to the method of Yoe and Kirkland (*18*), and then determine the palladium content of the sample by reference to a calibration curve prepared from data obtained from standard palladium solutions that have been taken through the TBP extraction procedure. Combine that portion of the solution, taken for spectrophotometric measurements, with the remainder of the solution and transfer the whole to a 60-ml. separatory funnel and reserve for the separation of palladium from platinum. When the sample contains 50 μg. or more of palladium, and an aliquot has been taken from it for the separate determination of palladium, add 2 ml. of the *p*-nitrosodimethylaniline reagent, 15 ml. of ethyl alcohol, and transfer the mixture to a 60-ml. separatory funnel.

Extract the palladium–*p*-nitrosodimethylaniline complex with two or three separate 10- to 15-ml. portions of chloroform. If milligram amounts of palladium are to be separated, add an additional 1 to 2 ml. of *p*-nitrosodimethylaniline reagent and continue the extraction with further portions of chloroform until the aqueous phase is light yellow to colorless.

Filter the aqueous phase (or aliquot thereof) through a Whatman No. 31 paper into a 400-ml. beaker, add approximately 2 ml. of concentrated sulfuric acid and approximately 5 ml. of concentrated perchloric acid, evaporate the solution to fumes of sulfur trioxide and then cool to room temperature. Boil the sample with 12*N* hydrochloric acid to convert platinum to the chloro-complex and then determine the platinum content spectrophotometrically by the method of Ayres and Meyer (*2*) or by the procedure of Faye and Inman (*11*).

(c) The Separation of Iridium from Rhodium. Transfer the rhodium–iridium fraction obtained in (a) to a 250-ml. beaker, evaporate nearly to dryness, and treat with a few drops of concentrated nitric acid to destroy iodides. Convert the rhodium and iridium to their chloro-complex by the repeated addition and evaporation of 2- to 3-ml. portions of 12*N* hydrochloric acid. Take up the final residue of salts with 5 ml. of 6*N* hydrochloric acid and wash the resultant solution into a 60-ml. separatory funnel with an additional 5 ml. of 6*N* hydrochloric acid. Add 5 ml. of equilibrated TBP and 5 ml. of hexane and shake the funnel and contents for 1 minute. Transfer the lower aqueous phase to a second funnel and repeat the extraction step. Drain the aqueous phase into a clean separatory funnel, wash with approximately 10 ml. of hexane, and reserve for the determination of rhodium by the stannous bromide method of Berman and Ironside (*7*). Combine the two TBP–hexane extracts in a separatory funnel and strip the mixture of iridium by shaking it with three separate 15-ml. portions of 1:9 hydrobromic acid. The stripping solution is then analyzed for iridium by Procedure (d).

(d) Determination of Iridium. Transfer the hydrobromic acid stripping solution from (c) to a 250-ml. beaker and evaporate it to dryness in the presence of a few milligrams of sodium chloride. Add 7 ml. of concentrated hydrobromic acid (which should not be colored), cover the beaker with a watchglass, and boil the solution until it has evaporated to 2.0 to 2.5 ml. (as judged visually). Transfer the solution to a 25-ml. volumetric flask by washing with 3 ml. of concentrated hydrobromic acid and 7 ml. of 25% (v./v.) phosphoric acid. Place the flask in a boiling water bath and, after 10 minutes, add 5 ml. of stannous chloride reagent as recommended by Berman and McBryde (*8*). Exactly 2 minutes after reagent addition, remove the flask and cool to room temperature in a cold water bath. Dilute the solution to the mark and measure the absorbance of the iridium complex at 402 mμ (*8*).

Determine the iridium content of the sample by reference to a calibration curve prepared from data obtained from standard iridium solutions that have been taken through the entire extraction procedure for the separation of iridium from rhodium.

RESULTS AND DISCUSSION

Extraction of Iodide Complexes of Platinum and Palladium with TBP. Yoe and Kirkland (*18*) developed a method for the simultaneous separation of submilligram quantities of platinum and palladium from other platinum group metals in which the iodide complexes of platinum and palladium are reacted with diethyldithiocarbamate and the resultant products are extracted into chloroform.

The present authors considered the possibility that rhodium and iridium do not form iodide complexes readily in a highly acid solution at room temperature, and that the iodide complexes of platinum and palladium [presumably $[PdI_4]^{-2}$ (*13*) and $[PtI_4]^{-2}$ (*1*)] might be amenable to separation from rhodium and iridium by extraction with a suitable solvent.

A second possibility for such a separation exists if iridium and rhodium remain as their chloro-complexes and iridium(IV) is reduced to iridium(III)

by the iodide medium, for it is known that the chloro-complexes of iridium (III) and rhodium are not extracted appreciably by TBP.

Experiments performed to determine the feasibility of this approach showed that at least 5 mg. of platinum or palladium, as the iodide complex, can be completely extracted from a solution that is 4.7*M* in hydrochloric acid with one 15-ml. portion of a 15% solution of TBP in hexane. In each of these experiments, the aqueous phase, after extraction, was analyzed by a suitable spectrophotometric method and the platinum metal under consideration was not detected.

Separate experiments with rhodium or iridium showed that, under conditions similar to those above, the extent of extraction of these elements was negligible.

Tributyl phosphate was chosen for use in the present investigation because it is capable of extracting the chloro-complexes of certain platinum metals (*5*, *17*) and therefore was considered to be a likely solvent for the iodo-complexes. A 15% solution of TBP in hexane was employed to lower the viscosity of the extractant and thus permit a cleaner separation of the liquid phases.

Recovery of Platinum and Palladium from TBP Extract. In the proposed extraction scheme, platinum and palladium had to be recovered from the organic phase prior to their separation by the steps described in Procedure (b). For this purpose, mixtures of 12*N* hydrochloric acid and 30% hydrogen peroxide, and also nitric acid solutions of various concentrations, were tested; however, only concentrated nitric acid (about 16*N*) proved to be satisfactory for the complete stripping of platinum and palladium from the extract.

Separation and Recovery of Iridium. Wilson and Jacobs (*17*) reported a method for the separation of iridium from rhodium by extraction with tributyl phosphate. These workers were concerned only with the isolation and determination of rhodium, for they discarded the iridium–TBP extract after the separation had been effected and gave no data to show the completeness of the extraction of iridium.

To determine the extractability of iridium with TBP, experiments were performed in which various known amounts of iridium stock solution were each evaporated to dryness in the presence of a few milligrams of sodium chloride and treated with 3 to 4 ml. of a 1:1 mixture of 12*N* hydrochloric acid and 30% hydrogen peroxide, to ensure that all the iridium was in the quadrivalent state. After evaporating to dryness and taking up in 6*N* hydrochloric acid, each sample was taken through the double batchwise extraction step with TBP according to Procedure (c). Because of the comparatively large quantities of iridium taken in these tests, the extent of extraction was determined by difference after analyzing the aqueous phase for unextracted iridium by Procedure (d). The results of these experiments are given in Table I.

Table I. Extractability of Iridium with TBP

Iridium taken, μg.	Iridium found, μg. (final raffinate)	Extraction, % (difference)
212	8	96.7
530	21	96.0
1060	18	98.3
1060	33	96.9
1060	28	97.4
5300	155	97.1
	Average	97.1

The results given in Table I show that at least 5 mg. of iridium can be extracted from a 6*N* hydrochloric acid solution with two separate 10-ml. portions of a 1:1 mixture of TBP and hexane with an average recovery of 97%.

In two subsequent experiments with 1060 μg. of iridium, three batch-wise extractions resulted in total recoveries of 99.1 and 99.2%, respectively.

Experiments showed that iridium can be readily recovered from the TBP extract by back-extraction with dilute aqueous solutions of hydrobromic, hydrochloric, or perchloric acids. A 1:9 aqueous solution of hydrobromic acid was chosen as the stripping agent in the proposed scheme of separation and analysis, because iridium is subsequently determined spectrophotometrically in a hydrobromic acid medium by a modification of the method of Berman and McBryde (*8*).

Determination of Iridium. The stannous chloride–hydrobromic acid method of Berman and McBryde (*8*) for the determination of iridium was chosen for use in the present work because of its comparatively high sensitivity. However, in early tests with standard iridium solutions, this method gave erratic results. Similar difficulty with this procedure has been reported by Tertipis and Beamish (*16*). Subsequent experiments in this laboratory showed that the addition of phosphoric acid to the iridium–hydrobromic acid system prior to reagent addition, gave highly reproducible results under the conditions described in Procedure (d). A satisfactory explanation for the stabilizing role of phosphoric acid cannot be given at the present time.

Table II. Separation of Platinum, Palladium, Rhodium, and Iridium

Taken, μg.				Found, μg.			
Palladium	Platinum	Rhodium	Iridium	Palladium	Platinum	Rhodium	Iridium
500	21	21	21	500	21	23	19
50	309	21	21	50	319	22	20
50	41	11	11	52	43	11	12
50	41	214	21	50	42	210	21
50	41	21	318	50	40	21	325
25	21	255	318	24	22	266	320
567	500	510	530	555	490	511	515
1134	1000	510	1060	1120	1025	497	1044
1701	2000	510	2120	1715	1990	507	2125

When 100 μg. or more of an individual platinum metal was to be determined, aliquots were taken from fractions for analysis.

APPLICATION OF PROPOSED METHOD

A number of synthetic mixtures, each containing various known amounts of platinum, palladium, rhodium, and iridium, were prepared from the stock solution of the respective platinum metals. Each sample solution was evaporated to dryness in the presence of a few milligrams of sodium chloride, treated with a mixture of 12*N* hydrochloric acid and 30% hydrogen peroxide, and again evaporated to dryness. The residue of salts was then treated according to the Recommended Procedure for the separation and determination of the individual platinum metals. The results obtained in these experiments are given in Table II and show that the proposed scheme is suitable for the separation of both microgram and milligram quantities of platinum, palladium, rhodium, and iridium, and also that it is applicable to mixtures in which the ratio of one platinum metal to others is comparatively high.

LITERATURE CITED

(1) Ardagh, E. G. R., Seaborne, F. S., Grant, N. S., *Can. Metals* **8**, 117, 140 (1924).
(2) Ayres, G. H., Meyer, A. S., ANAL. CHEM. **23**, 299 (1951).
(3) Barefoot, R. R., McDonnell, W. J., Beamish, F. E., *Ibid.* p. 514.
(4) Berg, E. W., Lau, E. Y., *Anal. Chim. Acta* **27**, 248 (1962).
(5) Berg, E. W., Senn, W. L., Jr., *Ibid.*, **19**, 12 (1958).
(6) *Ibid.*, p. 109.

(7) Berman, S. S., Ironside, R., *Can. J. Chem.* **36**, 1151 (1958).
(8) Berman, S. S., McBryde, W. A. E. *Analyst* **81**, 566 (1956).
(9) Berman, S. S., McBryde, W. A. E., *Can. J. Chem.* **36**, 835 (1958).
(10) Currah, J. E., McBryde, W. A. E., Cruikshank, A. J., Beamish, F. E., IND. ENG. CHEM., ANAL. ED. **18**, 120 (1946).
(11) Faye, G. H., Inman, W. R., *Ibid.*, **33**, 278 (1961).
(12) *Ibid.*, **34**, 972 (1962).
(13) Fraser, J. G., Beamish, F. E., McBryde, W. A. E., *Ibid.*, **26**, 495 (1954).
(14) Kirkland, J. J., Yoe, J. H., *Ibid.*, p. 1340.
(15) Sen Gupta, J. G., Beamish, F. E., *Ibid.*, **34**, 1761 (1962).
(16) Tertipis, G. G., Beamish, F. E., *Ibid.*, p. 623.
(17) Wilson, R. B., Jacobs, W. D., *Ibid.*, **33**, 1650 (1961).
(18) Yoe, J. H., Kirkland, J. J., *Ibid.*, **26**, 1335 (1954).

RECEIVED for review February 18, 1963. Accepted April 8, 1963.

Behavior of Dialkyl Phosphorodithioic Acids in Liquid Extraction Systems

RAQUEL H. ZUCAL[1] and JOHN A. DEAN
Department of Chemistry, University of Tennessee, Knoxville, Tenn.
THOMAS H. HANDLEY
Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

▶ **The solubility and acidity of the diethyl, diisopropyl, di-*n*-butyl, and diisobutyl esters of phosphorodithioic acid in water and the distribution of each between CCl_4, methyl isobutyl ketone, or *n*-amyl acetate and HCl-NaCl solutions have been studied. From the data, the acid dissociation constants and the partition coefficients were calculated. No evidence was found for dimerization of dialkyl phosphorodithioic acids in the organic phase. These constants are discussed, together with data for the dialkyl phosphates. The acid dissociation constant is somewhat larger and the partition coefficient is much larger when comparing di-*n*-butyl phosphorodithioic acid with di-*n*-butyl phosphate.**

DIALKYL phosphorodithioic acids have been screened in acid media for their selectivity in extraction of metal ions (*7*), but little is known about extractants which contain thiono and thiolo phosphorus groups. Hence, the principal objective of this investigation was to establish the general behavior of several individual esters of this class of reagents. The use of liquid-liquid partition to investigate the equilibria of dialkylphosphorodithioic acids in solution seemed most applicable among methods which have been employed to study similar equilibria in view of the strength of these acids and the ultimate employment of the information to metal extraction systems.

EXPERIMENTAL

Special Reagents. Dialkyl phosphorodithioic acids. Methods for preparation and purification have been described, and commercial sources of the reagents listed (*7*).

Methyl isobutyl ketone, technical grade, was distilled before use.

Apparatus. Extractions were performed with a Burrell wrist-action shaker. pH measurements were made with a Beckman Model G pH meter which had been calibrated with a phthalate buffer (pH = 4.01 at 25° C.) and checked against a 0.1*N* HCl buffer (pH = 1.10) which contained an appropriate quantity of NaCl to adjust the ionic strength.

Titrations were performed with microsyringe pipets, 0.5- and 1.0-ml. capacity.

Procedure. Equal volumes, 5 ml., of both phases were contacted for a period of 2 hours at 25° C. Phase separation was assisted by centrifugation at 2000 r.p.m. for 10 minutes. The acid concentration in the aqueous phase was determined from a pH measurement or, when $[H^+] > 0.1M$, by an alkalimetric titration. An extractive two-phase method was employed with the organic phase. The concentration of phosphorodithioic acid was determined by an iodometric titration (*3*, *4*).

The change in volume due to mutual solubility of the solvents can be neglected for the system CCl_4-water and, although it is about 5% for methyl isobutyl ketone–water and *n*-amyl acetate–water, corrections were not attempted.

Reagent Solubility in Aqueous Media. The solubility of di-*n*-butyl phosphorodithioic acid as a function of HCl or NaCl concentration was obtained by saturating the aqueous phase with the pure reagent during a shaking period of 1 hour at 30° C. Results are shown in Figure 1. The solubility of the diisobutyl ester was determined also in HCl medium; results superimposed essentially on the curve for the di-*n*-butyl ester.

Dependency of Distribution Ratio on Concentration of Reagent in Organic Phase. Two methods were suggested by Dyrssen (*5*) to establish whether dimerization of the reagent occurred in the organic phase and, incidentally, to determine the partition coefficient, $P_r = [HR]_o/[HR]$ of the reagent between the aqueous and organic phases when the acid dissociation constant is known. The subscript *o* signifies the organic phase.

In one case, the hydrogen ion concentration established by the reagent distributing between an organic solvent and an aqueous solution of a univalent salt of a strong acid is plotted as a function of reagent concentration in the organic phase, C_{org}. For such a system,

$$C_{org} = 2\,K_2\,(P_r/K_a)^2([H^+][R^-])^2 + (P_r/K_a)[H^+][R^-]$$

where K_2 is the dimerization constant of the reagent in the organic phase and K_a is the acid dissociation constant in water saturated with the organic solvent. A plot of log C_{org} *vs.* log $[H^+][R^-]$ is shown in Figure 2 for solutions of di-*n*-butyl phosphorodithioic acid shaken with an equal volume of 1*M* NaCl. For each of the organic solvent–water systems the points fell reasonably close to the straight line drawn with a slope equal to one although considerable scatter prevailed. A slope of one implies that the reagent exists only as a monomer in the organic phase and the term involving the dimerization constant may be neglected. Subsequent data will lend further support.

In the second case, the distribution ratio, *D*, of the reagent between the particular organic solvent and an aqueous solution of HCl was studied as a function of total reagent concentration. For such a system,

$$D = 2\,K_2\,(P_r/\phi)^2\,C_{aq} + P_r/\phi$$

where $\phi = 1 + K_a/[H^+]$. On double logarithmic coordinates, a plot of *D vs.* the equilibrium concentration of reagent in the aqueous phase, C_{aq}, for a series of fixed HCl concentrations, gives a series of horizontal lines as shown

[1] Present address, Comision Nacional Energia Atomica, Buenos Aires, Argentina.

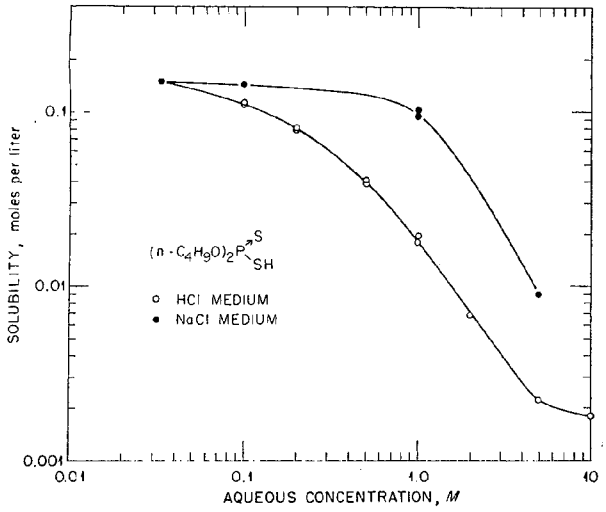


Figure 1. Solubility of di-*n*-butyl phosphorodithioic acid in HCl and NaCl media at 30° C.

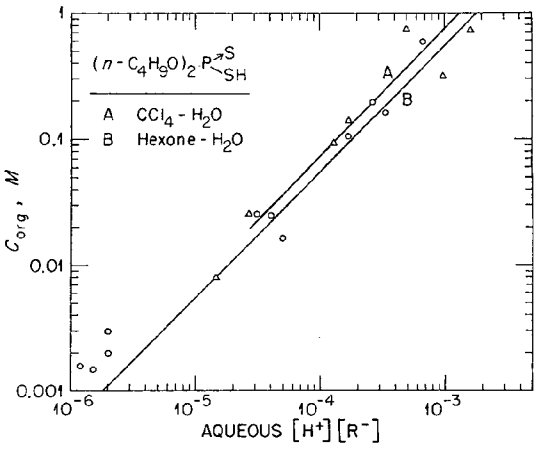


Figure 2. Distribution of di-*n*-butyl phosphorodithioic acid between an organic solvent and an aqueous solution 1.0M in NaCl

Solvent pairs: A, CCl_4–water; B, methyl isobutyl ketone–water

in Figure 3. The distribution ratio is independent of C_{aq} which once again indicates that no perceptible dimerization occurs in the organic phase for the di-*n*-butyl ester.

Acid Dissociation Constant and Partition Coefficient. For systems in which only one associated molecular species is formed and partitions, and no higher species are formed in either phase, the equilibria involved are the acid dissociation constant and the partition coefficient of the molecular species. The distribution ratio is given by:

$$D = [HR]_o([HR] + [R^-])^{-1}$$

and by appropriate substitution:

$$1/D = 1/P_r + K_a/P_r[H^+] \text{ or}$$
$$D = P_r(1 + K_a/[H^+])^{-1}$$

A plot of $1/D$ *vs.* $1/[H^+]$ is shown in Figure 4 for the diethyl ester. For the longer chain esters the intercepts become very small values and involve a long graphical extrapolation, an indication that the partition coefficients are large numbers.

On double logarithmic coordinates, a plot of D *vs.* $[H^+]$ provided two limiting conditions. On the plateau, $D = P_r$. Extrapolation of the two linear branches of the curve to their intersection gives K_a. In addition, the ratio P_r/K_a is given by $1/[H^+]$ when $D = 1$ and $P_r >> 1$. Data for the diethyl, diisopropyl, di-*n*-butyl, and diisobutyl esters are shown in Figure 5 for the system, CCl_4–water. Data for the di-*n*-butyl ester in two additional solvent systems are shown in Figure 6. The solid line drawn through each set of points represents the distribution ratio with the values of K_a and P_r from Table II inserted in the above expression.

Influence of Salt Concentration. Certain peculiarities observed in metal extraction systems when high concentrations of electrolytes were present in weakly acid solutions prompted a study of the influence of NaCl upon the distribution ratio of the di-*n*-butyl phosphorodithioic acid. Results are shown in Table I for the system CCl_4–0.05*M* HCl. Comparable data were obtained with the methyl isobutyl ketone–aqueous HCl system. Low concentrations of sodium chloride, 0.2*M*, depressed significantly the distribution ratio of the reagent for all reagent concentrations, whereas higher concentrations increased markedly the

Table I. Influence of Electrolyte Concentration on Distribution Ratio of Di-*n*-butyl Phosphorodithioic Acid

[HR] total, *M*	[HCl], *M*	[NaCl], *M*	Distribution ratio
0.90	0.05	...	35
	0.05	0.2	22
	0.05	2.0	120
0.20	0.05	...	27
	0.05	0.2	9
	0.05	2.0	85
0.045	0.05	...	18
	0.05	0.2	4
	0.05	2.0	73
0.0052	0.05	...	10
	0.05	0.2	0.9
	0.05	2.0	58
0.00064	0.05	...	28
	0.05	0.2	0.5
	0.05	2.0	100
0.172	None	1.0	14
	None	2.0	21
	None	5.0	94

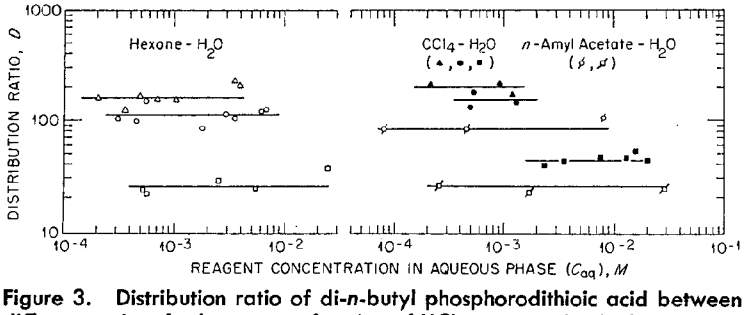


Figure 3. Distribution ratio of di-*n*-butyl phosphorodithioic acid between different pairs of solvents as a function of HCl concentration in the aqueous phase

Triangles, 1.0M HCl; circles, 0.5M HCl; squares, 0.1M HCl

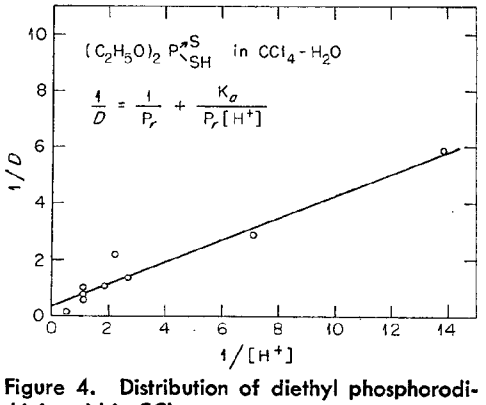


Figure 4. Distribution of diethyl phosphorodithioic acid in CCl_4–water system

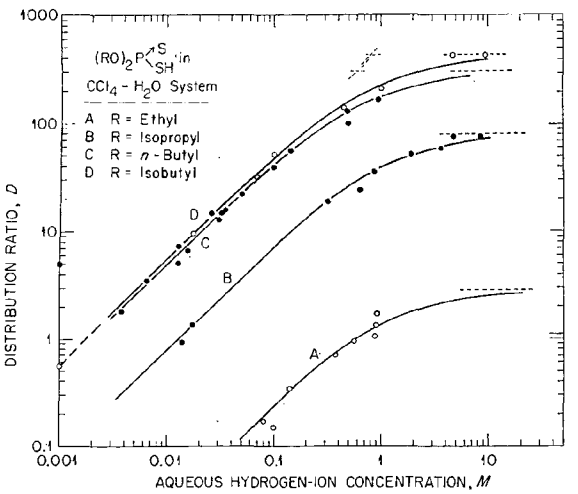


Figure 5. Distribution ratio of various dialkyl phosphorodithioic acids between CCl_4 and water as a function of hydrogen ion concentration in the aqueous phase

Curve A, diethyl ester; curve B, diisopropyl ester; curve C, di-n-butyl ester; curve D, diisobutyl ester

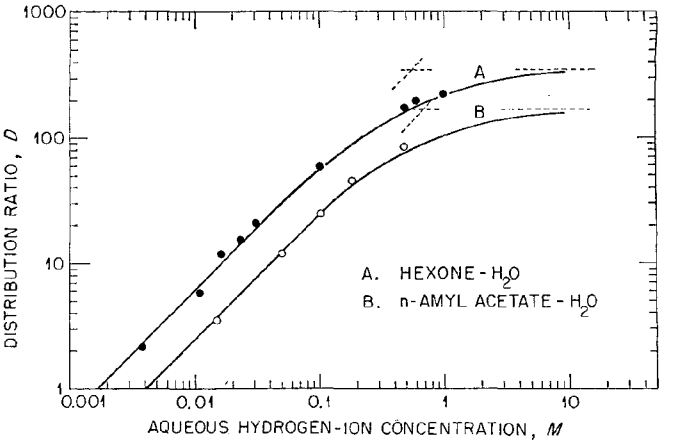


Figure 6. Distribution ratio of di-n-butyl phosphorodithioic acid between solvents as a function of hydrogen-ion concentration in aqueous phase

Curve A, methyl isobutyl ketone-water; curve B, n-amyl acetate-water

distribution ratio. As the reagent concentration decreased, the effect of increased salt concentration became more marked. Results would indicate extensive solvation of the reagent by water molecules in the aqueous phase and, in fact, Bode and Arnswald (*3*) reported a stable trihydrate sodium salt.

DISCUSSION

The dialkyl phosphorodithioic acids are quite strong acids. Because of this fact, it was impossible to maintain a constant, but low, ionic strength in the aqueous phase. At high concentrations of hydrogen ion the experimental points showed some scatter. However, the use of three different solvent systems provided a check upon the experimental value of the acid dissociation constant. From the data shown in Figures 2 through 6, values for K_a and P_r were selected which provided the most coherent fit with the experimental data. These values are collected in Table II. Because we are dealing with two phases at equilibrium, the values of the acid dissociation constants refer to an aqueous phase which has been saturated with an organic solvent; similarly, the partition coefficient of the reagent refers to the ratio of the concentration of HR in an organic phase saturated with an aqueous phase to the concentration of HR in an aqueous phase saturated with an organic phase. This stipulation must be borne in mind when comparing values obtained in different pairs of solvent. The more accurate measurements of the distribution ratio are naturally those for which D equals, or is not far removed from, unity. Thus, values of $D = 1$ (denoted $pH_{1/2}$ in metal extraction systems) are more readily determinable than the individual values of P_r or K_a to which it is related by the expression:

$$pH_{1/2} = pK_a + \log P_r$$

Fortunately, it is the ratio P_r/K_a which is actually required in expressions dealing with metal extraction systems.

Perusal of Table II indicates only a small change in the acid dissociation constant among the several dialkyl esters, but a very large change in the partition coefficients. Each increases in the order: diethyl < diisopropyl < di-n-butyl < diisobutyl. From the limited number of esters studied, it appears that chain branching among isomers brings about an increase in the value of the partition coefficient and the acid dissociation constant. Among the solvent pairs employed, CCl_4–water and methyl isobutyl ketone–water behaved alike; but in *n*-amyl acetate–water the reagent shows a slightly smaller value for the partition coefficient.

The dialkyl phosphorodithioic acids are somewhat stronger than are the dialkyl phosphates. Dyrssen (*5*) reported $pK_a = 1.00$ for di-*n*-butyl phosphate as compared with 0.22 for the dithioic acid ester. On comparing the partition coefficients for the two classes of reagents, wherein Dyrssen and Liem (*6*) reported for the dibutyl phosphate a value $\log P_r = 0.34$ in $CHCl_3$ and $\log P_r = 1.36$ in methyl isobutyl ketone, the partition coefficients for the dithioic acids are an order of magnitude larger, a major difference between the two classes of reagents.

No evidence for dimerization in the organic phase was detected in this study, a second major difference. Hydrogen bonding involving the thiol group has been reported from infrared studies in concentrated solutions of dithioic acids in CCl_4 (*1*). However, frequencies assigned to the P → S group remain constant only if the immediate environment of the phosphorus atom or thiono group does not change. Dyrssen and Liem (*6*) pointed out that an increase in the partition coefficient seems to be combined with a decrease in the dimerization constant for di-*n*-butyl phosphate. Many solvents conform to the relationship, $K_2P_r^2 = 5 \times 10^3$. If true here, $K_2 \leq 0.08$ (methyl isobutyl ketone) and ≤ 0.05 (CCl_4). If association does occur, it must be slight in the dilute solutions employed. Furthermore, the degree of association of dialkyl phosphates has been found to exceed that of dialkyl

Table II. Characteristic Constants for Dialkyl Phosphorodithioic Acids

(Ionic strength = 1.0 except when $[H^+] > 1M$)

Alkyl group	Solvent system	$pH_{1/2}$	$\log P_r$	pK_a
Ethyl	CCl_4-water	0.35	0.45	−0.10
Isopropyl	CCl_4-water	1.89	1.90	0.00
n-Butyl	CCl_4-water	2.70	2.52	0.22
	Methyl iso butyl ketone–water	2.77	2.54	0.25
	n-Amyl Acetate– water	2.40	2.23	0.18
Isobutyl	CCl_4-water	2.74	2.63	0.10

phosphorothioates (*8*). According to cryoscopic data (*2, 9*), the molecular weight of diethyl and di-*n*-butyl phosphorodithioic acids in benzene does not depend on concentration, in the range permitted by the method, and agrees with the theoretical value of the monomer.

ACKNOWLEDGMENT

The authors thank James A. Durbin for his assistance.

LITERATURE CITED

(1) Allen, G., Calclough, R. O., *J. Chem. Soc.* 3912 (1957).
(2) Baldwin, W. H., Higgins, C. E., U. S. Atomic Energy Comm., *Rept.* **ORNL-3320,** pp. 54–5 (1962).
(3) Bode, H., Arnswald, W., *Z. Anal. Chem.* **185,** 99 (1962).
(4) Busev, A. I., Ivanyutin, M. I., *J. Anal. Chem. (Russian)* **11,** 559 (1956).
(5) Dyrssen, D., *Acta Chem. Scand.* **11,** 1771 (1957).
(6) Dyrssen, D., Liem, D. H., *Ibid.*, **14,** 1091 (1960).
(7) Handley, T. H., Dean, J. A., ANAL. CHEM. **34,** 1312 (1962).
(8) Popov, E. M., Thesis, Moscow Univ., 1958.
(9) Popov, E. M., Kabachnik, M. I., Mayants, L. S., *Russian Chem. Revs.* 362 (1961).

RECEIVED for review November 16, 1962. Accepted April 8, 1963. Presented at Southeastern Regional Meeting, ACS, Gatlinburg, Tenn., November 1962. Miss R. H. Zucal is indebted to the International Atomic Energy agency for the award of a fellowship.

Di-*n*-butyl Phosphorothioic Acid as an Extractant for Metal Ions

THOMAS H. HANDLEY

Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

▶ Di-*n*-butyl phosphorothioic acid (5 w./v. % in CCl_4) was evaluated as a reagent for extracting metal ions from aqueous solutions of HCl or H_2SO_4. The results are presented in two periodic table type charts as plots of log distribution ratio (*D*) vs. log $[H^+]$. Of 32 metal ions studied, 18 extracted in significant amounts. In general, metal ions that form insoluble sulfides have the highest *D*. The relative order of extraction of 11 metal di-*n*-butyl phosphorothioate complexes was determined. The effect of di-*n*-butyl phosphorothioic acid concentration on the *D* values for Ag^+, Hg^{+2}, Zn^{+2}, and In^{+3} was investigated. The influence of various organic solvents on the *D* values for Hg^{+2} and Zn^{+2} was studied. The limits of extraction for Ag^+, Hg^{+2}, and Pd^{+2} were in the parts per billion range. The nature of the zinc di-*n*-butyl phosphorothioate complex was investigated.

THE dialkyl phosphoric acids, $(RO)_2P(O)OH$, have been investigated extensively and used widely as solvent extraction reagents (*5, 6, 15, 16*). More recently, the dialkyl phosphorodithioic acids, $(RO)_2P(S)SH$, have been found to be useful solvent extraction reagents (*2, 3, 10*). The dialkyl phosphorothioic acids, $(RO)_2P(O)SH$, appear to occupy a position intermediate between the dialkyl phosphorodithioic and the dialkyl phosphoric acids with respect to certain properties (*13, 14*). The study of such a mixed acid that contains both an oxygen and a sulfur atom attached to the phosphorus atom is of interest. Although sulfur and oxygen atoms bear a formal resemblance to each other, their tendencies for complex formation differ greatly.

The dialkyl phosphorothioic acids exhibit tautomeric equilibrium (*12, 13*) as follows:

$$\underset{\text{Thiono}}{(RO)_2\overset{\overset{S}{\|}}{P}-OH} \rightleftharpoons \underset{\text{Thiol}}{(RO)_2\overset{\overset{SH}{|}}{P}=O} \qquad (1)$$

Because of the similarity of the acid properties of the sulfur and the oxygen acids of phosphorus, the equilibrium does not favor either isomer. Therefore, reaction of di-*n*-butyl phosphorothioic acid with a metal ion of high electroaffinity would be expected to produce stable complexes with coordination through sulfur. Baldwin (*1*) has made infrared studies of di-*n*-butyl phosphorothioic acid and several of its complexes. He reported that in CCl_4 solution 90% of the acid is in the thiono form, whereas the silver complex exists mainly as the thiol isomer. Thus, the reaction of di-*n*-butyl phosphorothioic acid with any one of certain metal ions causes a shift of the equilibrium toward the thiol form and a transfer of the reaction center. Hydrogen bonding has been reported for di-*n*-butyl phosphorothioic acid (*9*) and is interpreted as being inter- and not intramolecular (*19*).

EXPERIMENTAL

Reagents. DI-*n*-BUTYL PHOSPHOROTHIOIC ACID, $(n\text{-}C_4H_9O)_2P(O)SH$, molecular weight, 226. This compound is not available commercially; it was prepared as follows. Equimolar quantities of di-*n*-butyl hydrogen phosphite and sulfur were reacted in benzene while an equimolar quantity of ammonia gas was bubbled into the reaction mixture during a period of approximately 1 hour (*7*). The ammonium di-*n*-butyl phosphorothioate thus formed was purified by recrystallization from a mixture of benzene and *n*-hexane. The melting point of the purified ammonium di-*n*-butyl phosphorothioate was 157–9° C. The free acid was obtained after acidification of the ammonium di-*n*-butyl phosphorothioate with aqueous mineral acid, extraction of the di-*n*-butyl phosphorothioic acid into benzene or ether, and removal of the solvent by evaporation. The free acid is a viscous liquid that has a slight odor.

It is not known whether di-*n*-butyl phosphorothioic acid is toxic; however, it should not be significantly more toxic than the dialkyl phosphorodithioic acids, which have been reported to be only slightly toxic (*17*).

Titration of a 5% solution of the acid in ethyl alcohol with a solution of sodium hydroxide showed that the acid is monobasic; the titration curve is indistinguishable from that of a strong monobasic acid.

A 5 (w./v.) % solution (0.221*M*) of di-*n*-butyl phosphorothioic acid in CCl_4 was used for the extraction studies. This solution is stable for days if kept at room temperature and away from ultraviolet radiation.

Appropriate radioactive tracers were used to determine the total concentration of each metal in each phase.

All other reagents were of reagent grade.

Instrumentation and Apparatus. A Geiger-Müller counter (G-M) was used to measure beta-emitting radioisotopes.

A gamma scintillation counter was used to measure gamma-emitting radioisotopes.

Extraction Apparatus. A 50-ml. centrifuge tube and a mechanical stirrer were used to effect all equilibrations between the aqueous and organic phases.

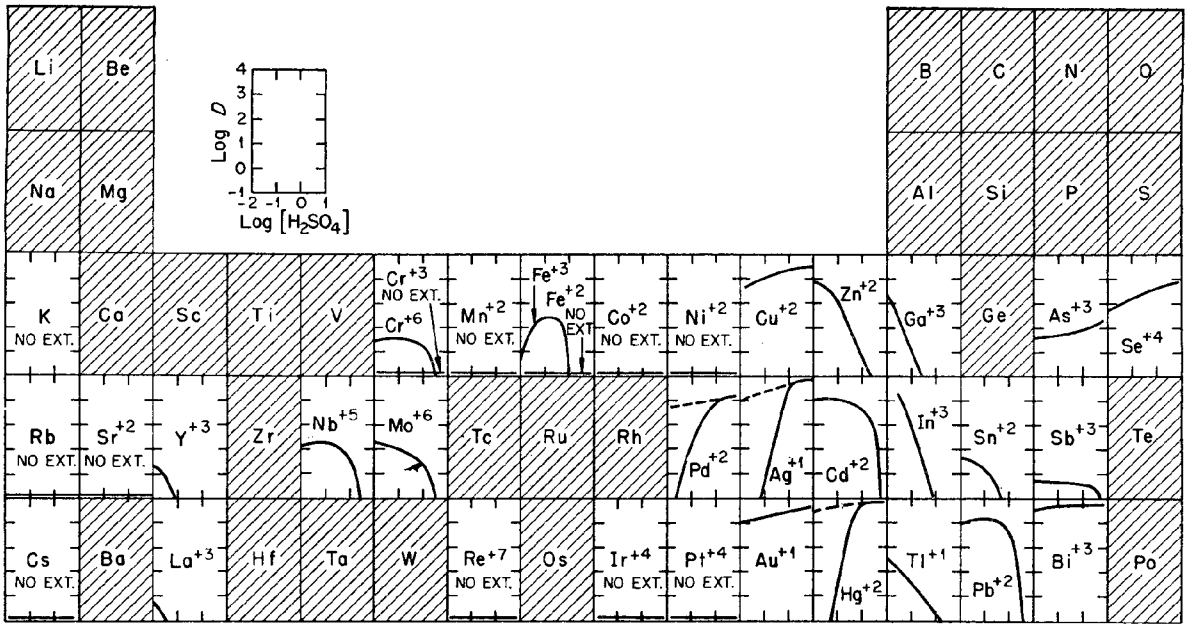


Figure 1. Extraction of metal ions from H_2SO_4 with di-*n*-butyl phosphorothioic acid

Organic phase. 0.221 *M* $(C_4H_9O)_2P(O)SH$ in CCl_4
Aqueous phase. $[H_2SO_4]$, *N* shown [metal ion], 0.5 mg./ml.
Volume of each phase, 5 ml.

Procedure. The data from which the *D* values were calculated were obtained as follows: A 5-ml. aqueous phase was prepared that contained the predetermined concentration of the selected mineral acid, the radioactive tracer of the metal ion to be tested, and the metal ion in concentration of 0.5 mg. per ml. The tracer and carrier added were always in the same oxidation state. To the aqueous phase was added 5 ml. of 5 (w./v.) % di-*n*-butyl phosphorothioic acid in CCl_4. Extractions were conducted at room temperature (27° C.) for 10-minute periods; preliminary experiments indicated that equilibration was attained in considerably less than 10 minutes. Separation of the phases was hastened by centrifugation. The concentration of total metal in each phase was determined by counting a suitable aliquot in either a gamma scintillation counter or a G-M counter, as required. The sum of the quantities of total metal in the two phases equaled the quantity added initially within the experimental error of 2 to 3%.

RESULTS AND DISCUSSION

Log-log plots of *D* *vs.* $[H^+]$ in H_2SO_4 and in HCl solutions are shown in Figures 1 and 2, respectively. The data are for single equilibrations.

For metal ions having a *D* value ≥ 10, the curves are of several general types. In one, the absolute value of the negative slope, throughout a large portion of the curve, is identical with the ionic charge of the metal ion—e.g., 2 for Zn^{+2}, and 3 for In^{+3}. For this group of ions, *D* is inversely proportional to $[H^+]^n$. At the lower $[H^+]$'s studied, however, the curves become linear, and this relationship is no longer valid because of a decrease of P, for di-*n*-butyl phosphorothioic acid and competition between its complexes and other complexes—e.g., Cl^-, OH^-, and SO_4^{-2}. In another type of curve, the group of metal ions has a high and reasonably constant *D* over the range of $[H^+]$ studied. Among the metal ions in this group are Ag^+, Cu^{+2}, Hg^{+2}, Pd^{+2}, and Bi^{+3}. From the data available, it is not possible to assign a numerical value to the dependency of *D* on $[H^+]$ for this group of ions. The *D* represented by the dashed portions of the curves is discussed below in the section on effect of $[HR]_o$ on *D*.

In the HCl system, the sudden decrease of *D* at higher $[H^+]$ can be attributed to the formation of chloro complexes, change in the activity coefficient of ions present in the aqueous phase, or a decrease in the concentration of di-*n*-butyl phosphorothioic acid in the aqueous phase. Tests with Hg^{+2} and Bi^{+3} in which $[HR]_o$ was held at slightly greater than the stoichiometric concentration (if a 2 to 1 and 3 to 1 ratio for Hg^{+2} and Bi^{+3}, respectively, are assumed) and chloride ion concentration was increased, showed a decrease in *D* with increase in chloride ion concentration. Other tests with Hg^{+2} and Bi^{+3} showed that with an aqueous phase 6*M* in LiCl twice the stoichiometric amount of di-*n*-butyl phosphorothioic acid was necessary for maximum *D*; with an aqueous phase 0.2*N* in H_2SO_4 only a slight excess over the stoichiometric amount was needed for a maximum *D*. Qualitative tests have shown that di-*n*-butyl phosphorothioate is more rapidly oxidized to the disulfide in an HCl than in an H_2SO_4 system of equal $[H^+]$. Oxidation decreases the $[HR]_o$ and can affect *D*. Qualitative tests have shown that the rate of oxidation is affected by temperature and by exposure of the system to irradiation. Therefore, high temperatures should be avoided, and solutions of di-*n*-butyl phosphorothioic acid should be kept out of direct sunlight. Lowering the temperature to 1° C. did not cause *D* to increase; however, increasing the temperature to 80° C. caused *D* to decrease significantly.

Pd^{+2} and Fe^{+3} were the only metal ions observed to have visible color reactions with di-*n*-butyl phosphorothioic acid. Examination of the organic phase by absorption spectrometry showed that the di-*n*-butyl phosphorothioate complexes of Pd^{+2} and Fe^{+3} have maximum absorbancies at 277 and 292 mμ, respectively. The complexes of Ag^+, Cu^{+2}, Zn^{+2}, Bi^{+3}, and In^{+3} with di-*n*-butyl phosphorothioic acid in CCl_4 were also studied by absorption spectrometry; they did not exhibit a maximum.

Ammonium di-*n*-butyl phosphorothioate, which is appreciably soluble in water, forms sparingly soluble crystalline precipitates with a number of heavy-metal ions, among which are Ag^+, Hg^{+2}, Pd^{+2}, and Bi^{+3}. The evaluation of di-*n*-butyl phosphoro-

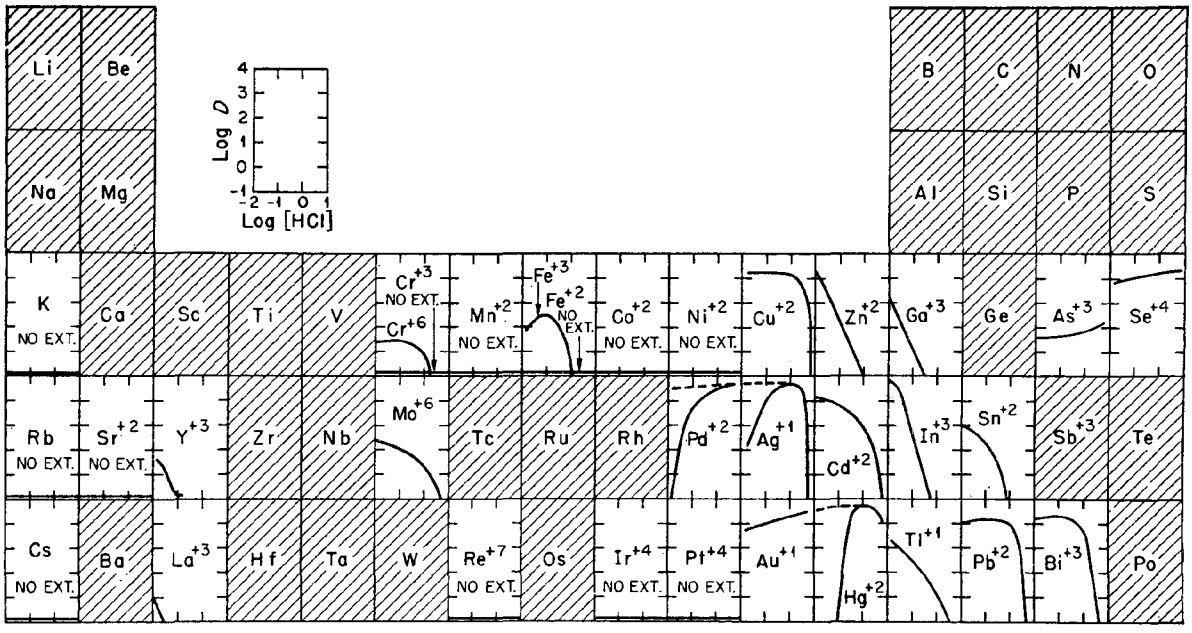


Figure 2. Extraction of metal ions from HCl with di-*n*-butyl phosphorothioic acid

Organic phase. 0.221 *M* $(C_4H_9O)_2P(O)SH$ in CCl_4
Aqueous phase. [HCl], *N* shown [metal ion], 0.5 mg./ml.
Volume of each phase, 5 ml.

thioic acid as a gravimetric reagent is beyond the intended scope of the present study and will be deferred.

The partition coefficient, P_r, of di-*n*-butyl phosphorothioic acid as a function of $[H^+]$ has been studied (*11*).

Effect of $[HR]_o$ on *D*. The effect of $[HR]_o$ on *D* at fixed $[H^+]$ for Zn^{+2} and In^{+3} is shown in Figure 3. Since di-*n*-butyl phosphorothioic acid was present in large excess over the metal ion at all times, this figure is actually a plot of *D vs.* uncombined di-*n*-butyl phosphorothioic acid. Over a wide range of $[H^+]$ and $[HR]_o$, the slope of the line for Zn^{+2} is 2; for In^{+3} the slope is 3. For Zn^{+2} and In^{+3}, the *D* value varies directly with $[HR]_o^n$. As has been shown (Figures 1 and 2), *D* for Zn^{+2} and In^{+3} varies inversely as $[H^+]^n$. For Ag^+ and Hg^{+2}, the results of a study of *D vs.* [HR] are shown in Figure 4; the [HR] was that at the beginning of the extraction. In those tests, the aqueous phase was 0.1*N* HNO_3–0.2*M* $NaNO_3$, a composition chosen to avoid complications that might result from the competition among anions. If it is assumed that the stoichiometric mole ratio of di-*n*-butyl phosphorothioic acid to metal ion is 1 to 1 for Ag^+ and 2 to 1 for Hg^{+2}, then for the initial part of the curve, which has a slope of 1.2, the metal ion is present in excess. For this portion of the curve, the amount of Ag^+ extracted is in a mole ratio of 1 to 1 with the di-*n*-butyl phosphorothioic acid added. No free di-*n*-butyl phosphorothioic acid could be detected in either phase. At the point of sudden change of slope, the total number of moles of di-*n*-butyl phosphorothioic acid is only slightly greater than the stoichiometric amount required for combination with the Ag^+.

In a study of *D vs.* $[Ag^+]$ at constant initial [HR], the reverse of this type of curve was obtained. At the intersections of the extrapolated straight-line portions of the Ag^+ curves (Figure 4), the number of moles of di-*n*-butyl phosphorothioic acid as read on the abscissa is equal to the number of moles of Ag^+ present initially. For the initial part of the curve for Hg^{+2}, which has a slope of 1.2, the mole ratio of Hg^{+2} extracted to di-*n*-butyl phosphorothioic acid added is 2 to 1. Again, no free

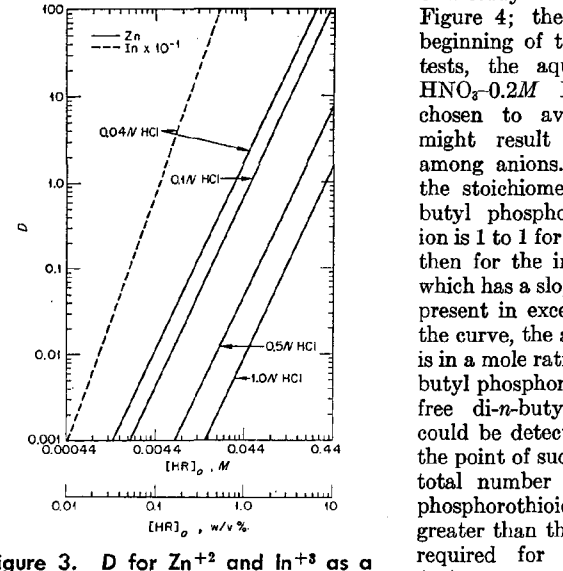


Figure 3. *D* for Zn^{+2} and In^{+3} as a function of $[HR]_o$

Organic phase. CCl_4, $[HR]_o$ as shown
Aqueous phase. $[In^{+3}]_i$, 0.1 mg./ml.
$[Zn^{+2}]_i$, 0.5 mg./ml.
Volume of each phase, 5 ml.

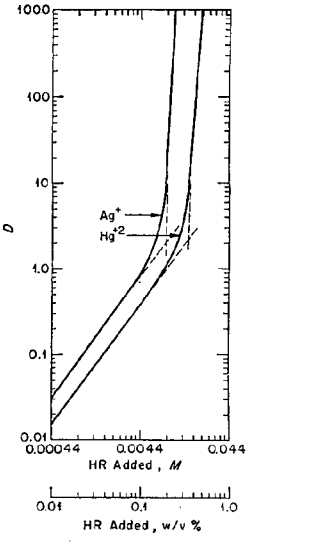


Figure 4. *D* for Ag^+ and Hg^{+2} as a function of initial [HR]

Organic phase. CCl_4, initial [HR] as shown
Aqueous phase. 0.1 N HNO_3 and 0.2*M* $NaNO_3$
$[Hg^{+2}]$, 1.5 mg./ml.
$[Ag^+]$, 1.0 mg./ml.

reagent was detected in either phase. At the intersection of the two extrapolated parts of the curve, the mole ratio of Hg^{+2} extracted to di-*n*-butyl phosphorothioic acid added is 1 to 2. The sudden change in slope (Figure 4) is not understood clearly. It may be due to the presence of polynuclear species formed by bonding. However, in a study of *D vs.* $[Ag^+]$ at constant initial [HR] the reverse of the type of curve shown in Figure 4 was obtained.

It has been suggested (*8*) that under the conditions of the extraction, for Ag^+ and Hg^{+2}, as soon as the metal complex is formed, it is extracted. In the region of incomplete extraction, an increase in [HR] will increase the amount of metal complex formed, and therefore the amount of metal ion extracted. The addition of the stoichiometric quantity of HR results in complete complexation of the metal ion. The value of *D* therefore increases rapidly to a constant value, which is the distribution coefficient of the complex. Using cryoscopic methods, Baldwin (*1*) determined that the apparent molecular weight of silver di-*n*-butyl phosphorothioate is two times the theoretical value if a 1 to 1 mole ratio is assumed. It has been shown (Figures 1 and 2) that for Ag^+ and Hg^{+2} a definite value cannot be assigned to the dependency of *D* on $[H^+]$ because of the very high experimental values of *D* within the range of $[H^+]$ tested. The same holds true for $[HR]_o$; however, it is necessary to maintain an excess of $[HR]_o$ over the stoichiometric amount for combination with the metal ion in order to obtain a maximum *D*. When competing anions are present, much more than the stoichiometric amount is necessary to obtain a maximum *D*.

At low $[H^+]$, the concentration of an electrolyte—e.g., NaCl, $NaClO_4$, Na_2SO_4—must be $\geq 0.25M$ in order to obtain a maximum *D*. The dashed lines in Figures 1 and 2 represent values of *D* when the electrolyte concentration of the aqueous phase is $\geq 0.25M$. The effect of electrolyte concentration on *D* for Hg^{+2} is shown in Table I (columns 3 and 4) when organic solvents other than CCl_4 are used—e.g., benzene, toluene, etc. It is not known why this phenomenon is peculiar to Ag^+, Hg^{+2}, and Pd^{+2}.

Since the relationship between acidity and complex stability (*4*) has been established for certain complexers, it was expected that the stability constants would not be high. However, for the di-*n*-butyl phosphorothioate complexes of Ag^+ and Hg^{+2} they have been reported to be 10.8 and 23.6, respectively (*20*).

Since di-*n*-butyl phosphorothioic acid is a reducing agent, the oxidation state of the metal ion after extraction may not always be the same as in the aqueous phase. Cr^{+6} is reduced to Cr^{+3} and Au^{+3} is reduced to Au^+; however, Au^+ is not reduced to the metal under the extraction conditions. Probably Tl^{+3} is reduced to Tl^+, since the slope of the line (Figures 1 and 2) is 1.

Relative Order of Extraction. The relative order of extraction of the metal di-*n*-butyl phosphorothioate complexes was determined by displacement of one metal ion by another.

A single chosen metal complex was obtained in an organic phase that contained no excess di-*n*-butyl phosphorothioic acid and no excess uncomplexed metal ion. An aqueous phase was prepared that was of optimum pH and contained the metal ion in excess over the stoichiometric amount required to react with the di-*n*-butyl phosphorothioic acid in the organic phase; the organic phase was a 5 (w./v.) % solution of the acid in CCl_4. The phases were equilibrated and then separated. The organic phase was washed several times with distilled water to remove any metal ion that may have been transferred to the organic phase by mechanical entrainment. To determine the relative extraction of the first chosen metal ion with respect to a second chosen metal ion, the organic phase prepared as just described was equilibrated with an aqueous phase that contained the second metal ion and that was prepared in the same way as the aqueous phase that contained the first metal ion. The data needed for determining the relative order of extraction were obtained by measuring the total concentration of each metal in each phase by radiochemical analysis. In like manner, the extraction of a third metal ion was compared with that of the second, and so on.

As a check on the order of extraction so established, di-*n*-butyl phosphorothioate complexes of Ag^+, Hg^{+2}, and Pd^{+2} were prepared by precipitation and recrystallization from organic media. An organic phase that contained known amounts of one of these complexes was used to check the order of extraction; the results agreed with the first technique described. The displacement series is:

$$Pd^{+2} > Au^{+3} > Cu^+ > Hg^{+2} > Ag^+ > Cu^{+2} > Bi^{+3} > Pb^{+2} > Cd^{+2} > In^{+3} > Zn^{+2}$$

When separations are made, the selectivity can be improved greatly if the extractant used is a metal di-*n*-butyl phosphorothioate rather than di-*n*-butyl phosphorothioic acid. Generally, the metal di-*n*-butyl phosphorothioate complexes have much greater chemical stability and, accordingly, are less subject to undesirable oxidation and hydrolysis reactions as compared with the acid. Therefore, the use of a specific metal di-*n*-butyl phosphorothioate complex as an extractant for those metal ions that are higher in the order of displacement can be of great advantage.

Effect of Solvent. The effects of different organic solvents on *D* of Hg^{+2} and Zn^{+2} are shown in Table I. The Hg^{+2} and Zn^{+2} ions were selected because each is typical of one of the groups mentioned above and because they were studied previously with the dialkyl phosphorodithioic acids (*10*). For Zn^{+2} the solvents CCl_4, *n*-hexane, and *o*-dichlorobenzene give the highest *D* under the conditions studied; however, oxygenated solvents—e.g., alcohols, acetates, and ethers—give a significantly lower *D*. For the $[H^+]$ studied, the *D* for Hg^{+2} is higher when alcohols are used as solvents than where CCl_4 is used. The small *D* found for Hg^{+2} with certain solvents—e.g., benzene, *o*-dichlorobenzene, etc.—at low $[H^+]$ agrees with results already men-

Table I. Effect of Solvent on *D* of Zn^{+2} and Hg^{+2}

Organic phase, $0.221M$ di-*n*-butyl phosphorothioic acid in solvent indicated
Aqueous phase, [HCl], as shown; $[Zn^{+2}]$ or $[Hg^{+2}]$, 0.5 mg./ml.

	D		
	Zn^{+2}	Hg^{+2}	
		HCl, *N*	
Solvent	0.03	0.05	0.5
Isoamyl alcohol	0.5	9,000	≥10,000
n-Butyl alcohol	0.7	≥10,000	≥10,000
Benzyl alcohol	0.5	2,800	≥10,000
Isoamyl acetate	0.1	430	920
Ethyl acetate	0.2	400	600
Isopropyl ether	0.1	220	290
Carbon tetrachloride	140	100	4,800
o-Dichlorobenzene	140	5	≥10,000
Chloroform	43	35	1,800
Benzene	75	6	1,600
n-Hexane	110	53	≥10,000
Toluene	68	110	≥10,000
Xylene	44	25	2,000

tioned for low electrolyte concentrations. The same phenomenon was observed when di-*n*-butyl phosphorodithioic acid was used as an extractant (*10*). The exact cause of this phenomenon is not understood clearly. It may be associated with bonding of the di-*n*-butyl phosphorothioate complex with the solvent and/or with the formation of polynuclear species.

Limits of Extraction. Essentially complete extraction of as little as 2 p.p.b. of Hg^{+2} was achieved in one equilibration between an aqueous phase 0.5*N* in mineral acid and an organic phase that was 5 (w./v.) % di-*n*-butyl phosphorothioic acid in CCl_4. The ions Ag^+ and Pd^{+2} in parts per billion concentrations were also extracted completely. The maximum amount of metal ion that can be extracted is limited by the extent of solubility of the complex in the solvent and by the initial $[HR]_o$.

Nature of Complex Formed. Figure 5 shows a plot of *D* as a function of $[HR]_o/[H^+]$ (*18*) for extraction results covering a range of $[HR]_o$ 0.06*M* to 0.44*M* and pH 0.25 to 2.5. It is clearly seen that *D* is approximately constant for a given value of $[HR]_o/[H^+]$, and over most of the range it varies directly as the second power of $[HR]_o/[H^+]$. This suggests and is consistent with ZnR_2 as being the predominant complex in the organic phase, provided the extractant is monomeric in the organic phase. The following equation represents the reaction:

$$2HR + Zn^{+2} \rightarrow ZnR_2 + 2H^+ \quad (2)$$

If dimerization occurs, this equation is no longer valid. In a study independent of solvent extraction, the zinc complex was prepared by precipitation and recrystallization from organic media. Analysis agreed with ZnR_2 as being the formula of the complex.

ACKNOWLEDGMENT

The synthesis of the di-*n*-butyl phosphorothioic acid by W. H. Baldwin is gratefully acknowledged.

LITERATURE CITED

(1) Baldwin, W. H., U. S. At. Energy Comm., Rept **ORNL-3320**, 54–5 (Oct. 5, 1962).
(2) Bode, H., Arnswald, W., *Z. Anal. Chem.* **185**, 99 (1962).
(3) *Ibid.*, p. 179.
(4) Calvin, M., Wilson, K. W., *J. Am. Chem. Soc.* **67**, 2003 (1945).
(5) Dyrssen, D., *Acta Chim. Scand.* **11**, 1277 (1957).
(6) *Ibid.*, **14**, 1100 (1960).
(7) Foss, O., *Ibid.*, **1**, 8 (1947).
(8) Freiser, H., University of Arizona, Tucson, Ariz., private communication, 1963.
(9) Gore, R. C., *Discussions Faraday Soc.* **9**, 138 (1950).
(10) Handley, T. H., Dean, J. A., ANAL. CHEM. **34**, 1312 (1962).
(11) Handley, T. H., Zucal, R. H., Dean, J. A., Southeastern Regional Meeting, ACS, Nov. 9–11, 1962, Gatlinburg, Tenn.
(12) Kabachnik, M. I., Mastryukova, T. A., *Zh. Obshch. Khim.* **25**, 1867 (1955).
(13) Kabachnik, M. I., Mastryukova, T. A., Radionova, N. P., Popor, E. M., *Ibid.*, **26**, 119 (1956).

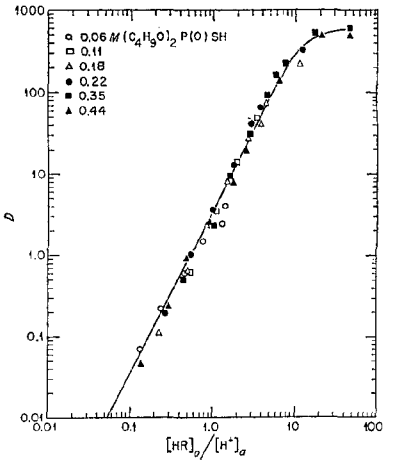


Figure 5. *D* for Zn^{+2} as a function of $[HR]_o/[H^+]$ at different $[HR]_o$

(14) Kabachnik, M. I., Opffe, S. T. Mastryukova, T. A., *Ibid.*, **25**, 653 (1955).
(15) Kimura, K., *Bull. Chem. Soc. Japan* **33**, 1038 (1960).
(16) *Ibid.*, **34**, 63 (1961).
(17) Monsanto Chemical Co., St. Louis, Mo., Tech. Data Sheet EBF-850 (1957).
(18) Rydberg, J., *Arkiv Kemi* **8**, 101 (1954).
(19) Thomas, L. C., Chittenden, R. A., Hartley, H. E. R., *Nature* **192**, 1283 (1961).
(20) Toropova, V. F., Saikina, M. K., Lietskaya, N. K., *Zh. Neorgan. Khim.* **6**, 2086 (1961).

RECEIVED for review October 22, 1962. Accepted April 22, 1963. Southeastern Regional Meeting, ACS, Gatlinburg, Tenn., November 1962.

Anion Exchange Studies in Tartrate Medium

The Separation of Manganese(II), Cobalt(II), Zinc(II), Copper (II), and Iron(III)

GERALD F. PITSTICK[1], THOMAS R. SWEET, and GERALD P. MORIE

Department of Chemistry, The Ohio State University, Columbus 10, Ohio

▶ **An anion exchange separation system is described which uses tartrate ion as an exchange medium. The data obtained from batch equilibrium studies at various pH values and tartrate concentrations were used as a basis for column separations. Radioisotopes were used for the batch equilibrium studies and for following the column separations. Rapid, clean separations were obtained for manganese(II), cobalt(II), zinc(II), copper(II), and iron (III) with Dowex 2-X8 resin in the tartrate form.**

IN RECENT YEARS many anion exchange equilibrium studies and separations have been made in which various inorganic acids, chelating agents, and organic acids have been used. Only a few of these investigations have involved separations from tartrate solutions.

Glass (*3*) separated americium and curium from 0.1*M* tartaric acid at pH 4.0. Antimony was separated from copper by passing a 2*N* HCl solution of the two metals through an anion exchange column which had been converted to the tartrate form (*1*). The antimony is retained on the column while the copper passes through. The distribution coefficients of zirconium and hafnium have been determined in tartaric acid (*4*), but no separations were reported. Gallium and aluminum also have been studied but separation was reported to be impossible (*5*).

The present communication reports the results of equilibrium studies of manganese(II), cobalt(II), zinc(II), cop-

[1] Present address: McClellan Air Force Base, Calif.

per(II), and iron(III) in tartaric acid solutions. The distribution coefficients were obtained by radioisotope measurements. From the distribution coefficients, conditions for column separations of these five metals were determined.

EXPERIMENTAL

Reagents. All reagents were reagent grade unless otherwise specified. The water used in all solutions and in resin treatment was double distilled and contained less than 1.0 p.p.m. impurity.

Tartrate solutions were made from *d*-tartaric acid. Fresh solutions were made approximately every 10 days.

Zinc(II), cobalt(II), and manganese (II) solutions were prepared as the chloride salt. Copper(II) and iron(III) solutions were prepared as the nitrate salt. Hydrochloric acid was added to the iron solution to prevent hydrolysis. Initial metal solutions were prepared 80 times more concentrated than that given as the final metal concentration. Two dilution processes were involved. The first dilution was accomplished by pipetting 0.25 ml. into a liter volumetric flask and diluting to the mark. This was transferred to a liter polyethylene storage bottle and the high specific activity radioisotope was added and thoroughly mixed. The second dilution took place when a volume of the metal solution was mixed with an equal volume of tartrate solution during the experiments.

The metal added due to the addition of the active isotope was about $10^{-7}M$ or less and could be neglected. The volume of added active solution was in all cases a small fraction of a milliliter.

The activity that was added was adjusted so that a 5-ml. portion of the final solution, after mixing with tartrate, would give an activity of 10,000 to 15,000 c.p.m. with the detector employed.

The particular isotopes used in this investigation were cobalt-60, manganese-54, iron-59, zinc-65, and copper-64. All of the active isotopes with the exception of manganese-54 were obtained from Oak Ridge National Laboratory, Oak Ridge, Tenn. The Mn^{54}, which is accelerator produced, was obtained from the Nuclear Science and Engineering Corp., Pittsburgh, Pa.

All of the isotopes, when received, were in a high state of purity with the exception of iron-59. When it arrived it was found to be contaminated with iron-55, cobalt-60, and manganese-54, and it was necessary to separate the cobalt-60 and manganese-54. Iron-55 decays by electron capture to stable manganese-55 and does not emit any measurable radiation.

Dowex 2-X8 anion exchange resins were obtained from the J. T. Baker Chemical Co., Phillipsburg, N. J. The mesh size 50–100 (0.297- to 0.149-mm. diameter beads) was selected for the batch determinations because of the ease of handling and control. Mesh size 200–400 (0.074- to 0.038-mm.) was selected for column operation because of its much faster equilibrium rates.

The resin was shaken with water and the water was quickly decanted to remove fine resin particles. This was repeated several times. It was then slurried into a $1^1/_2$-inch glass column plugged with glass wool and fitted with a stopper, Tygon tubing, and a screw clamp. The resin was first treated with approximately 3 column-volumes of $2M$ perchloric acid to remove any metallic impurities. It was washed with water and converted back to the chloride form by flushing with 5 to 8 column-volumes of $1N$ HCl. It was again washed with water and then converted to the tartrate form by treatment with $1M$ sodium tartrate. Treatment with tartrate was continued until the effluent gave a negative chloride test with silver nitrate. Finally the resin was again washed with water—about 10 column-volumes—removed from the column, and brought to constant weight in an oven at 110° C.

Apparatus. All quantitative activity measurements were made with a Radiation Instrument Development Laboratory (RIDL) Model 49-54 Scaler. The gamma detector employed was 2 inches in diameter by 2 inches thick, thallium activated, sodium iodide crystal coupled to an R.C.A. No. 6342A phototube with an external magnetic shield.

Samples were counted in 8-ml. screw cap glass vials. The sample holder consisted of a 1.8-cm. i.d. × 5.5-cm. vial holder fused to a glass jacket (similar to a 250-ml. beaker) which was fastened over the crystal. In this manner, constant geometry was maintained.

Fractions taken from the column were qualitatively analyzed on an RIDL Model 3302, 200-channel pulse height analyzer. The detector used was a 5- × 4-inch sodium iodide, thallium activated, well crystal.

A Beckman Model G pH meter equipped with an E-2 glass electrode was used for all pH measurements. Agitation of the metal–tartrate solutions with the resin was accomplished with a Burrell wrist-action shaker.

The ion exchange columns that were used were made from 8-mm. i.d. glass tubing. They were pulled to a tip so as to give a length of about 15 cm., and the tip was plugged with glass wool. A glass dropping tip was fitted with Tygon tubing and the flow was controlled with a screw clamp.

The eluent was introduced through a 125-ml. separatory funnel whose stem had been cut down to 1.5 inches. The stem of the separatory funnel was attached to the top of the column with Tygon tubing.

The columns were allowed to drip into an automatic fraction collector manufactured by Autonomos Instruments. This collector was set to automatically deliver 2-ml. fractions into 8-ml. vials.

Procedure. The distribution coefficients for the five metals as a function of pH and tartrate concentration were first determined. This was accomplished by placing about 500 ml. of the tartaric acid of the desired concentration (twice that given as the final concentration) in a 600-ml. beaker and adding small amounts of concentrated sodium hydroxide. Fifty-milliliter aliquots were removed by pipet at various pH intervals. These 50-ml. portions were placed in 150-ml. beakers and 50 ml. of active metal solution were added to each. The pH of each of these solutions was measured and was adjusted with $0.05N$ sodium hydroxide if necessary. Twenty-five milliliters were then pipetted into each of two bottles containing a weighed amount of dried resin in the tartrate form.

The solution remaining after the two portions were removed was placed in glass stoppered bottles and allowed to stand for several hours to determine if precipitation would occur. Precipitation was checked by comparing the activity of a 5-ml. portion after standing to an equal portion taken on first mixing.

The 60-ml. bottles containing the metal–tartrate solutions were placed on the shaker for a 12-hour period. After shaking, the resin was allowed to settle and the liquid was poured into 50-ml. beakers. Five milliliters were withdrawn by pipet and placed in 8-ml. vials for activity measurements. The pH of the solution was measured and recorded as the equilibrium pH. The activity of the 5-ml. portions was then measured and compared with the activity measurements of a 5-ml. portion of the original solution. The difference was a measure of the amount of metal taken up by the resin.

Twenty-five-milliliter volumes of solution and approximately 250 mg. of resin were used in all of the determinations, except where it was necessary to adjust these conditions in order to have a significant amount of metal remain in solution after equilibrium. In all cases, the molar ratio of resin to metal was maintained greater than 10 to 1 except in the case of iron, where it was necessary to reduce this ratio to approximately 6 to 1.

The distribution coefficient, K_d, is defined as

$$K_d = \frac{\text{concentration of ion in resin phase per gram of resin}}{\text{concentration of ion in soln. phase per ml. of soln.}}$$

Therefore

$$K_d = \frac{\text{c.p.m. in resin phase per gram of resin}}{\text{c.p.m. in soln. phase per ml. of soln.}}$$

Using the distribution coefficients obtained from the batch equilibrations, the conditions for a number of column separations were determined and these were tested experimentally.

In all the column separations, the column was brought to the pH and tartrate concentration at which the conditions for separation existed. Above pH 7, the best procedure was to convert the resin to the hydroxide form with $1N$ NaOH, wash with water, and then pass the tartrate solution through until the effluent pH matched the eluent

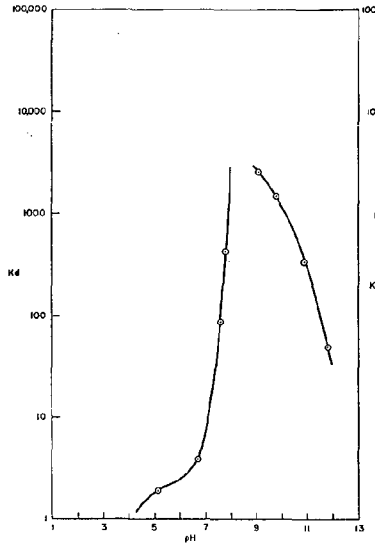


Figure 1. K_d *vs.* pH for Mn in 8.5×10^{-2}M tartrate

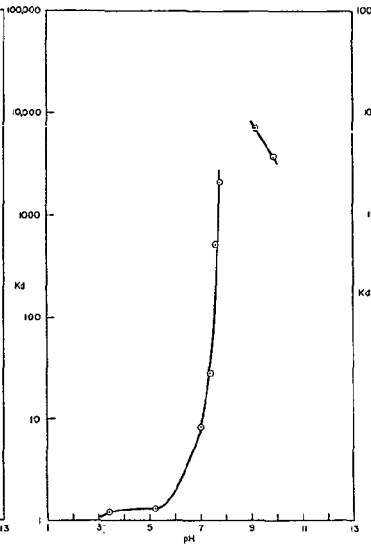


Figure 2. K_d *vs.* pH for Mn in 4.25×10^{-2}M tartrate

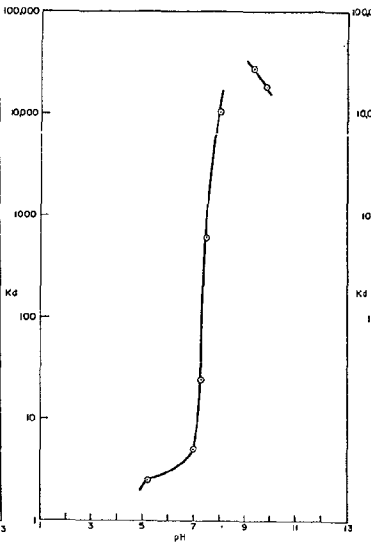


Figure 3. K_d *vs.* pH for Mn in 2.12×10^{-2}M tartrate

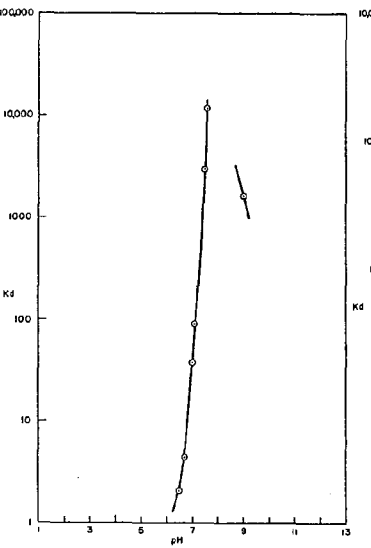


Figure 4. K_d *vs.* pH for Mn in 2.12×10^{-3}M tartrate

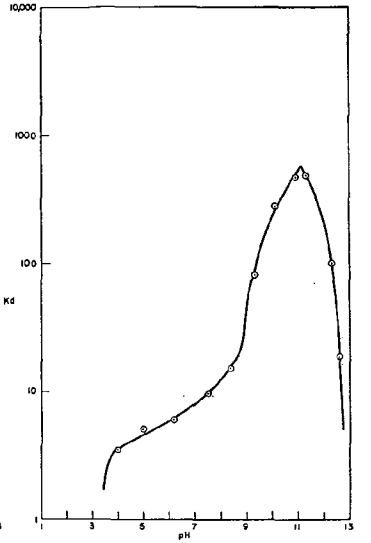


Figure 5. K_d *vs.* pH for Co in 8.5×10^{-2}M tartrate

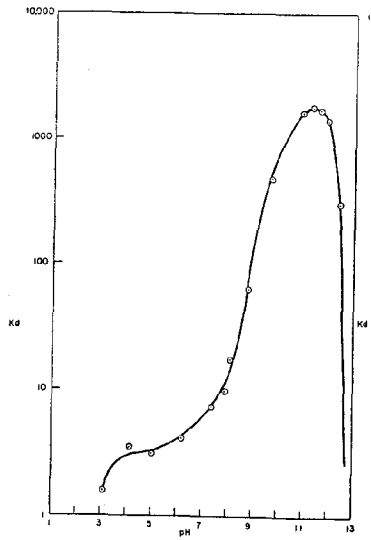


Figure 6. K_d *vs.* pH for Co in 4.25×10^{-2}M tartrate

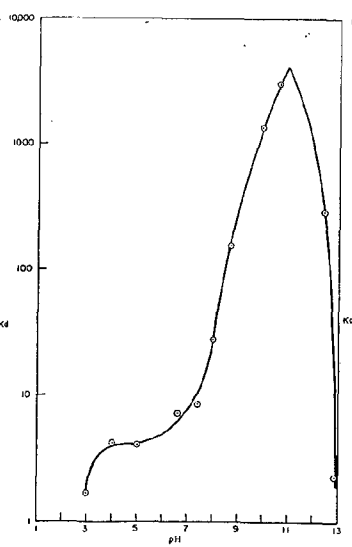


Figure 7. K_d *vs.* pH for Co in 2.12×10^{-2}M tartrate

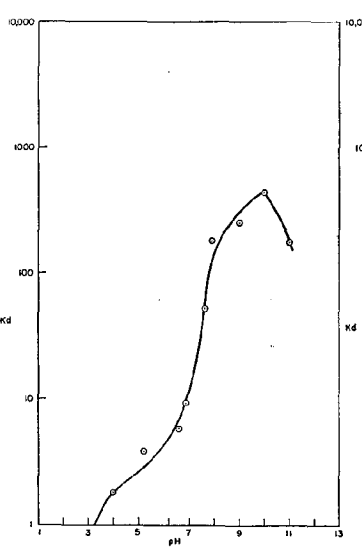


Figure 8. K_d *vs.* pH for Co in 2.12×10^{-3}M tartrate

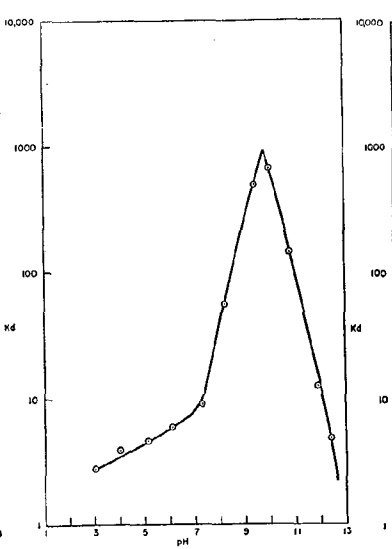


Figure 9. K_d *vs.* pH for Zn in 8.5×10^{-2}M tartrate

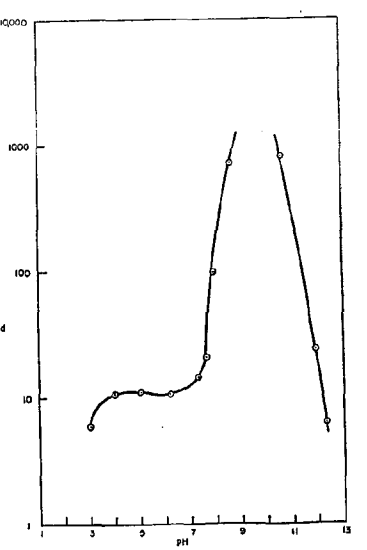


Figure 10. K_d *vs.* pH for Zn in 4.25×10^{-2}M tartrate

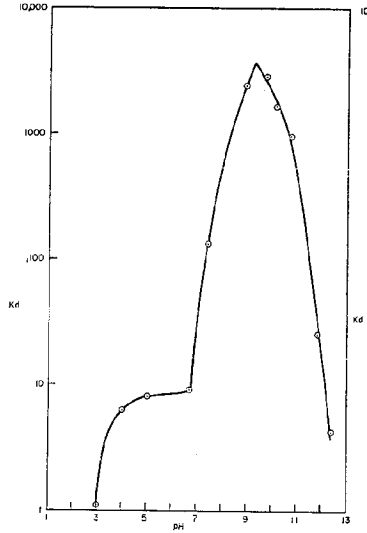


Figure 11. K_d *vs.* pH for Zn in 2.12×10^{-2}M tartrate

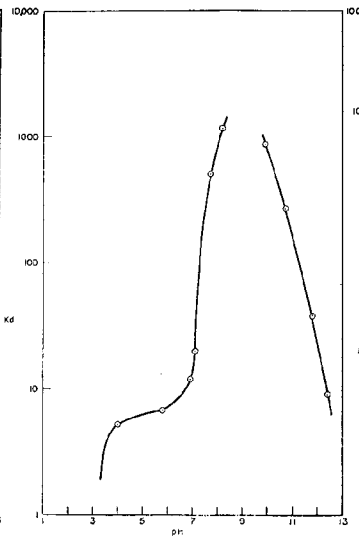


Figure 12. K_d *vs.* pH for Zn in 2.12×10^{-3}M tartrate

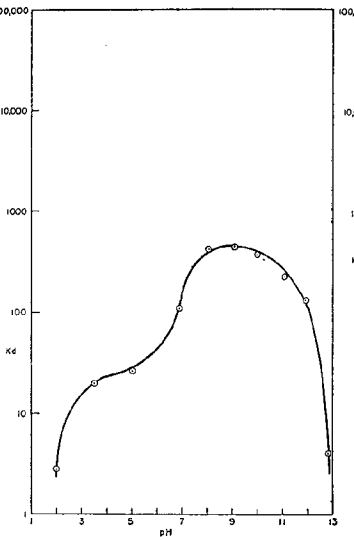


Figure 13. K_d *vs.* pH for Cu in 8.5×10^{-2}M tartrate

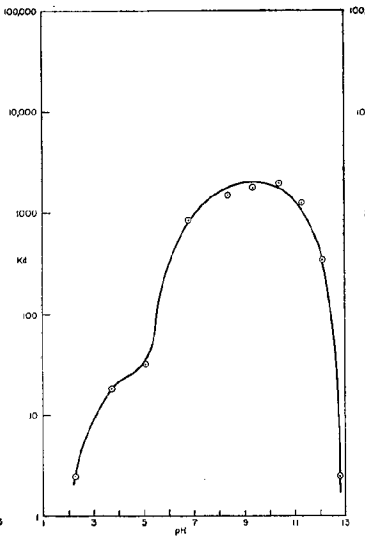


Figure 14. K_d *vs.* pH for Cu in 4.25×10^{-2}M tartrate

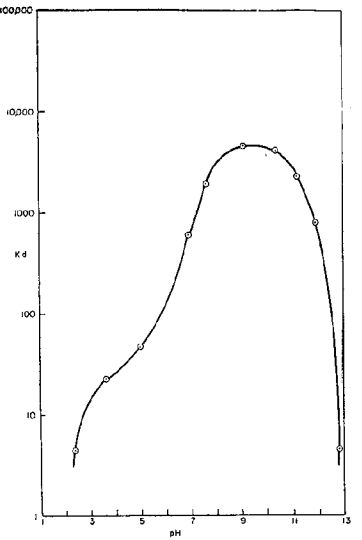


Figure 15. K_d *vs.* pH for Cu in 2.12×10^{-2}M tartrate

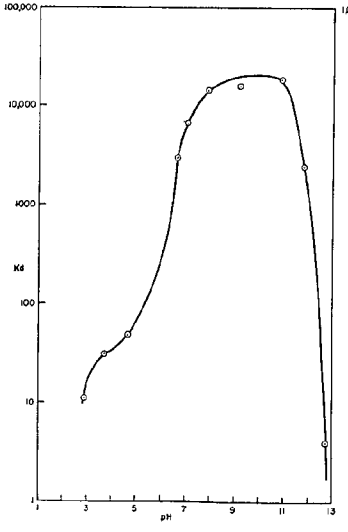


Figure 16. K_d *vs.* pH for Cu in 2.12×10^{-3}M tartrate

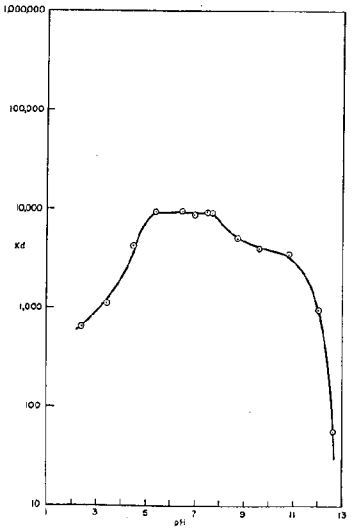


Figure 17. K_d *vs.* pH for Fe in 8.5×10^{-2}M tartrate

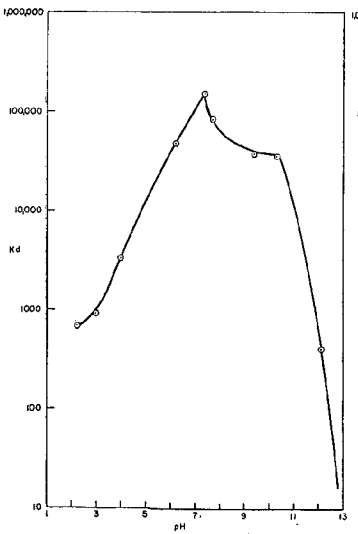


Figure 18. K_d *vs.* pH for Fe in 4.25×10^{-2}M tartrate

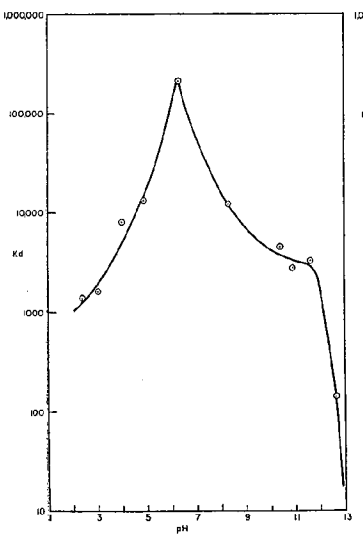


Figure 19. K_d *vs.* pH for Fe in 2.12×10^{-2}M tartrate

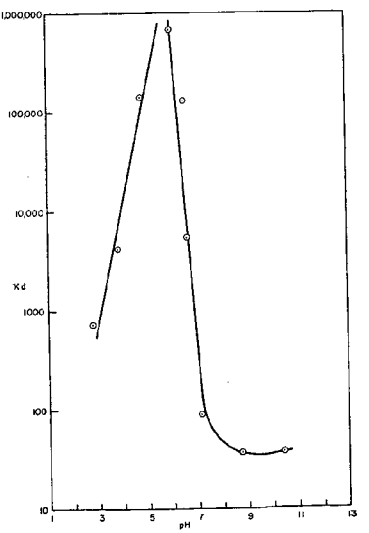


Figure 20. K_d *vs.* pH for Fe in 2.12×10^{-3}M tartrate

pH. Below pH 7, the column was left in the chloride form and treated with tartrate until the effluent pH matched the eluent pH.

After starting the separation, the column was connected to a 125-ml. separatory funnel containing the eluting agent. The column was allowed to flow into a fraction collector which collected 2-ml. portions of the effluent.

RESULTS AND DISCUSSION

The data resulting from the batch equilibrations are shown in Figures 1 through 20. These data were used as a basis for chromatographic column separations.

Figure 21 is an elution curve for a five-component mixture. The sample consisted of 2 ml. of a solution $2.12 \times 10^{-3}M$ in tartrate at pH 4.6, containing 13 μg. of Mn^{+2}, 14 μg. of Co^{+2}, 16 μg. of Zn^{+2}, 15 μg. of Cu^{+2}, and 14 μg. of Fe^{+3}. The resin depth was 10 cm. and the flow rate was approximately 3 to 4 drops per minute. The eluting agent was $2.12 \times 10^{-3}M$ tartaric acid at pH 4.5, since the distribution coefficients differed by a factor of two or more under these conditions. Iron was eluted with $1M$ HCl.

Similar separations of mixtures with fewer components have been performed in shorter columns. Rapid, clean separations of the metals were obtained, and in all cases the activity went to background between metals. This was determined by both scaler measurements and 200-channel analyzer measurements.

The flow rate used was well below the maximum that could have been used if more speed were desired. Studies by Boyd, Adamson, and Myers (*2*) have shown that the shape of the elution curve is nearly independent of flow rate, at rates below 1 ml. per sq. cm. per minute for size 200-mesh resin. Therefore, for the size column used, flow rates up to $^1/_2$ ml. per minute could probably have been used without affecting the elution curves.

Iron can be separated from the other four metals very rapidly and from almost any volume of solution because of its extremely high distribution coefficients as compared to other metals, especially at low pH values.

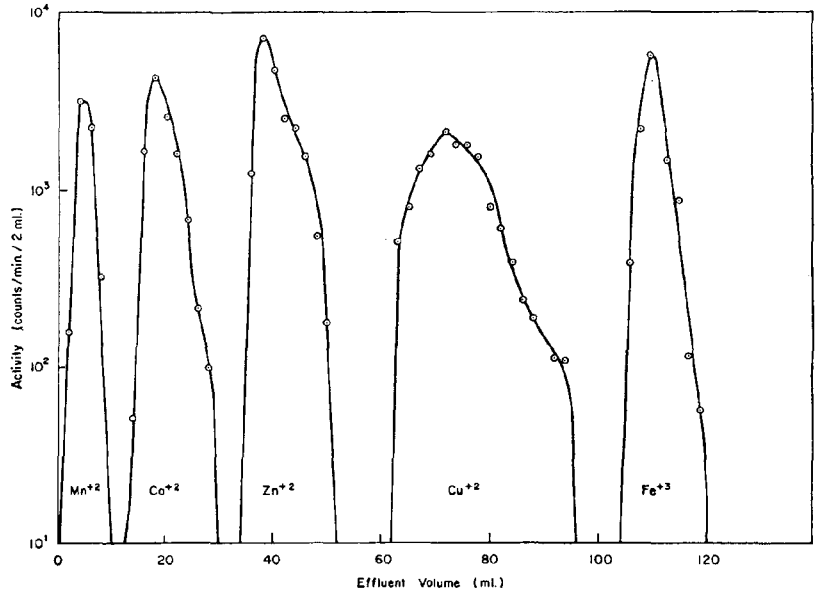


Figure 21. Separation of Mn, Co, Zn, Cu, and Fe

This method has some distinct advantages over many other anion exchange separations. In most cases, sharp bands with very little tailing are obtained. Usually, the ion used for elution is the same as that used to prepare the column. Therefore, it is possible to cycle one run immediately after another. In addition, it is unnecessary to use concentrated acids which may affect the resin after a period of time.

ACKNOWLEDGMENT

The authors are grateful to the United States Air Force for making it possible for one of them (G.F.P.) to undertake this study at The Ohio State University. The opinions expressed by the Air Force author are his own and do not reflect the policies or opinions of the United States Air Force or the Department of Defense.

LITERATURE CITED

(1) Barbanel, D. C., Voronina, N. I., *Uch. Zap. Leningr. Gos. Univ. Ser. Khim. Nauk* 19, 20–5 (1960); *C.A.* 55, 11184*a* (1961).
(2) Boyd, G. E., Adamson, A. W., Myers, L. S., *J. Am. Chem. Soc.* 69, 2836 (1947).
(3) Glass, R. A., *Ibid.*, 77, 807 (1955).
(4) Ryabchikov, D. I., Ermakov, A. N., Belyacva, V. K., Marov, I. N., *Zh. Neorgan. Khim.* 5, 1051–67 (1960); *C.A.* 55, 3260*i* (1961).
(5) Tsintsevich, E. P., Alimarin, I. P., Marchenkova, L. F., *Vestn. Mosk. Univ. Ser. Mat. Mekhan. Astron. Fiz. Khim.* 13, 221–7 (1958); *C.A.* 53, 10898*a* (1959).

RECEIVED for review November 13, 1962. ACCEPTED April 19, 1963. Taken in part from the M.S. thesis of Gerald F. Pitstick, The Ohio State University, Columbus, Ohio, 1962.

The Determination of Plutonium by (Ethylene dinitrilo)-tetraacetic Acid Titration

W. B. BROWN, D. R. ROGERS, E. A. MERSHAD, and W. R. AMOS

Monsanto Research Corp., Mound Laboratory, Miamisburg, Ohio

▷ A direct and an indirect (ethylene dinitrilo)tetraacetic acid (EDTA) titration for the determination of plutonium has been developed. A solution containing from 8 to 40 mg. of plutonium is buffered between pH 2.5 and 3.0, heated to boiling, and titrated with EDTA to a copper–1-(2-pyridylazo)-2-naphthol (Cu–PAN) end point. The indirect procedure is a continuation of the direct procedure. Ammonium fluoride solution, buffered at pH 3, is added to the titrated sample. Fluoride ions stoichiometrically demask EDTA from the plutonium chelate. The uncomplexed EDTA is titrated with standard copper solution to a PAN end point. For samples containing between 8 and 40 mg. of plutonium, the mean error of the direct method was less than ±0.1 mg., and the mean error of the indirect method was less than ±0.2 mg. The standard deviation of 10 titrations performed on samples containing 14.0 mg. of plutonium was ±0.08 for both the direct and the indirect methods. The indirect procedure is relatively free from interfering anions and cations.

SEVERAL ACCURATE techniques may be used for the determination of macroquantities of plutonium (*11*). However, only two methods are generally employed for the determination of semimicro amounts: amperometric titration of plutonium(VI) with iron(II) (*10*) and controlled potential coulometry (*17*). These methods are accurate and reliable, but a procedure not dependent upon electronic equipment is equally desirable.

The use of (ethylene dinitrilo)tetraacetic acid (EDTA) as an analytical reagent has been previously discussed (*18, 19*). Milner and Woodhead determined plutonium(III) by adding an excess of standard EDTA solution to a sample and back-titrating the excess reagent with standard thorium solution (*13*). Alizarin red S screened with methylene blue was the indicator for the titration. Cations which react with EDTA at pH 2.5 and anions which compete with EDTA for plutonium ions interfere. Paley and Chang titrated plutonium (IV) directly with EDTA at pH 1 using arsenazo as the indicator (*15*). After separation of plutonium by solvent extraction, Boase, Foreman, and Drummond added excess EDTA to the sample of plutonium(IV) and back-titrated the uncomplexed reagent with standard zinc chloride solution (*1*).

This paper presents a direct and an indirect complexometric titration procedure for the determination of plutonium.

EXPERIMENTAL

Apparatus and Reagents. This work was performed in stainless steel glove boxes and the usual precautions for handling radioactivity were observed (*11*). The reagent grade chemicals used in this procedure were obtained from the J. T. Baker Chemical Co., Phillipsburg, N. J., with the exception of the plutonium metal, which was obtained from the National Bureau of Standards, Washington, D. C.

A Beckman Zeromatic pH meter was used to make all pH measurements.

Standard Copper Solution (0.0200*M*). Dissolve 1.2721 grams of oxide-free copper shot (99.90%) in 20 ml. of 1 to 1 HNO_3. Dilute to 1 liter with deionized water.

Standard Zinc Solution (0.0200*M*). Dissolve 1.3102 grams of oxide-free zinc shot (99.8%) in 10 ml. of 1 to 1 HNO_3. Dilute to 1 liter with deionized water.

EDTA (0.0200*M*). Dissolve 7.2290 grams of disodium (ethylene dinitrilo)-tetraacetate dihydrate in 1 liter of deionized water and store in a polyethylene bottle. Standardize the EDTA solution against the standard zinc solution (*4*).

PAN (0.1%). Dissolve 0.1 gram of the indicator [1-(2-pyridylazo)-2-naphthol] in 100 ml. of ethanol.

Cu–EDTA Solution. Mix equivalent quantities of the standard copper solution and the standard EDTA solution (*4*). Store in a dropping bottle.

Standard Plutonium Solution (0.004184*M*). Polish the plutonium metal (99.97 ± 0.03%) with a metal polishing wheel in a dry argon atmosphere to remove the oxide. Dissolve 1.0000 gram of the metal in 2*N* HCl. Add 15 ml. of 3*N* H_2SO_4 and heat to fumes of SO_3. Continue fuming to incipient dryness, cool, and dilute to 1 liter with 0.5*N* H_2SO_4 (*12*).

Buffered Fluoride Solution (pH 3). Dissolve 10 grams of ammonium fluoride in 100 ml. of deionized water and add reagent grade hydrofluoric acid (48%) until the solution is buffered at pH 3.0. Dilute to 250 ml. with deionized water. Use polyethylene vessels for preparation and storage of the solution.

Recommended Procedure. Quantitatively transfer the sample solution, containing from 8 to 40 mg. of plutonium, to a 150-ml. beaker. Add 2 ml. of 1 to 1 H_2SO_4 and heat to fumes of SO_3. To destroy any organic matter which may be present, carefully add concentrated HNO_3, dropwise, to the fuming sample. Cool and wash down the cover glass and beaker walls with a minimum amount of 1*N* H_2SO_4. Heat to incipient dryness, cool, and dissolve the salts in approximately 10 ml. of 0.25*N* H_2SO_4. Add 3 to 5 ml. of glacial acetic acid to the sample and adjust the pH to between 2.5 and 3.0 by the dropwise addition of 10% sodium acetate. Do not allow the pH of the solution to exceed 3.0.

Heat the sample to boiling. Add 3 drops of PAN, 1 or 2 drops of Cu–EDTA solution, and titrate the sample with

Table I. Direct Titration of Standard Plutonium Solutions at pH 2.5 to 3.0 Using Cu–PAN as Indicator

Pu taken, mg.	No. of detns.	Pu found (mean value), mg.	Mean error, mg.
8.1	4	8.1	0.0
13.1	4	13.1	0.0
14.0	10	14.0	0.0
16.2	12	16.2	0.0
24.3	4	24.3	0.0
40.4	4	40.3	−0.1
13.1[a]	2	13.2	+0.1

[a] Plutonium(IV) oxidized to plutonium (VI) by divalent silver.

Table II. Indirect Titration of Standard Plutonium Solutions at pH 2.5 to 3.0 Using PAN as Indicator

Pu taken, mg.	No. of detns.	Pu found (mean value), mg.	Mean error, mg.
8.1	4	8.2	+0.1
13.1	4	13.1	0.0
14.0	10	14.0	0.0
16.2	16	16.2	0.0
24.3	3	24.2	−0.1
40.4	3	40.2	−0.2
13.1[a]	2	13.0	−0.1

[a] Plutonium(IV) oxidized to plutonium (VI) by divalent silver.

standard EDTA solution to a lemon-yellow end point. As the end point color of PAN indicator is approached, allow 1 minute between additions of EDTA.

After the end point has been attained, add 1 to 2 ml. of buffered fluoride solution to the sample. Titrate the released EDTA with standard copper solution. As the end point is approached, add 1 or 2 additional drops each of buffered fluoride solution and of PAN indicator solution. Titrate the sample to the faint pink end point color of the Cu–PAN complex.

RESULTS AND DISCUSSION

EDTA forms stable 1 to 1 complexes with plutonium(III), (IV), (V), and (VI) (*6–8, 11*). Because of the stability of these complexes, plutonium in any valence state may be titrated with EDTA by using a suitable end point indicator. This eliminates the need for a valence adjustment step in the determination. An indicator generally does not form a colored complex with all the valence states of plutonium; therefore, the indirect indicator, Cu–PAN, was investigated for end point detection. Flaschka and Abdine introduced the copper complex of PAN as an indicator for those cations with which PAN does not form a colored complex. They suggested that titrations be performed in hot solutions because of the sluggish reactivity of the indicator complex (*5*).

Direct Titration. The results of the direct EDTA titration of samples containing from 8 to 40 mg. of plutonium are shown in Table I. In this concentration range, the mean error of the direct procedure was less than ±0.1 mg. The standard deviation, calculated from 10 titrations performed on 14.0-mg. plutonium samples, was ±0.08.

The optimum pH range for the titration is between 2.5 and 3.0. At lower pH values the Cu–PAN end point reaction is sluggish and difficult to detect; at higher values, the plutonium(IV) ions may hydrolyze. Small quantities of sulfate ions are sufficient to inhibit the hydrolysis of plutonium(IV) (*2*); therefore, samples are converted to the sulfate prior to titration. Even in the presence of sulfate ions, hydrolysis of plutonium(IV) may occur when the hydrogen ion concentration drops below 10^{-3}. Because the hydrolysis reaction is irreversible, low results may be obtained if the pH of the sample is raised above 3.0. The rate of chelation of plutonium with EDTA is dependent upon the sulfate concentration of the sample. The reaction is rapid if the excess H_2SO_4 is expelled during the fuming of the sample as recommended in the procedure.

Indirect Titration. The results obtained by the indirect titration of samples containing from 8 to 40 mg. of plutonium are shown in Table II. At this concentration range, the mean error of the indirect procedure was less than ±0.2 mg. The standard deviation, calculated from 10 titrations performed on 14.0-mg. plutonium samples was ±0.08.

A comparison of the data presented in Tables I and II shows that fluoride ions stoichiometrically release EDTA from the Pu–EDTA complex.

Samples containing more than 40 mg. of plutonium cannot be titrated by the indirect procedure because the titration of the released EDTA with standard copper solution leads to such an intensely blue-colored solution of the Cu–EDTA complex that the end point color of the PAN indicator is obscured (*4*).

Interferences. Cations which titrate partially or completely between pH 2.5 and 3.0 interfere in the direct EDTA titration of plutonium. Twenty-three cations, listed in Table III, were added to solutions of known plutonium content. After the samples were treated according to the recommended procedure, they were analyzed by the direct and indirect EDTA titration methods. Cations which caused a mean error greater than twice the standard deviation of the methods were considered interferences. Fourteen cations listed in Table III interfered in the direct titration.

Cerium(III) and zinc partially interfered in the direct titration and also interfered in the indirect titration. These cations are incompletely complexed by EDTA below pH 4.5. Consequently, any small pH change which may occur after completion of the direct titration will cause a change in the amount of EDTA complexed with these cations. The error contributed by this phenomenon will depend upon the magnitude and the direction of the pH shift. Cerium(IV) hydrolyzed during the direct procedure and did not stoichiometrically interfere in the direct or the indirect titration. Thorium and aluminum quantitatively interfered in the direct and in the indirect procedures. Both cations react with stoichiometric amounts of EDTA at pH 2.5 to 3.0. Fluoride ions subsequently demask stoichiometric quantities of EDTA from these cations. Phosphate ions precipitate plutonium and interfere with the method.

Prior to the conversion to plutonium sulfate, plutonium may be quantitatively separated from interfering cations by either ion exchange (*3, 9, 11, 16*) or solvent extraction (*1, 11, 14*).

Xylenol Orange Indicator. Xylenol orange {3,3′-bis[*N*,*N*-di(carboxymethyl) - aminomethyl] - *o* - cresolsulfonphthalein} was found to be equivalent to Cu–PAN as an end point indicator for the direct titration of plutonium with EDTA. However, in the indirect titration no color change of xylenol orange was observed at the end point.

Table III. Interference Study of the Direct and Indirect Determination of Plutonium[a]

Pu taken, mg.	Interference		Direct		Indirect	
	Symbol	Added, mg.	Pu found, mg.	Mean error, mg.	Pu found, mg.	Mean error, mg.
15.6	Li(I)	3.0	15.7	+ 0.1	15.7	+ 0.1
15.6	Na(I)	3.0	15.7	+ 0.1	15.6	0.0
15.6	Ni(II)	3.4	29.6	+14.0	15.7	+ 0.1
15.6	Fe(III)	3.6	31.1	+15.5	15.5	− 0.1
12.9	U(VI)	3.0	12.9	0.0	12.8	− 0.1
12.9	U(IV)	3.0	12.9	0.0	12.8	− 0.1
12.9	Ce(III)	3.0	13.6	+ 0.7	13.5	+ 0.6
12.9	Ce(IV)[b]	3.0	13.3	+ 0.4	13.2	+ 0.3
13.1	Ba(II)	3.0	13.1	0.0	13.1	0.0
13.1	Ca(II)	3.0	13.1	0.0	13.1	0.0
13.1	Mg(II)	3.0	13.0	− 0.1	13.0	− 0.1
13.1	Cr(III)	3.0	13.4	+ 0.3	13.0	− 0.1
14.0	Al(III)	1.7	29.2	+15.2	29.1	+15.1
13.1	Cu(II)	3.7	25.5	+12.4	13.0	− 0.1
13.1	Bi(III)	3.6	18.5	+ 5.4	13.1	0.0
13.1	Au(III)	3.0	Destroys indicator			
13.1	Co(II)	3.0	Destroys indicator			
13.1	Np(IV)	5.0	13.1	0.0	13.1	0.0
13.1	Cd(II)	0.5	13.7	+ 0.6	13.0	− 0.1
13.1	Mn(II)	0.5	13.4	+ 0.3	13.1	0.0
13.1	Zn(II)	1.5	16.5	+ 3.4	13.7	+ 0.6
14.0	Th(IV)	5.2	19.2	+ 5.2	19.1	+ 5.1
13.1	Ag(I)	3.0	13.1	0.0	13.1	0.0

[a] Analyses performed in duplicate.
[b] Cerium(IV) hydrolyzed during direct titration.

LITERATURE CITED

(1) Boase, D. G., Foreman, J. K., Drummond, J. L., *Talanta* 9, 53 (1962).
(2) Drummond, J. L., Welch, G. A., *J. Chem. Soc.* 1958, 3218.
(3) Faris, J. P., Buchanan, R. F., U. S.

Atomic Energy Comm. *Rept.* TID 7606 (1960).
(4) Flaschka, H., Abdine, H., *Chemist-Analyst* **45**, 58 (1956).
(5) Flaschka, H., Abdine, H., *Mikrochim. Acta* 1956, 770.
(6) Foreman, J. K., Smith, T. D., *J. Chem. Soc.* 1957, 1758.
(7) Gel'man, A. D., Artyukhin, P. I., Moskvin, A. I., *Zh. Neorgan. Khim.* **4**, 1332 (1959); *Nucl. Sci. Abstr.* **13**, 18993 (1959).
(8) Kabanova, O. L., Danuschenkova, M. A., Paley, P. N., *Anal. Chim. Acta* **22**, 66 (1960).
(9) Kressin, I. K., Waterbury, G. R., ANAL. CHEM. **34**, 1958 (1962).
(10) Larson, R. P., Seils, C. A., Meyer, R. J., U. S. Atomic Energy Comm. *Rept.* TID 7606 (1960).
(11) Metz, C. F., ANAL. CHEM. 29, 1748 (1957).
(12) Metz, C. F., Waterbury, G. R., *Ibid.*, **31**, 1144 (1959).
(13) Milner, G. W. C., Woodhead, J. L., *Analyst* **81**, 427 (1956).
(14) Moore, F. L., Hudgens, J. E., Jr., ANAL. CHEM. 29, 1767 (1957).
(15) Paley, P. N., Chang, W. C., *Zh. Analit. Khim.* **15**, 598 (1960); *Nucl. Sci. Abstr.* **15**, 7305 (1961).
(16) Ryan, J. L., Wheelwright, E. J., *Ind. and Eng. Chem.* **51**, 60 (1959).
(17) Scott, F. A., Peekema, R. M., *Proc. U. N. Intern. Conf. Peaceful Uses At. Energy, Geneva, A/Conf.* **28**, 914 (1958).
(18) Welcher, F. J., "The Analytical Uses of Ethylenediaminetetraacetic Acid," Van Nostrand, New York, 1957.
(19) Wilkins, D. H., Hibbs, L. E., *Anal. Chim. Acta* **18**, 374 (1958).

RECEIVED for review August 10, 1962. Accepted March 11, 1963.

A Continuous Photometric Fluorine Analyzer

C. W. WEBER and O. H. HOWARD

Technical Division, Oak Ridge Gaseous Diffusion Plant, Union Carbide Nuclear Co., Oak Ridge, Tenn.

▷ A sensitive automatic analyzer has been developed for the continuous determination of elemental fluorine in gas mixtures. As the sample stream is passed through hot sodium chloride, the fluorine quantitatively liberates chlorine, which is measured at 360 mμ in a pressure-controlled flow colorimeter cell. The range of the analyzer, calibrated with standard fluorine-nitrogen mixtures, is 0.05 to 15 mole % of fluorine, using a 10-cm. cell at 500 mm. of Hg. The relative standard deviation of the fluorine analyzer is about ±1.5% above 0.8% fluorine, and the standard deviation is about ±0.04 (absolute) at lower levels. Initial response lag is 6 seconds, with full response in about 1 minute. The instrument is applicable in the presence of hydrogen fluoride and other gases which do not absorb radiation near 360 mμ or liberate chlorine from sodium chloride.

A CONTINUOUS determination of fluorine in a mixture of fluorine and nitrogen was needed for satisfactory control of a fluorination process. The operating range of concentrations was 0.3 to 10 mole % fluorine, to be controlled within ±0.05 to ±0.5%, respectively, throughout this range. Previous analytical control consisted of intermittent chemical analyses, which required constant manual effort to obtain an acceptable degree of process control. An automatic continuous analyzer was developed to reduce analytical costs and provide smoother process control.

A few continuous fluorine analyzers have been described in the literature. Weber (*5*) developed an automatic fluorine analyzer based upon pneumatic detection of the reduction of molar flow as fluorine reacts with sulfur dioxide; this analyzer was not sensitive enough for the low concentration range of interest. Staple and Grilly (*3*) determined fluorine continuously by measurement of the thermal conductivity of chlorine displaced from sodium chloride by the fluorine; this method also lacked the required sensitivity and precision. Staple, Schaffner, and Wiggin (*4*) utilized the liberation of bromine from sodium bromide by fluorine and the subsequent measurement of light absorption by the bromine; this method was not attractive because of reported bromine adsorption–memory effects.

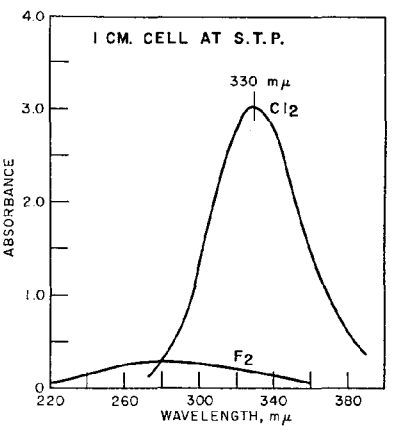


Figure 1. Ultraviolet absorption spectra of fluorine and chlorine

This report describes an automatic, continuous, fluorine analyzer which is basically similar to the bromine-displacement analyzer, except that the light-absorption measurement is made on chlorine displaced from sodium chloride by the fluorine. Adequate sensitivity and precision are obtained and no adsorption difficulties are encountered under the operating conditions established.

PRINCIPLE

Fluorine absorbs radiant energy only weakly in the ultraviolet and visible regions of the spectrum. Davis (*1*) reports an absorbance of 0.3, for a depth of 1 cm. at 0° C., 760 mm. of Hg, at the maximum absorption wavelength of 285 mμ (Figure 1). Chlorine, on the other hand, gives an absorbance of 3.0 at its maximum absorption wavelength of 330 mμ. Therefore, to achieve the desired sensitivity in the photometric fluorine analyzer, the fluorine sample is passed through hot sodium chloride, where it displaces an equivalent amount of chlorine:

$$F_2(g) + 2NaCl(s) \rightarrow Cl_2(g) + 2NaF(s)$$

The resulting gas then flows through a chlorine-sensitive colorimeter, which generates an electrical signal directly related to the concentration of fluorine in the sample.

CONSTRUCTION AND OPERATION

The analyzer (Figure 2) consists basically of a heated sodium chloride reactor, flow colorimeter, pressure-control system, flow limiter, a vacuum pump for drawing a continuous sample through the analyzer, and a recorder.

Sodium Chloride Reactor. The sodium chloride reactor is a nickel cylinder, 1-inch i.d. by 8 inches long. Approximately 100 grams of reagent grade, crystalline, sodium chloride is retained in the cylinder by nickel wool filters. It is designed so that it can be readily disconnected and one end removed for replacing the sodium chloride as needed. In operation the reactor hangs vertically within a cylindrical heater which maintains it at 250° C. The gas stream passes upward through the reactor.

The sodium chloride is heated because fluorine, at low concentrations (< 1%),

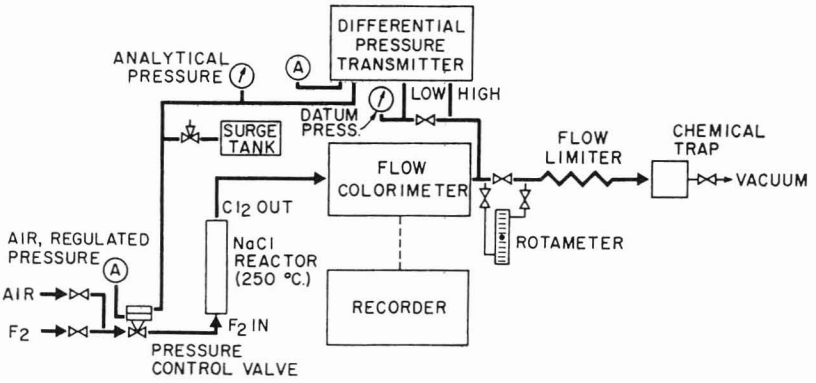


Figure 2. Schematic diagram of continuous photometric fluorine analyzer

does not react with pure sodium chloride at room temperature. Furthermore, some chlorine is adsorbed by sodium chloride below 200° C., introducing response lag and error. Low concentrations of fluorine will react with sodium chloride at room temperature, provided the sodium chloride has been initially heated to 200° C. in the presence of >5% fluorine. This suggested that unused sodium chloride might be satisfactory at room temperature if mixed with sodium fluoride; however, with 1% sodium fluoride in the sodium chloride, reaction was not complete at 0.4% fluorine. Kimball and Tufts (*2*) report that the presence of a small amount of sodium fluoride in the sodium chloride initiates the fluorine–sodium chloride reaction, without the application of heat; however, they worked with high concentrations of fluorine, which generated relatively high temperatures.

Evidence that sodium chloride adsorbs chlorine below approximately 200° C. was a temporary increase in chlorine emission occurring at about this temperature when a previously activated sodium chloride reactor was heated from room temperature to 320° C. while 0.4% fluorine in air was passed through it. Consequently, the stipulated operating temperature of 250° C. was selected, and has proved satisfactory. No other effects were seen on heating to 320° C., indicating that accurate temperature control of the sodium chloride reactor is not required.

The efficiency of conversion of fluorine to chlorine in the sodium chloride reactor was determined by passing chlorine standards through the analyzer and comparing the responses with those for corresponding fluorine standards. The results (Table I) show that, within the accuracies of the analyzer and standards, the conversion efficiency is 100%. This conclusion is supported by the visible sharp demarcation between the reacted and unreacted zones of a sodium chloride column which has been removed from the analyzer after partial consumption.

One 100-gram charge of the sodium chloride reactor is theoretically sufficient for approximately 300 hours of operation at an average fluorine concentration of 1% and a sample flow rate of 100 standard cc. per minute. However, the charge is usually renewed after 150 to 200%-hours of use; a larger reactor would require even less frequent attention.

Colorimeter. The colorimeter used in the analyzer is the Beckman Model 3700 flow colorimeter; a schematic diagram of the optical system is shown in Figure 3. The spectral filters are those provided by the manufacturer for chlorine measurement. The peak transmittance of the filters is at about 360 mμ. Although this does not coincide with the 330-mμ absorption peak for chlorine (Figure 1), sufficient sensitivity has been achieved for the application described.

Table I. Fluorine-to-Chlorine Conversion Efficiency in the Photometric Fluorine Analyzer

F_2 or Cl_2, mole %	Analyzer response, % of scale F_2	Analyzer response, % of scale Cl_2	Conversion efficiency (F_2/Cl_2), %
5.0	38	38	100
10.0	67	65	103
15.0	84	83	101

The 10-cm. glass sample cell provided with the colorimeter was replaced with a nickel cell with 1/16-inch-thick fluorothene windows, for resistance to fluoride corrosion (Figure 4). A thickness of fluorothene equal to that of the cell windows was also placed in the reference beam to compensate for the greater absorbance of the fluoroethene windows.

For zeroing the analyzer, which is accomplished by adjustment of the shutter in the reference beam of the colorimeter, provision is made for temporarily passing dry air through the analyzer, instead of fluorine sample gas.

A constant voltage transformer in the power line to the colorimeter minimizes the effect of line voltage fluctuations. Further signal stability was achieved by spring-loading the zeroing shutter so that it was less susceptible to vibration.

The cooling water, required by the colorimeter for cooling the tungsten source lamp, is also used to cool the tube carrying the gas from the hot sodium chloride reactor to the colorimeter cell.

A recording potentiometer, of greater sensitivity than the signal meter on the colorimeter, indicates and records the analytical signal; it has full scale ranges of 1 and 10 mv., corresponding to approximately 1 and 15% fluorine, respectively, at a pressure of 500 mm. of Hg at 25° C. in the 10-cm. colorimeter cell. The nonlinear response of

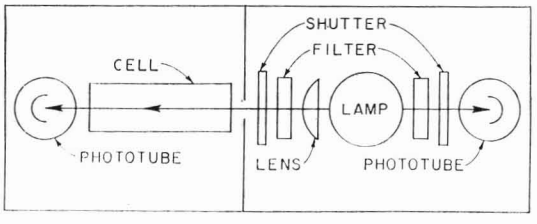


Figure 3. Schematic diagram of optical system of Beckman Model 3700 flow colorimeter

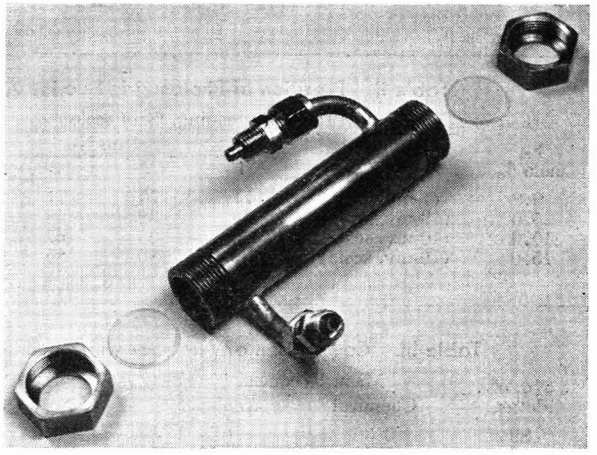


Figure 4. Optical cell

the 10-mv. range (see Figure 5) is peculiar to the electronic design of the colorimeter.

Pressure Control System. Since the analytical signal depends, for a given fluorine concentration, upon the pressure of the sample in the colorimeter cell, provision is made for automatically controlling this pressure. A differential pressure transmitter (Taylor, Model 206-RD), range 0 to 10 mm. of Hg, continuously senses the pressure and actuates a pressure control valve (Hoke, Inc., Part 1148) in the sample feed line to maintain the pressure at a preselected value. For a given desired operating pressure, the reference or "low" side of the transmitter is pressurized with dry air to 5 mm. of Hg below the desired operating pressure, and valved off. A manometer or Wallace-Tiernan gauge, temporarily attached to the system, serves to measure this reference (datum) pressure while it is being fixed. A small, inexpensive gauge permanently attached to the reference side of the transmitter will reveal any subsequent changes in the reference pressure. After the reference pressure has been so fixed, the desired operating pressure is obtained by appropriate adjustment of the pressure control valve until the receiver gauge in the transmitter output line reads midscale.

Use of a differential pressure transmitter in the manner described permits optimization of the range of the fluorine analyzer by selection of operating pressures appropriate to the fluorine concentrations of interest.

When the pressure control system is operating, the pressure oscillates with the opening and closing of the pressure control valve. To minimize the amplitude of the oscillations, a needle valve, connecting a 2-liter surge bottle to the transmitter output line, is adjusted until the transmitter receiver gauge indicates minimum pressure oscillation. With this device the pressure oscillation was reduced from ±1% to ±0.02% of the pressure.

Flow Limiter. The sample flow rate does not affect the accuracy of the analyzer, within reasonable limits. However, it does affect the response time and rate of consumption of the sodium chloride; therefore, the flow rate is limited to give an acceptable response time. The flow limiter is 20 feet of nickel tubing, 0.030-inch i.d., 1/8-inch o.d., in the form of a 2-inch diameter helix. It passes approximately 100 standard cc. of air per minute at a forepressure of 500 mm. of Hg, and a backpressure of essentially zero.

A glass rotameter, which can be connected in series with the flow limiter but is normally valved out, is occasionally valved in with clean air flowing through the analyzer, to detect possible plugging of the flow limiter by particulates from the sodium chloride reactor. A small amount of white powder, a mixture of sodium chloride and sodium fluoride, passes the nickel wool filter and accumulates in the bottom of the colorimeter cell over several weeks of operation of the analyzer; however, no significant plugging of the flow limiter has occurred during 10 months of use.

Chemical Trap. The chlorine and other corrosive gases, such as hydrogen fluoride which may be present in the sample stream, are removed in a chemical trap before the vacuum pump. Two gas mask canisters (Army, M-11), connected in series, are used for this purpose and are replaced when the sodium chloride reactor is recharged. Other types of traps, such as activated carbon or soda lime, would presumably serve equally well, and, of course, one of larger capacity would require less frequent attention. The particular selection was made for convenience and expediency during the development of the analyzer, and has not been further evaluated.

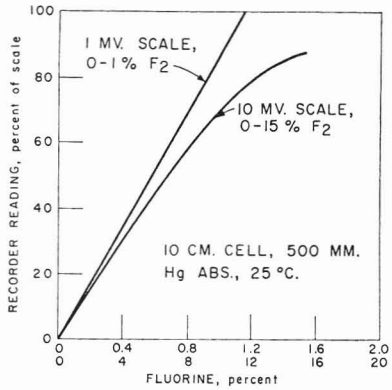


Figure 5. Calibration curves

Calibration. Calibration curves for the analyzer are shown in Figure 5. The analyzer is calibrated with standard mixtures of fluorine in nitrogen, prepared in nickel cylinders on an appropriate pressure-monitored manifold. A 2-liter cylinder at a total pressure of 30 p.s.i.a. is sufficient for about 20 minutes' operation of the analyzer at a controlled pressure of 500 mm. of Hg.

PERFORMANCE

Range. The range of the analyzer depends primarily upon the length of the colorimeter cell and the pressure of the gas in it. For example, under the conditions indicated in Figure 5—i.e., 10-cm. cell length and 500 mm. of Hg pressure—the lower limit is about 0.05% fluorine; the upper limit is about 15% because of the reduced sensitivity above this concentration. With an appropriately shorter cell, and/or lower pressure, up to 100% fluorine could be determined. Conversely a longer cell, and/or higher pressure, would provide a lower limit of detection. It is apparent from Figure 1 that a colorimeter filter with a transmittance peak at 330 mμ would provide more inherent sensitivity.

Response Time. The response time of the analyzer, the time required to attain 75% of a signal change after a change in fluorine concentration, is about 1 minute at a sample flow rate of 100 cc. per minute. Initial response, however, is noted in about 6 seconds.

Interferences. The analyzer is free from interference by the common components of air, or from other gases which do not absorb radiant energy in the 360-mμ region of the spectrum, and which do not react with sodium chloride to liberate chlorine. Hydrogen fluoride has no effect. Chlorine, bromine, uranium hexafluoride, and certain oxides of nitrogen are examples of gases that cause optical interference. Ozone and trifluorides of chlorine and bromine would probably interfere by liberating chlorine.

Servicing Requirements. Servicing the analyzer requires intermittent renewal of the sodium chloride, the chemical trap, and recorder chart; occasional replacement of the tungsten source lamp in the colorimeter; and cleaning of the colorimeter cell as indicated by inspection.

Precision and Accuracy. The relative standard deviation of the analyzer is about ±1.5% above 0.8%

Table II. Precision of Photometric Fluorine Analyzer

F_2, mole %	Recorder reading, % of scale	Run No. 1	Run No. 2	Run No. 3	Run No. 4	Relative std. dev., %
0.8	(1-mv. scale)	71	70	71	72	±1.2
5.0	(10-mv. scale)	39	38	38	38	±1.5
10.0	(10-mv. scale)	69	68	67	67	±1.4
15.0	(10-mv. scale)	86	86	85	84	±1.1

Table III. Comparison of Analyzer with Chemical Analysis

No. of detns.	Mean F_2 concn., % Chemical	Mean F_2 concn., % Analyzer	Difference, % (abs.) Mean	Difference, % (abs.) Std. dev.
89	0.30	0.34	+0.04	±0.04
6	5.48	5.56	+0.08	±0.22

fluorine (Table II). Comparison of analyzer results with determinations by a thiosulfate-titration method is presented in Table III, which indicates a standard deviation of at least ±0.04 (absolute) at lower levels.

ACKNOWLEDGMENT

The authors thank P. R. Kuehn, S. A. MacIntyre, and J. G. Million for their assistance in the early field-testing of the analyzer; R. D. High for providing standard gas mixtures; and the members of the Oak Ridge Gaseous Diffusion Plant Process Laboratory who made the comparative chemical determinations.

LITERATURE CITED

(1) Davis, W., U. S. At. Energy Comm. Rept. K-985 (Classified) (1953).
(2) Kimball, R. H., Tufts, L. E., *Ibid.*, MDDC-195 (1946).
(3) Staple, E., Grilly, E. R., *Ibid.*, MDDC-1565 (1947).
(4) Staple, E., Schaffner, J. G., Wiggin, E., *Ibid.*, MDDC-1610 (1946).
(5) Weber, C. W., ANAL. CHEM. 32, 387 (1960).

RECEIVED for review February 5, 1963. Accepted April 19, 1963. Southeastern Regional Meeting, ACS, Gatlinburg, Tenn., November 1962. Work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corp. for the U. S. Atomic Energy Commission.

The Ultraviolet Spectrometric Determination of the Three Isomeric Toluenesulfonic Acids in Excess of Aqueous Sulfuric Acid

HANS CERFONTAIN, HERMAN G. J. DUIN,[1] and LEO VOLLBRACHT[2]

Laboratory for Organic Chemistry, University of Amsterdam, The Netherlands

▶ Mixtures of the three isomeric toluenesulfonic acids in excess concentrated aqueous sulfuric acid can be determined quantitatively by multicomponent spectrophotometric analysis of the sulfuric acid solution on the basis of the ultraviolet absorption of the sulfonic acids. This determination is performed by subjecting the absorbances of the unknown mixture and of its constituents, gathered at a large number of wavelengths, to a least square treatment by an electronic computer. The para isomer is analyzed very accurately. The accuracy in determining the meta and ortho isomers is somewhat less satisfactory because of their high spectral similarity. *m*-Toluenesulfonic acid can be determined more accurately by multicomponent spectrophotometric analysis in oleum of about 10 weight % SO_3. In this solvent o- and p-toluenesulfonic acid are rapidly converted into toluene-2,4-disulfonic acid, so that only the sum of the amounts of o- and p-toluenesulfonic acid will be found in the oleum analysis.

IN CONNECTION with a study on partial rate factors of the sulfonation of toluene (*3*, *16*), a rapid and accurate method of analysis was needed for the quantitative determination of mixtures of the three isomeric toluenesulfonic acids in a large excess of concentrated aqueous sulfuric acid. The inverse isotope dilution method was successfully applied in preliminary experiments (*16*), but it did not seem attractive for routine analysis as the procedures are tedious. The cryoscopic method for the determination of the isomer ratio of a mixture of toluenesulfonic acids (*4*, *7*, *9*) was unfit to solve our problems in view of the relatively large quantities of sulfonic acid mixture required. The same difficulty applies to the isomer ratio determination proposed by Spryskov (*11*). The quantitative separation of small amounts of sulfonic acids from excess sulfuric acid seems very unattractive (*5*), thus making impossible gas chromatographic analysis of the sulfonic acids after their conversion to sulfonyl chlorides or to sulfonic esters (*8*). A spectrophotometric determination of the total amount of toluenesulfonic acids in an excess sulfuric acid was recently described (*10*). The spectrophotometric method, described for the determination of the ortho and para isomers in commercial mixtures of toluenesulfonamides (*14*), was not appropriate to solve our problem as no provision was made for the determination of the meta isomer.

The preliminary results of spectrophotometric analysis of multicomponent systems, obtained by Herschberg and Sixma in our laboratory, were very promising (*6*). Therefore the possibility of analyzing the toluenesulfonic acids in sulfuric acid solution by this method was investigated. The principles of the multicomponent spectrophotometric analysis have adequately been described (*6*, *13*). The analysis is based on a linear least square resolution of the absorption spectrum of the mixture to be analyzed in terms of the spectra of the pure components. To obtain maximal precision in the analysis, it is necessary to determine the absorbances of the mixture and the components at a large number of wavelengths (large relative to the number of components) and to perform the measurements at each wavelength as simultaneously as possible. The observed absorbances define an overdetermined system which, for the evaluation of the unknown concentrations, is subjected to a least square treatment by electronic computer (*6*). The applicability of the method depends on the differences in shape of the absorption spectra of the components.

The absorption spectra of the three isomeric toluenesulfonic acids in 82.4 weight % sulfuric acid are shown in Figure 1. The similarity in shape of the ortho and meta spectra may cause these two isomers to be subject to some interchange in the analysis. To minimize any possible interchange in the content of the meta and ortho isomer, the number of wavelengths, at which measurements have to be made, must be extremely large.

In weak oleum solution *o*- and *p*-toluenesulfonic acid are both rapidly converted into toluene-2,4-disulfonic acid (*15*), whereas the meta isomer forms a mixture of toluene-2,5- and toluene-3,5-disulfonic acid (*12*). The spectra in oleum of toluene-2,4-disulfonic acid and of the mixture resulting after sulfonation of *m*-toluenesulfonic acid show

[1] Present address: Research Laboratories of N.V. Philips-Duphar, Weesp, The Netherlands.
[2] Present address: Central Research Institute of AKU and affiliated Companies, Arnhem, The Netherlands.

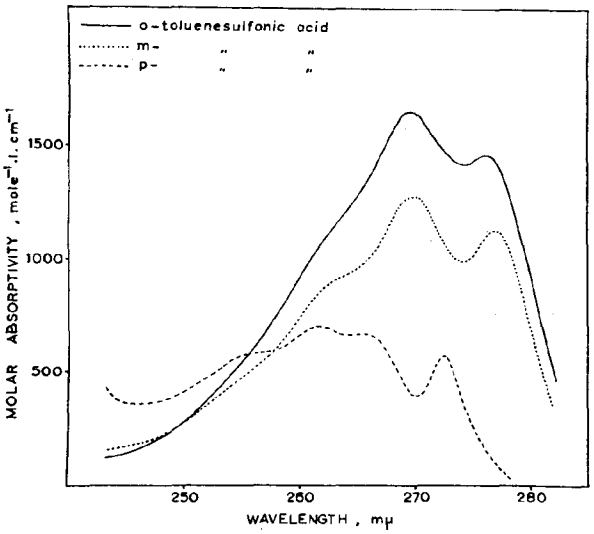


Figure 1. Absorption spectra of the three isomeric toluenesulfonic acids in 82.4 weight % sulfuric acid

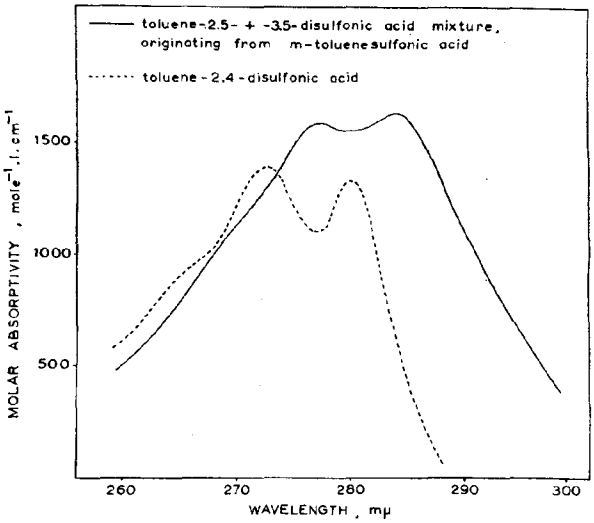


Figure 2. Absorption spectra of toluenedisulfonic acids in oleum containing 12.1 weight % SO_3

a fair difference in shape (Figure 2), in fact a greater difference than the spectra of *o*- and *m*-toluenesulfonic acid in aqueous sulfuric acid (Figure 1). Therefore, multicomponent spectrophotometric analysis in oleum will probably yield a more accurate value for the content of the meta isomer than the sulfuric acid analysis. However, the analysis in oleum will only produce two figures: the amount of *m*-toluenesulfonic acid and the sum of the amounts of the para and ortho isomers.

EXPERIMENTAL

Materials. The preparation and the purification of sulfur dioxide–free oleum and of the three isomeric toluenesulfonic acids were described previously (*1*, *16*).

Apparatus. The optical measurements were made manually with a Zeiss PMQ II spectrophotometer, equipped with a sliding cell holder which could accommodate eight quartz absorption cells of 1-cm. pathlength (*6*).

Procedure. Sulfuric Acid Analysis. Test mixtures were made by mixing appropriate amounts of the standard solutions of the three isomeric toluenesulfonic acids in 82.4 weight % sulfuric acid. The concentrations of the mixtures and of the reference solutions were chosen so as to have a maximal absorbance of 1.0 to 1.6 in the wavelength region employed. Consequently, for the determination of the isomer distribution, the lower limit of the total toluenesulfonic acid concentration is about 1.2 mmole liter^{-1}. Absorbances of the test mixtures and of the reference solutions in 82.4 weight % sulfuric acid were measured at 39 equidistant points between 243 and 281 mμ, as simultaneously as possible for a given wavelength—i.e., within 3 minutes.

Oleum Analysis. Test mixtures of the three toluenesulfonic acids were made in 81.9 weight % sulfuric acid. To 3.8 ml. of these solutions, and of the *o*-, *m*-, and *p*-toluenesulfonic acid reference solutions, 5.0 ml. of oleum of about 65 weight % SO_3 (sulfur dioxide free) was added under external ice cooling (all dilutions were determined accurately by weighing). The mixtures were left overnight to accomplish the complete conversion into disulfonic acids (*2*). Absorbances of the test mixtures, and of the reference solutions, were measured at 40 equidistant points between 260 and 299 mμ.

Calculations. The least square calculations were made with the electronic computer ARMAC according to the program previously described by Herschberg and Sixma (*6*). The computer was programmed so as to yield the concentrations of the components in the mixture, relative to those in the reference solutions. In addition, a quantity $\hat{s}$ was calculated, which may be regarded as an estimated standard deviation: $\hat{s}^2 = \Sigma r_i^2/(k-n)$, where n is the number of unknown concentrations in the mixture, k is the number of wavelengths at which the absorbances were measured, and Σr_i^2 is the sum of the squares of the residuals between the observed and calculated spectrum of the mixture (*6*). All calculations were performed on the assumption of the presence of a constant background, ΔA—i.e., an extra compound with constant absorbance in the wavelength region employed.

Table I. Analysis in Sulfuric Acid of Mixtures of the Three Isomeric Toluenesulfonic Acids in Excess 82.4 Weight % Sulfuric Acid

	Mixture 1		Mixture 2		Mixture 3		Mixture 4	
	Taken	Found	Taken	Found	Taken	Found	Taken	Found
Ortho, mole %	26.7	26.6	20.9	21.3	28.0	28.7	24.5	25.0
Meta, mole %	0.0	0.1	1.4	0.9	4.7	3.9	9.2	8.5
Para, mole %	73.3	73.3	77.7	77.8	67.3	67.4	66.3	66.4
Total sulfonic acid concn., mmole kg.$^{-1}$	0.991	0.991	1.041	1.040	0.953	0.953	0.965	0.965
$\Delta A \times 10^3$		2.5		2.7		2.3		−4.2
$\hat{s} \times 10^3$		1.3		1.2		0.9		1.0

RESULTS AND DISCUSSION

The composition of the toluenesulfonic acid test mixtures was chosen similar to that expected to be produced in the sulfonation of toluene, namely an ortho to para ratio of about 0.3 and a low meta content (*7*, *16*).

Analysis in Sulfuric Acid. The results of multicomponent spectrophotometric analysis of toluenesulfonic acid mixtures in 82.4 weight % sulfuric acid are shown in Table I. As expected from the shape in absorption spectra, the para isomer is analyzed very accurately, whereas the

Table II. Analysis in Oleum[a] of Mixtures of the Three Isomeric Toluenesulfonic Acids in Excess 81.9 Weight % Sulfuric Acid

	Mixture 1			Mixture 2			Mixture 3			Mixture 4		
	Taken	Found		Taken	Found		Taken	Found		Taken	Found	
Ortho, mole %	33.4	34.2	...[b]	33.0	64.6	...[b]	32.5	85.2	...[b]	31.3	24.4	93.7	...[b]
Meta, mole %	0.0	−0.1	−0.1	1.3	0.8	0.9	3.0	2.2	2.4	6.3	6.4	6.3	6.5
Para, mole %	66.6	65.9	...[b]	65.7	34.6	...[b]	64.5	12.6	...[b]	62.4	69.2	...[b]	93.5
Total sulfonic acid concn., mmole kg.$^{-1}$	1.476	1.473	1.470	1.465	1.462	1.466	1.452	1.449	1.451	1.425	1.428	1.436	1.425
$\Delta A \times 10^3$		−6.2	−6.6		−0.3	0.1		10.2	10.4		−1.4	−0.6	−1.7
$\hat{s} \times 10^3$		0.8	0.8		1.3	1.3		1.5	1.5		1.4	1.5	1.4

[a] Ten weight % SO_3.
[b] Assumed to be zero in the calculation.

accuracy in the ortho and meta isomers is less satisfactory: the mean deviations of the ortho, meta, and para isomers being 0.43, 0.53, and 0.08 mole %, respectively. The total amount of toluenesulfonic acid is determined accurately to within 0.1 of a per cent. The very low values of $\hat{s}$ indicate that the spectra of the mixtures can indeed be expressed as a linear combination of the simultaneously observed spectra of their constituents. The excellent resolution further implies that Beer's law is obeyed up to the concentrations employed for the reference solutions, that is up to 1 mmole liter^{-1} for *o*- and *m*-toluenesulfonic acid and 2 mmole liter^{-1} for *p*-toluenesulfonic acid.

The difference between the ultraviolet absorption spectrum of toluene-2,4-disulfonic acid and those of the three toluenemonosulfonic acids (see Figures 1 and 2) also enables the analysis of a mixture of these four acids in excess sulfuric acid. The sulfuric acid analysis of mixtures of the three toluenemonosulfonic acids and of mixtures of these acids with toluene-2,4-disulfonic acid has been successfully applied to sulfonation mixtures in sulfuric acid, varying in concentration from 0 to 98 weight % H_2SO_4.

Analysis in Oleum. The results of multicomponent spectrophotometric analysis of toluenesulfonic acid mixtures in 81.9 weight % sulfuric acid, after treatment of these mixtures with concentrated oleum, are shown in Table II. The data reveal that *p*- and *o*-toluenesulfonic acid are interchangeable in the analysis. This indicates that on sulfonation of these two isomers the same compound, toluene-2,4-disulfonic acid, is formed. It seems improbable that *o*-toluenesulfonic acid is partially converted into toluene-2,6-disulfonic acid as the absorption spectra of toluene-2,4- and of toluene-2,6-disulfonic acid between 260 and 299 mμ should have to be identical in that case. Because of the interchange between *o*- and *p*-toluenesulfonic acid in the oleum analysis, only one of these isomers is required as reference to determine the sum of the ortho and para isomer. The data in Table II show a slightly better agreement for *p*- than for *o*-toluenesulfonic as reference; moreover *p*-toluenesulfonic acid is more easily purified (*16*). The analysis in oleum with *m*- and *p*-toluenesulfonic acid as references seems therefore the most attractive one. For the test mixtures such an analysis gives rise to a mean deviation of 0.33 mole % both in *m*-toluenesulfonic acid and in the sum of *o*- and *p*-toluenesulfonic acid. The analysis of *m*-toluenesulfonic acid in oleum is slightly more accurate than that in sulfuric acid, as indicated by the mean deviation (0.33 *vs.* 0.52 mole %, respectively).

The oleum analysis has been successfully applied to sulfonation mixtures in aqueous and fuming sulfuric acid, varying in composition from 60 weight % H_2SO_4 (*17*) to 32 weight % SO_3.

CONCLUSION

For the quantitative determination of mixtures of the three isomeric toluenesulfonic acids in excess concentrated aqueous sulfuric acid it seems advisable to perform a multicomponent spectrophotometric analysis both in sulfuric acid and in oleum. The former analysis gives an accurate figure of the content of the para isomer and of the sum of ortho and meta, the latter one of the content of the meta isomer. The amount of the ortho isomer equals the difference of the last two figures.

ACKNOWLEDGMENT

The authors express their appreciation to the late F. L. J. Sixma for encouragement, to I. S. Herschberg for stimulating discussions and for carrying out the calculations on the ARMAC electronic computer, and to the Directors of the Mathematical Centre, Amsterdam, for placing the electronic computer ARMAC at their disposal.

LITERATURE CITED

(1) Cerfontain, H., *Rec. Trav. Chim.* **80**, 257 (1961).
(2) *Ibid.*, 298 (1961).
(3) Cerfontain, H., Kaandorp, A. W., Sixma, F. L. J., *Ibid.*, **79**, 936 (1960).
(4) Englund, S. W., Aries, R. S., Othmer, D. F., *Ind. Eng. Chem.* **45**, 189 (1953).
(5) Glogan, R. C., Halvorson, D. O., Sloan, W. J., *Ibid.*, **53**, 275 (1961).
(6) Herschberg, I. S., Sixma, F. L. J., *Koninkl. Ned. Akad. Wetenschap. Proc., Ser. B* **65**, 244, 256 (1962).
(7) Holleman, A. F., Caland, P., *Ber. Deut. Chem. Ges.* **44**, 2504 (1911).
(8) Kirkland, J. J., ANAL. CHEM. **32**, 1388 (1960).
(9) Lauer, K., Oda, R., *J. Prakt. Chem.* **143**, 139 (1935).
(10) Pinchas, S., Avinur, P., ANAL. CHEM. **30**, 2022 (1958).
(11) Spryskov, A. A., *Izvest. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol.*, **1958**, No. 6, p. 42; *C.A.* **53**, 16043*i* (1959).
(12) Spryskov, A. A., Yakovleva, T. I., *J. Gen. Chem. U.S.S.R.* **27**, 239 (1957).
(13) Sternberg, J. C., Stello, H. S., Schwendeman, R. H., ANAL. CHEM. **32**, 84 (1960).
(14) Stewart, F. N., Caldwell, J. E., Uelner, A. F., *Ibid.*, **31**, 1806 (1958).
(15) Suter, C. M., Weston, A. M., "Organic Reactions," R. Adams, ed., Vol. III, p. 151, Wiley, New York, 1947.
(16) Vollbracht, L., Cerfontain, H., Sixma, F. L. J., *Rec. Trav. Chim.* **80**, 11 (1961).
(17) Wanders, A. C. M., Kort, C. W. F., Laboratory for Organic Chemistry, University of Amsterdam, The Netherlands, private communication.

RECEIVED for review November 15, 1962. Accepted March 11, 1963.

Spectrophotometric Hydroperoxide Determination by the Use of Triphenylphosphine

ROBERT A. STEIN and VIDA SLAWSON

Department of Biological Chemistry, University of California, Los Angeles 24, Calif.

▷ A spectrophotometric analysis of hydroperoxides is described. The decrease in absorbance at 260 mμ when triphenylphosphine is oxidized to triphenylphosphine oxide by a hydroperoxide is a quantitative measurement of the hydroperoxide present. Quantitative values for autoxidized fats, H_2O_2, *t*-butyl hydroperoxide, and benzoyl peroxide are compared with those obtained by iodometric and ferric thiocyanate methods. Di-*s*-butyl peroxide does not react with the phosphine under the conditions specified.

THE REACTION of triphenylphosphine (TPP) with peroxides has been shown to yield triphenylphosphine oxide (TPPO) (*5*, *10*). Hydroperoxides react rapidly with the phosphine (*2*), whereas diperoxides must first dissociate into alkoxy radicals before reaction occurs (*10*). In this report we will show that under conditions that do not give an homolytic cleavage of diperoxides into radicals, it is possible to measure hydroperoxides quantitatively.

The ultraviolet absorption maxima of TPP and TPPO are sufficiently different so that the reaction may be followed spectrophotometrically. This method was used to determine a wide range of peroxide values in peroxidized fats, for hydrogen peroxide, benzoyl peroxide, and *t*-butyl hydroperoxide, and for demonstrating the lack of reactivity in di-*s*-butyl peroxide.

EXPERIMENTAL

Reagents. TPP (Matheson Coleman & Bell, No. TX-1490) was recrystallized from absolute ethanol, ϵ_{max}, 1.10×10^4 at 260 mμ [Literature value ϵ_{max}, 1.10×10^4 at 261 mμ (*6*)]. TPPO was prepared by the oxidation of TPP by 30% H_2O_2 in $CHCl_3$–acetone solution 1:2. ϵ, 1.52×10^3 at 260 mμ. Isopropyl alcohol, reagent grade (Baker and Adamson), was deoxygenated by bubbling nitrogen through it for 15 minutes on the steam bath. Cottonseed oil and corn oil were obtained from retail food stores. Soybean oil (Vegetable Oil Products, Wilmington, Calif.) was oxidized at 60° C. by aeration in the presence of 2 mg. per kg. each of $CuCl_2$ and $FeCl_3$. *t*-Butyl hydroperoxide which was synthesized (*7*) was assayed by iodometry and found to be 93.0%. Di-*s*-butyl peroxide was synthesized (*11*). Hydrogen peroxide was 30% (Merck Co.). Benzoyl peroxide (Matheson Coleman & Bell, No. BX-470). Di-*t*-butyl-*p*-cresol (Koppers Co., Inc.) was used as the antioxidant.

Ultraviolet absorption spectra were measured in 1-cm. silica cells in a Beckman DU spectrophotometer.

Reference Peroxide Methods. Iodometric 1: The method of Polister and Mead (*9*) was used with a modification to utilize isopropyl alcohol as solvent and a 12-minute reaction time at 60° C. Iodometric 2: The official A.O.C.S. method (*3*). Ferric thiocyanate: The aerobic procedure of Glavind and Hartmann (*4*) was modified to use chloroform–methanol 8:3 instead of chloroform–ethanol 8:3.

Triphenylphosphine Peroxide Method. The TPP reagent consists of 1 mg. of TPP and 0.1 mg. of antioxidant (di-*t*-butyl-*p*-cresol) in 1 ml. of isopropyl alcohol. This is conveniently prepared by weighing 25 mg. of TPP into a 25-ml. volumetric flask. The antioxidant, 2.5 ml. of an isopropyl alcohol solution containing 1 mg. per ml. of di-*t*-butyl-*p*-cresol, is added and the solution made up to volume with isopropyl alcohol. A peroxide sample containing about 2×10^{-3} meq. of peroxide is weighed into a 10-ml. flask and dissolved in 1 ml. of isopropyl alcohol. After addition of 1 ml. of TPP reagent, the flask is stoppered, swirled to mix, and inverted once to rinse the neck. The mixture is allowed to stand for 20 minutes at room temperature and brought to volume by the addition of isopropyl alcohol. A secondary dilution of 1 ml. to 10 ml. is made for spectrophotometric reading. The absorbance of the reaction mixture is measured at 260 mμ against isopropyl alcohol. A sample blank composed of a peroxide sample in isopropyl alcohol is measured at 260 mμ to correct for the initial absorbance of the samples. A reagent blank consisting of 1 ml. of TPP reagent and 1 ml. of isopropyl alcohol and subsequently treated as a sample is prepared with each series of samples.

Unless otherwise indicated, all figures represent the average of two determinations.

Calculations. Decrease in the absorbance of the reaction mixture at 260 mμ is used as a measure of hydroperoxide originally present. Since oxidation of TPP yields TPPO, which also has a significant absorbance at this wavelength, allowance must be made for contribution of TPPO to the absorbance of the total reaction mixture.

$$\text{Peroxide value (meq./kg.)} = \frac{A_r + A_s - A}{\text{sample weight}} \times 21.1$$

where A_r and A are the absorbances of the reagent blank and the reaction mixture, respectively. A_s is the absorbance of the sample blank calculated for the weight of sample in the reaction mixture. The 21.1, a constant, is a quotient obtained by dividing 2×10^5 (to convert to meq./kg. for the dilution specified) by the difference between the molar absorptivity of TPP (1.10×10^4) and TPPO (1.52×10^3) at 260 mμ.

RESULTS AND DISCUSSION

Comparison of Methods of Peroxide Determination. Soybean oil that was autoxidized to various peroxide values

Table I. Peroxide Values of Oxidized Soybean Oils

Meq. of peroxide per kg. of oil

Sample	TPP	Iodometry 1	Iodometry 2	Ferric thiocyanate
1	0.48	0.7	0.6	1.03
2[a]	10.6	10.8	12.2	16.8
3[a]	26.2	30.3	30.2	44.4
4[a]	64.7	69.2	71.4	96.9
5	90.0	98.5	96.9	170
6	269	278	263	488
7	594	577	380 (578[b])	1014
8	656	678	398 (685[b])	1190
9	1561	1624	...	2163

[a] Mixtures of samples 1 and 5.
[b] Single determination on 0.5-gram sample.

was analyzed by the TPP, two iodometric, and the ferric thiocyanate methods. The values for the two iodometric methods deviate from one another in a random manner. To be particularly noted is the fact that with but one exception the phosphine procedure gave lower results than iodometry (Table I).

It was previously noted (*2*) and verified in this study (see below) that a disubstituted peroxide does not react with TPP under the experimental conditions used here. Since the diperoxide does react with iodide to a slight extent, it may be considered that the differences in the values obtained by TPP and those obtained by iodometry are a measure of the disubstituted peroxides reduced by iodide ion. Thus, it may be concluded that the TPP method offers a more accurate measurement of hydroperoxide content than does iodometry.

The values obtained by the ferric thiocyanate method are much larger than those obtained by iodometry. The extreme susceptibility of this method to interference by atmospheric oxygen can result in values as high as three times those obtained by iodometry (*1*).

Samples of commercial cotton seed and corn oils from different sources were analyzed for peroxide values to determine the importance of composition of the oil on the method (Table II). The TPP values are not consistently lower than the iodometric values as is the case with the oxidized soybean oils. In fact, the TPP values are slightly larger than the iodometric values for the cotton and corn oils. This may represent the extent to which iodine is absorbed by the double bonds of the oil during the analysis. In the cotton seed and corn oil, the peroxides developed spontaneously and at these low levels are expected to consist of hydroperoxides which would be analyzed by both TPP and iodometry. The comparable low levels of peroxide in the soybean oil were made by dilution of an oil with a peroxide value of 90 with unoxidized oil. At the level of oxidation represented by peroxide value of 90, polymeric peroxides are probably present (*3*). A reduction of these diperoxides by iodide but not by TPP will cause the observed difference in values.

The Effect of Reagent/Sample Ratio. Varied amounts of soybean oil were analyzed for peroxide by a constant amount of TPP in order to determine the influence of the reagent/sample ratio on the reaction (Table III). As long as 86% or less of the reagent was consumed during the reaction, the determination had a precision of ±0.4. If more than 86% of the reagent is required to reduce all of the hydroperoxide, the reaction appears to be incomplete in the 20-minute reaction time with the resultant low value for the peroxide.

Table II. Effect of Oil Variety on Peroxide Value

Meq. of peroxide per kg. of oil

Oil	TPP	Iodometry 1	Iodometry 2	Ferric thiocyanate
Cottonseed 1	14.7	14.0	17.8	26.0
Cottonseed 2	29.7	26.6	28.7	41.0
Cottonseed 3	2.34	2.2	2.02[a]	2.87
Corn 1	3.87	2.2	1.41[a]	1.92
Corn 2	9.78	8.0	7.87	13.4[a]

[a] Single determinations.

Table III. Effect of Changing Reagent/Sample Ratio

Sample wt. soybean oil, gram	Per cent of 4.06 μmole reagent consumed	Peroxide value[a] meq./kg.
0.030	10	27.4
0.060	20	27.4
0.142	50	28.5
0.150	52	28.0
0.171	60	28.5
0.199	69	28.1
0.225	76	27.6
0.228	78	27.8
0.256	86	27.3
0.285	91	25.9
0.300	95	25.6

[a] Single determinations.

Reaction of Simple Peroxides. Using the concentrations of sample and TPP reagent specified above, hydrogen peroxide, *t*-butyl hydroperoxide, and benzoyl peroxide gave low values. By increasing the concentrations of TPP and peroxide 10-fold, but leaving the antioxidant concentration unchanged, the reaction went to completion and expected values were obtained (Table IV).

The reason for incomplete reaction of *t*-butyl hydroperoxide at the lower concentration is attributed to the well known dependency of reaction rates on concentrations. Time studies with the concentration given in the experimental section showed that the apparent *t*-butyl hydroperoxide concentration increased with reaction time longer than the 20 minutes specified. The apparent concentration increased from 54% at 20 minutes to 89% at 105 minutes. The fat peroxides did not show this slower reaction rate, nor did a 10-fold increase in reactant concentration result in higher peroxide values.

Di-*s*-butyl peroxide, which is a simple model of the di-*secondary* peroxides found in autoxidized fats, was unreactive using conditions outlined here for the TPP reaction. This evidence suggests that the diperoxides in autoxidized fats are unaffected by this reagent.

Effect of Added Antioxidant. Alcoholic solutions of TPP are oxidized slowly to the oxide presumably by atmospheric oxygen. This change is taken into account by a comparison of the reagent blank. However, the addition of an antioxidant decreases this autoxidation to a negligible amount, and a reagent blank is unchanged after as long as three hours.

Noninterfering Compounds. Several compounds with functional groups representative of possible autoxidation products from fats were tested for reaction with TPP. 12-Ketooctadec-10-enoic acid, 9,11-octadecadienoic acid, 2-butanone, and isobutyraldehyde caused no measurable oxidation of TPP in concentrations of sample and reagent specified in the experimental part.

Adherence to Beer's Law. Mixtures of TPP and TPPO obeyed Beer's law over a concentration range greater than that covered by the peroxider determinations.

Table IV. Analyses of Simple Peroxides

Per cent of theoretical

Peroxide	TPP	Iodometry 2	Ferric thiocyanate	TPP[a]
30% H_2O_2	81.7	96.0	48.3	98.3
t-Butyl hydroperoxide	54.0	95.5	95.9	100.3[b]
Di-*s*-butyl peroxide[c]	0	2.1[d]	...	...
Benzoyl peroxide	75.8[d]	98.6	...	102.8[d]

[a] Concentration of reactants were increased to 10 times the prescribed concentrations. [b] Reaction conducted in 95% ethanol. [c] Iodometry 1 gave 1.7%, constant boiling HI at 60° gave 6–10% in 45 minutes, and KI in refluxing isopropyl alcohol containing 1.5% acetic acid gave 8% in 24 hr. [d] Single determination.

LITERATURE CITED
(1) Chapman, R. A., McFarlane, W. D., *Can. J. Research* B 21, 133 (1943).
(2) Denney, D. B., Goodyear, W. F., Goldstein, B., *J. Am. Chem. Soc.* 82, 1393 (1960).
(3) Farmer, E. H., *Trans. Faraday Soc.* 42, 228 (1946).
(4) Glavind, J., Hartmann, S., *Acta Chem. Scand.* 9, 497 (1955).
(5) Horner, L., Jurgeleit, W., *Ann.* 591, 138 (1955).
(6) Jaffe, H. H., Freedman, L. D., *J. Am. Chem. Soc.* 74, 1069 (1952).
(7) Milas, N. A., Surgenor, D. M., *Ibid.*, 68, 205 (1946).
(8) "Official and Tentative Methods of the American Oil Chemists' Society," 2nd edition. A.O.C.S. Official Method Cd 8-53, 1960, American Oil Chemists' Society, Chicago.
(9) Polister, B. H., Mead, J. F., *J. Agr. Food Chem.* 2, 199 (1954).
(10) Walling, C., Basedow, O. H., Savas, E. S., *J. Am. Chem. Soc.* 82, 2181 (1960).
(11) Welch, F., Williams, H. R., Mosher, H. S., *Ibid.*, 77, 551 (1955).

RECEIVED for review December 21, 1962. Accepted April 29, 1963. Investigation supported by Public Health Service Research Grant H-4120 from the National Heart Institute, National Institute of Health, U. S. Public Health Service, Bethesda, Md.

Spectrophotometric Titration of Some Divalent Metals in Chloroform–Isopropyl Alcohol Solvent Mixture

ROY K. BEHM[1] and REX J. ROBINSON
Department of Chemistry, University of Washington, Seattle 5, Wash.

▶ **Dimethylglyoxime was used as a titrant of micro amounts of nickel(II) and cobalt(II) in a solution of 1:1 chloroform–isopropyl alcohol mixture. Spectrophotometric titrations of 0.4 to 4 μmoles of nickel(II) in 40 ml. of solvent were done with an over-all precision of 3 parts per thousand. Cobalt(II) in amounts of 1 to 4.5 μmoles was titrated with a precision of 2.5 parts per thousand. Palladium(II) and iron(II) form chelates, but react too slowly for titrations. Copper(II) could not be titrated because a mixture of several species of chelates in equilibrium was formed. Copper(II), iron (II), palladium(II), and cobalt(II) interfere in the titration of nickel(II). These metals and nickel(II) interfere in the cobalt titration.**

THE METHOD of spectrophotometric titrations has been applied to the determination of metals with organic precipitating or chelating agents in nonaqueous solvents by Boyle and Robinson (*1*), Marple, Matsuyama, and Burdett (*3*), and Takahashi and Robinson (*4*). Nonaqueous solvents, especially organic solvents, are desirable because they are capable of dissolving the organic precipitating agent and the metal chelate formed. In addition, the metal ion can be titrated directly in the organic phase without further involvement with the aqueous phase. The solvent, when properly chosen, may also enhance the color development of the chelate. Organic precipitating agents are especially applicable for such titrations because of their specific and sensitive reactions with metal ions. Spectrophotometric end point detection can be used to good advantage either in the visible or ultraviolet region. The factors of solvent, reagent, and spectrophotometric titrations combine to provide an effective means of titrating micro amounts of metal ions with high precision and accuracy.

In this work dimethylglyoxime was chosen as titrant because of its well known reactions with metal ions. A 1:1 mixture by volume of chloroform and isopropyl alcohol was chosen as solvent.

EXPERIMENTAL

Reagents. Standard solutions of 0.1*M* nickel and copper were prepared by dissolving Baker's analyzed reagent grade metal in a minimum amount of nitric acid and diluting to volume with distilled water. A standard solution of 0.1*M* cobalt was made by dissolving Merck high purity nickel-free cobalt in a minimum amount of hydrochloric acid and diluting to volume with distilled water. A 0.01*M* palladium solution was made by dissolving Fisher Scientific Co. pure palladium chloride in distilled water containing a minimum amount of hydrochloric acid to facilitate solution by forming $PdCl_4^{-2}$ and then diluting to volume with distilled water. A solution of iron was prepared 0.01*M* by dissolving Baker's analyzed reagent grade iron wire in a minimum amount of perchloric acid and diluting to volume. Nickel and palladium solutions were standardized gravimetrically with dimethylglyoxime. The cobalt solution was standardized gravimetrically as cobaltous sulfate. Dilute standard solutions were prepared by appropriate dilution of the previous standard solutions. Solutions of gold chloride made with Fisher Scientific Co. C.P., $AuCl_3 \cdot HCl \cdot 3H_2O$ and chloroplatinic acid made with Baker's 5% chloroplatinic acid solution, purity unspecified, were not standardized since preliminary exploratory tests proved unsuccessful. Eastman Kodak White Label dimethylglyoxime, melting point 239° C., was recrystallized four times from a 2:1 acetone–water mixture and was stored over anhydrous calcium sulfate. Standard solutions of dimethylglyoxime, ranging in concentration from 0.0008 to 0.005*M*, were prepared by weighing definite amounts, dissolving, and diluting to 500 ml. with chloroform–isopropyl alcohol solvent. Standardization against standard metal solutions showed that dimethylglyoxime solutions were stable for at least three weeks.

Chloroform was Mallinckrodt reagent grade.

Isopropyl alcohol was Eastman Kodak White Label, 98 to 99%.

n-Butylamine (Matheson Coleman and Bell), boiling range, 76° to 78° C., was distilled from an all glass apparatus.

Cyclohexylamine (Matheson Coleman and Bell), was treated with sodium and distilled from an all glass apparatus, boiling temperature 135° C.

Acetic acid was Merck, reagent grade, 99.8%.

Apparatus. A Beckman Model DU spectrophotometer was used for optical measurements, except for the spectrum of dimethylglyoxime which was taken on a Cary Model 11 recording spectrophotometer. Spectra were taken with pure solvent as reference in matched, 1-cm. silica cells. The metal chelate solutions were prepared by evaporating pipetted amounts of the aqueous metal ion solutions to crystals, dissolving, adding chelating agent, and diluting to volume with nonaqueous solvent. The spectrophotometric titrations were made with the DU spectrophotometer using the modified cell compartment as described by Boyle and Robinson (*1*), except that magnetic stirring was used. The titrant was measured with a 10-ml. Fischer and Porter microburet having a Teflon stopcock plug. The buret was attached to a 1000-ml. flat-bottomed flask connected to two microbubble

[1] Present address, Eastman Kodak Co., Rochester 3, N. Y.

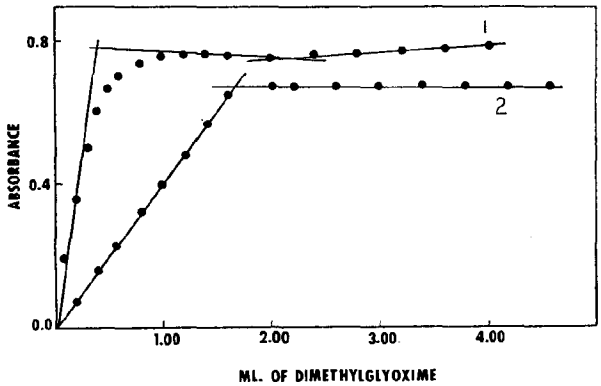


Figure 1. Titrations of nickel(II) and copper(II) with dimethylglyoxime

1. 5.98 μmoles of copper(II), 0.00534M dimethylglyoxime, 2.5% n-butylamine, in 1:1 chloroform–isopropyl alcohol mixture, at 410 mμ; 3:1 end point 0.370 ml.; 1:2 end point 2.182 ml.

2. 1.989 μmoles of nickel(II), 0.002470M dimethylglyoxime, 2.5% n-butylamine in 1:1 chloroform–isopropyl alcohol mixture, at 370 mμ; 1:2 end point 1.610 ml.

counters with Tygon tubing. The flask contained 200 to 300 ml. of the chloroform–isopropyl alcohol solvent to act as a reservoir of saturated vapor. The two bubble counters were half-filled to prevent escape of the vapors. Thus, the buret was effectively closed and solvent evaporation was restricted to about 0.02 ml. over a 24-hour period. The buret was calibrated at 1.0-ml. intervals using the densities reported in this work. The densities were obtained using a 50-ml. volumetric flask as a pycnometer and a constant temperature bath which could be regulated to ±0.1° C. Pipets and volumetric flasks were calibrated in the usual manner.

Absorption Spectra. Spectra were taken of dimethylglyoxime, chelates of nickel(II), cobalt(II), palladium (II), and iron(II) in chloroform–isopropyl alcohol solvent from 320 mμ to 600 mμ. Solutions were made to contain no excess chelating agent and, in general, contained chelates of molar ratios of 1:2, 1:1 or mixtures of such ratios. A more complex situation was found to occur in the case of copper. The metal chelates absorbed generally in the 320 to 450 mμ region. Dimethylglyoxime gave an absorption maximum at 238 mμ and absorbed only slightly from 320 mμ to 450 mμ. To determine the effect of acidity or basicity on the absorption of the chelates, spectra were taken of solutions of the metal chelates, containing 2.5% n-butylamine or 2.5% acetic acid. Generally the absorption of the chelates was increased in the presence of n-butylamine; in the case of the iron(II) chelate, however, the absorbance decreased. The presence of acetic acid caused the absorbance of all the metal chelates to decrease. The increases in absorption and slight bathochromic shifts occurring in basic solutions indicated greater stability of the metal chelates. Consequently the titrations were generally carried out in solutions made basic with an amine.

Titration Procedure. About 0.4 to 5 μmoles of dilute standard metal ion solution were pipetted into a 50-ml. beaker. The sample was evaporated under infrared light to a dewlike residue in a vacuum desiccator evacuated by a water aspirator. The salt crystals were dissolved in 40 ml. of solvent, either pure or containing acetic acid, n-butylamine, or cyclohexylamine. The beaker was placed in the rubber ring holder in the microcell compartment of the Beckman DU spectrophotometer and stoppered with a tight fitting cork lid to prevent evaporation. The solution was stirred magnetically for about 5 minutes. The proper wavelength was set and the sensitivity adjustment turned from 1 to 3.5 turns clockwise from the counterclockwise limit. The buret tip was inserted through the compartment lid and the cell compartment was made light tight by taping the edges of the compartment lids with black plastic tape. The buret was then connected to the flask containing the solvent to prevent solvent evaporation, and the titration was performed. The wavelength for titration was chosen so that each 0.1 ml. of titrant produced a change in absorbancy from about 0.01 to 0.08 unit. Absorbance values were kept between 0.0 and 0.700 for most titrations.

Conventional photometric titration procedures were followed in correcting absorbance readings for volume corrections and titrant volumes to 22° C. Conventional large scale plotting procedures were used to establish the end point to 0.001 ml. It was determined experimentally that the densities of 1:1 mixtures of chloroform–isopropyl alcohol solvent at different temperatures, over the 20° to 30° C. range, could be calculated from the equation:

$$D_t = 1.132 - 0.00133\ (t - 20°\ \text{C.})$$

RESULTS AND DISCUSSION

Nickel(II) nitrate was titrated at 370 mμ in solutions made basic with n-butylamine. The titrations showed that the nickel chelate had a molar ratio of 1:2 (nickel–dimethylglyoxime). Titration curve No. 2, shown in Figure 1, is typical. Results shown in Table I have both precision and accuracy. For the series of titrations the over-all precision was about 3 parts per thousand and the over-all average error was about 2%. When solutions of nickel(II) ions containing acetic acid were titrated, results were generally more variable and the resulting titration curves more rounded in the region of the

Table I. Titration of Nickel(II) with Dimethylglyoxime at 370 mμ

Nickel μmoles	Dimethylglyoxime Ml.	Mole/l., experimental	Mole/l., prepared
0.398	0.557	0.001427	
0.398	0.560	0.001422	
0.398	0.558	0.001426	
	Av.	0.001425	0.001385
	Av. Dev.	0.000002	
0.793	0.865	0.001834	
0.793	0.856	0.001853	
0.793	0.860	0.001845	
0.793	0.870	0.001823	
	Av.	0.001838	0.001772
	Av. Dev.	0.000010	
1.989	2.246	0.001772	
1.989	2.261	0.001759	
1.989	2.235	0.001780	
	Av.	0.001770	0.001772
	Av. Dev.	0.000007	
1.989	1.609	0.002472	
1.989	1.610	0.002471	
1.989	1.610	0.002471	
	Av.	0.002471	0.002470
	Av. Dev.	0.0000003	
3.970	5.702	0.001393	
3.970	5.650	0.001405	
3.970	5.690	0.001395	
	Av.	0.001397	0.001385
	Av. Dev.	0.000004	

Table II. Titration of Cobalt(II) with Dimethylglyoxime at 370 mμ

Cobalt μmoles	Dimethylglyoxime Ml.	Mole/l., experimental	Mole/l., prepared
0.911	1.090	0.000836	
0.911	1.092	0.000834	
0.911	1.101	0.000828	
0.911	1.101	0.000828	
	Av.	0.000832	0.000822
	Av. Dev.	0.000004	
1.818	2.182	0.000833	
1.818	2.181	0.000834	
1.818	2.182	0.000833	
	Av.	0.000833	0.000822
	Av. Dev.	0.0000003	
4.555	5.220	0.000873	
4.555	5.244	0.000869	
4.555	5.242	0.000869	
	Av.	0.000870	0.000822
	Av. Dev.	0.000001	

end point, indicating reduced chelating strength.

Interferences were noted with Co(II), Cu(II), Fe(II), and Pd(II) present when titrating 2 μmoles of nickel. The reactions were much slower and the results were high by 2 to 3% with as little as 1 μmole of copper or iron, 2 μmoles of cobalt, or 5 μmoles of palladium present.

The titration of cobalt at 370 mμ gave results (Table II) with a precision of about 2.5 parts per thousand and an average error of about 3%. These titrations were performed in solutions of cobalt(II) made basic with cyclohexylamine. Cobalt(II) was the chloride, although acetate, perchlorate, or nitrate was equally satisfactory. Cobalt solutions made basic with *n*-butylamine, as in the nickel titrations, were unsuitable because the titration reaction proceeded very slowly with subsequent drift of absorbance readings. The titration curve was similar to the curve of the nickel titration; however, with cobalt, the molar ratio of the complex was 1:1.

Cobalt titrations suffered interference in the presence of Ni(II), Pd(II), Fe(II), and Cu(II). When titrating 4.5 μmoles of cobalt, the presence of as little as 0.4 μmole of nickel or 1 μmole of palladium produced results high by about 3%. With as little as 1 μmole of iron or copper present, the reaction slowed to an unusable rate.

The titration of a number of other metals was tried but unsuccessfully. Gold and platinum formed no chelates under these conditions. Iron(II) and palladium reacted too slowly to be practically determined. With palladium, breaks in the titration curve at 389 mμ occurred at molar ratios of 1:1 and 1:2 (palladium–dimethylglyoxime). Copper(II) could be titrated at 410 mμ in the presence of *n*-butylamine but yielded a titration curve which was too rounded at the end point to yield accurate results. Breaks in the curve (Figure 1) occurred at molar ratios of 3:1 and 1:2 (copper–dimethylglyoxime).

Brummet and Hollweg (*2*) also determined nickel and copper in a nonaqueous medium with dimethylglyoxime as chelating agent, but not by a spectrophotometric titration procedure. Two μmoles of nickel or copper in a methanol–benzene medium were reacted with an excess of dimethylglyoxime and the two hydrogen ions liberated per nickel ion titrated potentiometrically with 0.1*N* sodium hydroxide. They obtained a mean deviation of 0.2% for nickel. Although they gave no specific value for copper, they indicated that it could be determined accurately. This is about the same precision obtained by the present authors for the direct titration of μmole quantities of nickel and cobalt spectrophotometrically.

LITERATURE CITED

(1) Boyle, W. G., Jr., Robinson, R. J., ANAL. CHEM. **30**, 958 (1958).
(2) Brummet, B. D., Hollweg, R. M., *Ibid.*, **28**, 448 (1956).
(3) Marple, T. L., Matsuyama, George, Burdett, L. W., *Ibid.*, **30**, 937 (1958).
(4) Takahashi, I. T., Robinson, R. J., *Ibid.*, **32**, 1350 (1960).

RECEIVED for review July 9, 1962. Accepted April 11, 1963.

Spectrophotometric Determination of Aldrin

HAKON O. FRIESTAD

Department of Pharmacology and Toxicology, The Veterinary College of Norway, Oslo, Norway

▷ The described method depends upon the possibility of converting aldrin to dihydroaldrin nitrosochloride by means of nitrosylchloride. This compound, reacting in the tautomeric oximform, forms dihydrochlorketoaldrin, which, in turn, reacts with *m*-dinitrobenzene and potassium hydroxide, yielding a violet-red derivative, extractable with chloroform. The absorbance of the resulting solution obeys Beer's law over the range studied (0 to 100 μg.). Recovery experiments show promising results when applied to samples of both animal and vegetable origin.

THE MOST FREQUENTLY applied method for the determination of micro amounts of the insecticide aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene), seems to be the modification of the Danish and Lidov (*4*) colorimetric method described by O'Donnell *et al.* (*9*). It is based on the reaction of phenylazide with the chlorine-free double bond of aldrin, whereby a triazole derivate is formed. This derivate acts as azocomponent when coupled with diazotized 2,4-dinitroaniline. The resulting red color solution is measured spectrophotometrically.

This paper describes another spectrophotometric method which has certain advantages compared to the aforementioned one. It does not require, for instance, a specially designed glass apparatus, and the highly explosive and unstable phenylazide is not used.

This method is based on aldrin reactions not described previously. Nitrosylchloride, produced from ethyl nitrite and hydrochloric acid, reacts with aldrin at the chlorine-free double bond whereby dihydroaldrin nitrosochloride is formed. This reacts in the tautomeric oximform and by heating in acid solution it is saponified to the corresponding ketone. The carbonyl compound reacts in alcoholic solution with *m*-dinitrobenzene and potassium hydroxide resulting in a red-violet colored solution which makes a spectrophotometric determination possible. The reaction scheme is shown in Figure 1.

This technique of converting hydrocarbons to ketones via the nitrosochlorides has been used frequently in terpene chemistry since Tilden discovered that nitrosyl chloride reacts with double bonds. Wallach (*11*) has described a standard method for the developing of nitrosochlorides which we successfully used in macroscale on aldrin. The nitroso compound was not isolated but converted directly to dihydrochlorketoaldrin (III) by heating the acid solution. As far as the author is aware, dihydrochlorketoaldrin has not been described previously. The compound may be purified by sublimation (from 150° C.), whereby small triangular prismatic crystals are formed, melting at 192° to 196° C. The quantitative elemental analysis of the purified compound gave the following results:

	C %	H %	Cl %	O %
	34.91	2.00	58.95	4.14 (diff.)
Calculated for (III):				
($C_{12}H_7OCl_7$)	34.70	1.70	59.75	3.85

The infrared transmittance curve of the compound is shown with the corresponding aldrin spectrum in Figure 2. The strong absorption at 1775 cm.$^{-1}$ indicates the presence of a carbonyl group. The absorption at the relatively high frequency is a result of the strain in the five-membered ring and of the chlorine atom in α-position to the carbonyl group. The peak at 1600 cm.$^{-1}$ indi-

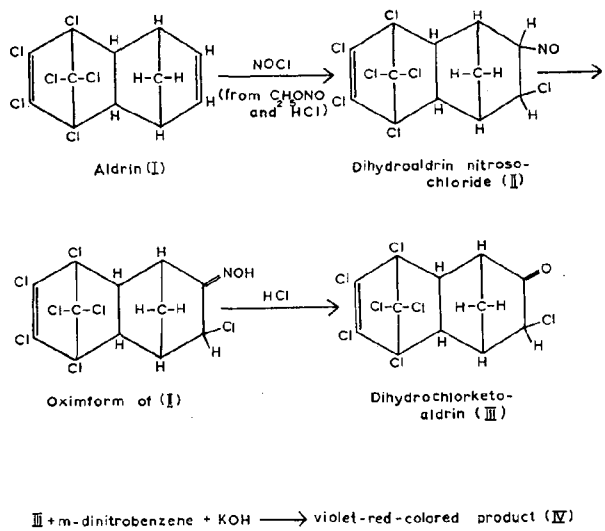


Figure 1. Chemistry of method

cates a —C = C— bond. The double bond in the chlorinated ring thus is intact.

Another fact also confirms the presence of a carbonyl group in the isolated compound. It reacts with *m*-dinitrobenzene and potassium hydroxide giving a colored compound. As shown by Bittó (*1*) this reaction is characteristic for carbonyl compounds. The reaction has previously been applied in colorimetric analysis; for example, by Zimmermann (*12*) for the determination of 17-ketosteroids, and by Schechter and Hornstein (*10*) for the analysis of lindane. In the last mentioned a ketone is used to determine *m*-dinitrobenzene formed from the lindane. The mechanism of this reaction has not yet been established.

EXPERIMENTAL

Apparatus. Spectrophotometer, Beckman Model DU, or equivalent, with 10-mm. absorption cells.

Reagents. Ethyl ether, free from peroxides.

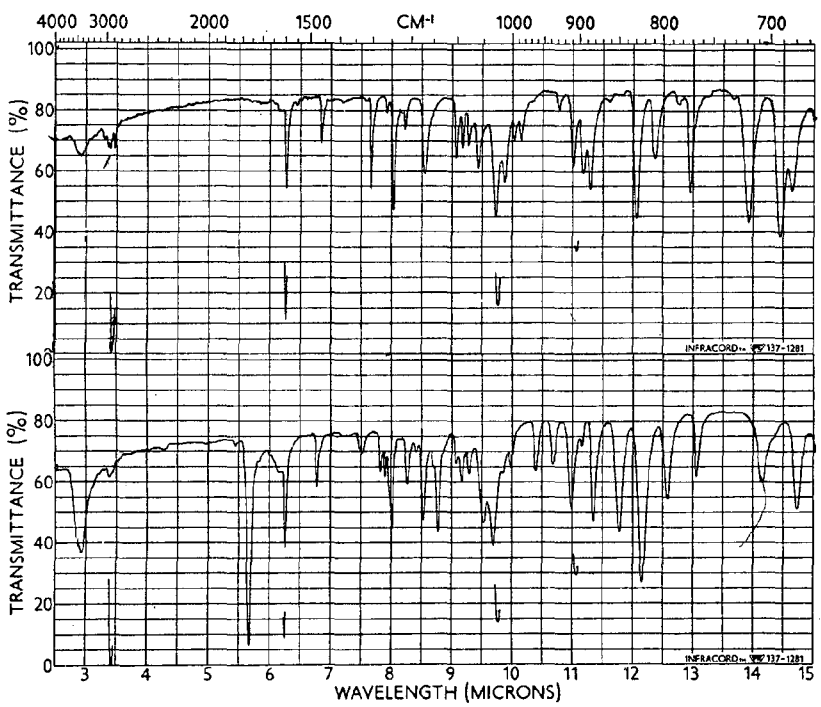


Figure 2. Infrared transmittance curve for aldrin (upper) and dihydrochlorketo-aldrin (lower) in KBr (1:200)

Ethyl nitrite. This compound, which has a boiling point of 17° C., is difficult to obtain commercially, but may be produced as follows [Gattermann-Wieland (*6*)].

In a distillation flask dissolve 37 grams of sodium nitrite in 70 ml. of water and add 60 ml. of ethanol. While stirring this mixture add (by drops) 42 ml. of concentrated hydrochloric acid. The temperature should be kept lower than 5° C. by use of an icebath. Connect the flask to a condenser and place on a waterbath. Slowly increase the temperature of the waterbath to 40° C. Collect the distillate in a flask placed in an icebath. This ethyl nitrite may be kept for 1 to 2 weeks if stored in a refrigerator (−15° C.) in a bottle with glass-stopper. In this method it is used in the form of a freshly prepared 30% ether solution.

Aldrin standard solution. An ether solution containing 10 μg. per ml. of aldrin.

Procedure. To a 10-ml. ether solution of the aldrin sample in a 100-ml. Erlenmeyer flask with glass-stopper, add 2 ml. of 30% ethyl nitrite–ether solution, and 1 ml. of concentrated hydrochloric acid. Secure the flask with the glass-joint-stopper and allow the solution to stand at room temperature overnight (12 hours minimum). The following day add 25 ml. of diluted hydrochloric acid (1 to 4) and place the flask without stopper for 30 minutes on a boiling waterbath. Leave the flask undisturbed on the bath; the ether will then evaporate without boiling over. After cooling to room temperature, pour the solution into a 250-ml. separatory funnel. Rinse the flask with 50 ml. of water, and then with 50 ml. of ether and transfer the rinsings to the funnel. Wash the flask once more with 50 ml. of ether and transfer the ether to a second 250-ml. separatory funnel. Shake the first funnel for approximately 1 minute, let the layers separate, and transfer the aqueous portion to the other separatory funnel. Shake this funnel for 1 minute and discard the aqueous portion. Wash the ether in the first and second funnels successively with 50 ml. of water; repeat it with another 50-ml. portion of water. Combine and drain the ether extracts into a 250-ml. Erlenmeyer flask by filtering through a 2-cm. layer of anhydrous sodium sulfate, which is kept in position in a Gooch crucible holder (about 40 mm. in diameter) by a cotton plug. Rinse the two separatory funnels with 15 ml. of ether and filter the ether through the layer of sodium sulfate. Repeat this procedure twice. To the solution, add a glass bead and a drop of mineral oil and evaporate the ether on a boiling waterbath. The last milliliters are removed at room temperature by rotating the flask horizontally. Dissolve the residue in 3 ml. of ethanol, add at least 0.1 gram of *m*-dinitrobenzene and 1 ml. of 40% potassium hydroxide and shake the flask carefully for approximately half a minute. Stopper the flask and place it for 30 minutes in a thermostat bath at 30° C. From this point on,

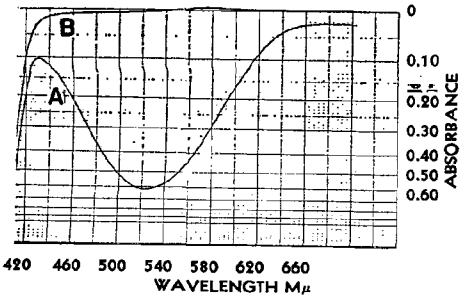


Figure 3. *A.* Absorbance curve for colored product of dihydrochlorketoaldrin(III), *m*-dinitrobenzene, and KOH
B. Reagent blank

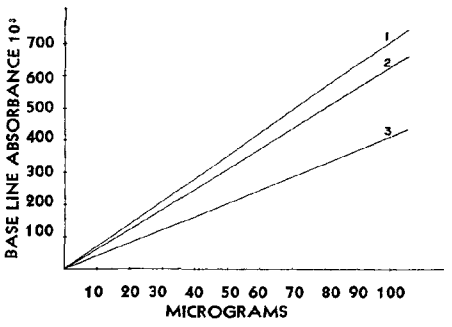


Figure 4. Calibration curves
1. Theoretical curve for aldrin calculated from 2
2. Dihydrochlorketoaldrin
3. Actual curve for aldrin carried through method

bright light should be avoided. Pipet into the flask 5 ml. of chloroform and 5 ml. of water, and shake the flask for a few seconds before the contents are transferred to a test tube. Transfer immediately, with a pipet, most of the still unclear chloroform layer to a second test tube which contains 0.5 gram of anhydrous sodium sulfate. Provide the test tube with a polyethylene stopper and shake the tube until the solution is optically clear. Decant the solution into an absorption cell and read the absorbance at 525, 670, and 440 mμ against chloroform.

Calculate the base line absorbance according to the following formula:

$$A_{BL} = A_{525} - A_{670} - 0.63 \cdot (A_{440} - A_{670})$$

Read the aldrin contents of the sample from a calibration curve, prepared in the same manner, with 0, 1, 2, 4, 6, 8, and 10 ml. of aldrin standard solution (0 to 100 μg.).

Application of Method. When determining residues of aldrin by this method, in most cases a preceding "clean-up" of the extract of the sample is required.

In the recovery experiments, described under Results, the fat-samples are mixed with anhydrous sodium sulfate in a mortar until a fairly dry consistency is obtained. Thereafter the mixture is extracted 3 times with 50 ml. of petroleum ether (b.p. 40° C.) by shaking mechanically, each time for 5 minutes. The combined extracts are then filtered, evaporated to approximately 20 ml., and partitioned between petroleum ether and dimethylformamide according to the method described by Mills (*7*) for acetonitrile extraction. This process is followed by a chromatographic purification described by Blinn, Gunther, and Mulla (*2*). The column is pre-wet with petroleum ether. It is preferable, however, to use 100 ml. of ether as eluting solvent instead of *n*-hexane. The radish samples are treated in the same way as the fat samples, except that the extraction with dimethyl formamide is omitted.

RESULTS AND DISCUSSION

The color solution resulting from dihydrochlorketoaldrin (III), *m*-dinitrobenzene, and potassium hydroxide in alcohol has a dirty, red-brown color. It is, therefore, extracted with chloroform to obtain a clear, violet-red color. A similar chloroform extraction has been used successfully in a method by Cahen and Salter (*3*) for the determination of 17-ketosteroids.

To separate the chloroform it is necessary to add water. The amounts of alcohol, potassium hydroxide, chloroform, and water are chosen to ascertain a quick separation of the layers and the strongest possible color. In Figure 3, *A* indicates the absorbance curve of the chloroform extract obtained as described in the aforementioned process, by direct reaction of 90 μg. of dihydrochlorketoaldrin in 3 ml. of ethanol. It shows an absorption peak at 525 mμ. *B* represents the absorbance curve for a reagent blank. Both were read against pure chloroform as reference.

Certain background absorption may occur, which has an especially disturbing effect when the aldrin amount is less than 20 μg. It was therefore advantageous to read the absorbance also at 670 and 440 mμ, and estimate the base line absorbance as described by Erne (*5*).

$$A_{BL} = A_{525} - A_{670} - \frac{670 - 525}{670 - 440} \times (A_{440} - A_{670}) = A_{525} - A_{670} - 0.63 \times (A_{440} - A_{670})$$

In the first experiments with this method, the reaction I-III was carried out with glacial acetic acid as solvent. To avoid acetic acid in the ether extract, the acid solution was partly neutralized before the extraction and the extract was washed with alkali. However, this led to loss of dihydrochlorketoaldrin, probably because this compound also exists in an acid enol-form, and under salt formation escapes the ether extract when washed with alkali.

The conversion of aldrin to dihydroaldrinnitrosochloride (II), requires a rather long time. After 10 to 12 hours at room temperature, the maximum reaction yield seems to be obtained. Further prolongation of the reaction time is unnecessary, but has no unfavorable effect on the result. The reaction does not follow the reaction scheme (Figure 1) quantitatively. This is apparent from Figure 4. Curve 2 shows the absorbance values for color solutions of dihydrochlorketoaldrin-standards.

Curve 1 represents the absorbance calculated from curve 2, provided the yield is 100%. By comparing this with the actual calibration curve for aldrin, curve 3, one arrives at a total yield of 58% for the entire process. Increasing the nitrosylchloride concentration, as an attempt to increase the yield, resulted in lower absorbance values. This is probably due to excessive amounts of nitrosylchloride not being removed sufficiently from the ether with the water washings. Experiments with standard solutions of dihydrochlorketoaldrin to

Table I. Recovery of Aldrin Added to Different Samples

Sample	Aldrin added (μg.)	A_{BL}	Aldrin found (μg.)	Recovery, %
Omental fat (from cow)	0	−0.002	0	...
Omental fat (from cow)	10	0.020	5	50
Omental fat (from cow)	10	0.025	6	60
Omental fat (from cow)	50	0.133	33	66
Omental fat (from cow)	50	0.129	32	64
Radishes	0	−0.003	0	...
Radishes	50	0.155	38.5	77

which were added small quantities of nitrosylchloride also resulted in weaker colored solutions.

The yield remained unchanged when increasing the hydrochloric acid contents five times.

The reproducibility of the method was tested by determinations of aldrin standard solutions. Analysis on different days of 20 samples of 50 μg. of aldrin gave A_{BL} values between 0.175 and 0.233, with a mean value of 0.201 and a standard deviation ±0.015.

The effect of the method, when applied to residue determinations, was tested after addition of known quantities of aldrin to some samples of animal (omental fat from cow) and vegetable (radish) origin. The aldrin was isolated as described in Application of Method. The results given in Table I show a recovery of 50 to 77%. The recovery could probably be increased by improving the chromatographic purification technique. However, the experiments prove that the principle of the analysis is fully applicable in residue determinations of aldrin.

It may be noted that the characteristic color in the last step of the reactions constituting the base for the method described herein is not obtained with every nitrosochloride-forming compound; the resulting nitrosochloride must also be convertible to a keto-compound—i.e., the unsaturated compound from which the nitrosochloride is derived must possess a hydrogen atom at least at one double bond carbon atom.

Thus, the method has a certain specificity for aldrin. Interference will occur, however, if the samples or reagents contain compounds having carbonyl groups, or if carbonyl-containing compounds are formed during the reactions. Such conditions may perhaps be encountered when determining residues of aldrin in terpene-rich crops, because terpene compounds, as mentioned above, frequently are converted to ketones by means of the same reactions.

Table II. Base Line Absorbance for 25-mg. Samples of Different Insecticides Carried through Described Method

Insecticide	A_{BL} values
Lindane	0.000
p,p'-DDT	0.004
Diazinon	−0.025
Systox	−0.015
Dieldrin (techn. product recryst. 4 times)	0.336
Dieldrin (techn. product recryst. 8 times)	0.221
Endrin (techn. product recryst. 4 times)	1.600
Endrin (techn. product recryst. 8 times)	1.030

To determine whether others of the commonly used insecticides interfere in the reaction by forming similar colored products, some of them were analyzed by the same method. All these experiments were carried out with samples of 25 mg., which represents 100 to 1000 times the quantities used in aldrin experiments. Samples of high purity were used, except for dieldrin and endrin which were technical products. The latter were purified by recrystallizations from methanol. The results are shown in Table II.

Dieldrin and endrin were the only compounds giving colored chloroform solutions. With regard to dieldrin, the explanation might be that the commercially available product contains some aldrin. As known, dieldrin is produced from aldrin by oxidation with hydrogen peroxide. The fact that the absorbance values are lower after 8 recrystallizations than after 4 supports this theory. Likewise, the interference in the endrin samples is probably due to a certain amount of isodrin in the product. Isodrin, the stereoisomer of aldrin, reacts quite probably according to the reaction scheme (Figure 1). However, this is not experimentally proved.

O'Donnell, Johnson, and Weiss (*8*) have utilized the principle of the phenylazide method in a spectrophotometric analysis for dieldrin. This could be done after conversion of dieldrin into a partially dechlorinated aldrin compound.

With a similar technique, it might be possible to apply the principle of the herein described method for determining dieldrin, possibly also endrin. This would be valuable as aldrin is readily converted to dieldrin in crops as well as in animal tissue, and the full survey of the contamination after using aldrin thus necessitates determinations of dieldrin too.

ACKNOWLEDGMENT

The author is grateful to Gudrun Bergseng for technical assistance.

LITERATURE CITED

(1) Bittó, B. von, *Ann.* **269**, 377 (1892).
(2) Blinn, R. C., Gunther, F. A., Mulla, M. S., *J. Econ. Entomol.* **53**, 1129 (1960).
(3) Cahen, R. L., Salter, W. T., *J. Biol. Chem.* **152**, 489 (1944).
(4) Danish, A. A., Lidov, R. E., ANAL. CHEM. **22**, 702 (1950).
(5) Erne, K., *Acta Pharmacol. Toxicol.* **14**, 158 (1958).
(6) Gattermann, L., Wieland, H., "Die Praxis des organischen Chemikers," 36th ed., p. 133, Walter de Gruyter & Co., Berlin, 1954.
(7) Mills, P. A., *J. Assoc. Offic. Agr. Chemists* **42**, 734 (1959).
(8) O'Donnell, A. E., Johnson, H. W., Jr., Weiss, F. T., *J. Agr. Food Chem.* **3**, 757 (1955).
(9) O'Donnell, A. E., Neal, M. M., Weiss, F. T., Bann, J. M., DeCino, T. J., Lau, S. C., *Ibid.*, **2**, 573 (1954).
(10) Schechter, M. S., Hornstein, I., ANAL. CHEM. **24**, 544 (1952).
(11) Wallach, A., *Ann.* **253**, 249 (1889).
(12) Zimmermann, W., (Hoppe Seylers) *Z. Physiol. Chem.* **233**, 257 (1935).

RECEIVED for review February 6, 1962. Resubmitted October 29, 1962. Accepted February 4, 1963.

Comparison of Two Colorimetric Methods for Determination of Copper in Mineral Oils

J. M. HOWARD and H. O. SPAUSCHUS

Major Appliance Laboratories, General Electric Co., Louisville, Ky.

▶ The carbamate method has been adapted to the determination of dissolved copper in mineral oils. The copper is extracted with acetic acid and determined colorimetrically as the carbamate complex which has an absorption maximum at 440 mμ in carbon tetrachloride–acetic acid solution. This method is compared with the neocuproine method of Zall, McMichael, and Fisher. Both methods obey Beer's law over the concentration range of 2 to 200 μg. of copper per 50 ml. of final solution. Absorbance of the copper–carbamate complex is 1.6 times that of the neocuproine complex, thus providing greater sensitivity for the former. Iron does not interfere with copper determination by the neocuproine method, but a slight modification of the carbamate method is required if iron is present.

PETROLEUM PRODUCTS, in contact with copper or copper alloys, gradually dissolve small quantities of the metal. In certain applications the presence of dissolved copper in petroleum products initiates or accelerates undesirable chemical effects. For example, it has been reported that dissolved copper (*a*) causes heavy deposits in the precombustion chamber of some Diesel engines (*11*), (*b*) accelerates the oxidation of transformer oils (*5, 10*), and (*c*) produces copper plating on steel bearings in refrigeration compressors (*7–9*). In the course of investigation of the mechanism of (*c*), a precise analytical method for determination of small quantities of dissolved copper in mineral oil was adapted and tested extensively in this laboratory. In this method, copper is extracted with acetic acid, complexed as the carbamate (*6*), and the absorbance at 440 mμ is determined in carbon tetrachloride–acetic acid solution.

Various methods for the determination of copper in oil are reported in the literature. The standard method (*1*) involves ashing the sample and then determining the copper content of the ash. Other workers have used sulfuric (*4*), alcoholic hydrochloric (*3*), and dilute nitric (*9*) acids to extract the copper before determination. More recent work has utilized ion exchange (*2*) to concentrate the copper. In 1957, Zall, McMichael, and Fisher (*11*) reported the development of an improved method requiring no separation or concentration of the copper, which is complexed with neocuproine and determined spectrophotometrically in chloroform solution. This paper describes the carbamate method and presents a comparison with the neocuproine method.

EXPERIMENTAL

Apparatus and Reagents. All absorbance measurements were made on a Cary recording spectrophotometer using fused silica cells of 20-mm. light path.

Reagents included: 2,9-dimethyl-1,10-phenanthroline hemihydrate (neocuproine), sodium diethyldithiocarbamate (0.2% aqueous solution), and metallo organic copper (copper content determined electrolytically after wet ashing) and iron compounds (National Spectrographic Laboratories, Inc., Cleveland, Ohio). All other reagents were analytical reagent grade.

Procedures. NEOCUPROINE METHOD. Reference (*11*).

CARBAMATE METHOD. Weighed quantities of standard copper solution (47.9 μg. of Cu per gram of mineral oil) were transferred to 125-ml. separatory funnels containing 10 ml. of mineral oil to give a satisfactory working volume. Ten milliliters of glacial acetic acid were added and each separatory funnel was vigorously shaken for 3 minutes. The solution was allowed to separate into two phases and the acid phase was transferred to a 250-ml. separatory funnel. The stem of the 125-ml. funnel was washed with 1 to 2 ml. of acetic acid after transfer and the washings were added to the 250-ml. funnel. This extraction procedure was repeated with two additional portions of acetic acid. Ten milliliters of the carbamate solution were then added to the combined acid extracts and the two solutions were thoroughly mixed by shaking. The brown copper–carbamate complex was extracted with three 10-ml. portions of carbon tetrachloride following the same procedure as for the original acid extraction. The carbon tetrachloride extracts were transferred to 50-ml. volumetric flasks, 10 ml. of acetic acid (to remove any turbidity) were added, and the volumes of solutions were made to 50 ml. with additional carbon tetrachloride. A blank consisting of all reagents, with the exception of the copper solution, was carried through the procedure and used as the reference solution during absorbance measurements. All absorbance measurements were made at a wavelength of 440 mμ.

Table I. Carbamate Method

Known copper, μg.	Predicted copper, μg.	Difference, μg.
2.2	1.8	−0.4
4.8	5.5	+0.7
7.6	6.7	−0.9
10.2	9.7	−0.5
23.9	25.3	+1.4
29.4	30.3	+0.9
37.2	37.5	+0.3
43.6	43.9	+0.3
49.6	51.4	+1.8
88.1	85.4	−2.7
121.0	117.0	−4.0
140.6	141.4	+0.8
170.7	171.8	+1.1
201.9	203.3	+1.4

The standard deviation is ±1.03.

Table II. Neocuproine Method

Known copper, μg.	Predicted copper, μg.	Difference, μg.
2.2	3.3	+1.1
4.6	4.8	+0.2
9.6	10.5	+0.9
11.8	13.2	+1.4
24.6	21.0	−3.6
51.7	52.9	+1.2
73.5	75.7	+2.2
99.8	95.9	−3.9
123.8	123.0	−0.8
150.3	149.8	−0.5
176.1	175.7	−0.4
200.4	203.0	+2.6

The standard deviation is ±1.24.

RESULTS AND DISCUSSION

Precision and Accuracy. The data from 14 analyses by the carbamate method and 12 analyses by the neocuproine method show that the two methods obey Beer's law over the range of 2 to 200 μg. of copper. The least squares lines for the standard curves are:

Carbamate method: Absorbance = 0.0082 (μg. of copper) + 0.0002

Neocuproine method: Absorbance = 0.0051 (μg. of copper) − 0.0068

Over these concentration ranges the intensity of the copper–carbamate complex is 1.6 times that of the neocuproine complex.

The least squares lines were used to predict the copper values for each standard solution. These predicted values were then compared to the known values and the standard deviations were calculated (Tables I and II).

Effect of Iron. In studies of the mechanism of solution and transfer of copper in mineral oil (*7*), the oil samples contained dissolved iron as well as copper. Consequently, experiments were conducted to determine whether dissolved iron interfered with the copper determination. A number of standard copper solutions containing known concentrations of iron (added as metallo organic iron) were run by each method. No modification of the neocuproine method was necessary to correct for the presence of iron, but the following addition was used with the carbamate method.

The combined acetic acid extractions were brought to pH 9 or greater with ammonium hydroxide (1:1) and 1.0 gram of citric acid was added before the addition of the carbamate solution (*6*).

The effect of iron is shown in Table III.

Table III. Effect of Dissolved Iron on Copper Determination

Copper added, μg.	Iron added, μg.	Copper Recovered, μg.	Difference, μg.
CARBAMATE METHOD			
39.0	40.0	38.1	−0.9
54.4	110.0	57.2	+2.8
NEOCUPROINE METHOD			
57.1	58.6	56.2	+0.9
102.1	104.8	101.3	−0.8

SUMMARY

Dissolved copper in the range of 2 to 200 μg. per gram of mineral oil can be determined with high accuracy ($\sigma \simeq 1$ μg. of Cu) by either the neocuproine or carbamate method. The procedures for these methods are much less complex than those required by earlier methods. The neocuproine method is the simpler and quicker of the two. The carbamate method offers an advantage at low concentrations since the copper–carbamate complex has a greater absorbance than the copper–neocuproine complex.

LITERATURE CITED

(1) American Society for Testing and Materials, Philadelphia, Pa., "Part 5, Fuels, Petroleum, Aromatic Hydrocarbons, Engine Antifreezes," *A.S.T.M.* D-810-48, 1952.
(2) Buchwald, H., Wood, L. G., ANAL. CHEM. 25, 664 (1953).
(3) Hackett, C. E. S., *Anal. Chim. Acta* 12, 358 (1955).
(4) Kreulen, D. J. W., *J. Inst. Petroleum* 38, 449 (1952).
(5) Massey, L., *Ibid.*, 38, 281 (1952).
(6) Sandell, E. B., "Colorimetric Determination of Traces of Metals," 3rd ed., Vol. 3, p. 444, Interscience, New York, 1959.
(7) Spauschus, H. O., *ASHRAE J.*, in press.
(8) Steinle, H., Kältetechnik 7, No. 4, 101 (1955).
(9) Steinle, H., Seeman, W., *Ibid.*, 3, No. 8, 194 (1951).
(10) Thompson, C. N., *J. Inst. Petroleum* 44, 295 (1958).
(11) Zall, D. M., McMichael, R. E., Fisher, D. W., ANAL. CHEM. 29, 88 (1957).

RECEIVED for review December 13, 1962. Accepted March 28, 1963.

Quantitative Radiochemical Procedure for Analysis of Polonium-210 and Lead-212 in Minerals

HUGH T. MILLARD, Jr.[1]

Division of Geological Sciences, California Institute of Technology, Pasadena, Calif.

▷ **A method for the analysis of polonium-210 (138.4-day half life) and lead-212 (10.6-hour half life) in zircons and other natural systems has been developed. The procedure employs spontaneous electrodeposition on silver for the isolation of polonium-210 and controlled-potential electrogravimetric separation of lead-212 plus added lead carrier. A diethyldithiocarbamate extraction procedure for the lead was developed to be used prior to plating in the presence of ions which precipitate at the pH used for lead deposition. The amounts of the deposited nuclides are then determined by alpha-counting. The effects of temperature, volume, and inhibiting ions on the yield and rate of deposition of polonium were also studied. The procedure was calibrated using minerals whose lead-210 and thorium-232 contents had been determined by other methods; it was tested on a composite uraninite-thorite mixture. Finally, it was applied in the analysis of four zircon samples and one uranothorite sample.**

ACKNOWLEDGE of the degree of disequilibrium in the radioactive decay chains in natural materials is of value in explaining geochronological inconsistencies and in more general studies of the geochemistry of the members of these chains. Rosholt (*20–22, 24, 25*) has reported methods for the detailed study and classification of the various types of radioactive disequilibria found in geological samples. He divides the chains into groups, each having a relatively long-lived parent which can be assumed to be in radioactive equilibrium with its immediate daughters. The uranium group contains two parent nuclides: 4.5×10^9-year uranium-238 and 7.1×10^8-year uranium-235. The parents of the other groups in the uranium-238 series are: 8.0×10^4-year thorium-230, 1622-year radium-226, 3.8-day emanation-222 (radon group), and 22-year lead-210 (lead group). The parent of the only other group in the uranium-235 series is 34,300-year protactinium-231 (protactinium group). All of the daughters in the thorium series have sufficiently short half lives to provide only one group in this series, the thorium group.

The objective of this study was to find alternative procedures for analyses of the lead and thorium groups and to apply these procedures to mineral separates with particular attention to uranium and thorium systems in nature. Assuming that the thorium series is ordinarily in radioactive equilibrium in geological samples, quantitative analysis for any member of the thorium group allows us to find the thorium-232 content. In the uranium-238 series the loss of lead group members from a sample can only produce short-term disequilibrium due to the short half life of lead-210 (22 years). However, because this group comes at the end of the chain, the knowledge of its amount relative to uranium is helpful in evaluating the state of radioactive equilibrium farther up the chain. This state of equilibrium may be affected by the gain or loss of

[1] Present address, Department of Chemistry, University of California, San Diego, La Jolla, Calif.

uranium-234, thorium-230 (ionium), radium-226, or emanation-222 (radon), and is of special importance when evaluating age data which is based upon the lead-206 content.

Electroplating procedures naturally suggested themselves as alternatives to the precipitation separations used by Rosholt because they require a minimum amount of manipulation of the sample solution and yield radionuclides in a form convenient for counting. All of the nuclides in the lead group may be electroplated but since alpha-counting was to be used, polonium-210 (138.4-day half life) was chosen for the determination. Lead-212 (10.6-hour half life) and bismuth-212 (60.5-minute half life) in the thorium group have combinations of half-life and decomposition potential which make them suitable for the determination of this group.

Bagnall (*3*) has reviewed the literature pertaining to the electrochemical deposition of polonium up to 1957. In recent years, the spontaneous deposition of polonium on less noble metals (silver, copper, and nickel) has been used to separate its isotopes from lead and bismuth targets (*18, 30*) and from lead-210 and bismuth-210 (*32*), and for its analysis in biological materials (*4, 16, 29, 31*) and radioactive minerals (*2*). Extensive studies of the spontaneous deposition of polonium on silver (*4, 9, 26, 29, 34*) have lead to the conclusion that elevated temperatures are needed for high yield and smooth deposition. Significant quantities of ferric iron and the ions of metals more noble than polonium (gold, platinum, tellurium, and mercury) interfere with its deposition, but these can be reduced prior to plating (*13, 34*).

Recently used methods for separating radioactive lead isotopes include precipitation (*10*), dithizone extraction (*1, 11, 33*), ion exchange (*6–8, 12, 15*), and electrochemical (*14, 32*) procedures.

EXPERIMENTAL

Apparatus. Polonium Plating Apparatus. The apparatus used to plate polonium consisted of a beaker (ordinarily a 100-ml. beaker for solution volumes less than 75 ml.) covered by a watch glass through which a hole had been bored. A silver-foil disk (punched from Matheson Reagent Grade Silver foil, 0.005 inch thick), 1.25 inches in diameter with a 0.13-inch diameter center hole, was suspended by means of a glass rod passing through the center hole in the disk and up through the hole in the watch glass. The back and edges of the silver-foil disks were coated with Glyptal to prevent plating on these surfaces and this gave a plating area of about 7.0 sq. cm. The solution was stirred with a magnetic stirring bar 1 inch in length. The stirrer also served to support the beaker. The stirring motor Variac was set at half scale and the magnetic stirrer rotated at about 500 r.p.m.

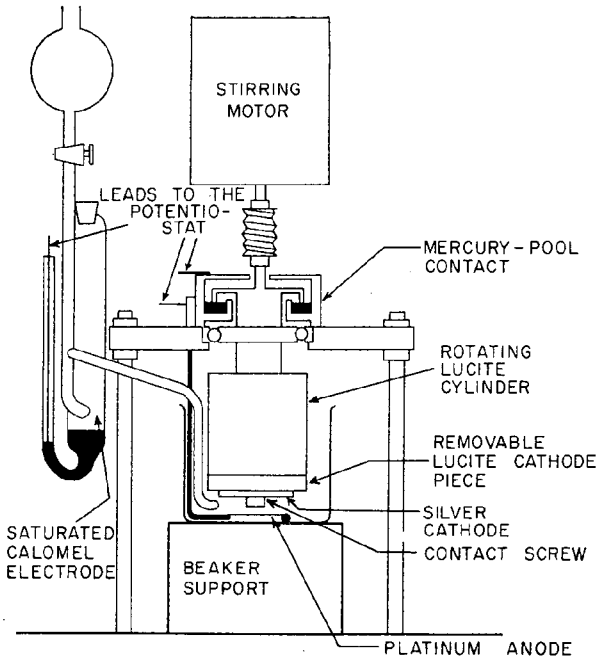


Figure 1. Apparatus for the controlled-potential deposition of lead

Lead Plating Apparatus. The apparatus used for the controlled-potential electrodeposition of lead is shown in Figure 1. The parts were mounted on a Sargent Electroanalyzer to provide the stirring motor. A transistorized potentiostat was designed to control the potential of the working electrode to ±20 mv. when the cell current was in the range 0 to 200 ma. The saturated calomel electrode arm could be rotated to allow removal of the Lucite cathode piece. The silver-foil disk used as cathode was identical to the disks used to plate polonium except that a glass-disk backing with a thin coating of grease as a seal was used instead of Glyptal to prevent plating on the rear surface.

Counting Apparatus. The scintillation detector used to count the alpha-radiation consisted of a zinc sulfide screen applied with rubber cement to the face of an RCA 5819 or DuMont 6292 multiplier phototube. The detector was mounted inside a light-tight box into which the sample could be introduced for counting. The multiplier phototube was coupled to a conventional electronic scaler and high-voltage power supply.

Solutions and Sources. Except where noted, reagent grade chemicals and reagents were used throughout this work.

Polonium-210 Solution. A stock polonium-210 solution was prepared from a radium-D-E-F solution. This was done by spontaneous deposition of the polonium-210 from a 0.5*N* HCl medium onto a silver-plated platinum base at 95° C. The silver and polonium were then dissolved in nitric acid. The silver was precipitated as silver chloride and separated by filtration, and the solution evaporated to dryness. The residue was then taken up in 0.5*N* HCl. These plating and precipitation steps were repeated to purify the polonium-210 and the final solution was diluted to 250.00 ml. in a volumetric flask to give a stock polonium-210 solution (0.5*N* in HCl). When prepared, this solution contained about 1700 alpha-c.p.m./5 ml. It was used over a period of 2.5 years to prepare working polonium-210 solutions which contained about 70 alpha-c.p.m./5 ml. The specific activity of the polonium-210 in these working solutions was determined from time to time by evaporating 1-ml. aliquot portions to dryness on silver-foil disks and counting the alpha-activity on these.

Lead Carrier Solution. Lead chloride (0.6712 gram, Baker's Reagent Grade) was dissolved in about 200 ml. of hot distilled water and the pH adjusted to about 4 with very dilute HCl. This solution was then diluted to 250.00 ml. in a volumetric flask giving 10.00 mg. of lead/5 ml. Blank runs were made by carrying aliquot portions of this solution through the plating procedure. The alpha-activity due to the lead carrier was found to be negligible.

Katanga Pitchblende Ore, MS-OR. This ore contains 44.96% uranium and the lead group is 94.5% of the equilibrium amount, or 42.5% equivalent uranium (*22*). A 50.00-ml. working solution was prepared from 0.0199 gram of this ore using aqua regia for its dissolution.

Happy Jack Uraninite Ore, GS-64/51. This ore contains 72.8% uranium and the lead group is 94.9% of the equilibrium amount, or 69.1% equivalent uranium (*23*).

THORIUM NITRATE [BAKER'S REAGENT GRADE, $Th(NO_3)_4 \cdot 4H_2O$]. A 100.00-ml. working solution was prepared from 0.4020 gram of this material using concentrated HCl for its dissolution. The thorium series in this material was not in radioactive equilibrium.

KIVU THORITE ORE. This ore contains 53.6% thorium and 0.1% uranium (*19*). Samples used for analysis ranged in size from 5 to 10 mg., and these were dissolved with aqua regia.

URANIUM-THORIUM SOLUTION. A 250.00-ml. working solution was prepared from 0.0259 gram of the Happy Jack uraninite and 0.1223 gram of the Kivu thorite ore using aqua regia for their dissolution. Analysis for the uranium content of this solution by the isotope dilution method indicated that there were 372 ± 4 μg. of uranium per 5 ml. of the solution as compared to the expected value of 379 μg. of uranium per 5 ml. calculated on the basis of the uranium content of the uraninite and thorite.

PACOIMA CANYON ZIRCON. This zircon contains 208.2 ± 1.0 p.p.m. uranium and 63.0 ± 1.0 p.p.m. thorium (*28*).

A 0.0958-gram sample was fused with 0.5 gram sodium peroxide and the entire sample analyzed.

A 100.00-ml. working solution was prepared by fusion of 1.8478 grams of zircon with 10 grams of sodium peroxide and 5.00-, 10.00-, or 15.00-ml. aliquot portions used for analysis.

A 500.00-ml. working solution was prepared by borax fusion of 0.5529 gram of zircon, the silica separated by HF treatment, and a 150.00-ml. aliquot portion used for analysis.

A 500.00-ml. working solution was prepared by peroxide fusion of 0.6564 gram of zircon, the silica separated by HF treatment, and 150.00-ml. aliquot portions were used for analysis.

SIERRA ANCHA 4 ZIRCON. This zircon contains 1807 ± 18 p.p.m. uranium (*27*). A 250.00-ml. working solution was prepared from 0.0556 gram of this material using a total of 11 grams of Na_2O_2 and 2 grams of NaOH for decomposition. Twenty-five-milliliter aliquot portions were used for each analysis. Analysis for the uranium content of this solution by the isotope dilution method showed 11.97 ± 0.12 μg. of uranium per 25 ml. of solution rather than the 10.05 μg. per 25 ml. expected on the basis of the uranium content of the zircon.

SIERRA ANCHA 1–6 ZIRCON. This zircon contains 6486 ± 65 p.p.m. uranium (*27*). A 250.00-ml. working solution was prepared from 0.0247 gram of this material using 2 grams of Na_2O_2 and 0.5 gram of NaOH for decomposition. Twenty-five-milliliter aliquot portions were used for each analysis. Analysis for the uranium content of this solution by the isotope dilution method showed 16.41 ± 0.16 μg. of uranium per 25 ml. of solution rather than the 16.02 μg. per 25 ml. expected on the basis of the uranium content of the zircon.

HOPI BUTTES ZIRCON. This zircon contains 3421 ± 34 p.p.m. uranium and 7000 ± 2000 p.p.m. thorium (*27*). The thorium value was calculated from the lead isotopic compositional and alpha-counting data. A 250.00-ml. working solution was prepared from 0.0332 gram of this material using 2 grams of Na_2O_2 and 0.5 gram of NaOH for decomposition. Twenty-five-milliliter aliquot portions were used for each analysis.

MARBLE MOUNTAIN URANOTHORITE. This uranothorite contains 3.29% ± 0.03 uranium and 30% ± 5 thorium (*27*). A 249.9-ml. working solution was prepared from 0.1057 gram of this material and 5.00-ml. aliquot portions used for each analysis. Analysis for the uranium content of this solution by the isotope dilution method showed 72.4 ± 0.7 μg. of uranium per 5 ml. of solution. Uranium (73.6 μg.) per 5 ml. was expected on the basis of the uranium content of the uranothrite.

The flux used to decompose the zircons normally consisted of 2 grams of Na_2O_2 plus 0.2 gram of NaOH. A sample of this flux was analyzed for its uranium content by the isotope dilution method and for its polonium-210 content according to the recommended procedure. The results indicated 0.07 Po-210 c.p.m. [or 0.2 μg.e (microgram equivalent) U]/2 grams of Na_2O_2 − 0.2 gram of NaOH and 2.0 μg. U/2 grams of Na_2O_2 − 0.2 gram of NaOH.

Recommended Procedure. Ordinarily, a solution of the sample should be prepared from which aliquot portions may be taken for analysis. The sample should be decomposed either with mineral acids and evaporated to dryness or by fusing with the sodium peroxide flux for 15 minutes in a nickel crucible. Slurry the residue or solidified melt with 0.1*N* HCl and separate any silica by centrifugation. Transfer the silica precipitate to a Teflon beaker, add 12 grams of perchloric acid and 25 grams of HF, and evaporate to dryness. Dissolve the residue in 0.5*N* HCl, combine with the main solution, and dilute to the desired volume in a volumetric flask while maintaining the HCl concentration at 0.5*N*. With some zircon samples, the HCl concentration may have to be as high as 2*N* to prevent precipitation.

Remove an aliquot portion of this sample solution for analysis (preferably 25 ml. or less, but it may be as much as 150 ml.). Add 5.00 ml. of the lead carrier solution and dilute to 25 ml. with 0.5*N* HCl if the solution volume is less than this. Add 0.26 gram of hydrazine dihydrochloride for each 25 ml. of solution. Deposit the polonium on a silver-foil disk at room temperature for a length of time determined by the volume of the solution. Overnight (12 hours) is a sufficient length of time if the solution volume is 150 ml. or less. The solution should be covered with a watch glass and stirred during deposition. Use small quantities of 0.5*N* HCl to wash the watch glass and sides of the beaker after about two-thirds of the plating time has elapsed. These washings are allowed to flow into the plating solution. At the conclusion of plating, remove the silver-foil disk, rinse with 0.5*N* HCl, and air-dry. The polonium-210 alpha-activity may be counted when convenient.

The volume of the solution remaining from the polonium deposition is reduced to about 30 ml. and 0.60 gram of sodium tartrate dihydrate added. The pH of this solution is adjusted to between 4.5 and 5.0 by the dropwise addition of 5*N* NaOH. The lead carrier is then deposited electrochemically for 30 minutes at room temperature on a second, previously weighed silver-foil disk. The cathode potential during this deposition is controlled at −0.70 volt *vs.* the saturated calomel reference electrode and the solution is stirred. Electrolysis is concluded by quickly lowering the beaker of solution (while the current and stirring motor remain on) and flushing the deposit free of electrolyte with distilled water. The silver-foil disk is cleaned of grease with benzene, rinsed with alcohol, and air-dried. The yield of lead carrier is determined by reweighing the disk plus the deposit of lead and subtracting the initial weight of the disk. After waiting about 5 hours for the alpha-activity supported by lead-212 to reach transient equilibrium, the alpha-activity decaying with a half life of 10.6 hours is observed for several half lives and the activity corresponding to zero decay time (conclusion of deposition) is calculated.

REDUCTION PROCEDURE. If the surface of the silver-foil disk is darkened during the deposition of polonium (due to the presence of ferric ion or the ions of gold, platinum, tellurium, or mercury), the following reduction step should be performed prior to the separation of polonium: The aliquot portion of the sample solution is evaporated to incipient dryness and the residue dissolved in as small a volume of 7*N* HCl as possible. Add the amount of hydrazine dihydrochloride which would normally be used (the solution should be saturated with hydrazine dihydrochloride at this point), cover with a watch glass, and maintain the temperature just below the boiling point of the solution for 30 minutes. Cool the solution slowly, dilute it with distilled water until the concentration of HCl is 0.5*N*, and separate any precipitate which has formed. If the solution is yellow at this point, due to the presence of ferric ion, warm until colorless and then deposit the polonium.

EXTRACTION OF LEAD. If the sample is zircon or if some other element is present which will precipitate when the pH is adjusted to about 4.7, then the lead-212 plus lead carrier must be extracted with diethyldithiocarbamate prior to plating. The HCl concentration of the solution remaining after deposition of polonium is raised to 1*N* and the lead extracted with two 10-ml. portions of carbon tetrachloride, each of which contains 0.25 gram of diethylammonium diethyldithiocarbamate. The yellow carbon tetrachloride solution turns brown during extraction. Separate the carbon tetrachloride phase and

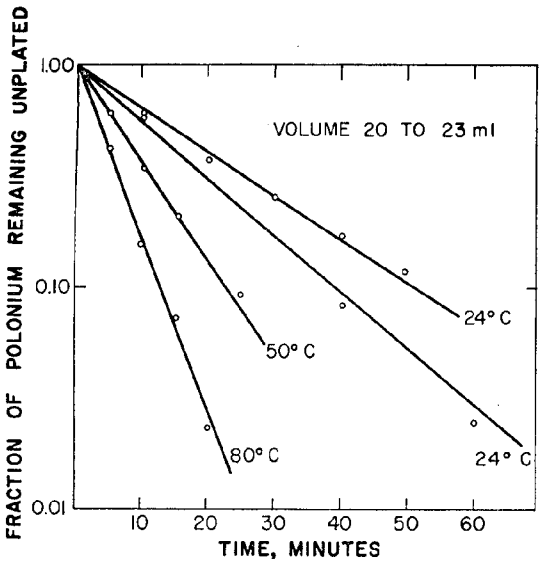


Figure 2. Fraction of polonium remaining unplated after various periods of deposition as a function of the solution temperature

Each solution initially contained 130 c.p.m. of polonium-210 alpha activity

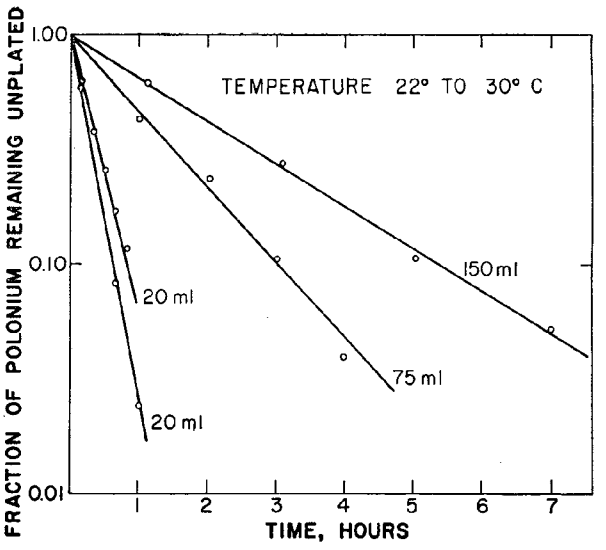


Figure 3. Fraction of polonium remaining unplated after various periods of deposition as a function of the solution volume

Each solution initially contained 130 c.p.m. of polonium-210 alpha-activity

evaporate to dryness. Destroy the organic material by adding 5 ml. of concentrated nitric acid and then 5 ml. of 60% perchloric acid. The solution is heated until dense white fumes appear, then an additional 5 ml. of 60% perchloric acid is added and the solution is evaporated to dryness. The small residue is treated with 2 ml. of 6*N* HCl and 25 ml. 0.5*N* HCl is added. If any residue remains at this point, the solution is warmed until all material has dissolved. Finally, 260 mg. of hydrazine dihydrochloride and 600 mg. of sodium tartrate dihydrate are added, the pH is adjusted to about 4.7 with NaOH, and the lead deposited for 1 hour. Zero decay time now corresponds to the time of extraction rather than to the conclusion of deposition.

Treatment of Counting Data. The corrections to be applied to the counting data are:

Background (5 to 20 c.p.h. for the polonium-210 plating but may be higher for the lead-212 plating, presumably due to the codeposition of some polonium-210 with the lead and the growth of lead-210 supported polonium-210)

Decay since removal from radioactive equilibrium—i.e., since deposition or extraction

Polonium-210 from the sodium peroxide flux (0.07 c.p.m./2 grams of Na_2O_2 – 0.2 gram of NaOH)

Plating yield (in the case of lead)

Standardization of the Procedure. A thick alpha-source was prepared as a counting standard by diluting 0.0328 gram of the Happy Jack uraninite with 0.9948 gram of ferric oxide and grinding the powder to ensure adequate mixing. The diameter of this standard was the same as that of the silver-foil disks so that it had the same counting geometry as the disks. All counting data were referred to this standard alpha-source and it in turn was calibrated against polonium-210 and bismuth-212–polonium-210 alpha-sources, prepared by carrying standard materials through the recommended procedure. Thus, these standard materials served to calibrate the procedure and all counting data for unknown samples were ultimately referred to them. The material used to calibrate the polonium-210 procedure was the Katanga pitchblende, while that used for the lead-212 procedure was the Kivu thorite. These materials were chosen because the state of radioactive equilibrium existing in them had already been determined by established procedures in other laboratories. The counting data obtained for these materials are presented in Table I where μg.e represents microgram equivalents. This unit is used to indicate the weight in micrograms of chain parent (uranium or thorium) required for the radioactive equilibrium support of the amount of daughter nuclide found to be present in a sample (*22*).

Table I. Calibration of the Procedure Using the Katanga Pitchblende and the Kivu Thorite

Weight sample, mg.	Wt. equiv. U, mg.	Corrected activity, c.p.m.	Specific activity, c.p.m./μg.e U
Katanga pitchblende, MS-OR, 42.5% equiv. U at Pb^{210}			
1.99	0.846	249.4	0.2947
1.99	0.846	242.0	0.2860
1.99	0.846	242.0	0.2860
1.99	0.846	238.9	0.2824
1.99	0.846	256.2	0.3026
1.99	0.846	255.7	0.3021
		Av. and std. dev.	0.2923 ± 0.0088
	Wt. equiv. Th, mg.		Specific activity, c.p.m./μg.e Th
Kivu thorite, 56.3% Th			
5.6	3.15	279.1	0.0886
5.6	3.15	285.4	0.0906
9.3	5.24	478.4	0.0913
		Av. and std. dev.	0.0902 ± 0.0014

RESULTS AND DISCUSSION

Polonium-210 Procedure. The results of experiments performed to determine the minimum plating time for polonium for various combinations of volume and temperature are shown in Figures 2 and 3. The two platings at 24° C. and 20 ml. in each figure provide an indication of the reproducibility of these data. The fraction

of polonium remaining unplated in each solution was calculated from the amount finally plated after a long period of time and not from the amount initially present in the solution. The yields based on the amount initially present ranged from 93 to 95%. It is evident from these graphs that relatively high yields of polonium can be obtained within reasonable lengths of time from solutions kept at room temperature, and therefore the temperatures of the solutions are not elevated in the recommended procedure.

An attempt was made to estimate the degree to which lead or bismuth co-deposit with polonium. The results indicated that only 0.5% or less of the available lead-212 or bismuth-212 is deposited on the platings in the absence of lead carrier and only 0.2% or less when 10 mg. of lead carrier is used. Thus, the codeposition of lead-212 and bismuth-212 becomes a problem only if the ratio of the activity of the thorium group to that of the lead group is very large, as is the case for thorite ores. When these conditions prevail in a sample, any alpha-activity supported by the lead-212 may be allowed to decay to negligible levels before determining the polonium-210 activity.

Since ferric ion and the ions of mercury, tellurium, platinum, and gold interfere with the deposition of polonium, provisions were made in the procedure for eliminating these interferences when they occur. Most of the methods devised to deal with these substances involve their reduction to a less troublesome oxidation state. A series of experiments was performed to devise a method for their removal by the use of hydrazine alone. The results of these experiments are summarized in Table II. The absence of yellow color in the solution was accepted as an indication that the iron had been reduced to the ferrous state. Solutions 1–3 and 7 demonstrate that complete reduction of the ferric ion can take place only after dilution of the 7*N* HCl to 0.5*N*. If this procedure is followed, approximately 2 mg. of ferric ion per 30 ml. of solution ($10^{-3}M$) can be tolerated. Solutions 4–6 indicate that a mixture of 1 mg. or more of mercury, tellurium, platinum, and gold definitely inhibits polonium deposition even though the reduction procedure in 7*N* HCl is followed. In solution 7, the amounts of these ions were reduced to 0.2 mg. and the reduction procedure in 7*N* HCl appeared to be adequate. This amount for any of these elements is much higher than that anticipated in zircon and most other materials to which this procedure was applied. In any event, whenever low yields of polonium were obtained, the silver surface was blackened; thus the criterion used to establish whether the hydrazine reduction step was required in the subsequent analysis of portions of the sample was the presence of darkening of the silver surface.

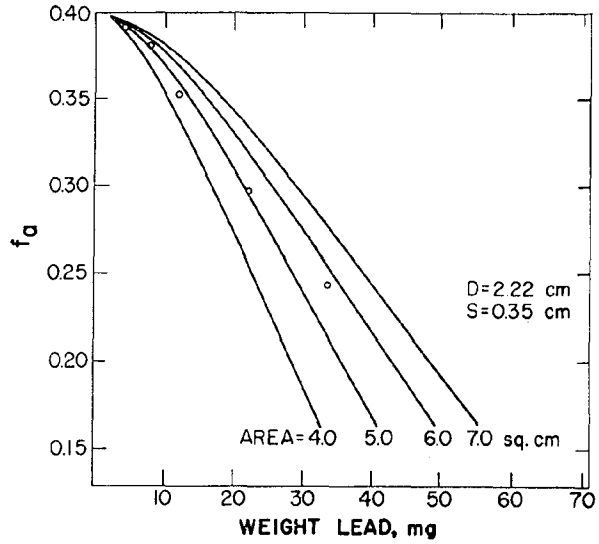


Figure 4. Average fractional solid angle, f_a, subtended by the detector as a function of the weight of lead for various deposit areas

The open circles are the points obtained from the plating experiment

Lead-212 Procedure. The recommended procedure for the determination of lead-212 is an adaptation of the controlled potential electrogravimetric method for the analysis of lead which was developed by Lingane (*17*).

The fractional attenuation of the bismuth-212 and polonium-212 alpha-radiation due to its passage through the lead carrier was determined as a function of the weight of lead carrier plated because this weight varied from plating to plating. An experiment was performed in which the alpha-activity from a polonium-210 deposit was determined after each successive plating of lead carrier over it. The results are shown in Figure 4 as open circles. The curves show the average fractional solid angle, f_a, subtended by the detector. These were calculated for polonium-210 alpha-radiation as a function of the weight of lead through which it must pass for various deposit areas. The source-to-detector distance, S, is 0.35 cm. and the radius of the circular alpha-detector, D, is 2.22 cm. Since the actual fractional solid angle for the counting geometry

Table II. Removal of Interference by Mercury, Tellurium, Platinum, Gold, and Ferric Ion in the Deposition of Polonium-210

	Weights of reagents, mg.						HCl concentration during reduction	Heating time during reduction, min.	Solution color after reduction	Total Po deposition time, hr.	Fractional recovery of Po^{210}
Solution	Hg	Te	Pt	Au	Fe^{+3}	Hydrazine					
1					10	260	7*F*	60	Yellow	3	0.21
2					10	130	0.5*F*	10	Colorless	0.8	0.92
3					2	130	0.5*F*	10	Colorless	2.5	0.98
4	2	2	2	3		130	No reduction step			3	0.18
5	2	2	2	2		260	0.5*F*	30		19	0.26
6	1	1	1	1		260	7*F*	50			
							0.5*F*	10		2	0.92
7	0.2	0.2	0.2	0.2	2	260	7*F*	60	Yellow		
							0.5*F*	20	Colorless	2.8	0.96

Solutions 2–6: 5.00 ml. Po^{210} working soln., 5.00 ml. Th-232 soln., 10 mg. Pb carrier.
Solutions 1, 7: 5.00 ml. Po^{210} working soln.

was only known to about ±0.05 and the detection efficiency for the zinc sulfide screen was unknown, the experimental points were fitted to the curve whose slope over the linear portion most closely matched their own. This turned out to be the curve for a deposit area of 5.0 sq. cm. which is less than the geometric area of 7.0 sq. cm. presumably because of graininess in the deposit. Figure 5 shows the 5.0 sq. cm. curve calculated for the weighted average of bismuth-212 and polonium-212 alpha-radiation It is evident that even for the maximum weight of lead carrier deposited (10 mg.), the reduction in the bismuth-212 and polonium-212 alpha-activity is of the order of only 2%. These curves represent geometries in which the activity lies at the bottom of the layer of lead, while in the actual situation the activity is distributed throughout the lead. Thus, the attenuation of bismuth-212 and polonium-212 alpha-radiation for lead deposits obtained from the procedure is only about 1% and no attenuation correction was applied to the counting data.

The fact that zirconium precipitates when the pH of the solution is raised prior to the deposition of lead necessitated the separation of lead from the solution prior to the pH adjustment when zircons were to be analyzed

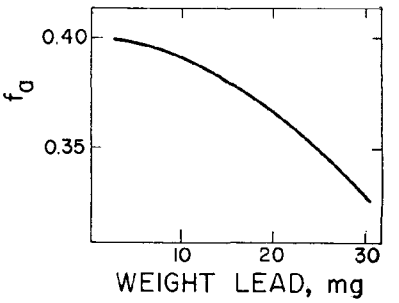


Figure 5. Average fractional solid angle, f_a, subtended by the detector as a function of the weight of lead for a deposit area of 5.0 sq. cm. for bismuth-212–polonium-212 alpha-radiation

Table III. Results of Analyses Performed on the Uranium-Thorium Solution

	Time since solution prepared, days	Corrected activity, c.p.m.	Wt. equiv. U Found, μg.	Wt. equiv. U Taken, μg.	Ratio
Po-210	6	82.4	281	358	0.787
	12	87.0	297	358	0.836
	29	85.1	291	358	0.813
	300	88.9	304	358	0.848
	400	99.6	340	358	0.949
	475	95.9	328	358	0.916
	750	95.5	336	358	0.938
	820	96.9	341	358	0.952
			Wt. equiv. Th Found, μg.	Wt. equiv. Th Taken, μg.	Ratio
Pb-212	6	88.4	980	1377	0.712
	12	79.8	885	1377	0.643
	29	73.1	811	1377	0.589
	300	112.9	1252	1377	0.909
	400	117.3	1301	1377	0.945
	475	126.9	1407	1377	1.022
	750	103.3	1178	1377	0.855
	820	119.4	1361	1377	0.988

Uranium-thorium solution (500 ml.) was used for each run.

Table IV. Results of Analyses Performed on the Pacoima Canyon Zircon

	Solution	Time since solution prepared, days	Corrected activity, c.p.m.	Wt. equiv. U Found, μg.	Wt. equiv. U Equilibrium value, μg.	Fraction of equilibrium value
Po-210	1	20	4.02	13.8	19.9	0.694
	2		7.86	26.9	38.4	0.701
			3.86	13.2	19.2	0.693
		80	11.32	38.7	57.6	0.675
		150	11.17	38.2	57.6	0.665
	3	2	1.18	4.0	34.5	0.118
	4	1	11.54	39.5	41.0	0.963
		2	11.51	39.4	41.0	0.960
		12	11.60	39.6	41.0	0.965
		357	3.34	11.4	12.3	0.927
			Av. and std. dev. (for solution 4)			0.954 ± 0.018
				Wt. equiv. Th Found, μg.	Wt. equiv. Th Equilibrium value, μg.	
Pb-212	1	20	0.30	3.4	6.0	0.567
	2		0.64	7.1	11.6	0.612
			0.36	4.0	5.8	0.690
		80	1.07	11.9	17.5	0.680
		150	1.11	12.4	17.5	0.709
	4	1	1.98	22.0	12.4	1.77
		2	1.10	12.2	12.4	0.98
		357	0.41	4.7	3.7	1.27
			Av. and std. dev. (for solution 4)			1.34 ± 0.40

Extraction was considered to be the most convenient method of separation and the procedure using diethyldithiocarbamate was worked out using the data of Bode and Neumann (5).

Analyses of Samples. Each sample solution was analyzed over long periods of time to confirm that the state of equilibrium in the uranium series had not been distributed during preparation of the solution. The criterion used was the absence of change for the polonium-210 analyses. This test is good only if no lead-210 is lost during preparation.

The composite uranium-thorium solution prepared from portions of the Happy Jack uraninite and the Kivu thorite provided high activities of polonium-210 and lead-212. Precipitates formed in a 0.5*N* HCl solution during the dissolution of these samples, and these precipitates were separated by filtration. The separate analysis for uranium in this solution by the isotope dilution method indicated that no uranium had been lost. However, as shown in Table III, the results of analyses performed on aliquot portions of this solution over a period of 820 days indicate that neither polonium-210 nor lead-212 was in radioactive equilibrium at the time these solutions were prepared and required relatively long periods to return to equilibrium. Thus, it is important that the entire amount of any sample be dissolved.

Attempts to analyze for polonium-210 in the Pacoima Canyon zircon illustrate the need in the procedure for the recovery of ions adsorbed on the silica precipitate and the importance of using a sodium peroxide flux rather than a borax flux. The results are shown in Table IV. The first two solutions of this material were prepared using sodium peroxide but the silica which resulted upon acidification was simply separated by filtration and no attempt was made to recover adsorbed decay chain members. The recovery of polonium-210 was only about 70% and remained con-

stant over a period of 150 days. The third solution was prepared using a borax flux. In addition, a recovery of material adsorbed on the silica was made by evaporating silicon as the tetrafluoride. The recovery of polonium-210 from an aliquot portion of this solution was only about 12% of the equilibrium value indicating that polonium was probably being lost during the borax fusion which was conducted at 1100° C. for several hours. Finally a fourth solution of zircon was prepared using a sodium peroxide flux but still recovering material adsorbed on the silica by treatment with HF. The results of the analyses for polonium-210 in aliquot portions of this solution indicate that all of the polonium-210 was recovered and that the lead group in this zircon is almost in radioactive equilibrium with the uranium. The low thorium content made analysis for lead-212 by this procedure difficult until the diethyldithiocarbamate extraction procedure was applied. However, even when the extraction procedure was used, a large standard deviation was still observed due to poor counting statistics.

The polonium-210 and lead-212 in the Sierra Ancha 4 zircon, the Sierra Ancha 1–6 zircon, the Hopi Buttes zircon, and the Marble Mountain uranothorite were analyzed according to the recommended procedure with the results shown in Table V. The U/aliquot content for the zircon solutions is based on the analyzed uranium contents of the zircons rather than the isotope dilution analyses of the solutions themselves because the additional uranium in these solutions presumably originates in the sodium peroxide flux. Unfortunately, the lead-212 data for these zircons cannot be interpreted with respect to the state of equilibrium because the thorium contents are not accurately known. The lead-212 content found in the Sierra Ancha 4 zircon presently provides the best value for its thorium content. The polonium-210 in this zircon appears to be close to the equilibrium amount. On the other hand, the polonium-210 contents found for the Sierra Ancha 1–6 zircon, the Hopi Buttes zircon, and the Marble Mountain uranothorite depart widely from the anticipated equilibrium values. The rate of growth of the polonium-210 activity in the Sierra Ancha 1–6 zircon solution corresponds to the polonium-210 half life. The maximum polonium-210 content to be expected from this growth to equilibrium was computed by a least squares fit to the data and is shown in Table V in place of the average for the analytical results.

Table V. Analytical Results for the Remaining Samples

Sample	Time since solution prepared, days	Po-210 Corrected activity, c.p.m.	Po-210 Wt. equiv. U, μg.	Pb-212 Corrected activity, c.p.m.	Pb-212 Wt. equiv. Th, μg.
Sierra Ancha 4 zircon (10.05 μg. U/aliquot portion)	47	2.52	8.87		
	71	2.57	9.04		
	95	2.61	9.18	0.117	1.33
	128	2.58	9.08	0.092	1.05
Av. and std. dev.			9.04 ± 0.13		1.19
Fraction of equilibrium value			0.900		
Sierra Ancha 1–6 zircon (16.02 μg. U/aliquot portion)	48	1.78	6.26		
	70	1.72	6.05		
	96	1.86	6.55	0.388	4.43
	129	1.99	7.00	0.523	5.97
	203	2.17	7.64		
Av.					5.20
Anticipated equilibrium value and std. dev.			8.97 ± 0.18		
Fraction of equilibrium value			0.560		
Hopi Buttes zircon (11.36 μg. U/aliquot portion)	5	2.65	9.33		
Fraction of equilibrium value			0.821		
Marble Mountain uranothorite (6.95 μg. U/aliquot portion 634 μg. Th/aliquot portion)	54	7.77	27.3		
	73	7.72	27.2	58.8	671
	142	8.10	28.5	64.8	740
Av. and std. dev.			27.7 ± 0.7		706
Fraction of equilibrium value			0.399		1.114

ACKNOWLEDGMENT

The author expresses his appreciation to Dr. L. T. Silver for the samples, analytical data, and advice generously provided.

LITERATURE CITED

(1) Alberti, G., Bettinali, C., Salvetti, F., *Ann. Chim. Roma* **49**, 193 (1959); *C.A.* **53**, 16421*e* (1959).
(2) Ancarani, L., Riva, L., *Comit. Nazl. Ric. Nucl.* **CNG-31** (1959); *C.A.* **54**, 10666*f*.
(3) Bagnall, K. W., "Chemistry of the Rare Radioelements," Academic Press, New York, 1957.
(4) Black, S. C., *U. S. At. Energy Comm., Rept.* **UR-463**, 1956.
(5) Bode, H., Neumann, F., *Z. Anal. Chem.* **172**, 1 (1960).
(6) Chen, Y., Wong, C., *J. Chinese Chem. Soc., Ser. II* **6**, 55 (1959).
(7) Dedek, W., *Monatsber. Deut. Akad. Wiss. (Berlin)* **1**, 502 (1959); *C.A.* **55**, 16206*i* (1961).
(8) Dedek, W., *Z. Anal. Chem.* **173**, 399 (1960); *C.A.* **54**, 17151*b* (1960).
(9) Feldman, I., Frisch, M., ANAL. CHEM. **28**, 2024 (1956).
(10) Godt, K. J., Sommermeyer, K., *Atomkernenergie* **5**, 282 (1960); *C.A.* **55**, 138*i* (1961).
(11) Gorsuch, T. T., *Analyst* **84**, 170 (1959).
(12) *Ibid.*, **85**, 225 (1960).
(13) Haissinsky, M., *J. Chim. Phys.* **33**, 97 (1936).
(14) Harrison, A. D. R., Lindsey, A. J., Phillips, R., *Anal. Chim. Acta* **13**, 459 (1955).
(15) Kahn, M., Langhorst, A. L., *J. Inorg. Nucl. Chem.* **15**, 384 (1960).
(16) Krebs, C. A., Whipple, G. H., *U. S. At. Energy Comm., Rept.* **UR-501**, 1957.
(17) Lingane, J. J., "Electroanalytical Chemistry," Interscience, New York, 1958.
(18) Pauly, J., *Bull. Soc. Chim. France* 1960, 2022; *C.A.* **55**, 11233*i* (1961).
(19) Poulaert, G., *Chimia (Aarau)* **12**, 116 (1958).
(20) Rosholt, J. N., Jr., "Advances in Nuclear Engineering," Vol. II, Part 2, p. 300, Pergamon, New York, 1957.
(21) Rosholt, J. N., Jr., ANAL. CHEM. **26**, 1307–11 (1954).
(22) *Ibid.*, **29**, 1398 (1957).
(23) Rosholt, J. N., Jr., U. S. Geological Survey, Denver, Colo., private communication, 1961.
(24) Rosholt, J. N., Jr., "Proceedings of the Second U.N. Conference in the Peaceful Uses of Atomic Energy," Vol. 2, p. 230, United Nations, Geneva, 1958.
(25) Rosholt, J. N., Jr., *U. S. Geol. Surv. Bull.* **1084-A**, (1959).
(26) Samartseva, A. G., *Trudy Gosudarst. Radiev. Inst.* **4**, 253 (1938); English translation by Rabinowitch, E., *AEC-tr-730; C.A.* **33**, 4512[3] (1939).
(27) Silver, L. T., Division of Geological Sciences, California Institute of Technology, Pasadena, private communication, 1962.
(28) Silver, L. T., McKinney, C. R., Deutsch, S., Bolinger, J., *J. Geol.* **71**, 196 (1963).
(29) Smith, F. A., Della Rosa, R. J., Casarett, L. J., *AEP Rept.* **UR-305** (1955).
(30) Templeton, D. H., Howland, J. J., Perlman, I., *Phys. Rev.* **72**, 758 (1947).
(31) *U.K.A.E.A. Rept. IGO-AM/W-167* (1958).
(32) Verbersik, V., *Z. Anal. Chem.* **175**, 405 (1960); *C.A.* 55, 5189*f* (1961).
(33) Von Gunten, H. R., Buser, W., Houtermans, F. G., "Proceedings of the Second U. N. International Conference on the Peaceful Uses of Atomic Energy," Vol. 2, p. 239, United Nations, Geneva, 1958.
(34) Whitaker, M. D., Bjorksted, W., Mitchell, A. C. G., *Phys. Rev.* **46**, 629 (1934).

RECEIVED for review March 25, 1963. Accepted April 26, 1963. This work was supported by the Atomic Energy Commission under Contract AT(04-3)-427.

General Applicability of the Channels Ratio Method of Measuring Liquid Scintillation Counting Efficiencies

ELIZABETH T. BUSH

Nuclear-Chicago Corp., 333 East Howard Ave., Des Plaines, Ill.

▶ Determination of the counting efficiencies of liquid scintillation samples as a function of the ratio of the count rates in two channels of the pulse height spectrum is examined for a much wider variety of quenching agents, solvent systems, and fluor concentrations than previously reported. The behavior of the curves of efficiency *vs.* channels ratio is examined as a function of small changes in multiplier phototube and discriminator voltages and other instrumental variables, and the over-all accuracy of the method is assessed. It is concluded that the method is much more widely applicable than is generally realized and that extremely useful results are obtainable when instrumental parameters are properly chosen.

One of the outstanding advantages of liquid scintillation counting has been its ability to accept a wide variety of radioactive sample materials without the necessity of converting them to uniform chemical composition. This has resulted in great saving of sample preparation time, but has presented the alternative problem of determining counting efficiency individually for each sample composition. Recently, a method was described by Baillie (*1*), and subsequently by Herberg (*3*) and Bruno and Christian (*2*), by which efficiency could be quantitatively related to the ratio of the counting rates in two channels of the pulse height spectrum of a liquid scintillation beta spectrometer. If the instrument provides for counting in two channels simultaneously, each sample need be counted only once, and no further operations on the samples are necessary to determine the counting efficiency. This provides significant advantages over the traditional methods of internal standardization or dilution.

A calibration curve can be established by counting a series of samples of varying efficiencies (degrees of quenching), but containing known amounts of radioactivity. The observed counting efficiency, E, is plotted against the ratio, R, of the counting rates in the two channels. When unknowns are counted under identical instrumental conditions, the channels ratios may be calculated and the corresponding efficiencies read from the curve.

Baillie, Bruno, and Christian (*1*, *2*) reported on quenching correction (E *vs.* R) curves for nine quenching agents, some of which were colored. Bruno and Christian found that a single curve sufficed for C^{14} samples quenched with any of five different substances, both colored and colorless. They studied only one solvent-fluor system, but suggested that different curves would be found for other solvents. Baillie, on the other hand, found diverging curves for colored and chemically quenched (colorless) samples of C^{14}, but reported that dilution of his (unspecified) solvent with secondary solvents gave the same curve as other chemical quenching agents.

In each case, the investigators were able to determine counting efficiency from the measured ratio with an accuracy comparable to or surpassing that of other methods. But while the calibration curves remained unchanged for months in one laboratory, in the other it was necessary to recalibrate every few days.

It appears that relatively few investigators have taken advantage of this potentially simple and rapid method of determining counting efficiency, because they are not sure either as to how many calibration curves are required for the different solvent and sample types they are using, or how the precision of the method is affected by instrumental variables such as voltage drifts. The present study is addressed to these problems.

EXPERIMENTAL

The isotopes studies were C^{14} and H^3. An attempt was made to include the solvent and fluor systems and the reagents most commonly used to prepare such samples, as well as a wide variety of quenching agents, including biological material. The effects of fluor concentration and of sample volume were also studied. Table I lists the fluors, solvents, and sample materials used.

The study included about 50 sample compositions containing H^3 and about 70 with C^{14}. Samples were counted in 20-ml. vials of No-Sol-Vit glass supplied by the Wheaton Glass Co.

H^3 or C^{14} was added to all samples in the form of labeled toluene. Since toluene was not a component of all the sample compositions to be studied, it was necessary to introduce it in amounts which could not significantly dilute

Table I. Components of Samples Used in Quenching Correction Studies

Solvent–fluor systems	Secondary solvents
Toluene + PPO[a]	Methanol
Toluene + PPO + POPOP[b]	Ethanol
Toluene + PBD[c]	Xylene
Dioxane + PPO + POPOP	Anisole
Dioxane + PPO + POPOP + naphthalene	1,2-Dimethoxyethane
	Ethylene glycol
	2-Methoxyethanol
	Other Components
Hyamine hydroxide	Urine
Ethanolamine	Blood precipitate from acetone
Water	Blood precipitate from $ZnSO_4$ + NaOH
Acetone	Blood supernatant from $ZnSO_4$ + NaOH
Benzoic acid	Liver homogenate supernatant from $ZnSO_4$ + NaOH
Oleic acid	Liver homogenate precipitate from $ZnSO_4$ + NaOH
Potassium hydroxide	Iodine
Tributyl phosphate	Yellow wax
Alanine	Indigo
Adenine	Methyl violet
Albumin	Crystal violet
Insulin	Malachite green
	Oxygen

[a] 2,5-Diphenyloxazole.
[b] 2-*p*-Phenylenebis(5-phenyloxazole).
[b] 2-(4-Biphenylyl)-5-phenyl-1,3,4-oxadiazole.

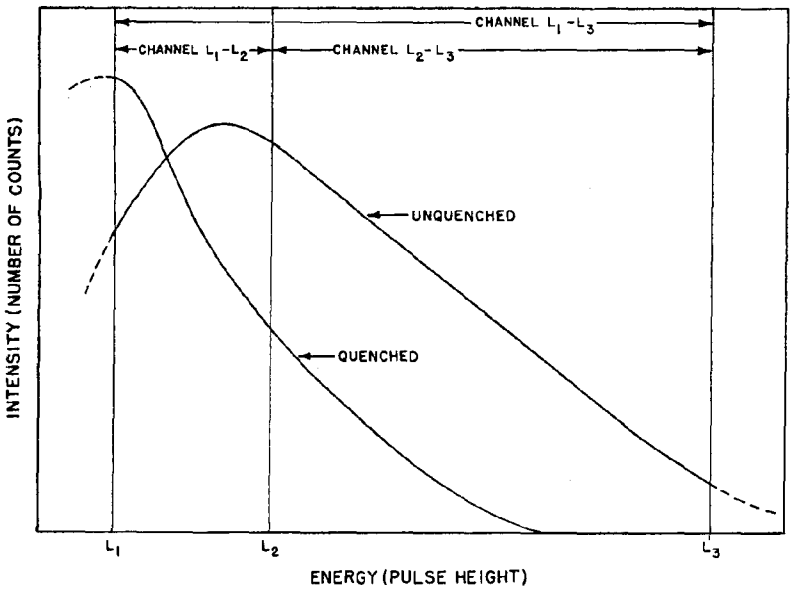


Figure 1. Spectrometer channels in relation to beta spectra

these samples, or fail to dissolve in them. In the largest group of samples, each received 100 μl. of active toluene. These samples had volumes of 10 ml., except for some which were prepared to study the effect of sample volume, and which ranged from 3 to 18 ml. A significant source of error in the internal standardization method, the difficulty in measuring a small volume of active solution, was therefore present in this part of the experiment. In order to assess its contribution to the over-all error, two further sets of samples were studied, containing 3 ml. of C^{14}-toluene and 1 ml. of H^3-toluene, respectively, in 10- or 11-ml. total volume. The activity in each of the foregoing samples was 2.68×10^4 or 1.71×10^4 d.p.m. of C^{14} or 3.28×10^5 d.p.m. of H^3. A series of low-activity samples of each isotope was also prepared in order to evaluate the channels ratio method at counting rates close to the background level.

Counting times were generally long enough to accumulate at least 20,000 counts in each channel, except in the case of the low activity samples.

The liquid scintillation counters, manufactured by Nuclear-Chicago Corp., included both two- and three-channel models. The criteria for choosing the counting channels were that the statistical errors of counting should be minimized, and that the plot of efficiency *vs.* channels ratio should have a useful slope over the desired range of efficiencies and be as nearly linear as possible. The more nearly linear the calibration curves, the fewer points are needed to establish them accurately.

To minimize statistical errors, the total portion of the spectrum which is included within the counting channels should be used in calculating the efficiency. This may be done either by dividing the spectrum into two adjacent channels and summing their counts, or by using one wide channel (from which the efficiency is calculated) and one narrow channel which is included within it. With reference to Figure 1, where the output pulse height spectrum of the (beta) counter is displayed in relation to three variable discriminator levels, these alternatives correspond to counting in channels L_1-L_2 and L_2-L_3, or channel L_1-L_3 plus either channel L_1-L_2 or L_2-L_3. For a given total number of counts, statistical uncertainty in the value of the ratio is smallest when the ratio is unity. It is probably desirable that the greatest deviation from unity occurs for unquenched samples. Since these may, in general, be expected to have the highest count rates, less time will be necessary to achieve the desired statistical precision in the channel with the lower rate.

RESULTS

The shapes of the E *vs.* R curves are determined by the positioning of the spectra in the counting windows and, therefore, by the gain and discriminator settings. Samples with varying degrees of quenching cannot all be counted with their best efficiencies at a single setting. It is sometimes necessary to compromise between better efficiency and linearity of the curve. Since a principal objective of the present work is to present data for a wide range of quenching agents and efficiencies, the curves displayed here represent what were felt to be the best operating conditions for this large spread of samples. For a group of samples showing a smaller range in quenching, higher efficiency and better linearity may be obtained by optimizing the conditions for that group.

It was found that adjacent channels were most suitable for counting H^3, with the L_1-L_3 efficiency plotted against the ratio of the counts in the upper window to those in the lower [$R = (L_2\text{-}L_3)/(L_1\text{-}L_2)$]. R is a much more slowly varying function of E for H^3 than for C^{14}. Use of adjacent channels gives the maximum change in R. When this ratio is plotted for C^{14} over a wide range of efficiencies, a very nonlinear curve results. Overlapping channels were therefore used for C^{14}, with L_1-L_3 efficiency plotted *vs.* $R = (L_1\text{-}L_2)/(L_1\text{-}L_3)$.

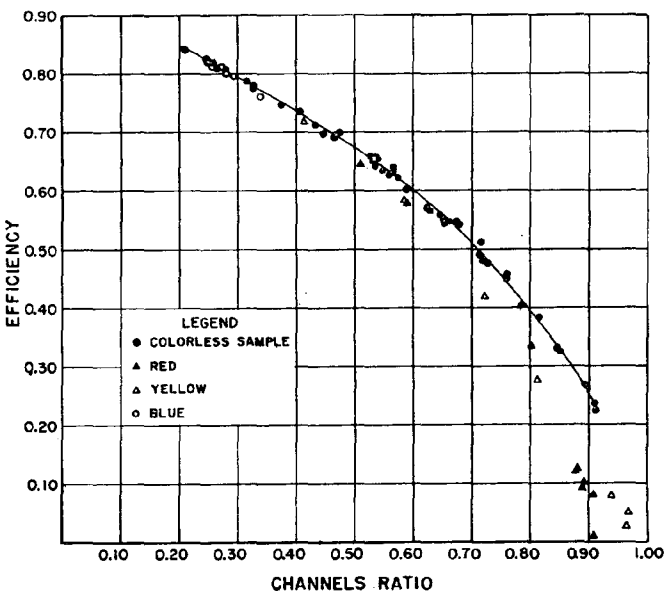


Figure 2. Quenching curve for C^{14} samples containing 100 μl. of labeled toluene

Wide-channel (L_1-L_3) efficiency *vs.* ratio of counts in channels $(L_1\text{-}L_2)/(L_1\text{-}L_3)$

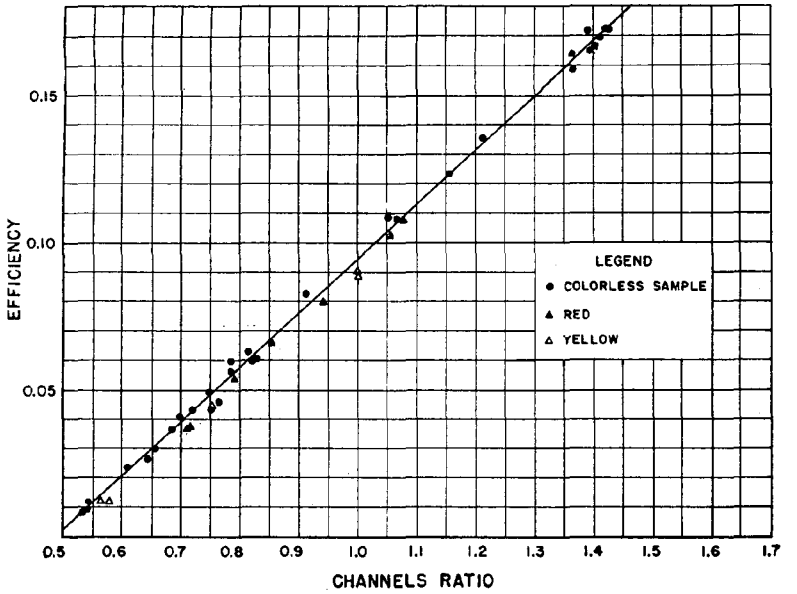


Figure 3. Quenching curve for H^3 samples containing 100 μl. of labeled toluene

Total efficiency in channels L_1-L_2 plus L_2-L_3 vs. ratio of channels $(L_2-L_3)/(L_1-L_2)$

The behavior of the E *vs.* R curves will be discussed as a function of the several variables which were studied.

Sample Composition. Carbon-14 Samples. A single quenching correction curve sufficed for all solvents, fluors, and quenching agents studied, so long as samples were not highly colored. Lightly colored samples containing biological materials such as urine, Hyamine solutions of blood, liver homogenate, etc., in which the quenching was chiefly chemical in nature, fell on this same curve. Highly colored samples diverged from the curve of chemical quenching as color became more intense. This agrees with Baillie's findings. Figure 2 shows the data for about 70 samples containing 100 μl. each of toluene-C^{14}. All the colored samples falling below the main curve were rather intense solutions of dyes, colored wax, or iodine, with the exception of the three yellow samples at the bottom. These were blood samples of medium color intensity whose quenching was primarily chemical. Blue samples exhibited little quenching, as might be expected from the fact that the fluorescent emission spectrum is peaked at 3500 to 4500 A.

Samples which separated into two liquid phases showed anomalous behavior, as did partially frozen samples. Solidly frozen dioxane samples usually fell on the curve. Counting was done at about −2° C. unless otherwise indicated.

Results for colorless samples containing 3 ml. of toluene-C^{14} showed a reduced dispersion of points about the curve, indicating a reduced error due to pipetting. Eight quenching agents or secondary solvents were represented in this set. Since these samples were made up before the larger set, their compositions were unselected with respect to the data of Figure 2. Samples containing the same quenching agents show a random distribution around the curve in Figure 2.

Tritium Samples. Data for H^3 samples containing 100 μl. of labeled toluene are shown in Figure 3. All samples fall very nearly on a single curve, although highly colored samples have slightly higher values of R for given values of E. This latter effect was also shown by samples containing PPO without POPOP. On the basis of these data samples were selected whose points fell below, above, and on the curve, and samples having these compositions were made up with 1 ml. of H^3-labeled toluene. The improved precision in measuring activity is indicated in Figure 4. (The average deviation from the curve of points for colorless samples is 0.098% in efficiency in the latter case, compared with 0.21% in the former.)

This last group of samples was counted in four different instruments. Intensely colored samples were found to deviate from the curve of chemical quenching by an average −0.5% in efficiency, with a maximum observed deviation of −0.75%. Samples containing PPO as the only fluor showed a maximum observed deviation of −0.9%. The results for PBD and PPO + POPOP in various fluor concentrations and with different solvents and quenching agents were consistent with a single curve, with one exception: In one of the four instruments a small negative deviation in efficiency (less than 1%) was also shown by samples containing dioxane plus naphthalene.

The effect of phase separation was similar to that in C^{14} samples. Some samples which were apparently solidly frozen did not fall on the curve, while others did.

Duplicate Samples. A number of duplicate samples were made in the course of this work. Although pipetting was done with all reasonable care, the efficiencies of duplicate samples might differ by 1 or 2% in absolute value. This amounted to fractional differences of up to 10%

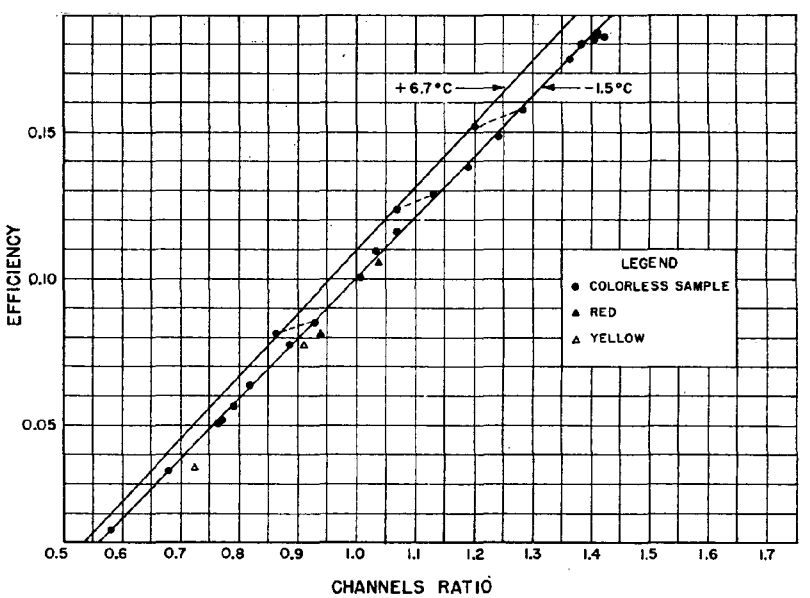


Figure 4. Quenching curves for H^3 samples containing 3 ml. of labeled toluene at −1.5° and + 6.7° C.

at lower efficiencies, which was more than could reasonably be accounted for by errors in pipetting of reagents. Nevertheless, these appeared to be differences in the degree of quenching, since the samples showed the expected relationships between efficiency and channels ratio: their points fell on the expected curves. These differences might be attributed to aging processes during the time intervals of days or weeks between preparation of the "duplicate" samples. Prepared samples were stored in the counter at −1.5° C., while scintillation solutions and other ingredients were stored at room temperature. Some difference may be due to the vials themselves.

Although the labeled material was volatile, there was usually no evidence of evaporation from the vials for several weeks. Adsorption of labeled compounds on the glass might present a problem in the aging of some other types of samples. This would be expected to shift the pulse height spectra toward lower energy. We have observed this phenomenon in liquid scintillation counting of high specific activity salts of P^{32}.

Temperature. H^3 curves were sensitive to temperature, as shown in Figure 4. The dotted lines connect points for the same samples, showing that with an increase in temperature E decreased slightly, while R decreased considerably.

C^{14} curves were not very sensitive to temperature. Although the same effects were operative on the pulse height spectra of the two isotopes, the C^{14} curves were "temperature-compensated." A decrease in E was accompanied by an increase in R which moved C^{14} points along the curve. An average error of less than 1% in efficiency was found in using a calibration curve for −1.5° C. to determine the efficiency of samples at +7° C.

Certain Optical Effects. Samples containing light-colored precipitates or filter paper on the bottoms of the vials did not deviate from the curves. A sample containing carbon black on the bottom fell far from the curve. (The activity was in solution in all cases.)

A gel sample of toluene plus Cab-O-Sil fell on the curve when first prepared, and showed very little quenching. Subsequently its efficiency decreased greatly without a corresponding change in R. Upon examination, the gel was then found to be distributed unevenly over the sides of the bottle. It is possible that with the right viscosity and great care in handling, reproducible results might be obtained with gel samples; but this study was not pursued.

Sample volume could be varied from 3 to 18 ml. in the case of C^{14} without causing deviations from the curve, and over a somewhat narrower range for H^3. Efficiency was slightly higher at 10 to 15 ml.

Severe "fogging" of the vials, simulated by a light coating of soap, caused deviations in efficiency of 1 to 2%, usually positive, for C^{14}. Normal fogging or fingerprints are not expected to cause errors.

Instrument Parameters. The effects on the curves of small changes in multiplier phototube high voltage and discriminator value were studied to assess the errors to be expected from instrumental drifting. It was determined that no measurable error could be expected from possible drifts in discriminator values. The expected error from high voltage drifts may be expressed as follows for a tritium curve of the type shown: for the maximum change in high voltage permitted by the regulator for a 30-volt line voltage change, the absolute value of E as determined from R would vary by 2×10^{-4} at 1% efficiency, or by 5×10^{-4} at 15% efficiency. That is, the error in the calculated activity of a sample (given by $\Delta E/E$) would range from 2% at $E = 0.01$ to 0.33% at $E = 0.15$. This is the maximum allowable error. In actual practice, the curves were not observed to drift outside the limits predicted by counting statistics over periods of many weeks. The curves were reproducible after changing the high voltage and discriminator values if the controls were accurately reset. This latter is an important requirement. In routine work it would seem to be good practice to count a set of sealed quenched standards in every run, just as background and unquenched standard samples are usually counted.

Level of Radioactivity. A set of samples was made up to have net count rates near the background level. C^{14} samples contained 107 d.p.m., and their count rates varied from about 0.75 to 2 times background in each channel, depending on the amount of quenching. Tritium samples contained 820 d.p.m., and varied in count rate between 0.35 and 7 times background in each channel. The quenching agent used was acetone. Net count rates were calculated for each sample, using the measured background rates for each sample type. The efficiencies and ratios based on the net count rates showed the same relationships as those of higher activity samples.

Background measurements were made on many sample compositions, but no general relationship between background rate and efficiency was found for either H^3 or C^{14}. Some factors in the variation of that part of the background due to the sample system are: (1) chemical quenching, (2) color quenching, (3) fluor type and concentration, (4) fluorescence of components other than the scintillation solute, (5) efficiency for γ-ray interaction, (6) efficiency for Cherenkov radiation, (7) natural content of contemporary carbon, (8) natural activity of the vial, and (9) phosphorescence of some sample materials. In so far as the effects of these could be separated, an estimate was made of the amount by which the background rate changed when each factor was varied independently. (Sample phosphorescence was not studied.) The observed limits of these changes may be of some general interest, since it is necessary to estimate the possible uncertainty in the background and the magnitude of the resulting error in order to choose appropriate counting procedures for samples of low activity. The following are the (approximate) maximum observed variations in background in the summed H^3 channels with changes in each of those factors which could be distinguished, expressed as percentage changes in the background rate of a sample of pure toluene + PPO + POPOP: chemical quenching, 10%; color quenching, 55%; fluor (presence or absence of secondary solute), 11%; solvent system (including effects of 4, 5, 6, and 7 above), 15%; and vial, 15% (all vials were from a single shipment by the Wheaton Glass Co.). The magnitude of the variation in the C^{14} window was generally less, while in the lower energy H^3 channel alone it was higher.

Chemical quenching is distinguished from dilution in this context by letting it refer to the change in efficiency produced by adding to a given solvent system not more than 30% by volume of colorless quenching agents. No correlation was observed between efficiency and background rate in samples containing different chemical quenching agents. In a series of samples having increasing amounts of the same quenching agent, the background rate sometimes, but not always, varied monotonically with efficiency. The background of colored samples always decreased with increasing concentration of quencher.

It is not always feasible, or even possible, to control all of the above-mentioned factors in preparing blanks for low activity samples. It is therefore of interest to compare the errors caused by using incorrect background rates in the channels ratio and other methods of efficiency determination. In the channels ratio method the values of both the ratio and the net count rate used in calculating the activity may be in error if the true background rates in each channel are not known. These errors may be additive or they may partially cancel each other, depending upon the particular counting conditions

Table II. Error in Calculated Value of Disintegration Rate Due to Background Variation of −20% from Its Assumed Value

(Calculations for tritium samples having net count rates of 150 c.p.m. at various efficiencies)

Channels ratio method				Internal standardization method
R	E	E'	$\frac{D'-D}{D}$	$\frac{D'-D}{D}$
1.50	0.2064	0.2027	−0.022	0.040
1.25	0.1532	0.1481	−0.0069	0.040
1.00	0.1000	0.0941	+0.020	0.040
0.85	0.0681	0.0623	+0.047	0.040
0.75	0.0468	0.0405	+0.109	0.040

employed. When internal standardization is used, the error introduced by uncertainty in the value of the background count rate appears only in the calculation of the net count rate.

The relative magnitudes of the errors of these two methods were compared for an actual set of counting conditions. The error introduced by using the wrong value for the background count rate will be called the "background error," defined as the fractional difference, $(D'-D)/D$, between the true disintegration rate, D, of the sample and the apparent value, D', calculated as follows:

$$D = C/E \quad (1)$$

$$D' = C'/E' \quad (2)$$

where C is the true net count rate, E the true counting efficiency, $C' = C + \Delta B$, ΔB being the difference between the assumed and actual values of the background rate, and E' is the apparent efficiency. It is assumed that $E = E'$ for the internal standardization method—i.e., that the background rate cancels out of the expression for the efficiency.

Using the channels ratio method, E' is determined in the following way: A standard calibration curve is established by counting high activity samples, so that no background error is involved. The background rates of an unquenched sample are measured in each channel. The ratio of the true net counting rates of a low activity sample in the two channels is adjusted for a given background change in each channel: $R' = (C_1 + \Delta B_1)/(C_2 + \Delta B_2)$, where the subscripts identify appropriate channels for the isotope in question. The new ratio R' is then used to find E' from the calibration curve.

It is obvious that if $E' = E$, as in the internal standardization method, the tractional error in the disintegration rate equals the fractional error made in determining the net count rate, since from Equations 1 and 2

$$D'-D = \frac{C'-C}{E}$$

$$\frac{D'-D}{D} = \frac{C'-C}{ED} = \frac{C'-C}{C}$$

If, however, $(C'-C)/E = (E'-E)/E$, it is easily shown that $D'-D=0$, and there is no background error. By using the channels ratio method, this situation may be achieved or approached in many cases by proper choice of the counting conditions. This depends on being able to obtain, simultaneously, certain values of the slope of the curve of E *vs.* R and of the ratios of the sample and background rates in each channel. For a given set of counting conditions and a given background change the background error will vary from positive to negative over a range of efficiencies, passing through zero at some value. Samples having a restricted spread of efficiencies about this value will be counted with a very small background error.

Table II illustrates this for H^3 samples having net count rates of 150 c.p.m., or five times background, at all efficiencies. The assumed value of the background was that observed for an unquenched sample: 10 and 20 c.p.m. in the lower and upper energy channels, respectively. The true value of the background was taken as 20% lower than the assumed value. An experimental curve of E *vs.* R was used. This was a "typical" curve similar to that of Figure 3, with counting conditions chosen according to the general criteria set forth earlier, rather than with any reference to background error. For this particular curve, the background error became zero at about 15% efficiency. Other values of the gain and discriminator settings were investigated, and it was found that for a change of 20% in the background rate the background error for H^3 samples could be made less than the fractional error in the count rate alone—i.e., the background error of the internal standardization method—for all but the most highly quenched samples. Zero background error was made to occur at any efficiency down to 7% (not necessarily the lower limit). For C^{14} samples, zero error could be obtained for medium and highly quenched samples.

In addition to the two methods already discussed, efficiency may be determined by either of two dilution techniques (4). One involves successive additions of scintillation solution to a sample, with repeated countings. Since the background is a function of sample volume as well as degree of quenching, it appears that it would be very tedious to determine an appropriate background rate for each count. The other method requires a series of samples having the same total volume but decreasing amounts of the radioactive (quenching) material. It might be hoped that one could avoid the necessity of having a blank for each dilution by using a single background value, that of the unquenched sample, and that the background error would disappear in an extrapolation to infinite dilution. In the one experiment of this kind which was performed in the course of this work, the fractional error in net count rate increased with the decreasing activity and yielded a background error of 5% at infinite dilution.

DISCUSSION AND CONCLUSIONS

Baillie has shown that by the proper choice of instrumental parameters the C^{14} efficiency in channel L_1-L_3 can be made numerically equal to the ratio $(L_2-L_3)/(L_1-L_3)$ over a limited range of efficiencies. This ratio thus provides a very convenient measure of efficiency, but it suffers in general from greater statistical uncertainty than the ratio $(L_1-L_2)/(L_1-L_3)$. The latter approaches the value of 1 as quenching increases, while the former approaches 0.

Use of a special calibration curve is necessary for highly colored C^{14} samples. It appears that all colors follow one curve, at least until quenching becomes very severe. The error which will be made in using a single curve for H^3 samples is small.

Samples prepared and sealed in a nitrogen atmosphere are ordinarily employed as standards in liquid scintillation counting. These have higher counting efficiencies than samples in equilibrium with the oxygen in air and cannot be used directly to standardize solutions which are counted in ordinary vials, unless a correction is made for quenching in the latter. The use of a quenching correction curve offers a very convenient method of standardizing a laboratory solution. A curve may be established by counting a set of variously quenched samples of the unknown solution, using a tentative value for the activity. The sealed standard is then counted and the curve is normalized to this point. Obviously, such an extrap-

olation to higher efficiency should be carried out on a curve which is fairly linear in this region.

The use of a "duplicate" sample to determine counting efficiency may result in an unexpectedly large error, particularly at lower efficiencies. The channels ratio of the individual sample gives a more reliable measure of its efficiency.

The channels ratio method offers the following advantages over internal standardization or dilution techniques for determining efficiency: only a single counting is necessary in a two-channel instrument; the measurement can be repeated at any time, because the sample remains unaltered; and certain sources of error are eliminated, such as the assumption that efficiency is the same before and after adding an internal standard and measuring errors in pipetting small volumes. On the other hand, when activity is very low a longer counting time will be necessary to achieve a given statistical precision in the value of the ratio than to achieve the same accuracy in the counting rate. This extra counting time must be weighed against the time required of personnel to perform the sample manipulations involved in other methods.

ACKNOWLEDGMENT

Thanks are expressed to Ariel G. Schrodt and Richard B. Frank for helpful discussions in the course of this work.

LITERATURE CITED

(1) Baillie, L. A., *Intern. J. Appl. Radiation Isotopes* **8**, 1 (1960).
(2) Bruno, G. A., Christian, J. E., ANAL. CHEM. **33**, 650 (1962).
(3) Herberg, R. J., *Ibid.*, **32**, 1468 (1960).
(4) Peng, C. T., *Ibid.*, **32**, 1292 (1960).

RECEIVED for review August 8, 1962. Accepted April 15, 1963. Division of Analytical Chemistry, 141st Meeting, ACS, Washington, D. C., March 1962.

Neutron Activation and Radiochemical Determination of the Molybdenum, Chromium, and Iron Content of Individual Stainless Steel Microspheres

PHILIP A. BENSON and CHESTER E. GLEIT

TRACERLAB, Division of Laboratory for Electronics, Richmond, Calif.

▶ Stainless steel microspheres, with weights between 4.7×10^{-9} and 3.9×10^{-8} gram, are isolated on methyl methacrylate films. After measurement of particle diameters by optical microscopy, the specimens are encapsulated in lead foil and irradiated with an intense flux of neutrons. Radiochemical procedures are used to isolate the Mo^{99}, Cr^{51}, $Fe^{55,59}$, and Np^{239} fractions. The abundance of molybdenum, chromium, and iron in the individual spheres is determined from the measured activities. The experimental error is attributed to three principal sources. Uncertainty in particle diameters as measured by optical microscope produced a relative error of 6 to 11%. Radiochemical variations led to a relative error of 5%. Contamination of the sample was successfully controlled in the Mo and Cr analyses. Impurities in the encapsulating lead foil were the largest source of error in the iron determination.

ACCURATE chemical analysis of samples as small as 10^{-9} gram is required in research programs related to the characterization of air-borne particulate matter and interplanetary dust. Neutron activation analysis is a valuable analytical method for such small samples. Through the use of high intensity neutron sources and subsequent radiochemical analysis over 30 elements can be quantitatively measured in amounts smaller than 10^{-12} gram. In practice, sensitivity is limited by contamination. The experiment described in this paper was undertaken to develop suitable handling techniques and to determine the practical limits of sample size, accuracy, and reproducibility in performing such analyses.

Activation analysis, based on measurements of induced radioactivity, is essentially free of errors produced by contamination of the specimen after irradiation. Carrier solutions composed of stable isotopes, which are added in the first step of the radiochemical separations, and standard blank corrections minimize errors due to accidental additions of stable species. However, special techniques must be employed in isolating the samples to minimize contamination prior to the irradiation. In the present work, the individual stainless steel microspheres are carried on 10^{-7}-gram films of methyl methacrylate. To prevent loss of activated species during irradiation by nuclear recoil the particles are encapsulated in high purity lead foil and are then irradiated in high purity quartz ampoules.

Iron, molybdenum, and chromium have been determined in a variety of samples by activation analysis. Several papers discuss the determination of chromium in meteorites (*3*, *10*), alloys (*11*), and high purity metals (*2*). Chromium is determined by quantitatively measuring the activity of 28-day Cr^{51}. This species is produced by neutron capture of stable Cr^{50}. After radiochemical purification, the intensity of the 0.32-m.e.v. γ-ray of Cr^{51} is measured. Molybdenum is determined in a similar manner employing the Mo^{98} (n,γ) Mo^{99} reaction. However, 66-hour Mo^{99} is usually assayed by measuring its beta radiation with a Geiger-Müller or proportional counter (*1*, *5*, *7*). To correct for Mo^{99} produced by the fission of uranium, a sample of natural uranium is irradiated simultaneously with the samples and the ratio of Mo^{99} arising from U^{235} (n,f) Mo^{99} and Np^{239} arising from the U^{238} (n,γ) $U^{239} \rightarrow Np^{239}$ reaction is determined. The samples are then analyzed for Np^{239}, and an equivalent amount of Mo^{99} is subtracted from the Mo^{99} in the samples to correct for uranium impurity. Iron yields two radioactive isotopes on activation, arising from the nuclear reactions: Fe^{54} $(n,\gamma)Fe^{55}$ and Fe^{58} $(n,\gamma)Fe^{59}$. A method of counting these two radioisotopes simultaneously to increase sensitivity has recently been described (*4*).

EXPERIMENTAL

Standards and Reagents. Appropriate amounts of iron, molybdenum, and chromium salts were dissolved and diluted to 1 liter with conductivity water to yield a solution containing approximately 20 mg. of the element per ml. Five milliliters of redistilled HNO_3 were added to the iron carrier to prevent hydrolyzation. Dilute solutions of these standards

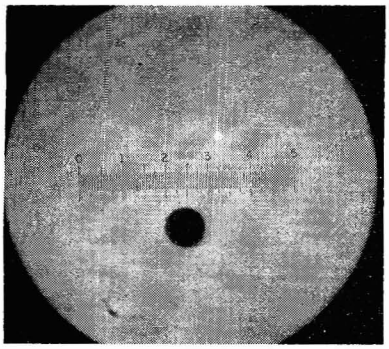


Figure 1. Typical stainless steel ball, highly magnified

Major scale divisions separated by approximately 10 microns

were prepared by successive dilution of the stock solutions. The standard iron solution contained 47.10 μg. of Fe per ml., the standard chromium solution contained 41.88 μg. of Cr per ml., and the molybdenum solution contained 4.56 μg. of Mo per ml. A tracer solution containing 509 d.p.m. per ml. of Np^{237} was prepared. Its purity was checked by electroplating an aliquot on a platinum disk and counting in an alpha spectrometer.

Scavenge Carriers. Solutions of Zr, La, Ag, Cu, and Fe containing approximately 10 mg. of the elements per ml. were prepared by dissolving their nitrate salts in water or dilute nitric acid. A solution of Ba scavenge carrier was also prepared containing 50 mg. of Ba per ml.

Preparation of Samples. Samples of number 316 stainless steel microspheres, obtained from the Linde Co., Division of the Union Carbide Corp., East Chicago, Ill., were transferred to a glass microscope slide with a dissecting needle. A drop of 1 to 15 solution of methyl methacrylate in amyl acetate was added to the slide and allowed to harden, forming a cast of the particles. Single microspheres (Figure 1) with diameters of approximately 12 microns were isolated from the methyl methacrylate film by cutting out a square of the plastic approximately 75 microns square with a micromanipulator. A razor blade fragment served as a cutting tool. The square of plastic was transferred to a clean slide with a thin tungsten needle which had been sharpened to a point of single-crystal thickness by means of $NaNO_2$ etching. The plastic square was dissolved in a drop of the 1 to 15 methyl methacrylate–amyl acetate solution, which was then allowed to harden. When the drop of methyl methacrylate solution was added, the cutout dissolved and convection currents existing in the drop of solution caused the particles and extraneous materials to be distributed throughout the entire drop. This process was repeated until the cutout contained only the desired microsphere, free from other particles and foreign debris.

After the last isolation had been completed, the diameter of the particle was measured using a filar micrometer equipped with a 12.5× Ramsden ocular (Bausch and Lomb Number 31-16-50). The filar micrometer was calibrated with a Bausch and Lomb Number 31-16-90 stage micrometer. All measurements were made through a 97× oil immersion objective. The numerical apertures of both the condenser and objective were 1.25. The spheres were illuminated by an American Optical Co. Ortho-Illuminator B, using a green filter with a transmittance peak at 5300 A. Standard corrections (*6*) were applied to obtain the true diameter. Replicate measurements of the diameter along several axes were performed.

Single particles, measuring 10.4 to 21.2 microns in diameter, were selected for analysis. A square of the plastic no larger than 50 microns on an edge was cut out as before. The cutout was placed on a 3-mm.-diameter disk of high purity lead foil, 35 mg. per sq. cm. thick (Figure 2). A second lead-foil disk was then placed over the particle and sealed by crimping to make a tight envelope. These manipulations were performed in an isolated, pressurized clean room to avoid contamination of the samples by dust and other foreign materials.

The lead foils were sealed in quartz ampoules, 3-mm. i.d. by 4-mm. o.d. by 2 cm. long, made from Supersil quartz tubes (Amersil Quartz Division, Engelhard Industries, Hillside 5, N. J.). The quartz tubes contained a helium atmosphere to avoid oxidation of the lead envelope during irradiation. The excellent heat transfer characteristics of helium helped to prevent the melting of the lead foil from the heat generated during irradiation by gamma radiation inside the nuclear reactor. An aluminum irradiation container was designed to improve further heat transfer to the reactor coolant.

Fifty-microliter aliquots of the standard solutions were evaporated to dryness in quartz ampoules. The standards were prepared in a glove box. A stream of nitrogen was blown over the tubes to hasten evaporation and prevent bubble formation. The standards, samples, blank lead foils, natural uranium, and blank quartz tubes were placed in the aluminum irradiation capsule and irradiated in the in-core position of the General Electric Test Reactor, Vallecitos, Calif., at a thermal neutron flux of 3.1×10^{14} neutrons per sq. cm. per second for 20 days or 567 megawatt-days.

Dissolution and Separation. After the irradiation, the quartz ampoules were removed from the irradiation capsule and cleaned by boiling sequentially in aqua regia, 6*N* NaOH, 6*N* HCl, and distilled water to remove surface contamination. The lead foils were removed from the quartz ampoules and placed in beakers containing 20 mg. of standard iron, chromium, and molybdenum carriers. The lead was dissolved in dilute HNO_3 and the solution equilibrated with HF. The solution was evaporated to dryness, the fluoride

Figure 2. Stainless steel ball cast in 50-micron methyl methacrylate film and mounted at center of 3-mm. lead disk

Point of tungsten needle can be seen above particle

was complexed with H_3BO_3, and HCl was added until the solution was 8*N* in HCl. The chromium was removed from the iron and molybdenum by absorbing the latter elements on a column of Dowex AG 1 × 8 anion exchange resin. Iron was separated from molybdenum by eluting the iron from the resin with 0.5*N* HCl. The molybdenum was eluted from the column with a basic ammonium acetate solution. The neptunium was separated from the iron by reduction of the neptunium in $NaHSO_3$ and coprecipitation of the fluoride with LaF_3.

The chromium fraction was radiochemically purified using standard radiochemical procedures (*9*). The chromium was extracted with acetylacetone into benzene (*8*), the complex was destroyed with HNO_3 and $KBrO_3$, and $Fe(OH)_3$ and $La(OH)_3$ scavenges were performed on the supernate. The chromium was reduced with $NaHSO_3$, and $Cr(OH)_3$ was precipitated with ammonia. The chromium was dissolved in dilute HNO_3 and again oxidized to chromate. The $Fe(OH)_3$ and $La(OH)_3$ scavenges were repeated, and a CuS scavenge was performed after acidification of the solution to 1*N* in HCl. A $BaSO_4$ scavenge was performed and $Cr(OH)_3$ was precipitated with ammonia. The chromium was dissolved and oxidized to chromate with $KBrO_3$. A $Fe(OH)_3$ scavenge was performed and the chromium was precipitated as $BaCrO_4$. The precipitate was then filtered and mounted for counting.

The iron sample was purified using methods previously described (*4*). After LaF_3 and $BaZrF_6$ scavenges were performed, the iron was precipitated as the sulfide. The iron sulfide was dissolved in aqua regia, AgCl and $(Zr)_3(PO_4)_4$ were precipitated, and CuS was then precipitated from the acid solution. Iron was precipitated as the sulfide, redissolved in HCl, and extracted from 8*N* HCl into diisopropyl ether. The iron was back-extracted into water, re-extracted into diisopropyl ether from 8*N* HCl, and finally back-extracted into water. The iron was then electroplated on a copper disk from an ammonium carbonate–ammonium phosphate solution.

Table I. Concentration of Mo, Cr, and Fe in 316 Stainless Steel Microspheres

Sample No.	Diameter, microns	Particle wt., grams $\times 10^9$	Mo wt., grams $\times 10^{11}$	Mo concn., %	Cr wt., grams $\times 10^{10}$	Cr concn., %	Fe wt., grams $\times 10^9$ Fe^{55}	Fe wt., grams $\times 10^9$ Fe^{59}	Fe concn. (Fe^{55+59}), %
1	21.2	39.51	87.7	2.22	58.5	14.8	25.2	25.9	64.7
2	17.4	21.85	(64.2)	(2.94)	26.7	12.2	13.9	13.3	62.3
3	14.0	11.38	20.3	1.78	14.2	12.5	2.4	3.2	24.6
4	12.9	8.90	18.3	2.06	8.1	9.1	7.5	7.5	84.2
5	12.6	8.30	17.4	2.10	11.0	13.2	8.7	8.9	106.0
6	11.8	6.81	14.1	2.07	7.3	10.7	2.7	2.9	40.8
7	11.5	6.31	12.1	1.91	7.2	11.4	2.7	2.6	41.9
8	11.4	6.15	12.4	2.01	6.1	10.0	1.6	2.4	32.6
9	11.4	6.15	12.5	2.04	4.7	7.6	4.1	4.0	65.6
10	11.2	5.83	8.7	1.49	...	...	7.4	6.7	12.2
11	10.6	4.94	10.8	2.19	5.2	10.5	6.8	7.8	148.0
12	10.4	4.67	7.0	1.49	5.2	11.2	3.0	3.1	65.3
Mean concentration				1.94		11.2			62.4
Standard deviation				±0.25		±2.0			±37.4
Nominal concentration of 316 stainless steel				2.0		12.0			62.5

The molybdenum fraction was purified using a rigorous radiochemical decontamination procedure. Iron, zirconium, and tellurium scavenge carriers were precipitated from the molybdenum solution with NH_4OH and molybdenum was precipitated with Cupron (α-benzoinoxime) after acidification of the solution with HNO_3. Oxalic acid was added to prevent the coprecipitation of niobium. Sodium nitrite was added to reduce vanadium and chromium to their lower valence states and, thus, prevent their coprecipitation. The precipitate was dissolved in a mixture of HNO_3 and $HClO_4$. The entire decontamination procedure was repeated. Cesium and tungsten scavenge carriers were added before absorption of the molybdenum on the anion exchange column to aid in the decontamination of these elements. The final molybdenum-Cupron precipitate was ignited in a muffle furnace at 500° C. for 1.5 to 2 hours. The MoO_3 was ground to a fine powder and mounted on a filter paper for counting.

The purification procedure for the neptunium samples has been described (*4*). The neptunium fraction was separated by anion exchange chromatography using HCl and extraction of the neptunium into a 0.4*M* solution of TTA (thenoyltrifluoroacetone) in benzene. The neptunium was back-extracted and electroplated for counting.

Counting Procedures. The Mo^{99} was counted immediately after mounting on a Tracerlab CE-2 continuous flow methane end-window proportional counter. The samples were counted daily for two weeks to verify radiochemical purity. After the sample is prepared, the observed activity increases because of the growth of the Tc^{99m} daughter of Mo^{99}. The Tc^{99m} reaches equilibrium after about 36 hours, and the equilibrium mixture then decays with the typical 66-hour half life of Mo^{99}. In no case do the conversion electrons of Tc^{99m} increase the counting rate of the Mo^{99} activity by more than 3%. As samples of low activity necessitated long counting periods, a correction was made for sample decay during the measurement.

The Cr^{51} was counted on the gamma-spectrometer coupled to a Technical Measurement Corp., Model 404, 400-channel pulse-height analyzer. The activity associated with the 320-k.e.v. photopeak was determined by subtracting background and numerically fitting a Gaussian curve of appropriate width.

The Fe^{59} was counted on a Tracerlab P-20 scintillation counter and decayed weekly until four counts were taken. The Fe^{55} was counted on a Tracerlab AW argon-filled end-window proportional counter using a 157 mg. per sq. cm. beryllium absorber. The sample was also counted through a combination of the beryllium absorber and a 16.7 mg. per sq. cm. lead absorber to eliminate the Fe^{55} x-rays. The activity of Fe^{55} was then determined by subtracting the count rate with lead absorber from the count rate without the second absorber.

RESULTS AND DISCUSSION

Table I summarizes the results of this investigation. The diameters of the particles chosen for this study range between 10.4 and 21.2 microns. The accuracy of the measurement of particle diameter is limited principally by the resolving power of the optical microscope. Theory predicts that the limit of resolution is equal to the wavelength of the illuminating light divided by twice the average of the numerical aperture of the objective and condenser systems, or approximately 0.2 micron. In practice the limit of resolution in optical microscopy is never less than 0.2 micron (*12*) and is usually greater than 0.3 micron in studies of opaque objects. Based on the manufacturer's specifications, the error in the stage micrometer is ±0.1 micron. Reproducibility of the filar micrometer setting has been measured by several skilled microscopists in our laboratory and found to be less than ±0.2 micron. The overall error in particle diameter is, therefore, believed to be approximately ±0.4 micron. In the case of the largest particle, this will produce a 6% error in particle volume. For the smallest particle this error will be 11%.

The weights of the individual particles were calculated from the measured diameter and independent measurements of particle density. A separate study (*13*) of particles from a similar lot indicates that the variation in density with particle size in the diameter range under investigation is less than ±3%.

In general no unusual problems were encountered in the determination of molybdenum. With the exception of the smallest particle, over 10,000 counts were accumulated for each particle. This reduced the statistical counting error to less than 1%. In general, chemical yield was ~40%. However, in one case (particle 2) the chemical yield was exceptionally low (4.1%). This yield is not considered reliable. A small correction was required to allow for Mo^{99} produced by the fission of uranium contained in the lead foil. This factor was obtained from measurements of Np^{239} and Mo^{99} in blank lead foils irradiated simultaneously with the specimens and from the Np^{239} content of the lead-encapsulated, stainless steel microspheres. In the case of the smallest particle, 5% of the observed Mo^{99} activity is ascribed to the lead foil. The over-all relative error in determining the weight of Mo^{99} in the individual microspheres, therefore, is not believed to be appreciably larger than that obtained in neutron activation analysis of larger samples, or approximately ±5%.

The fifth column of Table I lists the percentage abundance of molybdenum in the individual particles. Particle 2 has been omitted in the calculation of the mean because of the low chemical yield. This value varies from the mean by four standard deviations. The mean value and standard deviation are listed solely for illustrative purposes. Since the largest single source of error is the measurement of particle diameter, the values of the larger particles are believed to be more accurate. The relative error of 13%, therefore, merely reflects the average error over the entire size range.

The chromium results are similar in quality to those obtained for molybdenum. The blank lead foils were shown by neutron activation analysis to contain 0.15 p.p.m. of chromium. Therefore, 12% of the observed chromium activity associated with the smallest particle was derived from the lead foil and proportionately less in the case of the larger particles. As the chromium content of the lead foil is probably not

uniform, the inability to apply this correction accurately probably contributes significantly (±5%) to the over-all standard error.

The major error in the iron values was produced by the inability to correct adequately for the concentration of iron in the lead foil. A previous study of similar high purity lead foil (*4*) showed a variation amounting to a factor of 6.8 among 12 similar pieces of foil. In the case of the smallest particle in this study, 39% of the observed iron activity is calculated to have been produced by activation or iron impurities in the lead foil. A value of 3.79 p.p.m. iron in the foil was used for all specimens. It is obvious that this was not a satisfactory correction in all cases. The concentration of iron was calculated independently from the results of Fe^{55} and Fe^{59} activities. In general, the concentration calculated from each of these activities agreed to within 6%. However, those cases in which the concentration of iron differed most markedly from the mean value also displayed the largest discrepancies between the concentration calculated from the Fe^{55} data and that of Fe^{59}.

In general, the data indicate that this technique has sufficient accuracy for use in many studies. The analytical error in the analysis of the larger particles is similar to that obtained in neutron activation analysis of much larger samples. In the case of the smaller particles, contamination from the surrounding media and uncertainties in particle diameter contributed appreciably to the observed error. The former can be reduced by the use of smaller encapsulating envelopes. The error in particle diameter can be greatly reduced by the use of ultraviolet light or electron microscopy.

LITERATURE CITED

(1) Alimarin, I. P., Jakovlev, T. U. V., Zhabin, A. I., *Geokhim. i Anal. Khim.* 1955, 58.
(2) Atchison, G. J., Beamer, W. H., ANAL. CHEM. **24**, 1812 (1952).
(3) Bate, G. L., Potratz, H. A., Huizenga, J. R., *Geochim. et Cosmochim. Acta* **18**, 101 (1960).
(4) Benson, P. A., Holland, W. D., Smith, R. H., ANAL. CHEM. **34**, 1113 (1962).
(5) Bowen, H. J. M., *Intern. J. Appl. Radiation Isotopes* **5**, 277 (1959).
(6) Cadle, R. D., "Particle Size Determination," pp. 126–9, Interscience, New York, 1955.
(7) Fukai, R., Meinke, W. W., *Nature* **184**, 815 (1959).
(8) McKaveney, J. P., Freiser, H., ANAL. CHEM. **29**, 290 (1957).
(9) Pijck, J., "Radiochemistry of Chromium," Natl. Acad. Sciences–Natl. Research Council, Rept. NAS-NS 3007 (1960).
(10) Smales, A. A., Mapper, D., Morgan, J. W., Webster, R. K., Wood, A. J., *Proc. Second U. N. Intern. Conf. on Peaceful Uses of Atomic Energy, Geneva, 1958*, **2**, 242 (1959).
(11) Smith, R. R., Passell, T. O., Reeder, S. D., U. S. At. Energy Comm., Rept. AECD-3889 (1955).
(12) Stoney, G., *J. Roy. Microscop. Soc.* **1903**, 564.
(13) Wrigley, R. C., Gleit, C. E., unpublished data.

RECEIVED for review March 6, 1963. Accepted April 23, 1963.

Novel Radiotracer Method for Fluoride Determination

FLETCHER L. MOORE

Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

▶ A new, simple, rapid method for the determination of fluoride ion is based on the radiotracer principle. Under highly selective conditions, tantalum-182 is extracted from 6.5*M* sulfuric acid solution as a fluoride complex into diisobutylketone. The amount of radioactivity extracted is proportional to the fluoride ion concentration. The counting rate is linear over the range 400 to 840 μg. of fluoride ion; below 400 μg. it is nonlinear but reproducible and useful. The sensitivity is about 40 μg. of fluoride ion. The radiotracer method exhibits relatively high tolerance to some of the serious interferents of other methods. Several useful applications of the method are discussed.

THE QUEST for a simple, rapid, highly selective method for the determination of fluoride ion has produced a voluminous literature. A comprehensive review of the subject has been published recently (*3*). Interest in methods for the determination of fluoride has grown steadily because of the fluoridation of public water supplies, growing use of fluoride chemicals in many industrial processes, such as rocket fuels and the fluorocarbons, and fluoride pollution control of waste streams and air.

Most of the popular methods employ a metal dye complex, such as the zirconium alizarin (*3*) and thorium thoron (*2*) procedures. These types are noted both for high sensitivity and poor selectivity; a wide variety of interferences usually necessitate the preliminary separation of fluoride by distillation—a time-consuming technique which must be precisely controlled for high recovery. Essentially all current methods for fluoride are of the negative type; that is, the fluoride ion bleaches a metal dye indicator, and the decrease in color is measured colorimetrically. Similarly, previous methods using radiotracers (*4*, *6*) have depended on measuring the decrease in radioactivity after a particular reaction. Recently a positive colorimetric method for fluoride ion has been developed by Belcher, Leonard, and West (*1*).

The new approach taken in this work is of the positive type. Under highly selective conditions a radioactive metal tracer is extracted from an aqueous system as a fluoride complex into an organic solvent. The amount of radioactivity extracted is proportional to the fluoride ion concentration. Such a radiotracer technique has several appealing features over current methods for the determination of fluoride. Among these are speed, higher selectivity, adaptability to colored solutions, high tolerance for oxidants, and no critical pH or temperature control. Use of a radioreagent is particularly attractive because of the inherent sensitivity possible with tracers.

During the past few years, several chemists (*5*, *7*, *8*) have found that high selectivity for niobium and tantalum may be effected by the liquid-liquid extraction of fluoride complexes of these elements into various organic solvents. However, it appears that the very high sensitivity of tantalum tracer for fluoride ion in such systems has not been recognized previously. In this paper the writer exploits this observation in the development of a new radiotracer method for the determination of fluoride ion.

EXPERIMENTAL

Reagents. Standard Fluoride Solution, 1 mg./ml. Dissolve 2.2105 grams of dried ACS reagent grade sodium fluoride and make to 1 liter with distilled water. Store in a polyethylene bottle. The sodium fluoride was heated in an oven overnight at 105° C. before weighing.

Diisobutylketone Extractant. Extract the diisobutylketone with an equal volume portion of 0.5*M* sulfuric acid by mixing well for 2 minutes. Discard the aqueous phase. Centrifuge the treated solvent before storing in a borosilicate glass bottle.

Tantalum - 182 Radioreagent. $K_8Ta^{182}O_{19}$ is available from the Radioisotopes Department of the Oak Ridge National Laboratory, Oak Ridge, Tenn. Evaporate a suitable aliquot just to dryness, add several milliliters of concentrated nitric acid and again evaporate just to dryness. (The size of the aliquot will vary with the specific activity of the particular Ta^{182} solution shipment.) Add 100 ml. of reagent grade concentrated sulfuric acid and heat to fuming. Continue to heat at fuming temperature for 1.5 hours. Dilute the solution appropriately by adding reagent grade concentrated sulfuric acid to give a working stock solution. After cooling to room temperature and mixing well, determine the acidity and gamma counting rate. The radioreagent solution used in this work was of the composition:

Ta^{182}, 4.5×10^5 gamma c p.m./ml.

H_2SO_4, 17.82*M*

Total Ta, <1.0 μg./ml.

Procedure. Pipet an aliquot of the sample solution containing 400 to 840 μg. of fluoride into a 1-ounce polyethylene bottle. Pipet the appropriate amounts of distilled water, concentrated (standardized) sulfuric acid, and 1 ml. of the tantalum-182 radioreagent to produce a final 5-ml. aqueous solution which is 6.5*M* in sulfuric acid. Swirl gently to mix. Extract manually for 2 minutes with 5 ml. of the treated diisobutylketone. Transfer the contents into a 15-ml. glass centrifuge tube and centrifuge for 2 minutes in a clinical centrifuge. Carefully pipet 1 ml. of the top organic phase into a 10 × 75-mm. culture tube. Cork the tube and count the gamma radioactivity in a well-type scintillation counter. After correcting the counting rate for background, blank, and decay, determine the fluoride ion concentration by referring to a standard calibration curve. The calibration curve is prepared by running 400-, 500-, 600-, 700-, 800-, and 900-μg. portions of standard fluoride solution through the above procedure. If it is desired to use the lower, nonlinear part of the curve, run 100-, 200-, and 300-μg. portions of standard fluoride similarly. A new calibration curve should be run when fresh radioreagent is prepared.

DISCUSSION

Selection of Conditions. Radioreagent. For simplicity of measurement, a gamma-emitting radioisotope is desirable. On the basis of previous experience, antimony-125, niobium-95, and tantalum-182 were considered as radioreagents. These tracers have suitable half-lives, are easily measured in a conventional well-type scintillation counter, and are readily available.

Antimony-125 tracer was essentially inextractable by various solvents from a sulfuric acid–hydrofluoric acid medium. While it readily extracts from hydrochloric acid–hydrofluoric acid solutions, such systems exhibit poor selectivity. Niobium-95 tracer extracts efficiently from sulfuric acid–hydrofluoric acid solutions, but a relatively high concentration of hydrofluoric acid must be present. During experiments with tantalum-182 tracer, it was discovered that this tracer was highly sensitive to low fluoride ion concentrations. All subsequent work involved the use of the gamma emitter, tantalum-182 ($t_{1/2}$, 115 days).

Acid System. While tantalum-182 tracer may be extracted efficiently from hydrochloric acid–hydrofluoric acid or nitric acid–hydrofluoric acid solutions, the former system shows poor selectivity, and the latter system introduces the possibility of hydrolysis difficulties at high nitric acid concentrations.

Sulfuric acid was selected as the best acid system because high extractability of tantalum-182 tracer with concomitant high selectivity is possible. Concentrated sulfuric acid was found to maintain the tantalum tracer in solution effectively as the radioreagent, thereby eliminating the usual hydrolysis problems associated with macro levels of tantalum. Such radioreagent solutions were found to be stable for at least 5 months. In addition, sulfuric acid was found to exhibit a marked enhancement on the extraction of tantalum fluoro species—an effect which makes possible a sensitive and highly selective method for the determination of fluoride. This enhancement effect by sulfuric acid has been noted previously for niobium fluoride extractions (*5*). The 1.5-hour heating period for the radioreagent described under "Reagents" is probably unnecessary. Shorter heating periods may be found adequate. Also, it may be possible to eliminate the routine, nitric acid treatment; however, this requires further study.

Solvent. The main criterion in the selection of an organic extractant is that tantalum tracer be essentially inextractable from sulfuric acid solutions but highly extractable from sulfuric acid solutions containing low concentrations of fluoride ion. The secondary alcohol, diisobutylcarbinol, has been used previously in effective separation (*5*) of niobium and protactinium in a sulfuric acid–hydrofluoric acid system. However, exploratory experiments indicated that diisobutylcarbinol gave excessively high blanks with tantalum tracer from sulfuric acid solutions.

Diisobutylketone and methylisobutylketone were found to be excellent extractants for tantalum fluoro species from sulfuric acid solution. Diisobutylketone was selected as the extractant for further study on the basis of its greater immiscibility and inertness at higher sulfuric acid concentrations and the low blanks possible. Negligible sulfuric acid was found to extract into diisobutylketone; however, the solvent was pretreated in all cases by mixing well for 2 minutes with an equal volume portion of 0.5*M* sulfuric acid solution.

An interesting observation was that one may use an organic:aqueous ratio as low as 1:10 and still achieve the recovery possible with a 1:1 ratio. This fact is potentially useful for concentration purposes with very low levels of fluoride.

Pertinent variables were evaluated by the procedure described above. Experiments showed the desired inextractability of tantalum-182 tracer with diisobutylketone from aqueous solutions of varying sulfuric acid concentration up to 7*M*. Less than 0.2% extraction was found, thereby assuring low blanks in this system. It is recommended that a blank determination (no fluoride) be run when fresh reagents are prepared. Blanks usually averaged 0.04% or 40 gamma counts per minute per milliliter of extractant under the conditions described in this paper.

Figure 1 is a typical calibration curve showing the extraction of tantalum-182 tracer from 6.5*M* sulfuric acid solution as a function of fluoride ion concentration. The tantalum-182 tracer is very sensitive to the fluoride ion concentration. Excellent linearity is observed over the range 400 to 840 μg. The curve begins to flatten out above 840 μg. and is useful only in a qualitative manner in this region. The curve is nonlinear below about 400 μg. However, this does not preclude its use because it is quite reproducible. The sensitivity under the conditions of the prescribed procedure is about 40 μg. of fluoride ion.

The extraction of tantalum-182 tracer can be further enhanced by increasing the aqueous sulfuric acid concentration. Table I shows this marked sulfuric acid effect on aqueous solutions of extremely low hydrofluoric acid concentration. Higher concentrations of sulfuric acid tend to degrade the solvent and produce high blanks.

The extraction mechanism is of the ion association type and probably proceeds by the following oxonium type reaction:

$$Ta_2^{182}(SO_4)_5 + 14HF \rightleftharpoons 2H_2Ta^{182}F_7 + 5H_2SO_4 \quad (1)$$

$$H_2Ta^{182}F_{7(a)} + 2R_2CO_{(o)} \rightleftharpoons (R_2COH)_2^{+}Ta^{182}F_{7(o)}^{-2} \quad (2)$$

where the subscripts a and o refer to aqueous and organic phases, respectively. Equilibrium is reached in 2 minutes or less (Table II). Negligible extraction of radiotantalum occurs with nonoxygenated solvents, such as xylene or chloroform.

Effect of Diverse Ions. The prescribed procedure was employed at the 700-μg. fluoride level to investigate the effect of some diverse ions. Several of the major interferences of current procedures were intentionally tested. Table III shows the limiting amounts of several of these ions. Each value is the average of two or more determinations. Sulfate ion, a common interference in most fluoride methods, is a requirement in this new method. The method exhibits marked tolerance to anions in general; this is a result of the high acidity (6.5M sulfuric acid) from which the extraction is performed. Thus, the repression of the ionization of weak acids, such as acetic, citric, tartaric, and oxalic, renders them relatively innocuous. The orthoborate ion was the major anionic interference tested. Among the cations tested highest tolerance was found for thorium, with relatively good tolerance to the usual strong fluoride complexing ions—zirconium, iron, aluminum. A positive bias was noted for the higher levels of iron and calcium tested. Calcium precipitated at the 1-mg. level. The uranyl ion interfered seriously, even at the 60-μg. level exhibiting a positive bias.

Table I. Effect of H_2SO_4 Concentration on Extraction of Ta^{182} Tracer from Dilute HF Solution

H_2SO_4, M	HF, M	Ta^{182} extracted, %
5.3	0.0049	8.34
6.5	0.0008	0.20
	0.0049	19.15
7.5	0.0008	0.6
	0.0049	31.2

Table II. Extraction of Ta^{182} Tracer as a Function of Time

Time, min.	Ta^{182} extracted, %
0.5	39.1
1	39.1
2	45.9
3	43.7
4	46.2

Table III. Influence of Diverse Anions and Cations upon Fluoride Recovery

Diverse ion	Amount added	Fluoride recovery, %
Tartaric acid	0.255 mmole	97
Citric acid	0.264 mmole	98
Oxalic acid	0.168 mmole	99
Acetic acid	1.00 mmole	100
Phosphoric acid	0.17 mmole	96
	0.27 mmole	90
	0.34 mmole	9C
Boric acid	0.009 mmole	56
Nitric acid	0.50 mmole	103
	1.00 mmole	118
Hydrochloric acid	0.50 mmole	91
	1.00 mmole	88
Th(IV)	0.56 mg.	102
	1.12 mg.	103
	1.68 mg.	102
Zr(IV)	0.10 mg.	100
	0.21 mg.	95
	0.31 mg.	90
	1.03 mg.	62
Fe(III)	0.10 mg.	103
	0.30 mg.	108
	0.50 mg.	122
	1.00 mg.	152
Al(III)	0.11 mg.	90
	0.34 mg	78
	0.57 mg.	66
Ca(II)	0.20 mg.	109
	0.50 mg.	153
	1.00 mg. (precipitates)	150
UO_2(II)	0.012 mg.	92
	0.030 mg.	101
	0.060 mg.	127

Figure 1. Standard calibration curve

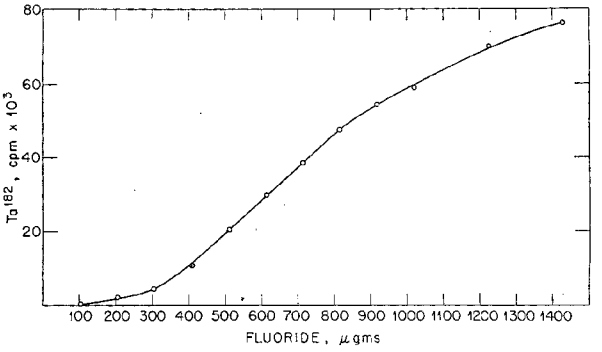


Table IV. Determination of Fluoride in Some Typical Samples

Sample	Fluoride found, μg. Thoron method	Fluoride found, μg. Radiotracer method
NaF	300	290
	500	488
	700	700
HF	980	1005
Process Sample-1	1020	1034
Process Sample 2	640	590
Process Sample-3	780	822

APPLICATIONS

The radiotracer method for fluoride should find many applications because of its simplicity, speed, sensitivity, and selectivity.

Some typical determinations of fluoride ion by this radiotracer method are shown in Table IV. The results compare favorably with the standard thoron procedure (*2*) as used at this laboratory. Interestingly, the process samples—P-1, P-2, P-3—were dark yellow and contained approximately 150 μg. per milliliter of niobium, thereby providing adverse conditions for a direct fluoride determination by the usual methods. Thus, a preliminary distillation was required in the colorimetric procedure. On the other hand, the fluoride ion was determined directly by the radiotracer method. In many cases, this new approach will eliminate the tedious distillation and color development steps. Again, when distillation is required to isolate fluoride, the radiotracer method may offer greater tolerance to excess H_2SO_4 or H_3PO_4 in distillates—a critical factor in current methods.

The radioreagent, tantalum-182, is readily available in high purity from Oak Ridge National Laboratory and is license-free in 10-μc. amounts.

Plans for future work in this area include studies of the increase in sensitivity of the method when higher specific activity tantalum-182 becomes available. It is also planned to adapt the radiotracer principle described to the analysis of fluorine and fluorides in air.

ACKNOWLEDGMENT

The assistance of Mrs. R. L. Towns in some of the tests is acknowledged.

LITERATURE CITED

(1) Belcher, R., Leonard, M. A., West, T. S., *J. Chem. Soc.* **1958**, 2390.
(2) Horton, A. D., Thomason, P. F., Miller, F. J., ANAL. CHEM. **24**, 548 (1952).
(3) Horton, C. A., in "Treatise on Analytical Chemistry," I. M. Kolthoff, P. J. Elving, eds. Part II, Section A, Vol. 7, pp. 207-334, Interscience, New York, 1961.
(4) Maeck, W. J., Booman, G. L., Elliott, M. C., Rein, J. E., ANAL. CHEM. **32**, 922 (1960).
(5) Moore, F. L., *Ibid.*, **27**, 70 (1955).
(6) Onstott, E. I., Ellis, W. P., *Ibid.*, **28**, 393 (1956).
(7) Stevenson, P. C., Hicks, H. G., *Ibid.*, **25**, 1517 (1953).
(8) Werning, J. R., Higbie, K. B., Grace, J. T., Speece, B. F., Gilbert, H. L., *Ind. Eng. Chem.* **46**, 644 (1954).

RECEIVED for review January 31, 1963. Accepted March 22, 1963. Work supported by the Division of Isotopes Development of the U. S. Atomic Energy Commission. Oak Ridge National Laboratory is operated by Union Carbide Nuclear Co. for the U. S. Atomic Energy Commission.

Fluorescence Techniques in the Microdetermination of Metals in Biological Materials

Utility of 2,4-Bis-[*N*,*N*′-di-(carboxymethyl)aminomethyl] fluorescein in the Fluorometric Estimation of Al^{+3}, Alkaline Earths, Co^{+2}, Cu^{+2}, Ni^{+2}, and Zn^{+2} in Micromolar Concentrations

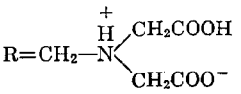
DONALD F. HOELZL WALLACH and THEODORE L. STECK
Harvard University Medical School, Boston 15, Mass.

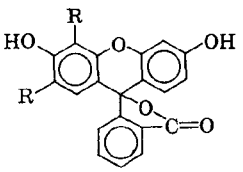
▶ The spectral and fluorescence changes that accompany the reaction of aluminum, the alkaline earth metals, cobalt, copper, nickel, and zinc with 2,4 - bis - [*N*,*N*′ - di - (carboxymethyl)aminomethyl] fluorescein have been examined as a function of pH and of concentration of reactants. The utility of the dye in the estimation of these metals in micro and submicromolar concentrations is illustrated. Approximate stability constants of the alkaline earth metal chelates have been computed from fluorescence measurements.

THE applications of fluorescence techniques to biological problems, recently reviewed by Udenfriend (*18*), have until lately been concerned primarily with the analyses of organic constituents of cells and tissues. However, the great sensitivity inherent in fluorescence methods is of immense advantage in the analysis of minute samples, and for this reason there is considerable interest in the development of fluorescence techniques for the measurement of the metal components of biological materials.

A logical approach to this problem was the introduction of metal chelating groups into fluorescent dyes with the hope of forming derivatives which would change fluorescence intensity and/or wavelength upon formation of metal complexes. This idea, implicit in the report of Anderegg *et al.* (*1*), was first put to test by Diehl and Ellingboe (*4*), who reacted fluorescein with iminodiacetic acid and formaldehyde, producing a mixture they termed "Calcein," which served as a fluorescent indicator for the complexometric titration of calcium at alkaline pH. The synthesis and some of the properties of pure bisdi-(carboxymethyl)aminomethylfluorescein have been reported by Körbl and Vydra (*7*, *8*).

Closely related indicators are "umbellicomplexone" (*6*, *22*) and "xanthocomplexone," prepared by the condensation of iminodiacetic acid and formaldehyde with umbelliferone and xanthone, respectively. The preparation of 2,4-bis-[*N*,*N*′-di-(carboxymethyl)-aminomethyl]fluorescein, **A**, has been reported by Wallach *et al.* (*20*), who also described the spectral and some of the fluorescent properties of this substance and presented the pK values for the various dissociable groups. The above-mentioned dyes are alike in the following respects: (1) They fluoresce at neutral pH but are nonfluorescent in strongly alkaline solutions; (2) they form fluorescent complexes with alkaline earth metals at high pH; and (3) they form nonfluorescent complexes with a number of heavy metals. Because of these properties, these dyes have been employed as fluorescent indicators in the complexometric titrations of a number of metals of biologic importance, such as calcium (*5*, *9*, *20*), magnesium (*13*), and several heavy metals (*22*, *23*), but have not, heretofore, been reported as reagents for the direct fluorometric estimation of these substances.





A

Wallach *et al.* (*20*) have presented three lines of evidence that the product of their condensation of fluorescein with iminodiacetic acid and formaldehyde is 2,4-bis-[*N*, *N*′-di-(carboxymethyl)aminomethyl]fluorescein: (1) dissimilarity of the dissociation constants of the two phenoxyl groups and the two imino nitrogens, indicating asymmetrical substitution of the methyliminodiacetic acid residues; (2) lack of metal-sensitive fluorescence reactions at high pH in the symmetrical bisdi - (carboxymethyl)aminomethyl derivatives of 2,7-diethyl- and 4,5-dimethylfluorescein; and (3) evidence for asymmetrical substitution obtained from the comparison of the infrared spectra of fluorescein tetraiodofluorescein, and the dye under discussion. On the basis of the foregoing evidence these authors proposed the above structure, **A**.

Below pH 4 this dye is in the form H_4A^{-2}. With increasing pH, the two phenoxyl groups and the two imino nitrogens dissociate sequentially with the successive formation of the species H_3A^{-3}, H_2A^{-4}, HA^{-5}, and A^{-6}. This report illustrates the fluorescence changes which accompany the formation of certain metal complexes as well as transitions in pH, and demonstrates the utility of 2,4-bis-[*N*,*N*′-di-(carboxymethyl)aminomethyl]fluorescein in the fluorometric determination of minute amounts of a number of metals.

MATERIALS AND METHODS

Reagents. WATER. Distilled water was passed through a mixed bed deionizer (Cartridge 0808, Barnstead Still and Sterilizer Co., Boston, Mass.) and had a conductivity of less than 2×10^{-6} ohm^{-1}.

POTASSIUM HYDROXIDE REAGENT. A 0.7 to 0.8*N* potassium hydroxide solution was prepared by diluting appropriate amounts of 45% potassium hydroxide solution (Baker's analyzed reagent) with deionized water. The solution was stored in a heavy-walled polyethylene bottle. Its normality was checked by titration with standard acid. It was diluted as needed.

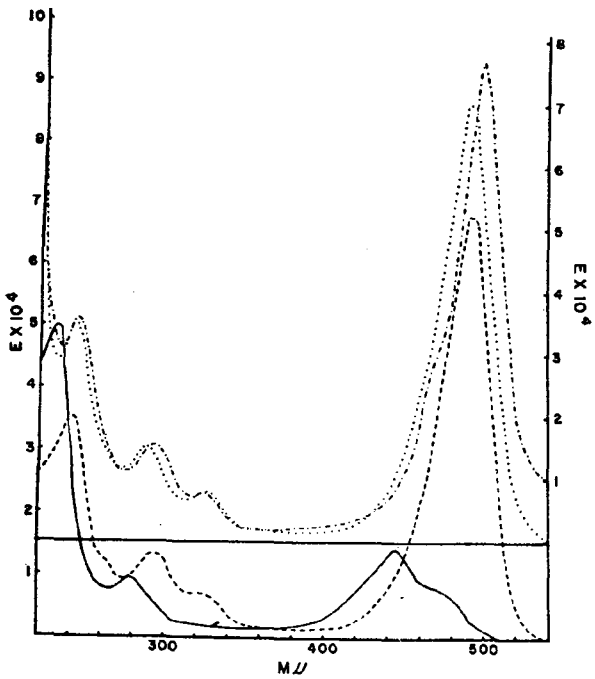


Figure 1. Absorbance spectrum of A under various conditions

—— 0.1M HCl
--- 0.1M tris(hydroxymethyl)aminomethane, pH 7.4
-·-· 0.1M KOH
···· 0.1M KOH plus 10-fold molar excess Ca^{+2}

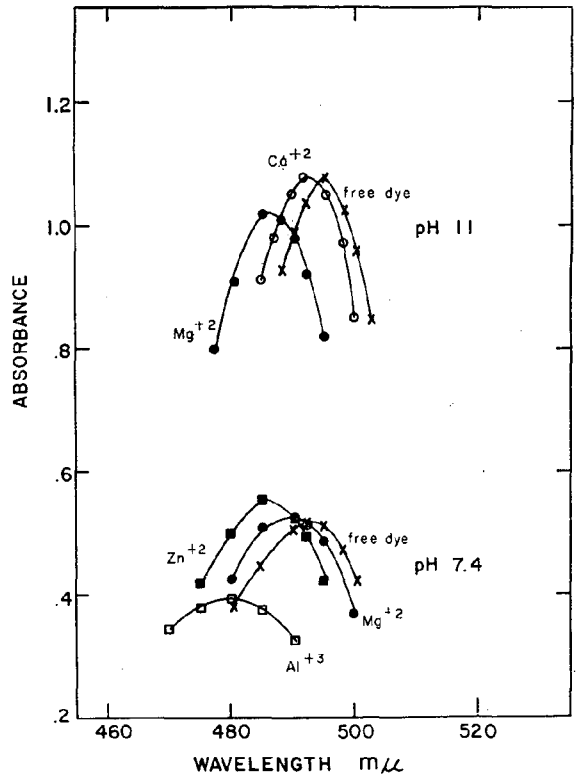


Figure 2. Effects of metal ions on absorbance spectrum of A

Visible absorption band

STANDARD Ba^{+2}, Ca^{+2}, AND Sr^{+2} REAGENTS (10m*M*). These were prepared from their respective carbonates (analytical grade) dissolved in a minimal amount of 0.1*N* hydrochloric acid. The solutions were stored in polyethylene bottles, and appropriate dilutions prepared when necessary.

STANDARD Al^{+3}, Co^{+2}, Cu^{+2}, Mg^{+2}, Mn^{+2}, Ni^{+2}, AND Zn^{+2} REAGENTS (10 m*M*). These were prepared from their respective sulfates (analytical grade) and stored in polyethylene bottles. They were diluted as needed.

DYE. The synthesis of **A** has been described (*20*). A 0.4m*M* stock solution was prepared by adding 26.3 mg. of crystalline dye to 50 ml. of deionized water in a 100-ml. borosilicate volumetric flask. Enough 0.7*M* potassium hydroxide was added to bring the material into solution and deionized water was added to make a volume of 100 ml. The stock solution was divided into 10-ml. aliquots in small polyethylene bottles and kept frozen in the dark. The dye is stable for at least a month when kept at 4° and in the dark.

STANDARD EDTA REAGENT (10m*M*). Twice recrystallized disodium (ethylenedinitrilo)tetraacetate (372 mg., Geigy Industrial Chemicals, Ardsley, N. Y.), dried for 18 hours at 105° C., was dissolved in 100 ml. of deionized water. The reagent was stored in a polyethylene bottle and diluted as needed shortly before use. Because of the ease with which EDTA solutions can become contaminated with calcium, the molarity of the solutions was checked frequently by titration against standard calcium reagent.

Tetramethylammonium hydroxide (10% aqueous solution, Eastman Organic Chemicals) was used directly.

Apparatus. Because of the ubiquity of calcium and the sensitivity of the method here described, the utmost care is needed to prevent accidental contamination of samples with calcium. All containers, pipets, burets, stirring rods, centrifuge tubes, test tubes, and cuvettes used in these experiments were washed initially in detergent (Lakesceal, Finger Lakes Chemical Co., Etna, N. Y.) followed by five rinses with distilled water. They were then rinsed twice with 1*N* nitric acid, five times with deionized water and twice with acetone (Spectral grade), and air-dried. Particular care was taken to avoid contamination by dust. A common source of calcium contamination is the cellulose tissue ordinarily used in the laboratory. Therefore low-ash filter paper—e.g., Whatman No. 42—was used to blot pipet and buret tips.

Pipets, micropipets, and microburets were of borosilicate glass. Centrifuge tubes were made of borosilicate glass or polyethylene. Test tubes and cuvettes were made of synthetic silica. All were washed according to the above procedure. Standard titrations were carried out with micrometer burets (SB2, Micrometric Instrument Co., Cleveland, Ohio) of 0.2- to 2-ml. capacity provided with a capillary tips drawn out to about 1-mm. external diameter. The burets were also washed according to the above procedure, but, prior to use, were rinsed twice with titrating reagent. They were refilled with reagent at least every 30 minutes.

All reagent bottles were made of polyethylene and were washed according to the above directions. Special care was taken to prevent dust contamination of caps.

Measurement of Fluorescence and Absorbance. Fluorescence measurements were made with an attachment to a Beckman Model DU ultraviolet spectrophotometer, using a Hanovia 150-watt d.c. xenon arc as light source. The current to the arc was maintained at 7.0 ± 0.1 amperes by means of a transistorized constant current power supply (Instrumentation Laboratories, Boston, Mass.). Light emerging from the monochromator was chopped at 60 c.p.s. Emitted light was viewed at right angles to the exciting beam with a Dumont 6292 multiplier phototube and the resulting a.c. signal amplified, demodulated, and measured with a null balancing voltmeter. Round cuvettes of synthetic silica with an internal diameter of 1 cm. were employed. Rectangular cuvettes with cemented edges could not be used because of extraction of magnesium from the cement lines. The fluid volume was 2 to 3 ml. Fluorescence intensity was expressed in arbitrary linear units. The stability of the

instrument, as measured with fluorescein standards, was better than 1% per hour. Fluorescence excitation and emission spectra were obtained with an Aminco Bowman recording spectrofluorometer.

Fluorescence was developed by mixing the reagents in polyethylene or synthetic silica tubes and incubating at 37° C. for 30 minutes. Thereafter the tubes were allowed to cool to room temperature (30 minutes). At any time within the succeeding 2 hours the reaction mixture was transferred to the fluorometer cuvettes and the fluorescence measured. Tubes were run in duplicate or triplicate. Individual measurements varied by less than 1%.

Absorbance measurements were carried out in a Beckman Model DU ultraviolet spectrophotometer.

Measurement of pH. pH measurements were carried out with an Instrumentation Laboratories Model 135 pH meter with an Ingold Type 403672 combination electrode. The variation of fluorescence intensity with pH was measured as follows: Two hundred milliliters of a $3.2 \times 10^{-6}M$ solution of **A** in $0.1M$ KCl and $2 \times 10^{-5}M$ EDTA was placed in a borosilicate beaker and the pH brought to about 12 with $1N$ tetramethylammonium hydroxide. The reaction mixture was then titrated to pH 2 to 3 in steps of 0.2 pH unit, using $1N$ HCl added with a micrometer buret. The fluorescence was measured on a 2-ml. aliquot after each acid addition and the sample was returned to the beaker afterward. The reaction mixture was stirred continuously using a Teflon-covered magnetic stirring bar. The total volume change in the titration was about 1% and each fluorescence reading was corrected accordingly. Similar titrations were also performed in the presence of Al^{+3}, Ca^{+2}, Mg^{+2}, and Zn^{+2}. In these instances the metal ion was added in excess of the EDTA present. The exact conditions for each case are stated in the Results section.

The excitation and emission maxima of **A** change with pH (*20*). At pH less than 3.5, the excitation maximum is at 444 mμ (corrected) and the emission maximum of the weak fluorescence is at 503 mμ. At neutral pH, the excitation maximum is at 492 mμ (corrected) and the emission maximum at 511 mμ. At pH 10, the excitation maximum is at 500 mμ and the emission maximum at 520 mμ. In the titrations described here the excitation wavelength was 495 mμ, with a slit width of 0.15 mm. No secondary filters were used, and the entire spectral output of fluorescence was monitored. This was permissible, since the instrumental blank was negligible under the conditions described. Furthermore, error introduced by the change in the spectral sensitivity of the photocathode between 503 and 520 mμ was also negligible.

An organic base was used in these experiments to avind electrode errors at high pH. The presence of EDTA was essential to avoid undesired fluorescence changes due to metal ion contamination.

RESULTS

Spectra. Absorption Spectra. Fluorescence Excitation and Emission Spectra. Figure 1 shows the absorption spectra of **A** at acid, neutral, and alkaline pH. The significance of the spectral changes accompanying alterations in pH has been discussed in detail (*20*). The corrected relative fluorescence excitation spectra (*11*) are identical to the absorption spectra. The fluorescence emission spectra of the dye show only single bands whose maxima depend on pH. The wavelength of the emitted light at a given pH is the same regardless of the wavelength of the exciting light. For a given quantum flux of exciting light, the intensity of the emitted radiation is maximal when the dye is excited at its visible absorption band, about 60% of maximum when excited at the 220-mμ peak, and about 40% of maximum when excited at the absorption band of the 3-OH.

Effects of Metal Ions on Visible and Ultraviolet Spectra of **A**. A large number of metal ions combine with **A**, producing alterations in the visible and ultraviolet portions of its spectrum. These spectral changes occur when the metal in question involves the

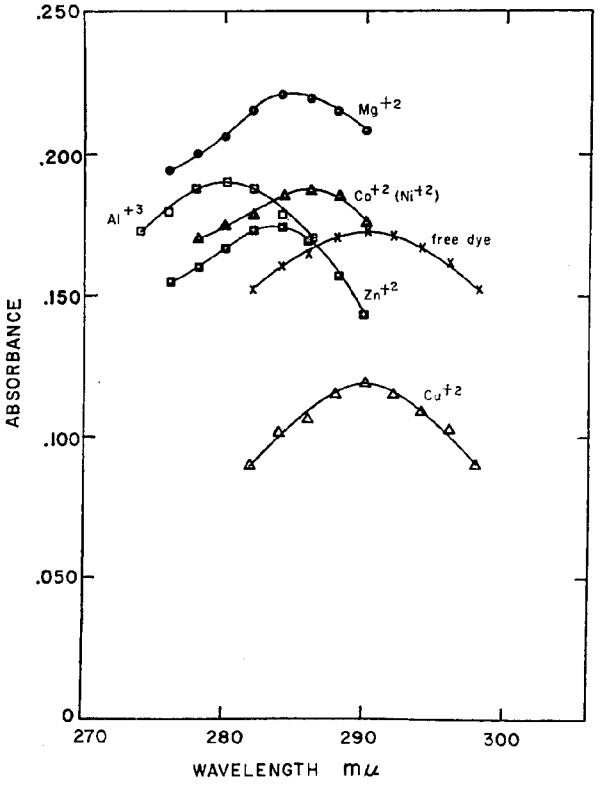


Figure 3. Effects of metal ions on absorbance spectrum of A

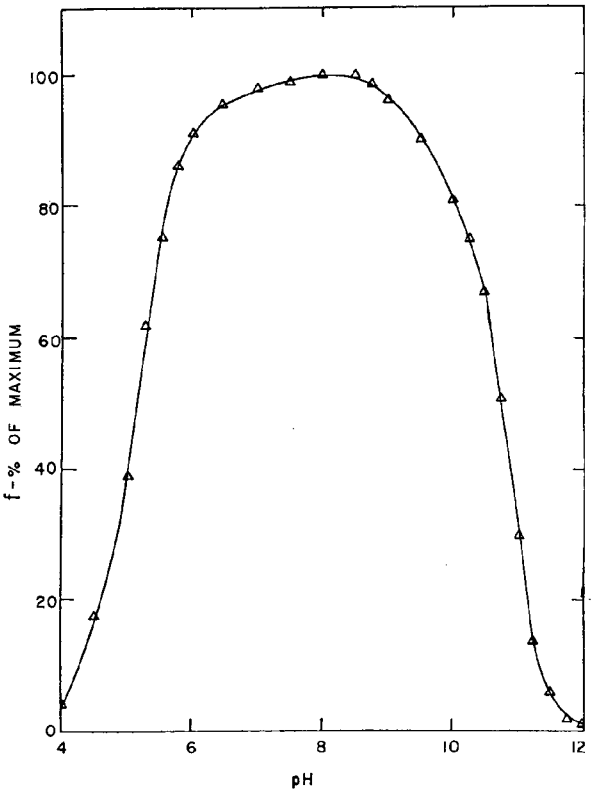


Figure 4. Variation of fluorescence of A with pH

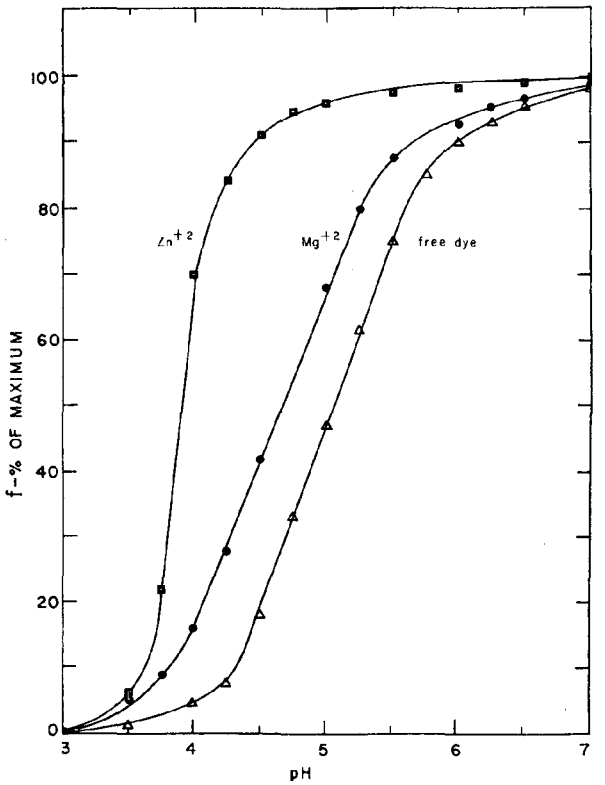


Figure 5. Variation of fluorescence of A with pH

Acid range

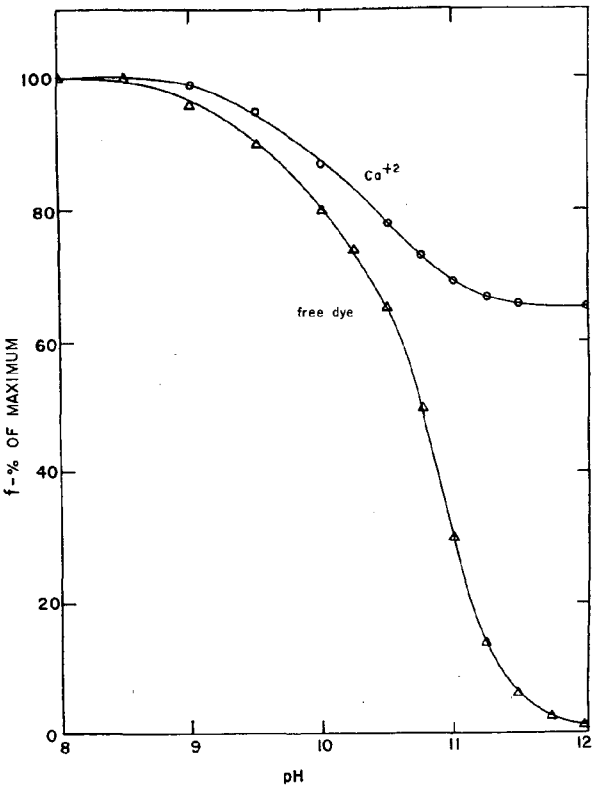


Figure 6. Variation of fluorescence of A with pH

Alkaline range

3-O$^-$, its adjacent imino nitrogens, or both as coordination partner(s). The resulting electron redistribution manifests itself by modifications in the position and/or intensity of the visible absorption band and the ultraviolet absorption band of the 3-O$^-$ (*20*). These spectral changes are relevant to the changes in fluorescence which accompany metal binding by **A** and are briefly illustrated here.

Figure 2 shows the types of shift produced in the visible absorption band at neutral and alkaline pH. Two groups of metals can be distinguished: (1) those that produce varying degrees of hypsochromic shift—i.e., Al^{+3}, Zn^{+2}, and Mg^{+2} at neutral pH and all of the alkaline earth ions at alkaline pH; (2) metals that produce no significant shift in the visible absorption band—Co^{+2}, Cu^{+2}, Mn^{+2}, and Ni^{+2}.

Figure 3 illustrates the changes produced in the 3-O$^-$ absorption band at pH 7.4. Here again the metals in the first group cause a distinct shift of the absorption band to shorter wavelengths. This effect is only very slight for Ba^{+2}, Ca^{+2}, and Sr^{+2} at this pH, but becomes pronounced at high pH where these metals are more strongly bound. The second group of metals produces either no spectral shift—e.g., Cu^{+2}—or only a slight one—e.g., Co^{+2}, Ni^{+2}, and Mn^{+2}. As can be seen from Table I, it is the metals in the first group which form fluorescent chelates with **A**. Metals in this category have strong affinities for the phenolate oxygen, whereas the metals in the second group which form nonfluorescent chelates, have a preferential affinity for basic amino nitrogens (*15*).

Table I. Fluorescence and A_{max} of 2,4-Bis-[*N,N'*-di-(carboxymethyl)-aminomethyl]fluorescein and Some of Its Metal Chelates

Metal ion	Fluorescence, arbitrary units	A_{max}, mμ
	At pH 7.4	
None	991	495
Mg^{+2}	992	490
Zn^{+2}	988	487
Al^{+3}	730	470
Mn^{+2}	80	495
Cu^{+2}	10	495
Co^{+2}	2	495
Ni^{+2}	4	495
	At pH 12	
None	10	500
Ca^{+2}	756	495
Sr^{+2}	756	495
Ba^{+2}	735	495

Measurements at pH 7.42 were made in 0.1*M* tris(hydroxymethyl)aminomethane, the others in 0.1*N* KOH. For fluorescence measurements concentration of **A** was $3.2 \times 10^{-6}M$, that of metal $3.2 \times 10^{-5}M$. Exciting wavelength 495 mμ. For absorbance measurements concentration of A was $2 \times 10^{-5}M$ and metal $10^{-4}M$.

Variation in Fluorescence of A with pH. The fluorescence intensity of **A** at various levels of pH is shown in Figure 4. Below pH 4 the dye is in the form H_4A^{-2} and its feeble fluorescence has an emission maximum of 503 mμ. Between pH 4 and 6 the fluorescence intensity increases sharply and the emission maximum shifts to 511 mμ. Comparison of these results with the spectrophotometric and acid-base titration data reported previously (*20*) indicates that the fluorescence changes in this pH range are associated with the dissociation of the 3-OH and concomitant symmetrical hydrogen bonding to the nearby imino nitrogens, leading to the formation of H_3A^{-3}.

Between pH 6 and 8.5 there are a further slight increase in fluorescence intensity and a shift in the emission maximum to 520 mμ. These changes, due to the dissociation of the 6-OH—i.e., formation of H_2A^{-4}—accompany the intensification of the visible absorption band and its shift from 492 to 500 mμ.

The decrease in fluorescence between pH 8.5 and 12 is associated with the titration of the less basic of the two imino nitrogens, ($H_2A^{-4} \rightarrow HA^{-5}$).

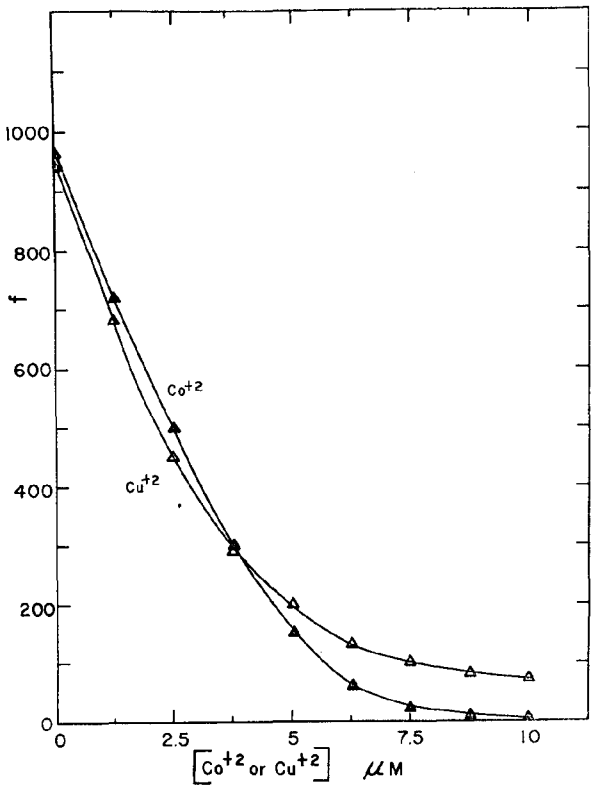


Figure 7. Extinction of fluorescence upon formation of cobalt and copper chelates of A

Buffer. Tris(hydroxymethyl)aminomethane, 0.1*M*, pH 8.5. Exciting wavelength 495 mμ. [A] = 5 × 10^{-6}*M*

Titration of the second imino nitrogen, leading to the formation of A^{-6}, is not accompanied by any fluorescence change.

As illustrated in Figure 5 for Mg^{+2} and Zn^{+2} and in Figure 6 for Ca^{+2}, the plot of fluorescence *vs.* pH is markedly influenced by the presence of metals which can form complexes with the dye.

Fluorescence Changes Accompanying Reaction of A with Various Metals. Alterations in Fluorescence Emission Spectrum. The complex of aluminum with **A** is the only one studied which has a significantly different emission spectrum from that of the free dye under similar conditions. Thus the emission maximum of the free dye at pH 2 is 503 mμ, whereas that of the aluminum complex is 511 mμ.

Decrease in Fluorescence Intensity. As noted in Table I, Co^{+2}, Cu^{+2}, Mn^{+2}, and Ni^{+2} (and presumably others) combine with **A** to form chelates which do not fluoresce in the pH range in which the free dye is fluorescent. The decrease in fluorescence of **A** [5 × 10^{-6} *M* in 0.1*M* tris(hydroxymethyl) aminomethane, pH 8.5] with increasing metal concentration (0 to 10 × 10^{-6}*M*) is illustrated for Co^{+2} and Cu^{+2} in Figure 7. These data suggest that the combination of 1 mole of metal with 1 of the dye leads to the disappearance of fluorescence. A plot of the increase in absorbance at 288 mμ, which accompanies metal binding, confirms this impression. The depression of fluorescence produced by Co^{+2}, Cu^{+2}, and Ni^{+2}, present in equimolar ratio to **A** (3.2 × 10^{-6}*M*), was measured over the pH range of 5 to 10. The results, shown in Figure 8, indicate that the binding of Co^{+2} and Cu^{+2} increases sharply with pH to pH 6 and then again above pH 8.5. The affinity of Ni^{+2} is considerably higher than that of Co^{+2} and Cu^{+2} and is independent of pH until above pH 8.5, where it also increases.

The above data suggest that **A** forms strong 1 to 1 chelates with Co^{+2}, Cu^{+2}, and Ni^{+2} between pH 6 and 8. The formation of the 1 to 1 chelate leads to the disappearance of fluorescence. A second mole of metal can presumably be bound by the second methyliminodiacetyl residue but with lesser affinity and with little or no further change in fluorescence intensity.

Increase in Fluorescence Intensity. Increase in fluorescence intensity due to the formation of fluorescent metal chelates can occur at acid, neutral, and alkaline pH.

Acid pH. As can be seen from Figure 5, Zn^{+2} and to a lesser extent Mg^{+2}, form fluorescent chelates between pH 5.5 and 3.5, where the fluorescence of the free dye is decreasing rapidly with increasing hydrogen ion concentration. This phenomenon is, however, of little analytical utility, since the affinity of **A** for these metals is very low in this pH range.

The situation is different with Al^{+3}, which forms fluorescent complexes with **A** even below pH 2. Figure 9 illustrates the relative increase in the fluorescence of the aluminum complex over that of the free dye between pH 2 and 5, using an exciting wavelength of 480 mμ. At

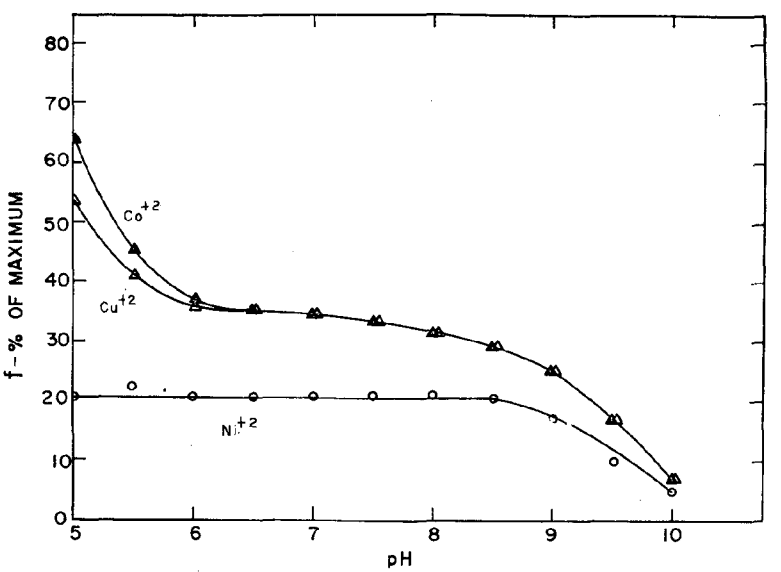


Figure 8. Effect of pH upon fluorescence extinction by Co^{+2}, Cu^{+2}, and Ni^{+2}

Exciting wavelength 495 mμ

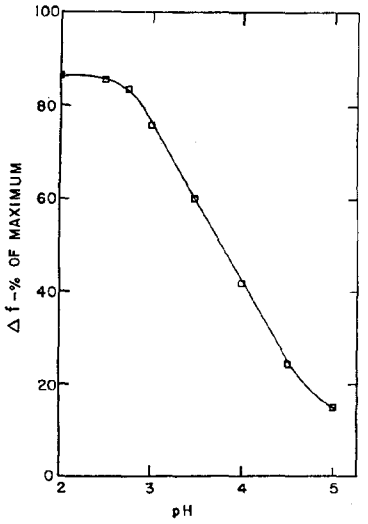


Figure 9. Effect of pH upon development of fluorescence with Al^{+3}

Exciting wavelength 480 mμ

pH 2 the free dye is weakly fluorescent, whereas the aluminum complex fluoresces intensely. The increase in the fluorescence of a $3.2 \times 10^{-6}M$ solution of **A** in $0.8N$ acetic acid with increasing aluminum concentration is given in Figure 10. It is clear that **A** can be used for the fluorometric determination of Al^{+3} in concentrations of $10^{-5}M$ and below.

pH 6 to 9. It can be shown spectroscopically that Ba^{+2}, Ca^{+2}, Mg^{+2}, Sr^{+2}, and Zn^{+2} form chelates with **A** between pH 6.5 and 8.5, but this is not accompanied by any change in fluorescence. Among the metals in this group, Zn^{+2} has by far the highest affinity for the dye in this pH range. The stability of the zinc chelate is sufficiently great that Zn^{+2}, even at low concentration, can displace Co^{+2} from its combination with **A**. This phenomenon is illustrated in Figure 11, which shows the development of fluorescence in a $3.2 \times 10^{-6}M$ solution of **A** in $0.1M$ tris(hydroxymethyl)aminomethane (pH 7.4) and $1.2 \times 10^{-5}M$ Co^{+2} with increasing concentrations of Zn^{+2} (0 to $6 \times 10^{-6}M$). This effect forms the basis for the fluorometric determination of zinc in micromolar concentrations.

Alkaline pH. Above pH 8.5 the fluorescence of the free dye diminishes with increasing pH. It becomes negligible at pH 13 and above. The alkaline earth metals form strongly fluorescent chelates with **A** at alkaline pH. This is illustrated in Figure 12, which shows the increase in the fluorescence of the calcium and magnesium chelates of **A** relative to that of the free dye between pH 8.5 and 13. The curves for Ba^{+2} and Sr^{+2} are identical to the calcium curve. The fluorescence yield obtained with magnesium is less than that obtained with equivalent amounts of calcium because of the removal of Mg^{+2} from solution as insoluble $Mg(OH)_2$. The fluorescence decrement in the magnesium curve above pH 12 is due to the same cause.

Figure 13 shows the increase in fluorescence of a $3.2 \times 10^{-6}M$ solution of **A** in $0.06N$ KOH with increasing concentrations of calcium and magnesium (0 to $6 \times 10^{-6}M$). The curves obtained with Ba^{+2} and Sr^{+2} are similar in shape but somewhat flatter than the calcium curve. These data show that **A** can bind 2 moles of alkaline earth metal per mole and that the reaction occurs in two discrete steps. The

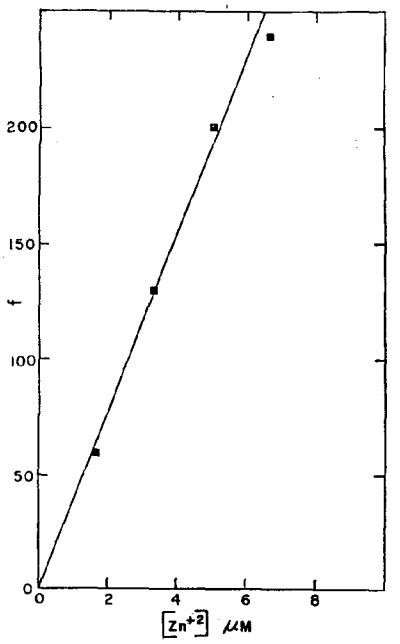


Figure 11. Development of fluorescence accompanying displacement of Co^{+2} by Zn^{+2}

Buffer. Tris(hydroxymethyl)aminomethane, 0.1 M, pH 7.4; [A] = $3.2 \times 10^{-6}M$; [Co_{total}] = $1.2 \times 10^{-6}M$
Exciting wavelength 495 mμ

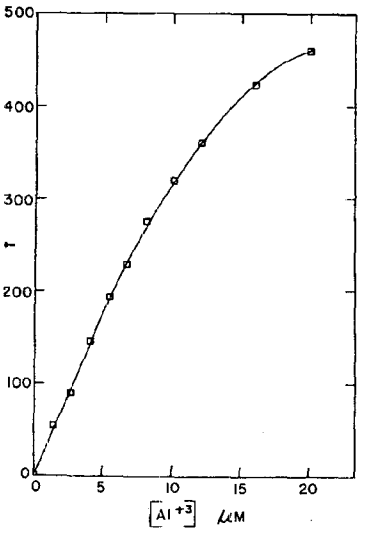


Figure 10. Variation of fluorescence intensity with Al^{+3} concentration

0.8N acetic acid. Exciting wavelength 480 mμ

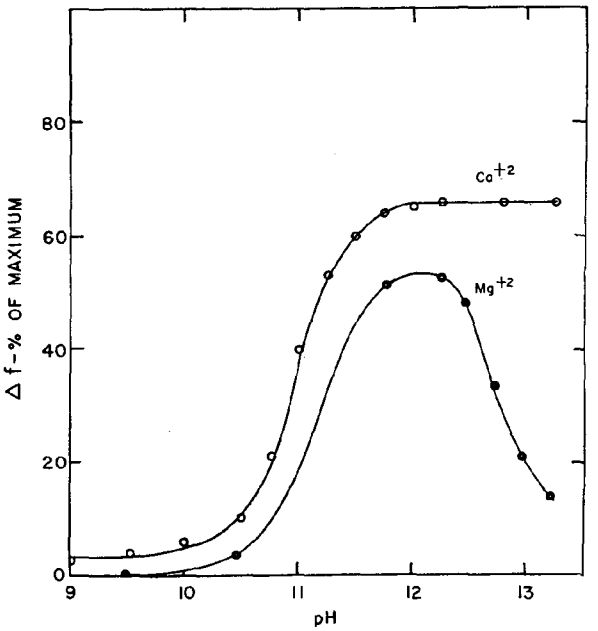


Figure 12. Effect of pH on development of fluorescence by Ca^{+2} and Mg^{+2}

Exciting wavelength 495 mμ. Data expressed relative to fluorescence of free dye, set to zero

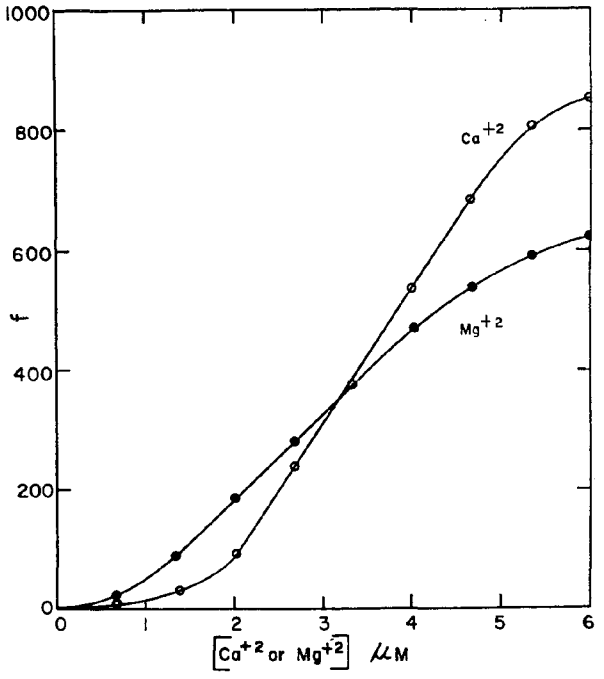


Figure 13. Variation of fluorescence intensity with concentration of Ca^{+2} and Mg^{+2}

0.06N KOH. Exciting wavelength 495 mμ

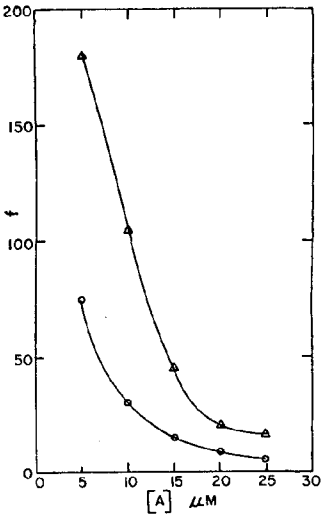


Figure 14. Variation of fluorescence intensity with concentration of A at fixed Ca^{+2} concentrations

0.1N KOH. Exciting wavelength 495 mμ
△ Ca^{+2}. 8×10^{-6} M
○ Ca^{+2}. 4×10^{-6} M

curves also indicate that formation of the 1 to 1 chelate is not accompanied by any increase in fluorescence. That this is indeed the case is illustrated in Figure 14, which shows that there is a decrease in the fluorescence produced at a given Ca^{+2} concentration as the concentration of **A** is raised.

It appears that, as with Co^{+2}, Cu^{+2}, and Ni^{+2}, the first ion of metal to react with each molecule of dye is bound much more avidly than the second one. This observation is entirely in accord with the findings of Schwarzenbach *et al.* (*16*) in (1-oxyphenylen-2, 6)-bis-(methylimino)diacetic acid. It is equally evident that the fluorescence change occurs only with the binding of the second metal ion. The sequence of reaction of **A** with the alkaline earth metals at pH 12 can be expressed as:

$$\mathbf{A} + M^{+2} \rightleftharpoons MA;\ K_1 = \frac{[MA]}{[A]\,[M^{+2}]} \quad (1)$$

$$MA + M^{+2} \rightleftharpoons M_2A;\ K_2 = \frac{[M_2A]}{[MA][M^{+2}]} \quad (2)$$

where [A] is the concentration of free dye, $[M^{+2}]$ the concentration of free metal ion, [MA] the concentration of the 1 to 1 metal chelate, $[M_2A]$ the concentration of the 2 to 1 complex, and $K_1 > K_2$. Approximate stability constants (K_2) for the reactions producing the fluorescence change with Ba^{+2}, Ca^{+2}, and Sr^{+2} can be determined from the following considerations (*12*):

$$K_2 = \frac{[M_2A]}{[MA][M^{+2}]} = \frac{[M_2A]}{[A_{tot} - M_2A - A][M_{tot} - M_2A - MA]} \quad (3)$$

At very high total concentrations of M, [A] will become negligible and $[M^{+2}]$ will approach $[M_{tot} - 2A_{tot}]$, where M_{tot} and A_{tot} are the total concentrations of metal and dye, respectively. Then

$$K_2 = \frac{[M_2A]}{[A_{tot} - M_2A][M_{tot} - 2A_{tot}]} \quad (4)$$

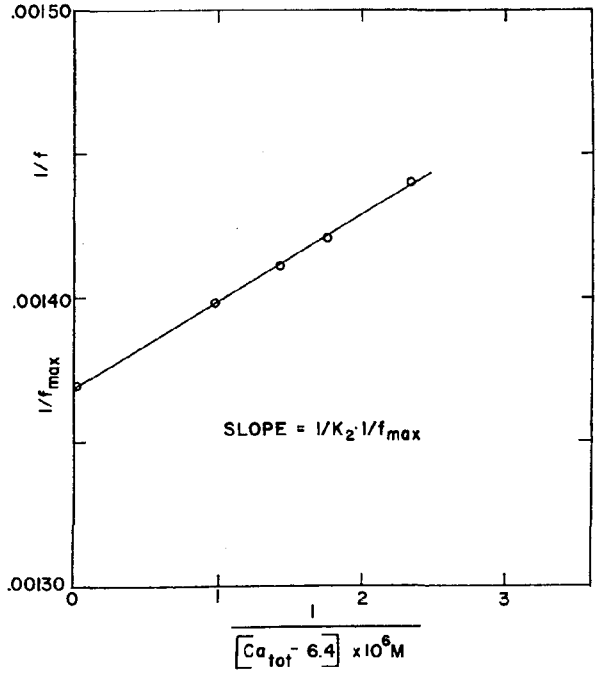


Figure 15. Graphic determination of K_2 for calcium

0.1N KOH. Exciting wavelength 495 mμ. For discussion see text

Table II. Stability Constants (K_2) of 2 to 1 Alkaline Earth Chelates of 2,4-Bis-[N,N'-di-(carboxymethyl)-aminomethyl]fluorescein

Metal ion	K_2[a],
Ba^{+2}	$10^{5.57}$ (5.49–5.65)
Sr^{+2}	$10^{5.86}$ (5.82–5.89)
Ca^{+2}	$10^{6.63}$ (6.54–6.69)
Mg^{+2}	$10^{7.90}$ (7.75–8.15)

[a] Means and range of three experiments. Values obtained in 0.1N KOH at 20° C. Ba^{+2}, Sr^{+2}, and Ca^{+2} values calculated from Eq. 6, and Mg^{+2} values from Eq. 9.

$[M_2A]$ is directly proportional to the fluorescence, f, at a given metal concentration and the maximal fluorescence, f_{max}, is proportional to the total dye concentration $[A_{tot}]$. Therefore,

$$K_2 = \frac{f}{(f_{max} - f)(M_{tot} - 2A_{tot})} \quad (5)$$

This can be rearranged to give:

$$1/f = 1/f_{max} \times 1/K_2 \times 1/(M_{tot} - 2A_{tot}) + 1/f_{max} \quad (6)$$

At very high concentrations of M, the plot of $1/f$ *vs.* $1/(M_{tot}-2A_{tot})$ approaches a straight line with an intercept of $1/f_{max}$ and a slope of $1/f_{max} \times 1/K_2$. From such a plot, K_2 can be determined. This method for the estimation of K_2 is illustrated in Figure 15 for Ca^{+2} in 0.1N KOH at 20° C. The K_2 values obtained by this technique are given in Table II.

Because of the very low solubility of $Mg(OH)_2$, the above technique cannot be applied directly to the determination of K_2 for this metal. An approximate value for this constant was obtained at several pH levels from the following considerations:

$$K_2 = \frac{f}{(f_{max} - f)[Mg^{+2}]} \quad (7)$$

where $[Mg^{+2}]$, the free magnesium ion concentration, is given by

$$[Mg^{+2}] = K_{sp}/[OH^-]^2 \quad (8)$$

K_{sp} being the solubility product constant of $Mg(OH)_2$ (1.2×10^{-11}) and $[OH^-]$ the activity of the hydroxyl ion under the conditions used. Then

$$K_2 = \frac{f}{(f_{max} - f)(K_{sp}/[OH^-]^2)} \quad (9)$$

Of the various components of this equation, $[OH^-]$ can be calculated for standardized KOH solutions from the activity coefficient values given in the International Critical Tables and f can be measured directly. The f_{max} for Mg^{+2} cannot be determined directly at high pH. There are, however, several reasons for the assumption that the f_{max} for magnesium is very close to that for Ca^{+2}: The fluorescence intensities obtained with excess Ca^{+2} and Mg^{+2} are identical up to about pH 10.2; at very alkaline pH the fluorescence intensity obtained immediately after addition of an excess of Mg^{+2} to the dye solution approaches the f_{max} for Ca^{+2}, but then falls off as equilibrium with the $Mg(OH)_2$ phase is approached; and the f_{max} values for Ba^{+2}, Ca^{+2}, and Sr^{+2} are essentially identical at alkaline pH.

On the basis of the above assumption, the f_{max} values for Ca^{+2} were substituted in Equation 10 and the K_2 for magnesium was calculated at several values of pH. The dye concentration used was $3.2 \times 10^{-6}M$ and the total calcium and magnesium concentrations were $1.67 \times 10^{-5}M$. The results are shown in Figure 16. The marked increase in the value of K_2 up to pH 12 is presumably related to the dissociation of the less basic of the two imino nitrogens in this pH range. The finding that **A** has a greater affinity for Mg^{+2} than for Ba^{+2}, Ca^{+2}, and Sr^{+2} is consistent with the observations of Schwarzenbach *et al.*(*16*) concerning the preferential affinity of the phenoxyl ion for Mg^{+2}. It is also a matter of considerable analytic importance in that it necessitates very high hydroxyl ion concentrations to prevent Mg^{+2} interference in the fluorometric determination of calcium.

The fluorescence intensity of HA^{-5} in aqueous solutions of potassium hydroxide or organic bases such as choline, tetramethylammonium hydroxide, and tetraethylammonium hydroxide is very low indeed in the absence of alkaline earth metals. However, in strong solutions of sodium hydroxide there is a very appreciable residual fluorescence. This phenomenon has also been reported to occur in Calcein, (*17*), umbellicomplexone (*6*), and xanthocomplexone (*6*).

The residual fluorescence of HA^{-5} depends not only upon the type of base used but also upon the viscosity and temperature of the solution. Thus, if the viscosity of a solution of HA^{-5} in 0.1N KOH and excess EDTA is raised by the addition of glycerol, there is a distinct increase in residual fluorescence. This effect is not observed with the species H_4A^{-2} nor with the nonfluorescent complexes of **A** with Co^{+2} as f. This phenomenon is analogous to the one detailed for Auramine O by Oster and Nishijima (*10*).

Analytical Implications. Limits of Sensitivity. The limits of sensitivity in fluorescence analyses clearly depend heavily on instrumental factors. These have been discussed in detail by Parker and Rees (*11*). However, since **A** has a fluorescence efficiency very near that of fluorescein and since it is excited at frequencies where intense light fluxes are readily obtained, very high sensitivity can be attained without elaborate instrumentation. This

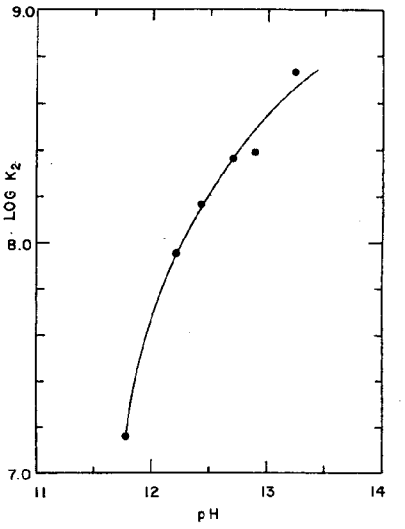


Figure 16. Variation of apparent K_2 for Mg^{+2} with pH

For discussion see text

point is illustrated in Figure 17, which shows the increase in fluorescence with increasing concentrations of the 2 to 1 complex of calcium in the range of 0 to $2.5 \times 10^{-8}M$. This experiment was performed in 0.1N KOH containing $10^{-7}M$ Ca^{+2} with a fluid volume of 1 ml., an exciting wavelength of 495 mμ, and a slit width of 1 mm. Under these conditions the limit of detection for calcium is about 10^{-12} mole.

The practical limits to the sensitivity of fluorometric analyses employing **A** are considerably higher than the limits of detection or even of precise measurement of the free dye or its fluorescent complexes. Definite limits of concentration are imposed by the stability constants of the various metal complexes of **A**, but of greater practical importance, particularly in analyses at alkaline pH, is the difficulty in avoiding alkaline earth metal contamination. With a limited number of precautions, however, fluorometric analysis of alkaline earth metals in micromolar concentrations and of Al^{+3}, Co^{+2}, Cu^{+2}, and Ni^{+2} at even lower levels is entirely practical.

Specific Applications. Detailed procedures for the fluorometric determination of the alkaline earth metals in biologic materials have been worked out and will be reported separately (*19*). The essentials of these techniques are as follows:

Calcium. This is measured in 0.7 to 0.8N KOH. The high hydroxide concentration is necessary to prevent magnesium interference. Sufficient calcium is added to dye reagent (3 to $6 \times 10^{-6}M$ in 0.7 to 0.8N KOH) to bring the standard curve into the linear range

(see Figure 13). For solutions and fine suspensions of biological materials ashing is generally not necessary. The method does not distinguish between Ca^{+2}, Ba^{+2}, and Sr^{+2}; 10^{-9} mole of Ca^{+2} can be determined with a standard deviation of not more than 5%.

Magnesium. The reagent for the fluorometric determination of magnesium is a 3 to 6 $\times$ $10^{-6}M$ solution of **A** in 0.03 to 0.06N KOH and 1.5 to 3.0 $\times$ $10^{-5}M$ ethylene glycol bis-(β-aminoethyl ether)-N,N'-tetraacetate (EGTA) (Geigy Industrial Chemicals, Ardsley, N. Y.). The latter reagent has a stability constant of $10^{10.7}$ for Ca^{+2} and $10^{5.4}$ for Mg^{+2} (*14*) contrasted with the values of $10^{6.6}$ and $10^{7.9}$ obtained for the 2 to 1 complexes of Ca^{+2} and Mg^{+2} with **A**. The relative affinities of EGTA and **A** for calcium and magnesium are such that magnesium can be determined specifically. As with the calcium method, sufficient Mg^{+2} is added to the reagent to bring it into the linear range. Ba^{+2} and Sr^{+2} do not interfere.

The theoretical limit of detection for Mg^{+2} is lower than that for Ca^{+2}, because of the higher affinity of **A** for magnesium. The practical range of sensitivity is in the micromolar region, similar to that reported for the bissalicylidene–ethylenediamine complex with magnesium (*21*).

The other metals discussed in this report have not been studied in detail from an analytical point of view. The fluorescence accompanying the displacement of Co^{+2} by Zn^{+2} should provide a relatively specific assay for the latter metal with a sensitivity greater than that obtained with 8-*p*-tolylsulfonylaminoquinoline (*3*).

The fluorometric determination of Co^{+2}, etc., with **A** will presumably require preliminary separations, although the greater stability of the nickel chelate, especially at acid pH, may permit specific determination of this metal.

The determination of Al^{+3} with **A** should be relatively free from interference and of a sensitivity comparable to that employing 8-OH quinoline. Specific conditions remain to be worked out.

DISCUSSION

The fluorescent dye, 2,4-bis-[N,N'-di-(carboxymethyl)-aminomethyl] fluorescein, is clearly a reagent of wide utility in the determination of trace amounts of a wide variety of metals. It is also of considerable interest with regard to mechanisms of fluorescence and of energy transfer. Detailed discussion of this topic is beyond the range of this report, but a hypothesis for the observed fluorescence phenomena is briefly presented below.

The intensity of the fluorescence emitted by **A** reflects the balance between the rate of deactivation of the excited molecules by light emission and the rate of deactivation by radiationless transitions. This balance depends upon the resonance energy and configuration of the molecule, determined largely by the electron configuration about the 3-OH, and the degree of energy transfer by collision between excited molecules and unexcited ones, determined largely by the configuration of the molecule.

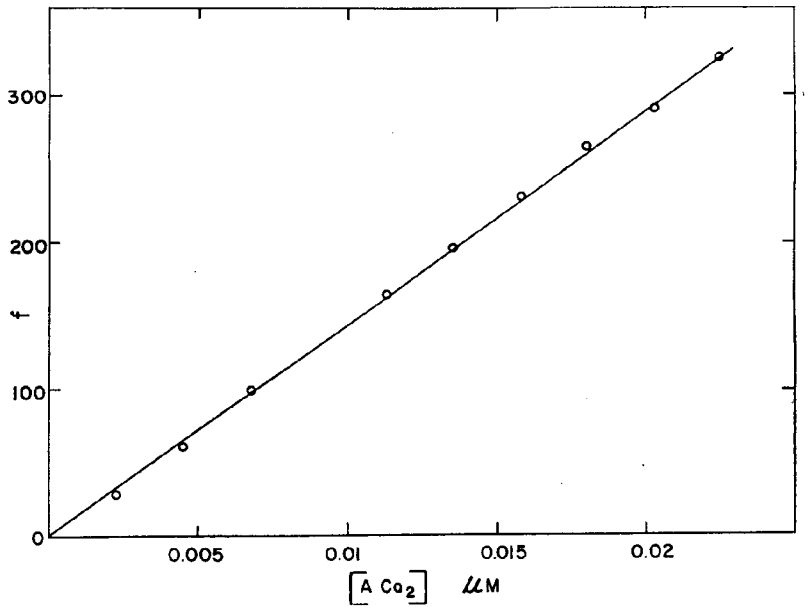


Figure 17. Variation of fluorescence with concentration of 2 to 1 chelate of calcium at very low concentration

0.1N KOH. Exciting wavelength 495 mμ

In species H_4A^{-2}, the H-O bond of the 3-OH is covalent and the dye therefore lacks the resonance structure necessary for high fluorescence efficiency. Furthermore, the two methyliminodiacetate residues, representing about 45% of the mass of the molecule, are freely movable, permitting ready energy transfer to other molecules by rotational diffusion. This leads to a further decrease in fluorescence efficiency (*6*, *10*)

In the fluorescent species H_3A^{-3} the oxygen of the 3-O^- is hydrogen-bonded to the two imino nitrogens, establishing a strong resonance system between the two phenoxyl groups. Steric considerations indicate that the two hydrogen bonds hold the two methyl iminodiacetate residues symmetrically about the oxygen atom, one above and one below the plane of the conjugated ring system. This situation is also true for the fluorescent species H_2A^{-4}. Both H_3A^{-3} and H_2A^{-4} fulfill the requirements of rigidity and planarity of the molecule and its resonance structure shown to be essential for fluorescence by Bozhevol'nov (*2*) and others.

In the weakly fluorescent species HA^{-5}, the electron cloud about the 3-O^- becomes noncoplanar, because of rupture of one of the H bonds. This also releases one of the two methyl iminodiacetate residues, with an associated increase of energy dissipation by rotational diffusion. In A^{-6} there is a change in resonance associated with the opening of the lactone ring. In addition, release of the second methyl iminodiacetate residue increases frictional dissipation of energy. The importance of the energy loss due to rotational diffusion of the methyl iminodiacetate residues is attested by the increase in the fluorescence intensity of HA^{-5} and A^{-6} in highly viscous solutions.

The above considerations assist in formulating an explanation for the fluorescence changes which accompany the chelation of various metals by **A**. In the case of the transitional metals, fluorescence disappears dramatically with the formation of the asymmetric 1 to 1 chelate, but there are no spectral shifts in the visible and only minor hypsochromic displacements in the 3-phenoxyl band. The lack of large hypso- and hypochromic changes even at pH 7.4 indicates that in the chelates of the above metals the 3-phenoxyl group remains dissociated and that the oxygen of this group is involved in partly covalent linkage with these metals, establishing a resonance state which does not permit fluorescence.

In the case of the alkaline earth metals at alkaline pH, the 3-O^- again plays a major role in the fluorescence changes. The metals are presumably first bound by the free methyl iminodiacetate and then enter the coordination sphere of the 3-O^- to form the asym-

metric 1 to 1 chelate. Binding of the second metal ion produces the symmetrical fluorescent structure, which is analogous to H_3A^{-3} in configuration. The strong hypsochromic shifts which accompany the fluorescent changes indicate that the M-O bonds of these metals are primarily ionic (*15*).

ACKNOWLEDGMENT

The authors express their appreciation to J. L. Oncley for his stimulating interest in these studies.

LITERATURE CITED

(1) Anderegg, G., Flaschka, H., Sallmann, R., Schwarzenbach, G., *Helv. Chim. Acta* **37**, 113 (1954).
(2) Bozhevol'nov, E. A., *Tr. Vses. Nauch-Issled. Khim. Reactivov* **23**, 147–165 (1959); *C. A.* **54**, 23723 (1960).
(3) Bozhevol'nov, E. A., Dziomenko, V. M., Serebryakova, G. V., USSR 120,029 (1960).
(4) Diehl, H., Ellingboe, J. L., ANAL. CHEM. **28**, 882 (1956).
(5) Dumont, P. A., *Ibid.*, **33**, 565–7 (1961).
(6) Eggers, J. H., *Talanta* **4**, 38 (1961).
(7) Körbl, J., Vydra, F., *Chem. Listy* **51**, (8) 1457 (1957).
(8) Körbl, J., Vydra, F., *Z. Anal. Chem.* 161, 200 (1958).
(9) Mori, K., *Arch. Biochem. Biophys.* **83**, 552 (1959).
(10) Oster, G., Nishijima, Y., *J. Am. Chem. Soc.* **78**, 1581 (1956).
(11) Parker, C. A., Rees, W. T., *Analyst* **85**, 587 (1960).
(12) Rossotti, F. J. C., Rossotti, H., "Determination of Stability Constants," McGraw-Hill, New York, 1961.
(13) Schirardin, H., Metais, P., *Path. Biol. Semaine Hop.* **7**, 418 (1959).
(14) Schouwenburg, J. Ch. Van., ANAL. CHEM. **32**, 709 (1960).
(15) Schwarzenbach, G., in "Chemical Specificity in Biological Interactions," F. R. N. Gurd, ed., Chap. X, Academic Press, New York, 1954.
(16) Schwarzenbach, G., Anderegg, G., Sallmann, R., *Helv. Chim. Acta* **35**, 1785 (1952).
(17) Svoboda, V., Chromy, V., Körbl, J., Dorazil, L., *Talanta* **8**, 249 (1961).
(18) Udenfriend, Sidney, "Fluorescence Assay in Biology and Medicine," Academic Press, New York, 1962.
(19) Wallach, D. F. H., Steck, T. L., in preparation.
(20) Wallach, D. F. H., Surgenor, D. M., Soderberg, J., Delano, E., ANAL. CHEM. **31**, 456 (1959).
(21) White, C. E., Cuttitta, F., *Ibid.*, **31**, 2083 (1959).
(22) Wilkins, D. H., *Talanta* **4**, 182 (1960).
(23) Wilkins, D. H., Hibbs, L. E., *Ibid.*, **2**, 201 (1959).

RECEIVED for review February 18, 1963. Accepted April 26, 1963. Supported by a grant from the National Institutes of Health (C-3943).

The Separation and Fluorescent X-Ray Spectrometric Determination of Zirconium, Molybdenum, Ruthenium, Rhodium, and Palladium in Solution in Uranium-Base Fissium Alloys

J. O. KARTTUNEN

Argonne National Laboratory, Argonne, Ill.

▶ The various elements are separated prior to the fluorescent x-ray determination because of either direct x-ray line interference or negative interference to the characteristic x-ray intensities caused by the presence of the other elements in the solution. Palladium is precipitated with dimethylglyoxime, and the precipitate is extracted with chloroform. The aqueous portion is made 6M in hydrochloric acid and is passed through a Dowex 1-X8 anion exchange resin. Zirconium and rhodium do not adsorb, uranium is eluted with 0.3M hydrochloric acid, ruthenium and molybdenum are eluted with 8M nitric acid. The various elements are then determined by counting their K alpha radiation using a lithium fluoride plane crystal for dispersion.

In the Experimental Breeder Reactor II, the fuel plates contain zirconium, molybdenum, ruthenium, rhodium, niobium, and palladium in addition to uranium. This reactor is initially fueled with enriched uranium fissium, but later will operate on plutonium fissium. In the pyrometallurgical processing of irradiated or spent fuel plates, studies have indicated that a certain group of the fission products cannot be removed and that these elements would tend to build up to an equilibrium value after several successive recycles of the fuel.

In subsequent pyrometallurgical processing studies, it has been ascertained that more fertile material will remain if the oxidative drossing of zirconium is not taken down to the lower limit. Therefore, typical fuel alloys (called fissium) now have compositions as shown in Table I, and the nonuranium portion can vary from 5 to 25% of the total alloy.

The principle of chemical analysis by fluorescent radiation has been discussed fully by Von Hevesy (*9*), Glocker (*5*), Birks (*2*), and Liebhafsky (*8*). The number of special applications of chemical analysis by x-ray fluorescence in published papers are too numerous to mention. Essentially, when a sample is bombarded with x-rays, the various chemical elements in the sample absorb this primary radiation and emit fluorescent radiation. Before an atom can emit fluorescent radiation, it must first absorb a primary photon. Thus the excitation efficiency of a chemical element is a function of its absorption coefficient. Therefore, in a complex sample all atoms absorb primary photons and all atoms emit fluorescent radiation, although not with the same efficiency; and the presence of one element affects the intensity of fluorescent emission of another.

Table I. Typical 10% Fissium Uranium-Base Alloy

Element	Wt. %
Zr	2.80
Mo	2.75
Ru	2.95
Rh	0.50
Pd	1.00
U	90.00

From the fluorescent intensity spectrum, Figure 1, it is seen that the high uranium content causes direct interference with molybdenum and with rhodium, masking both of them rather completely. In addition, attenuation or negative interference of the characteristic x-ray intensities occurs in the case of zirconium and ruthenium, which results from absorption of their radiation by the other elements in the sample. These interferences from the extraneous

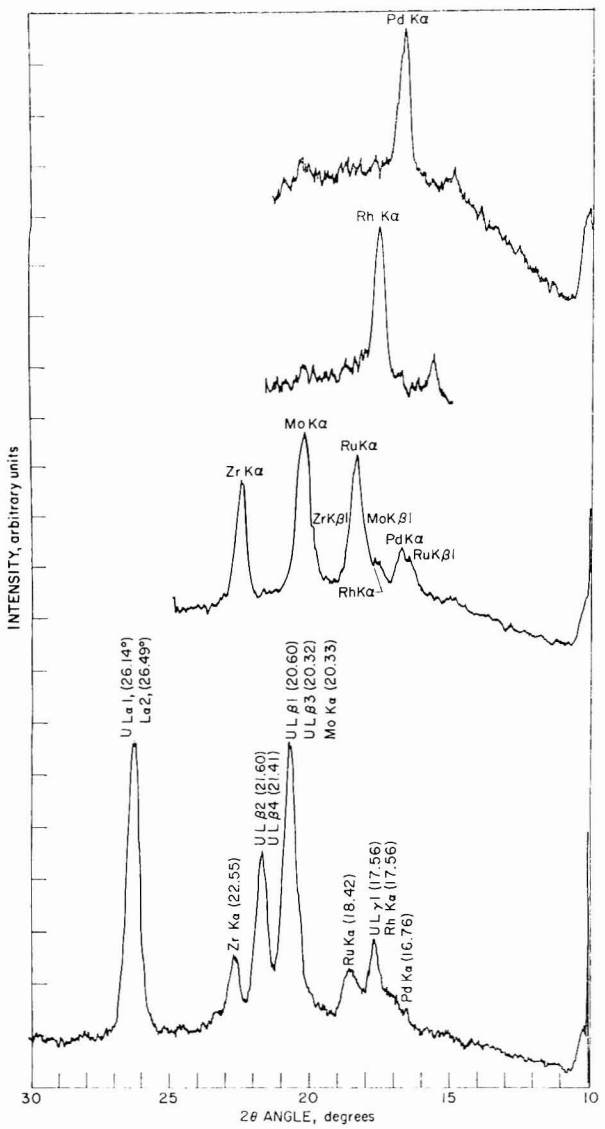


Figure 1. X-ray spectrogram of a simulated 10% fissium uranium-base alloy

Upper scans depict characteristic lines after separations

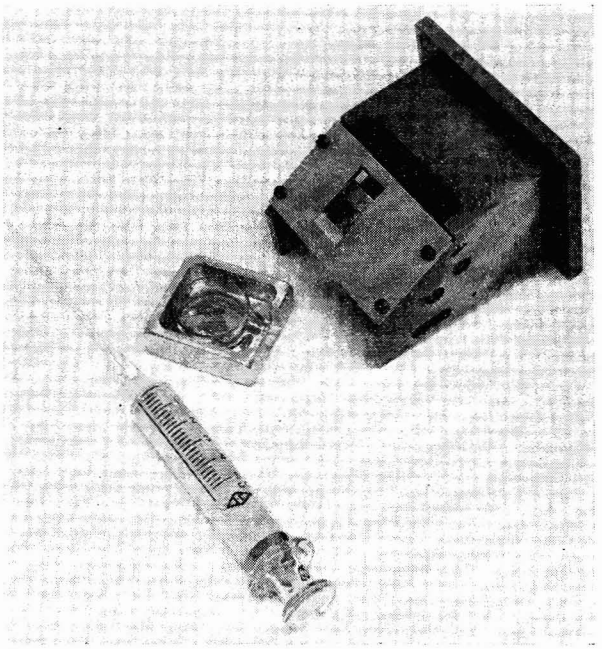


Figure 2. A liquid-sample cell and instrument specimen holder

chemical species in the sample may be dealt with by compensating for their effects by the use of internal standards (*1*), by calibration (*4*), or by removing them. Because the fissium alloys are rather complex and of varying composition (5 to 25% of nonfertile material), it is felt that the separation approach is the simplest.

EXPERIMENTAL

Apparatus. The x-ray spectrograph used was the General Electric XRD-5 instrument with no additional current stabilizer required other than that in the XRD-5 power supply. The primary x-radiation is provided with a Machlett AEG-50S tungsten target tube. The secondary radiation from the sample was analyzed by diffraction from a lithium fluoride crystal cut for the (200) plane. A parallel plate collimator, ratio 800 to 1, was interposed between the crystal and the counter. The instrument was operated at 50 k.v.p. and 50 ma.

All-glass sample cells are constructed from standard-wall borosilicate glass tubing and 0.07-mm. borosilicate cover disks. One large mouth arm is attached to the side of the cell body to facilitate the filling, washing, and drying cycle of each analysis. A cover disk is sealed directly to the cell body to provide a rigid yet relatively transparent x-ray window. (These cover disks have been attached to various cell bodies by fusing and also by means of adhesives.) The cell is cemented to an aluminum holder which is positioned in the instrument specimen holder as shown in Figure 2. Complete filling of the cell is easily done by holding it vertically and introducing the sample with a syringe-controlled transfer pipet.

A topaz crystal would give higher resolution, but the negative absorption interference and direct x-ray line interference in a few elements would still be present. Also the reflectivity of a topaz crystal is several times less than that of a lithium fluoride crystal. Since small amounts of sample are submitted, this greater reflectivity of the lithium fluoride crystal makes it the more useful crystal for the analysis of these elements in solution. The diffracted secondary radiation is detected with a xenon-filled proportional counter.

Reagents. Dowex 1-X8 anion exchange resin, chloride form, styrene type quaternary ammonium, 100 to 200 mesh, with an exchange capacity of 3.2 meq. per dry gram.

Standard solutions of the various elements were made by dissolving 99.9% pure metal pieces of the respective elements. All other chemicals were analytical reagent grade.

Matrix Influence. To control the final matrix composition and the elemental concentration within the limits for reliable analysis, solutions were evaporated to dryness and the evaporates were redissolved to the desired concentration in a selected solvent. From the results shown graphically in Figure 3, 1.0*M* hydrochloric acid was used as the final matrix composition whenever possible. Molybdenum salts do not dissolve readily in 1.0*M* hydrochloric acid or 1.0*N* sulfuric acid; so 4.0*M* hydrochloric acid was used as the matrix solvent for molybdenum and also for zirconium which has a tendency to hydrolyze rapidly in low acid concentrations. It is apparent from Figure

3, together with calculated linear absorption coefficients, that control over the solvent acid concentration must be somewhat rigorous if an inverse interference error is to be avoided.

Interferences. If uranium alone is removed from the solution of a uranium-base fissium alloy, the x-ray spectrogram of the fissium solution then is as depicted as the second scan in Figure 1. Direct x-ray line interference, and also negative absorption interference still exist. The simplest and most expedient solution is to separate the various elements to the desired extent.

Separation by Anion Exchange. The comprehensive survey of absorption characteristics in a hydrochloric acid medium presented by Kraus and Nelson (*7*) has resulted in a variety of analytical applications. Zirconium(IV) does not adsorb on an anion exchange resin when in 0 to 7*M* hydrochloric acid. Rhodium(III) ($RHCl_6^{-3}$) shows only negligible adsorption above 4*M* hydrochloric acid. Molybdenum(VI), ruthenium(IV), uranium(VI), and palladium(II) all are strongly adsorbed when in 6*M* hydrochloric acid.

For the zirconium determination, it is only necessary to take an aliquot from the solution that passed through the resin column, adjust the acidity as explained, and count the K alpha radiation. It is necessary to further separate rhodium from zirconium to determine the amount of rhodium present because the higher relative zirconium concentration causes a high negative absorption interference on the rhodium characteristic x-ray intensity. This is mainly due to the relatively large mass absorption coefficient of zirconium at the rhodium K alpha wavelength. As seen in Figure 4, when zirconium and rhodium are present as in their normal relative concentrations in the alloy, there is approximately a 24% loss in the characteristic x-ray intensity of rhodium due to the absorption of this radiation by the zirconium atoms present. Therefore, zirconium is extracted with 60% tributylphosphate in carbon tetrachloride. There is also a faster alternative approach where the zirconium is extracted with 0.1*M* trioctylphosphine oxide (Eastman Organic Chemical) in carbon tetrachloride and counted in this medium, and the

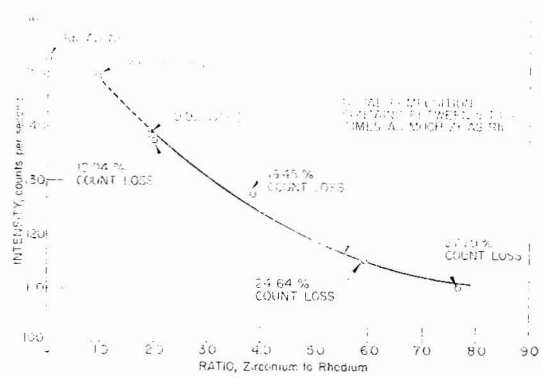


Figure 4. Zirconium interference on rhodium

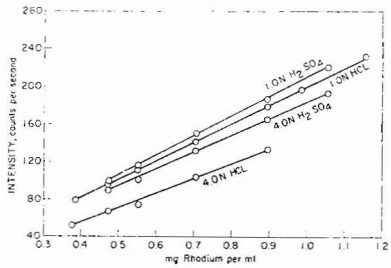


Figure 3. Relation of analytical sensitivity for rhodium in various solution matrices

rhodium remaining in the aqueous portion is adjusted with respect to acidity and counted as before.

The uranium(VI), molybdenum(VI), ruthenium(IV), and palladium(II) [Pd(II) is usually extracted as explained previously], are eluted from the resin column in the following sequence by equilibrium shifting. Uranium(VI) is eluted with 0.03*M* hydrochloric acid. Molybdenum(VI) and ruthenium(IV) are eluted from the anion exchange resin with 8*M* nitric acid (*3*). It was observed that palladium also could be quantitatively eluted from the anion exchange resin, but this elution required approximately 300 ml. of 8*N* nitric acid. For this reason and also because of the negative x-ray absorptive effect of larger concentrations of molybdenum and ruthenium present in the eluted solution, the preliminary extraction of palladium is performed. Since ruthenium and molybdenum are present in approximately equal quantities, it is not necessary to make any further separations but just to adjust the matrix, and then to count the molybdenum K alpha radiation and the ruthenium K alpha radiation.

Characteristics of Anion Exchange Resins and Treatment of Resin. Commercial resins almost always need some purification or pretreatment before they can be used in analytical applications. Undesirable ionic impurities may be removed by treatment with excess of the proper electrolyte solutions—for example, hydrochloric acid if the chloride form of the exchanger is desired. Often treatment with both concentrated and dilute electrolyte solutions is necessary because certain metallic impurities may remain strongly adsorbed if only one reagent is used. The Dowex 1-X8 anion exchange resin should be stored in 6*M* hydrochloric acid when not in use. It can be left in the glass column and prior to use the resin should be washed with 6*M* hydrochloric acid. distilled water, and again with 6*M* hydrochloric acid. It is important that all the fines in the resin are washed out prior to use, because these fines if washed into the sample elution solution will cause slightly low results due to their negative absorption effect on the secondary radiation.

Alternative Separations for Ruthenium and Molybdenum. In the event that only the determination for ruthenium and/or molybdenum is required, a very rapid separation can be made in both cases. For ruthenium, an aliquot is made 9*M* in nitric acid and the uranium, molybdenum, and zirconium are extracted to a non-influencing degree with 60% tributylphosphate (Commercial Solvents Corp.) in carbon tetrachloride. Two extractions are made, and one carbon tetrachloride wash is performed. A small amount of zirconium will not extract completely, but this does not influence the results when counting the ruthenium K alpha radiation.

In the case of molybdenum, an aliquot is adjusted to 10% in hydrochloric acid, 5 ml. of 10% ammonium thiocyanate are added, and after a 10-minute wait, the molybdenum thiocyanate complexes are extracted with butyl acetate. The red thiocyanate complex of quinquevalent molybdenum, the colorless hexavalent molybdenum complex, and the colorless trivalent molybdenum complex are all extracted

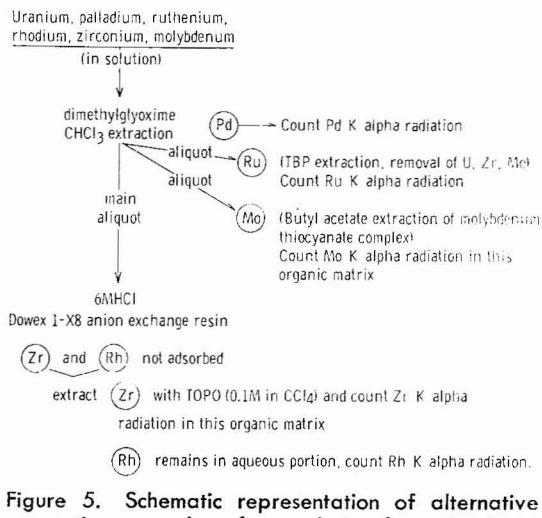


Figure 5. Schematic representation of alternative separation procedure for analysis of uranium-base fissium alloys

with butyl acetate. One extraction and one wash are sufficient. The wash is not absolutely necessary, but the precision is improved slightly by using it. It is only necessary to adjust the volume, and then to count the molybdenum K alpha radiation in the organic matrix.

Standardized Procedure. The standardized procedure is divided into 2 parts because Procedure B is considerably faster than Procedure A even though 2 additional extractions are involved in place of an anion exchange separation. The precision is also slightly better using Procedure B.

Procedure A: Accurately weigh a 0.5- to 2-gram sample of fissium alloy and transfer to a beaker. Cautiously treat the alloy with a solution of aqua regia that is 0.3*M* in hydrofluoric acid. When the reaction has subsided, boil gently until all of the alloy has dissolved, and make up to a suitable volume. With alloys of high fissium content complete dissolution is slow, and use of modified Carius tubes (*6*) in the dissolution is recommended. The tubes are of heavy-walled borosilicate glass, 15 × 20 mm., filling stem 4 × 8 mm., with a 2.5-mm. wall thickness. Add 9 ml. of concentrated hydrochloric acid and 1 ml. of concentrated nitric acid to 0.5 to 2 grams of accurately-weighed fissium alloy. Allow the alloy to react until most of the hydrogen that is released in the dissolution has escaped. This is important because high hydrogen build-up can cause explosions when the tube is being reopened after the dissolution procedure. If the above precaution is observed, no danger will exist. Seal the glass tube and place it in a steel secondary container, add solid carbon dioxide to compensate for the internal pressure within the glass tube when it is heated, and close the steel container. Then place the combination in a furnace at 300° C. overnight. Cool the modified Carius tube with a solid carbon dioxide–acetone mixture, open cautiously, and make the solution to volume.

Assuming that the palladium content is low (in a 5 to 10% fissium alloy), instead of taking an aliquot, take the entire sample to dryness and then redissolve with 4*M* hydrochloric acid. Adjust the solution to approximately 0.3*M* in hydrochloric acid and transfer it to a 125-ml. separatory funnel. Add 1 ml. of 1% dimethylglyoxime (Baker Analyzed reagent) in 95% ethyl alcohol for every 10 mg. of palladium. Allow to stand for 10 minutes, and then extract the palladium(II) dimethylglyoximate twice with 20 ml. of chloroform. Evaporate the chloroform extract to dryness on a hot plate (low setting), and dissolve the palladium(II) dimethylglyoximate with a small amount of aqua regia. Again take the solution to dryness, and then redissolve the palladium salts with 1.0*M* hydrochloric acid and make to volume so that the palladium concentration is between 0.3 mg. palladium per ml. to 1.5 mg. palladium per ml. One milligram of palladium per ml. gives an excellent counting rate. Set the goniometer of the XRD-5 x-ray spectrograph at the 2θ angle for palladium K alpha radiation (16.76°), and note the amount of time required to accumulate 100,000 counts. Determine the net count per second and by comparison with standards, determine the quantity of palladium present.

To the aqueous portion of the extraction above, add 5 ml. of concentrated nitric acid, and evaporate the solution to dryness. This nitric acid treatment is necessary to oxidize the elements to higher oxidation states for the following anion exchange separation. Redissolve the salts with 20 ml. of 6*M* hydrochloric acid, and pass the solution through a pretreated Dowex 1-X8 anion exchange resin. Drain the solution off at a rate of approximately 4 ml. per minute. Wash the beaker twice with approximately 5 ml. of 6*M* hydrochloric acid and pass the wash through the resin also. Zirconium(IV) and rhodium(III) do not adsorb under these conditions. Wash them from the resin column with 60 ml. of 6*M* hydrochloric acid. Retain this portion for the determination of zirconium and rhodium. Elute the uranium(VI) by means of equilibrium shifting with 70 ml. of 0.03*M* hydrochloric acid. Discard this uranium portion to waste. Finally, elute molybdenum(VI) and ruthenium(IV) from the anion exchange resin with 175 ml. of 8*M* nitric acid. Save this portion for the molybdenum and ruthenium determinations.

From the zirconium and rhodium portion above, take an aliquot and evaporate it to dryness. Redissolve the salts with 4.0*M* hydrochloric acid and make to a suitable volume, so that the zirconium concentration is from 0.3 mg. per ml. to 1.5 mg. per ml. Set the goniometer of the x-ray spectrograph at the 2θ angle for zirconium K alpha radiation (22.55°), and note the time required for the accumulation of 100,000 counts. By comparing the net count with that of zirconium standards, determine the quantity of zirconium present. Take the remaining major aliquot of the zirconium and rhodium portion to dryness, redissolve with 9*M* hydrochloric acid, and transfer to a 60-ml. separatory funnel. Extract zirconium twice with 60% tributylphosphate in carbon tetrachloride, and wash the aqueous portion containing the rhodium once with carbon tetrachloride. Evaporate the aqueous portion to dryness in a beaker, redissolve the rhodium salts with 1.0*M* hydrochloric acid, and adjust to a suitable volume so that the rhodium concentration is from 0.3 mg. to 1.5 mg. per ml. Set the goniometer of the x-ray spectrograph at the 2θ angle for rhodium K alpha radiation (17.56°), and note the time required for the accumulation of 100,000 counts. By comparing the net count with that of rhodium stand-

Table II. Typical Calibration Data

Results of a calibration, count rate *vs.* concn., for x-ray spectrometric determination of molybdenum in 4.0*M* HCl solution after Dowex 1-X8 anion exchange separation. 50 k.v.p., 50 ma.

A. Molybdenum alone through resin separation procedure

Mo, mg./ml.	Time for 100,000 counts (sec.)[a]	Total count rate, av. (c.p.s.)	Net count rate (c.p.s.)	μg. Mo per ml./net c.p.s.	Per cent deviation from mean
0.7106	271.87 270.63	368.66	144.79	4.91	+0.41
0.7881	259.89 258.39	385.89	162.02	4.86	−0.61
0.8409	252.25 251.40	397.11	173.24	4.85	−0.82
0.9971	233.17 233.34	428.71	204.84	4.86	−0.61
1.0560	228.44 229.09	437.14	213.27	4.95	+1.23
1.1004	223.07 222.68	448.67	224.50	4.90	+0.20
0	445.81 447.54	223.87			

B. Standard simulated fissium alloy

0.7405	268.09 268.11	373.00	150.56	4.92	+0.20
0.9990	235.11 234.75	425.66	203.22	4.92	+0.20
0.7323	267.23 268.48	373.33	150.89	4.85	−1.22
0.9810	236.80 236.81	422.30	199.86	4.91	...
1.0380	232.89 230.52	431.59	209.15	4.96	+1.02
1.0657	228.14 226.85	439.56	217.12	4.91	...
0	449.84 449.28	222.44			

[a] Sample cell was repositioned after each count.

Table III. Comparison of Palladium Recoveries

Palladium, mg./ml. Taken	Found	Variation, %	μg. Pd per ml./ net c.p.s.
(Controls with palladium alone through the procedure)			
1.044	1.006	−3.64	5.37
1.062	1.021	−3.86	5.38
0.898	0.372	−2.90	5.33
0.806	0.799	−0.87	5.22
0.756	0.727	−3.84	5.38
0.532	0.523	−1.69	5.27
0.688	0.679	−1.31	5.30
(Standard simulated fissium alloy)			
1.064	1.024	−3.76	5.38
1.064	1.025	−3.67	5.37
1.064	1.023	−3.85	5.38
0.678	0.669	−1.33	5.25
0.746	0.727	−2.55	5.31
0.848	0.825	−2.71	5.32
0.590	0.581	−1.52	5.26

Table IV. Comparison of Molybdenum Recoveries

Molybdenum, mg./ml. Taken	Found	Variation, %	μg. Mo per ml./ net c.p.s.
(Butyl acetate extraction procedure)			
(Controls with molybdenum alone through the procedure)			
0.289	0.289	0.00	2.62
0.475	0.465	−2.11	2.68
0.731	0.713	−2.46	2.69
0.292	0.289	−1.03	2.65
0.472	0.464	−1.69	2.67
0.774	0.751	−2.97	2.70
0.696	0.686	−1.44	2.66
(Standard simulated fissium alloy)			
0.2606	0.2521	−3.26	2.71
0.2606	0.2540	−2.53	2.69
0.423	0.415	−1.89	2.67
0.694	0.676	−2.59	2.69
0.825	0.823	−0.24	2.63
1.030	1.001	−2.82	2.67
0.2786	0.2778	−0.29	2.63

Table V. Comparison of Ruthenium Recoveries

Ruthenium, mg./ml. Taken	Found	Variation, %	μg. Ru per ml./ net c.p.s.
(TBP extraction of U, Mo, and Zr)			
(Controls with ruthenium alone through the procedure)			
0.9194	0.9012	−1.98	5.22
0.8885	0.8539	−3.89	5.32
0.9544	0.9211	−3.49	5.30
1.0454	1.0069	−3.68	5.31
1.0454	0.9991	−4.43	5.35
0.6742	0.6570	−2.55	5.25
0.7616	0.7321	−3.87	5.32
(Standard simulated fissium alloy)			
0.9234	0.8999	−2.54	5.25
0.8731	0.8377	−4.05	5.33
0.7516	0.7211	−4.06	5.33
0.6650	0.6506	−2.17	5.23
0.9882	0.9425	−4.62	5.36
1.023	0.9834	−3.88	5.32
1.125	1.084	−3.64	5.31

ards, determine the quantity of rhodium present.

Now returning to the molybdenum and ruthenium portion of the anion exchange separation, molybdenum and ruthenium will be present in approximately the same concentration and cause only slight interference in their respective determinations. Therefore, no further separation of these two elements is required. Take this portion to dryness, and redissolve in 4.0*M* hydrochloric acid, and make up to a suitable volume so that the concentration in each case is approximately 0.3 mg. to 1.5 mg. per ml. Count the ruthenium K alpha radiation at 18.42°, and count the molybdenum K alpha radiation at 20.33°. Compare the net count with standards containing similar concentrations of molybdenum and ruthenium, and even the slight interference mentioned above is compensated for.

Procedure B: Figure 5 shows a schematic representation of an alternative separation approach which is less time consuming even though additional manipulations are required. The purpose of this approach is to separate the constituents of the alloy as rapidly as possible in the event the determination of only a particular element is desired. It can be used equally well for the determination of all five of the minor constituents. The essential points have been discussed previously.

RESULTS AND DISCUSSION

The samples submitted for analysis usually are small chips or shavings with a total weight of only several grams. The ordinary wet chemical methods of analysis for these elements comprising the fissium alloys are time consuming and are otherwise tedious (color complexes are stable for only short periods of time, sometimes only one or two samples can be analyzed simultaneously, etc.). The separation procedures used here are new in the analysis of fissium alloys, and the time saving in the total analysis is approximately 20%. This is a rather complex alloy, but it illustrates the value of the fluorescent x-ray approach. It is necessary only to separate certain of the components of the alloy and then to count the isolated element's characteristic secondary radiation.

The characteristics of secondary x-ray emission and primary radiation scatter from a 10% fissium uranium-base alloy in dilute hydrochloric acid under the conditions of this study are depicted by the linear ratemeter scans reproduced in Figure 1. It illustrates features such as the peak to background intensity ratio, which determine the choice of the characteristic line whose intensity is correlated with element concentration for the basis of the method. The relatively high background intensity from dilute aqueous solutions has to be contended with since the use of energy-selective detectors cannot reduce it appreciably in this procedure. It arises in large part from diffuse scatter, coherent and Compton, of the exciting x-ray continuum as it impinges on the sample and surroundings.

The greatest source of error in precision in this method arises from errors in the chemical separations and not from detection or counting errors. The per cent average deviation in counting the same sample 15 times at random intervals over a 7-hour time period was only 0.28%. The per cent average deviation of values in the construction of standard curves of concentration *vs.* intensity was 0.38%.

Precision and Accuracy. Tables II through VII depict comparisons of the elemental recoveries using these procedures. The average per cent recovery for the dimethylglyoxime precipitation and chloroform extraction of the palladium dimethylglyoximate is 97.3%, and the relative standard deviation using the procedure is 1.17%. It is felt that the greatest loss of palladium occurs not in the precipitation or in the extraction, but in the complete dissolution of the palladium salt after the chloroform has been evaporated. For molybdenum, using the ammonium thiocyanate complexation and butyl acetate extraction, the per cent recovery of the method is approximately 98%, and the relative standard deviation of the procedure is 1.24%. More than 99% of the molybdenum is extracted; this was ascertained by checking the aqueous portion after the extraction of molybdenum. The variations shown in the amount of molybdenum found are due primarily to the other contributing factors in the procedure—accurate control of matrix, etc. In the method for

Table VI. Comparison of Zirconium Recoveries

Zirconium, mg./ml. Taken	Found	Variation, %	μg. Zr per ml./ net c.p.s.
(Anion exchange resin + TOPO extraction procedure)			
(Controls with zirconium alone through the procedure)			
1.130	1.098	−2.83	30.81
1.4568	1.4205	−2.49	30.68
1.259	1.244	−1.19	30.26
1.194	1.195	+0.08	29.87
1.668	1.648	−1.20	30.27
1.274	1.263	−0.86	30.16
1.764	1.720	−2.49	30.74
(Standard simulated fissium alloy)			
1.220	1.194	−2.13	30.64
1.314	1.320	+0.46	29.81
1.189	1.148	−3.45	30.98
1.088	1.068	−1.84	30.53
1.361	1.354	−0.51	30.11
0.8814	0.8595	−2.48	30.68
0.8000	0.7873	−1.59	30.44

ruthenium by extracting uranium, molybdenum, and some zirconium using tributylphosphate, the per cent recovery of ruthenium is approximately 96.5%, and the relative standard deviation using the procedure is 0.90%. The slight matrix deviations, the slight loss in incomplete extraction, and the slight attenuative effect of some zirconium, rhodium, and palladium in the solution are the chief contributing error factors.

The per cent recovery of zirconium using the anion exchange resin separation and the trioctylphosphine oxide approach is approximately 98%, and the relative standard deviation of the procedure is 1.44%. The per cent recovery of rhodium is approximately 95%, but the relative standard deviation of the procedure is 1.07%. Slight amounts of rhodium remain in the +4 oxidation state and remain on the resin column. Rhodium in the +2 oxidation state is also strongly adsorbed.

The rhodium recovery can be increased a bit by taking the solution to semi-dryness twice with 6*M* hydrochloric acid before passing the solution through the Dowex 1-X8 anion exchange resin. This alters the molybdenum, uranium, and ruthenium oxidation states slightly though causing poorer recovery elsewhere. It is permissible if the molybdenum and ruthenium are determined by the alternative procedures. Using the anion exchange separation approach for molybdenum, the per cent recovery of molybdenum is approximately 99%, and the relative standard deviation using the procedure is 1.02%. The poorest per cent recovery is in the resin separation of ruthenium; it is approximately 91%, while the relative standard deviation of the procedure is 1.38. The per cent recovery of zirconium using the resin separation, and counting in a 4.0*M* hydrochloric acid medium without separating rhodium from it, is approximately 99%, and the relative standard deviation of the procedure is 1.02%.

Table VII. Comparison of Rhoduim Recoveries

(Anion exchange resin + TOPO extraction of zirconium)

Rhodium, mg./ml. Taken	Found	Variation, %	μg. Rh per ml./ net c.p.s.
(Controls with rhodium alone through the procedure)			
0.6573	0.6354	−3.33	4.64
0.8297	0.7896	−4.83	4.71
0.5772	0.5567	−3.55	4.65
0.8976	0.8505	−5.25	4.73
0.9304	0.8914	−4.19	4.68
0.9883	0.9491	−3.97	4.67
0.9918	0.9295	−6.28	4.75
(Standard simulated fissium alloy)			
0.7408	0.6948	−6.21	4.75
0.6020	0.5832	−3.12	4.63
0.7525	0.7322	−2.70	4.61
0.9826	0.9331	−5.04	4.72
1.081	1.036	−4.16	4.68
0.8814	0.8448	−4.15	4.68
0.7432	0.7076	−4.79	4.71

ACKNOWLEDGMENT

It is a pleasure to recognize the contribution of P. J. Markovich who assisted in much of the analytical work.

LITERATURE CITED

(1) Adler, I., Axelrod, J. M., *Spectrochim. Acta* **7**, 91–9 (1955).
(2) Birks, L. S., "X-ray Spectrochemical Analysis," Interscience, New York, 1959.
(3) Buchanan, R. F., Faris, J. P., "Radioisotopes in the Physical Sciences and Industry," p. 361, International Atomic Energy Agency, Vienna, 1962.
(4) Burnham, H. D., Hower, J., Jones, L. C., ANAL. CHEM. **29**, 1827–34 (1957).
(5) Glocker, R., Schreiber, H., *Ann. Physik* **85**, 1089–102 (1928).
(6) Gordon, C. L., Schlecht, W. C., Wichers, E., *J. Res. Natl. Bur. of Stds.* **33**, 457, 1944.
(7) Kraus, K. A., Nelson, F., *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva*, **7**, 113 (1956).
(8) Liebhafsky, H. A., Pfeiffer, H. G., Winslow, E. H., Zemany, P. D., "X-ray Absorption and Emission in Analytical Chemistry," Wiley, New York, 1960.
(9) Von Hevesy, G., "Chemical Analysis by X-ray and Its Application," McGraw-Hill, New York, 1932.

RECEIVED for review January 10, 1963. Accepted April 29, 1963. Based on work performed under the auspices of the U. S. Atomic Energy Commission.

X-Ray Emission Analysis of Plutonium and Uranium Compound Mixtures

OSCAR MENIS, E. K. HALTEMAN, and E. E. GARCIA

Advanced Materials Center, Nuclear Materials and Equipment Corp., Apollo, Pa.

▶ **A timesaving and reliable x-ray emission method was developed for the simultaneous determination of plutonium and uranium in refractory oxide mixtures and fused alloys. The measurements of characteristic *Lα* lines of uranium and plutonium, with thorium used as an internal standard, were carried out after a fusion of the refractory mixtures in a flux of potassium pyrosulfate. A casting technique, which involves slow cooling of the molten flux mixture, was developed as a substitute for the more lengthy briquetting procedure. For samples of uniform composition, calibration curves and plutonium-to-uranium intensity ratios can be used. In these cases, the relative standard deviation is less than 0.4%. With complex mixtures containing a high percentage of other elements, thorium is used as an internal standard. A mechanism is also proposed to explain the positive curvature in the intensity ratio values for uranium to thorium and plutonium to thorium. This is due to the autoexcitation phenomena characteristic of uranium and transuranium elements.**

IN THE STUDY of uranium, plutonium, and other oxides as possible reactor fuel components, analysis of multicomponent systems is necessary. One of these systems is composed of a mixture of uranium and plutonium oxides in concentrations ranging from 0.5 to 25% PuO_2 and 75 to 99.5% UO_2. Analysis of such mixtures is a rather long process requiring separations (*7*).

In a search for less time-consuming procedures that still provide accurate results, the x-ray technique was studied. Examination of the emission spectra of uranium and plutonium shows that no serious mutual interference is to be expected and that both elements can be determined using the same sample. Furthermore, x-ray emission procedures are relatively free of interference from impurities and additives, and the oxidation state of the elements to be measured, which is an important consideration in plutonium solution chemistry, does not introduce errors in the results.

X-ray emission methods for the determination of uranium (*3, 5, 6, 9, 10, 12, 13, 16*) and plutonium (*4, 6, 15*) have already been reported. In general, solution techniques were favored for uranium, and a slurry method was de-

scribed for the determination of plutonium (*15*). The instability of fairly concentrated plutonium solutions, together with the higher risk of contamination stemming from the use of liquid samples in the spectrograph, made the use of solid rather than liquid samples more desirable. The refractory character of the oxides of uranium and plutonium made a fusion attack necessary to ensure complete dissolution and homogeneity of the sample (*2*).

In the selection of an internal standard, several elements were considered. Yttrium (*3, 5, 13, 15*), strontium (*4, 10, 12, 13*), and bromine (10, 13) have been used in the analysis of either plutonium or uranium. The uranium-to-thorium ratio has also been used (*1, 14*), although in this case thorium was not added as an internal standard but was already present in the sample. Since thorium is also an important material in nuclear technology, it was interesting to try it as an internal standard and, at the same time, to study its influence on the emission characteristics of uranium and plutonium.

The principal areas investigated include interaction of the emission lines and absorption edges of the three elements, relative effectiveness of various fluxes, methods for the preparation of suitable samples, and effect of variation in the composition of the samples.

EXPERIMENTAL

Instrumental. A Phillips Norelco Universal X-Ray Spectrograph, Model 52360, with its associated components, was used for the experimental work. Components included a lithium fluoride crystal ($2d = 4.0267$ A.); a tungsten target tube, type FA-60; a scintillation counter, type 52245; a pulse height analyzer, type 52332; and a scaler, type 421455. The x-ray tube was operated at 50 kv. and 35 ma. The sample holder compartment was enclosed in a glove box to eliminate the health hazard associated with handling plutonium.

Preparation of Standards. Standards were prepared by adding appropriate amounts of plutonium, uranium, and/or thorium solutions to a weighed amount of flux. Plutonium solutions were prepared by dissolving high purity metal in a sufficient amount of 6*N* hydrochloric acid and diluting to volume. The final concentration of hydrochloric acid was kept at 3–4*N* to avoid hydrolysis. The solutions were also standardized by an amperometric titration of the plutonium(VI) with ferrous sulfate (*11*).

Uranium solutions were prepared by dissolving uranous oxide in nitric acid and diluting to the desired volume. The solutions were standardized by titration with standard dichromate.

Thorium solutions were prepared by dissolving reagent grade thorium oxide in perchloric acid. It was standardized by an EDTA titration with xylenol orange as an indicator (*8*).

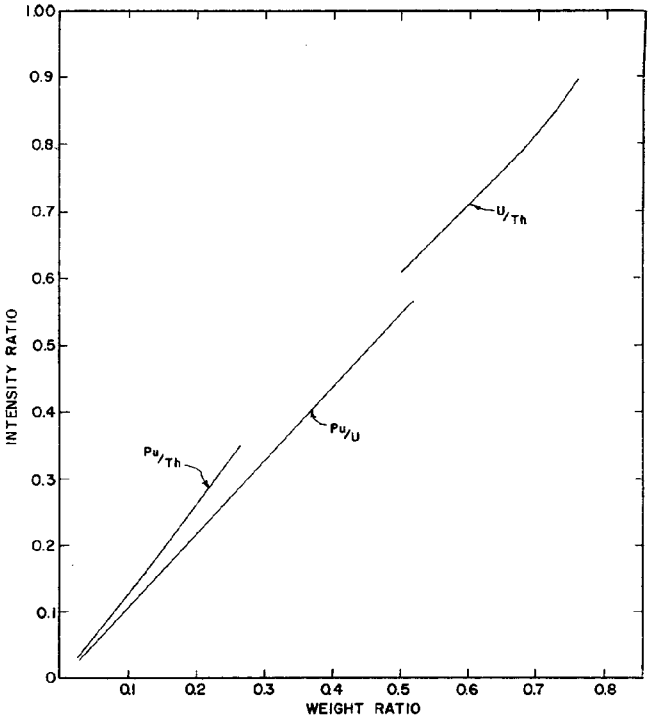


Figure 1. Calibration curves for uranium and plutonium with thorium as an internal standard

Preparation of Pyrosulfate Briquets and Cast Pellets. An appropriate sample size within the concentration range of the calibration curve was weighed and mixed with 10.00 grams of potassium pyrosulfate contained in a 30-ml. borosilicate glass beaker. This was fused at 450° C. for 2 hours or until the melt showed a clear solution. Where cast pellets were desired, the melt was allowed to cool to room temperature very slowly, usually overnight. The pellet surface was then polished with fine sandpaper. For the preparation of briquets, the fused mass was poured on a Teflon tray and allowed to cool, then ground in an agate mortar to approximately 200-mesh size. This powder was pressed at 900 p.s.i. to obtain briquets $1\frac{1}{4}$ inches in diameter, approximately $\frac{3}{8}$ inch thick.

Preparation of Calibration Curves. Calibration curves were prepared within a range of 20–30 mg. for uranium and 1–10 mg. for plutonium. When thorium was used as an internal standard, 40 mg. were added. The total weight of plutonium and uranium was kept at approximately 30 mg. Adequate amounts of the uranyl nitrate, plutonium chloride, and/or thorium perchlorate solutions were added to 10.00 grams of potassium pyrosulfate. The standards were dried either in an oven at 110° C. or under an infrared lamp. The other steps of the procedure have been described in the section on the preparation of briquets and cast pellets.

X-ray Measurements. Each sample was loaded into a sample holder having a Mylar window supplied with the instrument. The intensity of the $L\alpha 1$ lines was measured at 24.90° for plutonium, 26.15° for uranium, and 27.46° for thorium. Background intensity was measured at 24.18° and 29.18°. A fixed count technique was used, and a minimum of 128,000 counts were collected to avoid errors associated with the counting statistics.

From the data, intensity ratios for Pu/Th, U/Th, and Pu/U were computed using the intensities of the $L\alpha 1$ lines for uranium, plutonium, and thorium, corrected for background. The background correction was calculated assuming that the variation was linear between the matrix background readings at 29.18° and 24.18°.

In addition, ratios of the emission intensities of uranium and plutonium to the background readings were calculated. These ratios were plotted against corresponding weight ratios of the elements (against the weight of uranium or plutonium in the case of the metal-to-background ratios).

Pretreatment of Samples. Mixed oxide samples were usually prefired at 850° C. to avoid uncertainty in the composition of the oxides, then cooled and weighed. At this temperature, UO_2 is converted to U_3O_8, and the error associated with the unknown oxygen-to-metal ratio in the uranous oxide is eliminated.

Samples of fused plutonium mixed with Haynes alloy or tantalum were fired at 600° C. under a 5% hydrogen–95% nitrogen atmosphere for several hours. This treatment embrittles the metal and it can be ground easily.

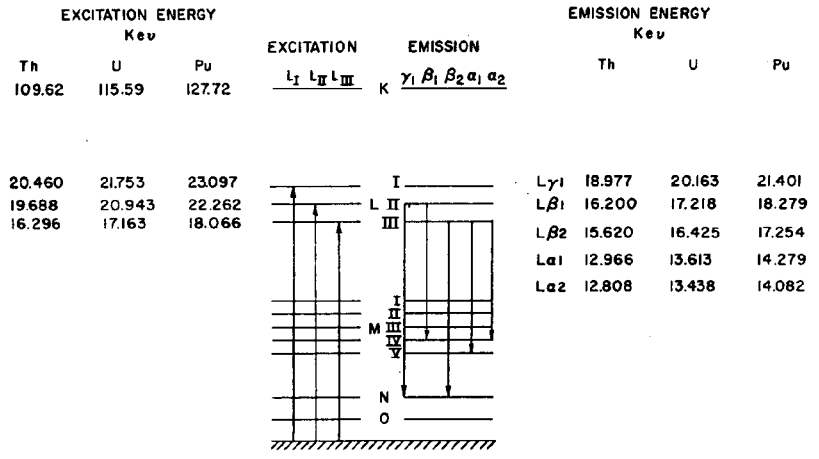


Figure 2. Simplified x-ray energy level diagram

After the firing, the pieces were broken and ground to 100-mesh size in a ball mill, to assure a homogeneous sample.

DISCUSSION

An examination of the results indicates that a linear relation exists between the intensity ratios and the concentration ratios for plutonium and uranium, while a positive curvature exists in the corresponding relationship for plutonium and thorium and uranium and thorium (Figure 1). In the case of two elements with no interfering absorption edges, a linear relation should be observed.

The nonlinearity in the case of Pu/Th and U/Th ratios is due to autoexcitation occurring in the L excitation and emission spectra of elements of atomic number 92 and above—i.e., uranium and transuranium elements. A simplified diagram of the x-ray energy levels in the 10- to 25-kv. range for thorium, uranium, and plutonium is shown in Figure 2. The K state levels for these elements are all greater than 100 kv. and are not excited using the available equipment. The M state levels are all less than 6 kv. and produce lines of low intensity which are readily absorbed by the atmosphere and are generally unsuitable for chemical analysis. The L levels are at excitation potentials convenient for producing emission lines for use in analysis and these are also shown in Figure 2. The energy of the three L excitation levels and of the strongest emission L lines for elements of atomic number 88 and above is plotted in Figure 3. It will be noted that for all elements below uranium the L III excitation energy is greater than the $L\beta 1$ emission energy. For uranium and transuranium elements the situation is reversed. The $L\beta 1$ emission energy is sufficient to cause L III excitation leading to $L\alpha 1$ emission. Thus, there exists a mechanism for the enhancement of the $L\alpha 1$ emission line relative to the $L\beta 1$ line for uranium and plutonium.

The intensity of the $L\alpha 1$ emission line is, therefore, due to emission from the direct excitation to the L III level and from the secondary process of excitation to the L III level by the absorption of $L\beta 1$ radiation. The intensity of the $L\beta 1$ emission line is also reduced by the increased absorption due to the L III excitation level. Thus, in the case of small concentrations of uranium or plutonium in a noninterfering matrix, the intensity of the direct $L\alpha 1$ emission line is proportional to the concentration of the heavy element. However, the intensity of the $L\alpha 1$ excited by the $L\beta 1$ radiation is proportional to the square of the concentration because of the dual process involved. This then leads to the nonlinearity in the intensity-to-concentration ratios for U/Th and Pu/Th (Figure 1). The linearity in the U/Pu ratios can be attributed to the fact that autoexcitation occurs in both elements and any differences in intensity would be second order effects.

Several fluxes were investigated in an attempt to obtain specimens suitable for x-ray measurements. The most important conditions sought were: ability to dissolve refractory uranium and plutonium oxides; low melting point; low x-ray absorption in the zone of the

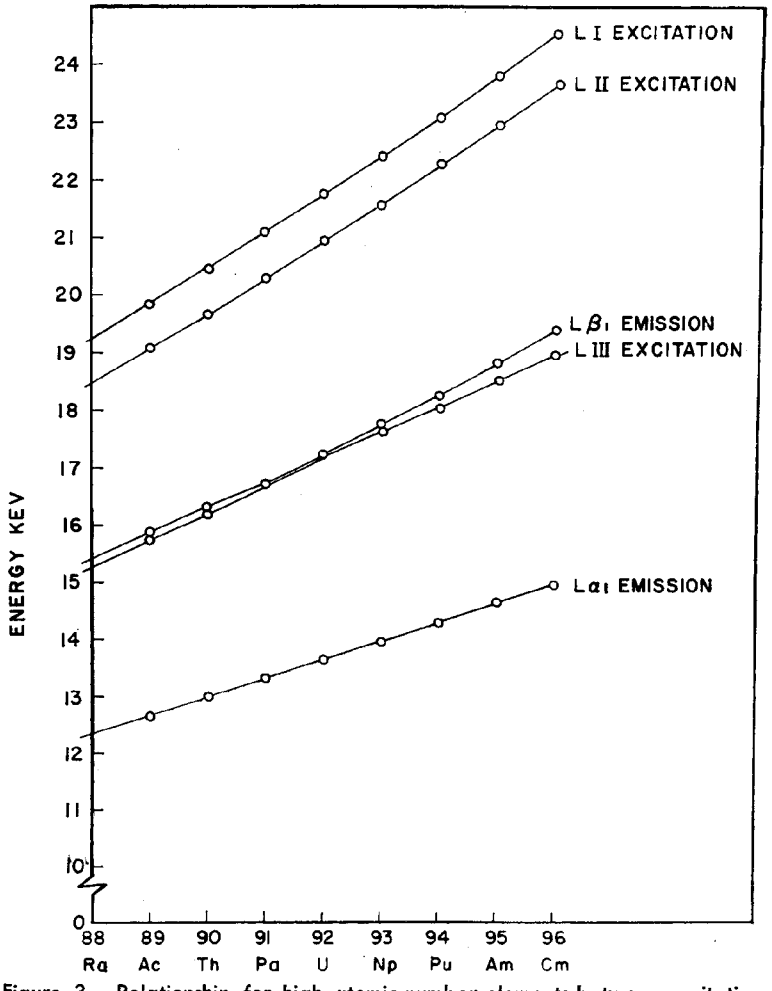


Figure 3. Relationship for high atomic number elements between excitation and emission energies

Table I. Reproducibility of Duplicate Determination of Uranium and Plutonium

	Rel. std. dev., based on series of duplicates						
	Pu/Th	U/Th	Pu/U	Pu/Bgd 29°	Pu/Bgd 24°	U/Bgd 29°	U/Bgd 24°
Thorium internal standard	2.5%	2.1%	2.8%	2.7%	2.3%	0.8%	1.3%
No internal standard	...	...	0.4%	1.4%	1.0%	1.0%	1.4%

spectrum to be used for the determination of uranium and plutonium; and good casting properties for pellets by direct cooling.

The principal fluxes studied were potassium pyrosulfate, sodium and lithium borates, potassium dichromate mixed with potassium pyrosulfate, and ammonium bifluoride. The borates have good casting properties and easily dissolve the refractory oxides, but their high melting point (approximately 950° C.) is a disadvantage. In addition, lithium borate attacks platinum ware. Mixtures of dichromate and pyrosulfate (1:9) cast well but are not an improvement over pyrosulfate alone. Ammonium bifluoride, which has been used to dissolve plutonium oxide, attacked uranium oxide only at temperatures over 100° C. with considerable sublimation that precludes the attainment of a reproducible matrix composition. Potassium pyrosulfate attacks even high-fired oxides, shows low x-ray absorption properties, and has a relatively low melting point. On the whole, it has more suitable properties than the other fluxes tried.

Table II. Comparison of Precision of X-Ray Emission and Amperometric Titration Methods

	X-Ray		
	Th internal standard	No internal standard	Amperometric titration
Determined Pu %	16.02	15.67	15.82
Rel. std. dev., %	1.3	0.7	0.6

A considerable saving in time and labor was achieved by the procedure developed for casting pyrosulfate pellets. This step required slow cooling to avoid cracking the pellets. It was necessary, however, to polish the surface of these pellets to improve the precision. The relative standard deviation with and without polishing was 0.9 and 3.2%, respectively. The poorer precision was evidently due to the uneven bottom surface of the beakers. Casting on a glass plate could possibly prevent it. For the same type of mixtures, the relative standard deviation of briquetted samples is 0.4%.

The reproducibility of the calibration curves in the presence of thorium, as expressed by the standard relative deviation between duplicates (Table I), is of the same order for both metal-to-thorium and plutonium-to-uranium ratios. If thorium is not used, the reproducibility of the plutonium-to-uranium ratio improves. This improvement can be attributed to either the elimination of spectral interference by thorium or to a more homogeneous matrix in the absence of thorium sulfate. The results based on the calibration curves of the metal-to-background ratios are more easily affected by changes in the composition of the samples and are, therefore, considered less reliable than those calculated from the plutonium-to-uranium ratio. However, in many cases of pure preparations of oxide mixtures, the plutonium-to-uranium ratio values yield enough information on the sample composition to make further calculation unnecessary. Thorium, as an internal standard, has been used, therefore, only in the analysis of more complex samples to minimize the effects of interferences.

The x-ray emission method has been applied to several different types of samples. Table II shows agreement between results obtained by x-ray emission and amperometric titration in a sample of mixed oxides. In this case, the pressed-briquet technique was used, with results calculated from the plutonium-to-uranium ratio and the weight of sample. Uranium was similarly determined. The relative standard deviation, in this case based on seven duplicate determinations, was better than 0.7%. When the method was applied to the determination of plutonium in Haynes alloy mixtures, thorium was used as an internal standard. Table III shows the precision of the determination of plutonium mixed with Haynes alloy or with tantalum.

Table III. Precision of Determination of Plutonium Found in Alloys

Type of sample	No. of determination	Pu content, %	R.S.[a]
Haynes Alloy No. 25[b]	8	49.6	0.6
Haynes Alloy No. 25	18	11.2	1.1
Haynes Alloy No. 25	7	3.60	1.1
Haynes Alloy No. 25	10	6.42	0.3
Tantalum	10	5.08	1.2

[a] R.S. = Relative standard deviation of the mean.
[b] Composition of Haynes Alloy No. 25: Cr 19.0–21.0%, Co 47.0–57.0%, N 9.0–11.0%, Fe 2.0% max., W 14.0–16.0%, Mn 1.0–2.0%

ACKNOWLEDGMENT

The assistance of J. R. Cherry in carrying out the analysis is gratefully acknowledged.

LITERATURE CITED

(1) Campbell, W. J., Clark, H. E., ANAL. CHEM. 27, 1884 (1955).
(2) Claisse, F., *Norelco Reptr.* 4, 3 (1957).
(3) Cope, J. H., *Ibid.*, 3, 41 (1956).
(4) Flikkema, D. S., Schablaske, R. V., U. S. Atomic Energy Comm. *Rept.* ANL-5804 (1957).
(5) Kehl, W. L., Russell, R. G., ANAL. CHEM. 28, 1350 (1956).
(6) Lambert, M., Proceedings Seventh Annual Conference on Industrial Applications of X-ray Analysis, Denver Research Institute, Denver, Colo., 1958, p. 193.
(7) Larsen, R. P., Seils, C. A., ANAL. CHEM. 32, 1863 (1960).
(8) Layton, F. L., Master Analytical Manual, Oak Ridge National Laboratory, Analytical Chemistry Division, Oak Ridge, Tennessee, U. S. Atomic Energy Comm. *Rept.* TID-7015 (1958), Methods 218771-900718771.
(9) Moak, W. D., Pojasek, W. J., U. S. Atomic Energy Comm. *Rept.* KAPL-1879 (1957).
(10) Pish, G., Huffman, A. A., ANAL. CHEM. 27, 1975 (1955).
(11) Seils, C. A., Larsen, R. P., Meyer, R. J., Proceedings Fourth Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., 1960, U. S. Atomic Energy Comm. *Rept.* TID-7606 (1961).
(12) Silverman, L., Hook, W. W., Moudy, L. A., ANAL. CHEM. 29, 1762 (1957).
(13) Smithson, G. H., Eager, H. L., Van Cleave, A. B., *Can. J. Chem.* 37, 20 (1959).
(14) Tournay, M., *Compt. Rend.* 234, 2527 (1952).
(15) Turnley, W. S., *Talanta* 6, 189 (1959).
(16) Wilson, H. M., Wheeler, G. V., U. S. Atomic Energy Comm. *Rept.* IDO-14393 (1957).

RECEIVED for review January 2, 1963. Accepted April 8, 1963. Presented at Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology at Gatlinburg, Tenn., October 1962. Work carried out under AEC Contract AT(30-1)-2389.

Inert Gas Fusion Determination of Oxygen in Vanadium, Niobium, and Tantalum

GEORGE J. KAMIN, JEROME W. O'LAUGHLIN, and CHARLES V. BANKS

Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa

▶ The inert gas fusion technique has been applied to the determination of oxygen in the Group V-A metals—vanadium, niobium, and tantalum. A platinum flux technique was satisfactory for the determination of oxygen in vanadium and a mixed nickel–platinum bath used with a platinum flux technique was satisfactory for niobium and tantalum. Oxygen contents from 100 to 1000 p.p.m. were determined on standard samples with relative standard deviation of 3% for vanadium and 5% for niobium and tantalum.

THE INERT gas fusion technique has been applied to the determination of oxygen in a number of materials. Since the availability of commercial instrumentation, it has become increasingly popular. Much of the original work dealt with the determination of oxygen in steels, but in the recent literature the technique has been applied to beryllium (*4*), zirconium and zircaloy (*3*), yttrium and yttrium fluoride (*1*), and mixed fluorides (*5*). Beck and Clark (*2*) have used the graphite capsule method for determining oxygen in various oxides and in organic compounds. This paper deals with the extension of the inert gas fusion method to the determination of oxygen in vanadium, niobium, and tantalum.

EXPERIMENTAL

Apparatus and Reagents. The basic instrument used was the Leco Oxygen Analyzer, No. 534-300, consisting of an induction furnace and conductometric bridge. The modifications made on this instrument, as well as outgassing, blanking, and calibration procedures, were discussed previously (*1*). The temperature was adjusted to at least 2000° C. as measured by an optical pyrometer.

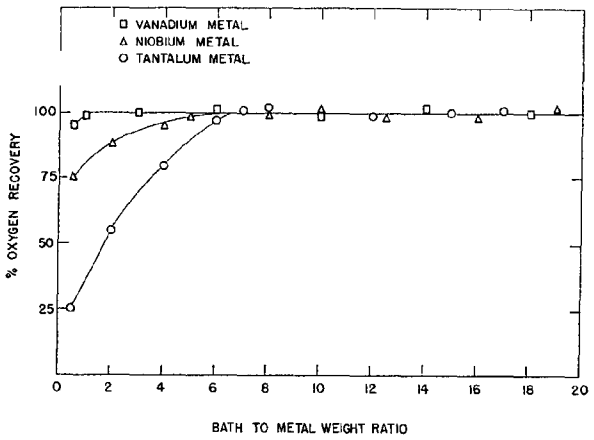


Figure 1. Studies of bath to metal ratios necessary for determination of oxygen in the Group V-A metals

Bath Conditions. Proper bath conditions play an important part in the evolution of the oxygen from a sample (*1*, *3*, *4*). The commonly used platinum flux technique involving a 1:1 ratio of platinum to sample was adequate for the determination of oxygen in vanadium, but much larger quantities of platinum were needed to achieve any meaningful results on niobium or tantalum. In the case of niobium, the platinum to niobium ratio of at least 8:1 was required, while for tantalum, the required ratio was 10:1. These large amounts of platinum present a major problem, in that they greatly restrict the number of uninterrupted consecutive analyses which can be performed because the volume requirements of the apparatus are rather restricted. This space problem is especially acute when samples containing less than 100 p.p.m. of oxygen are being analyzed. In an effort to overcome this problem, the use of other bath materials was investigated. Nickel has been previously used as a bath material (*4*) but it did not prove adequate for any of the Group V-A metals. Attempts at using a mixed platinum–nickel bath showed greater promise.

Because nickel contains more impurities than platinum, all the nickel and the initial charge of platinum were added to the crucible and allowed to outgas for approximately 1 hour at 1950° to 2000° C. The samples were also wrapped in at least an equal weight of platinum before analysis.

In the case of vanadium, it was found that a platinum–nickel bath containing as much as 75% nickel gave the same results as a pure platinum bath. Studies on the effect of composition of the platinum–nickel bath on the de-

Table I. Determination of Oxygen in Group V-A Pentoxides and Metals

V_2O_5		V		Nb_2O_5		Nb		Ta_2O_5		Ta	
O_2, μg.		O_2, av. p.p.m.		O_2, μg.		O_2, av. p.p.m.		O_2, μg.		O_2, av. p.p.m.	
Taken	Found[a]	V.F.	I.G.F.	Taken	Found[a]	V.F.	I.G.F.	Taken	Found[a]	V.F.	I.G.F.
147	155	2200	2160 ± 24	301	297	1450	1460 ± 20	162	153	480	415 ± 12
113	118	490	491 ± 15	178	176	450	460 ± 12	105	102	280	270 ± 10
68	66	210	214 ± 9	105	101	295	289 ± 10	88	91	160	155 ± 8
		180	181 ± 10	81	80	185	186 ± 5	58	60	80	70 ± 7
		127	118 ± 5	44	41	100	95 ± 6				
		107	102 ± 6								

[a] Determined by inert gas fusion method.

termination of oxygen in niobium showed that baths containing from 25 to 75% nickel yielded good results. A similar study on tantalum showed that baths containing from 25 to 50% nickel gave good results, the bath to sample ratio in each case being approximately 10:1. In both cases, the range of the results was far more satisfactory in the case of the mixed bath than with platinum alone. Though nickel alone tends to volatilize at temperatures above 1800° C., the platinum–nickel bath shows no signs of volatilization until 2200° C.

For analysis of vanadium, niobium, and tantalum, a 40% nickel bath was prepared and used with the platinum flux method. Studies on the bath to metal ratios necessary for the use of this bath are shown in Figure 1. The minimum bath to metal ratio for vanadium is 1:1, for niobium, 5:1, and for tantalum, 6:1. The bath to metal ratios were maintained by periodic addition of nickel with subsequent outgassing.

The use of the platinum–nickel bath permitted the analysis of 25–30 metal samples, before it was necessary to change the crucible, which was approximately double the number analyzed with platinum alone. There is, however, little volume decrease between the platinum–nickel bath and the platinum alone, because of the lower density of the nickel. The increased number of analyses would appear to be caused by increased solubility of the samples and graphite in the bath.

Procedure. After the bath was outgassed and the system calibrated (*1*), the crucible was preheated for 1 minute, the platinum-wrapped sample was introduced, heating was continued for 3 minutes, the power was shut off, the system was swept for 4 minutes, and the final oxygen content was calculated from the change in conductance.

RESULTS

The pentoxides of the Group V-A metals were analyzed and the results of these analyses are shown in Table I.

A comparison of the results obtained by the vacuum fusion and by the inert gas fusion methods on the Group V-A metals is also given in Table I. As can be seen, the results were in good agreement in the range from 100 to 1000 p.p.m. of oxygen content in the sample, except for the higher oxygen values on tantalum metal. Multiple analyses of the samples showed a relative standard deviation for vanadium of about 3%, and a relative standard deviation of about 5% for niobium and tantalum.

ACKNOWLEDGMENT

The authors thank V. A. Fassel and his coworkers for the vacuum fusion results.

LITERATURE CITED

(1) Banks, C. V., O'Laughlin, J. W., Kamin, G. J., ANAL. CHEM. 32, 1613 (1960).
(2) Beck, E. J., Clark, F. E., *Ibid.*, **33**, 1767 (1961).
(3) Elbling, P., Goward, G. W., *Ibid.*, **32**, 1610 (1960).
(4) Kallman, S., Collier, F., *Ibid.*, p. 1616.
(5) Potter, J. L., Murphy, J. E., Heady, H. H., *Ibid.*, **34**, 1635 (1962).

RECEIVED for review February 11, 1963. Accepted April 4, 1963. Division of Analytical Chemistry, 141st Meeting, ACS, Washington, D. C., March 1962. Contribution No. 1283 from the Ames Laboratory of the U. S. Atomic Energy Commission.

Semimicro Determination of Molecular Weight with a Dew-Point System

ANGELO DE ROS, OLIVIERO FAGIOLI, and PIERO SENSI

Research Laboratories, Lepetit S.p.A., Milan, Italy

▷ A new method for the semimicro determination of molecular weight is described. The method is based on the fact that the observation of the dew point provides a very accurate estimation of the beginning condensation and of the ending evaporation of the solvent on a surface whose temperature varies slowly, in the presence of the vapor of the solution at constant temperature. If a number of cells containing solutions of different molarities are used simultaneously with a common condensing surface, the disappearance of the various solvent films follows the order of the molar dilutions, even where the differences among the concentrations are very small. The method described presents the following features: ease of performance, possibility of repeating the measurements many times, good precision and accuracy, use of small quantities of substance (2 ml. of solution from 0.1 to 0.2*M*), quantitative recovery of the substance whose molecular weight has been determined, and the possibility of using substantially all the solvents having boiling points between 40° and 120° C.

MOLECULAR WEIGHT is usually determined by methods based on the variation of the vapor pressure of a solution relative to the pure solvent (cryoscopy, ebullioscopy, isopiestic, osmotic methods), the determination of vapor density, or functional group analysis (*1*). The more recent ones, which are microscale methods, utilize improvements in temperature measurements, such as amplified thermocouples and thermistors with low thermal capacities, high speed, and sensitivities not previously attained. These methods are very useful because of the small amount of substance required, but are rather delicate (*2–7*).

The problem of determining molecular weight using small quantities of substance is very important in organic chemistry, and in spite of the considerable amount of work cited, the problem seems not yet definitely solved. In this paper a new method, based on vapor pressure lowering of a solution, is described which can provide, in a semimicro scale, an easy and quick determination of molecular weight with good accuracy and with the possibility of using a very large number of solvents. The method is based on the fact that the observation of the dew point provides a very accurate estimation of the beginning condensation and of the ending evaporation of the solvent on a surface whose temperature varies slowly, in the presence of the vapor of the solution at costant temperature. If a number of cells containing solutions of different molarities are used simultaneously with a common condensing surface, the disappearance of the various solvent films follows the order of the molar dilutions even where the differences among the concentrations are very small.

EXPERIMENTAL

Apparatus. The apparatus is shown schematically in Figure 1. The cell block, *A*, is formed by a cylinder of copper electrolytically plated with platinum, 10 cm. in diameter and 3 cm. high. The six cells on the top surface are 2 cm. in diameter and 1 cm. deep, and are placed at the corners of a regular hexagon. The center of each cell is 3.2 cm. away from the axis of the block. To the undersurface of the block, a 1-watt heater, *B*, is screwed. The ground-glass disk, *C*, is 12 cm. in diameter and 0.23 cm. thick, with plane parallel surfaces. The bottom

surface was carefully ground with 3-micron grain corundum. The aluminum disk, *D*, is 10 cm. in diameter and 0.5 cm. thick, and is connected by an arm to an externally rotatable spindle, *E*. The assembled apparatus, Figure 2, shows the relative positions of the components. The differential thermocouple, *H*, whose two elements are connected to the block, *A*, and to the disk, *D*, is a copper-constantan one which gives an e.m.f. of about 38 μv. per °C. and has a resistance of 4 to 5 ohms. The e.m.f. of the thermocouple is amplified by a driftless d.c. amplifier (not shown). A fluorescent lamp is arranged so that the halos on the ground glass are easily visible. The apparatus, except for the latter two components, is enclosed in a thermally insulated polyethylene vessel with a transparent Plexiglas cover.

Materials. All solvents and solutes used in this study were C. Erba pure products. Analytical checks were in agreement with the literature data for the pure products.

Procedure. Five solutions of the chosen standard substance in the appropriate solvent are prepared. Usually these are 0.20, 0.17, 0.14, 0.11, and 0.08*M*. Two milliliters of each are introduced into five of the cells in order of their molarity. The solution containing the substance of unknown molecular weight is introduced into the sixth cell. The unknown molarity must be within the range of the five known ones. The ground surface of the glass disk is attached to the cell block by placing silicone grease spots on three small symmetrical areas on the edge of the block. The heater is then switched on, and the temperature of the block slowly and uniformly rises to a temperature slightly above room temperature. The temperature difference, Δt, between the heated block and the cooling disk for obtaining the best measurements depends mainly on the boiling point of the solvent (b.p.). The following formula has been found empirically, and it is useful for solvents boiling in the range 40° to 120° C. and at a room temperature between 18° and 25° C.:

$$\Delta t = (0.0147)\,(\text{b.p.}) - 0.347$$

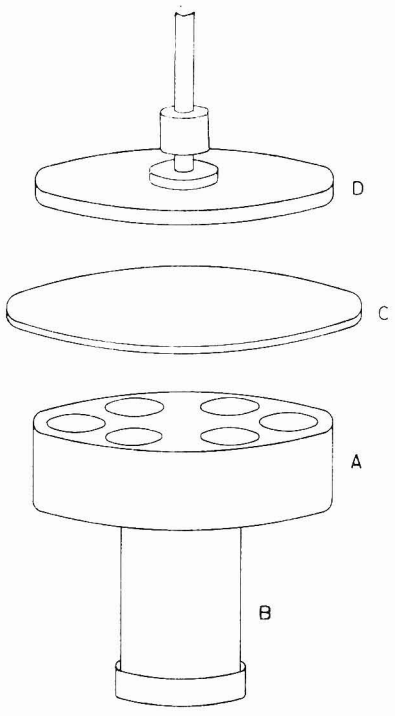


Figure 1. Schematic diagram of the dew-point apparatus for determining molecular weight

A. Cells bearing platinum-plated copper block
B. 1-Watt electric heater
C. Ground-glass disk
D. Aluminum cooling disk

At a uniform temperature and at equilibrium, in each cell the solvent is not present outside of the solution because its vapor pressure is greater than that of the solution. The solvent can be present in equilibrium with the solution only when its temperature is such that its vapor pressure is equal to that of the solution. To obtain this condition, the cooling disk is carefully put on the glass, with the external knob, and after 15 seconds it is raised and returned to the rest plate. Condensation halos of the solvent appear on the glass in correspondence to the cells and will tend to disappear as the glass disk gradually returns to the temperature of the block (Figure 3). From the time of disappearance of the first halo, corresponding to the solution of highest molarity, begin the measurements of the time of the consecutive disappearances of the other halos. If Δt has been appropriately chosen, the maximum disappearance time varies from 3 to 15 minutes except for the highest boiling solvents used (water, butanol) for which the time may be as much as 40 minutes. The halos can be made more visible if some form of appropriate lighting is provided and a lamp can accordingly be placed outside the vessel; reflections of light can be prevented by a black screen placed on the Plexiglas cover.

The disappearance times of the solutions of standard molarities are plotted against the molarity values; the disappearance time of the solution of unknown molarity, reported on the graph, will give by interpolation the value of molarity (Figure 4).

If the order of the molecular weight to be determined is completely unknown, preliminary tests can be made to find out the appropriate concentration range. For that, three standard solutions having molarities of 0.20, 0.10, and 0.05 are placed in three of the six cells, and the other cells are provided with solutions of the unknown product in concentrations varying by a known factor—for instance, 2. The described procedure is repeated several

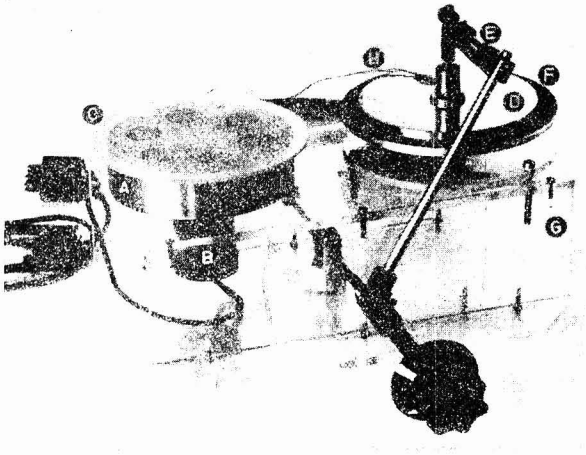


Figure 2. Main part of the dew-point apparatus

E. Spindle connected with the external knob
F. Rest support for cooling disk
G. Plexiglas base
H. Thermocouple

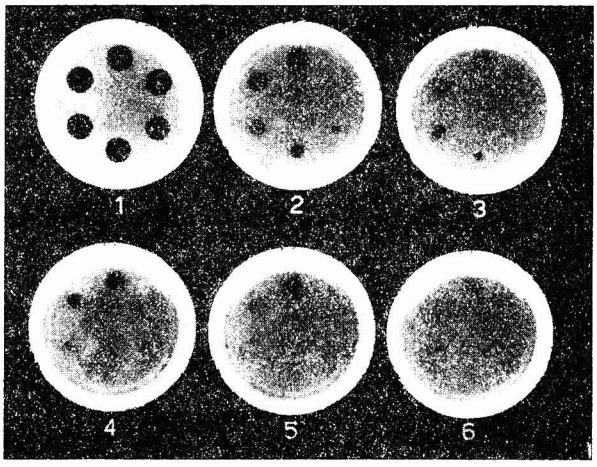


Figure 3. Example of disappearance of condensates of six solutions of various molarities

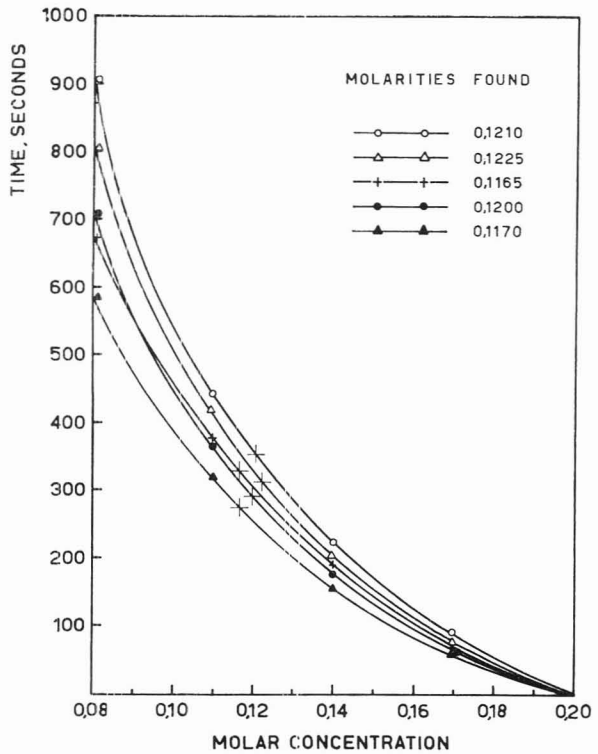


Figure 4. Example of five determinations of molecular weight of benzophenone in ethyl alcohol

For precision and accuracy data, see Table II

times with various concentrations of unknown product until the disappearance of at least one of the halos of the unknown solution occurs between two of the standard solutions.

RESULTS AND DISCUSSION

Determinations of molecular weight of different substances were made using 10 different solvents—namely, water, methanol, ethanol, butanol, methyl acetate, ethyl acetate, acetone, carbon disulfide, chloroform, and benzene. An appropriate reference substance was used for each solvent: urea for the first four, phenanthrene for the next five, and benzophenone for benzene. For each solvent, five solutions of known molarity varying from 0.2 to 0.08 of the reference substance were prepared. The molecular weight found is the mean of five consecutive determinations except in the case of methyl alcohol and ethyl alcohol, for which five determinations at one molarity (0.15) and five determinations at another molarity (0.12) were made. Figure 3 shows the curves for the determination of the molecular weight of benzophenone in ethyl alcohol (molarity 0.12) using urea as the reference substance. Table I gives all the values obtained in the determination of the molecular weight of three substances at two different molarities using methyl alcohol as solvent, and Table II gives the results for three substances using ethyl alcohol as solvent. The precision and accuracy data are also given in the tables. The relative standard deviation of the determinations is very low and the relative error for the molecular weights is in no case greater than 1.5%. The molecular weights obtained for some substances in other solvents are given in Table III. For the most of them the relative error is less than 3%; only occasionally it is greater. As in these last cases the relative standard deviation is never greater than ±2%, the fact that the relative error is greater than 3% can be attributed to phenomena of association. In fact, these discrepancies lead to molecular weights greater than the theoretical ones.

The sensitivity of the method depends mainly upon the smallest thickness of condensate which can be perceived on the glass disk. This thickness is approximately of the order of wavelengths in the visible range. Consequently, the amounts of heat required for evaporation and condensation are small, relative to the thermal capacities of the system, and therefore they cause substantially no disturbances to the regular pattern of heating and cooling of the glass. The thermal capacity of a glass disk weighing about 80 grams is

Table I. Determination of the Molecular Weight of Some Substances in Methyl Alcohol at Two Different Molarities

Standard reference substance: urea

Substance	Molarity Theor.	Molarity Found		Molarity Theor.	Molarity Found	
Benzoic acid	0.150		0.1490	0.120		0.1195
			0.1475			0.1215
			0.1485			0.1210
			0.1485			0.1200
			0.1475			0.1215
		Mean	0.1482		Mean	0.1207
		Rel. std. dev.	±1.5%		Rel. std. dev.	±1.3%
Mol. wt. 122.12		Mol. wt. calcd.	123.60		Mol. wt. calcd.	121.41
		Rel. error	+1.2%		Rel. error	−0.6%
p-Nitrobenzaldehyde	0.150		0.1495	0.120		0.1205
			0.1490			0.1200
			0.1510			0.1185
			0.1490			0.1175
			0.1500			0.1235
		Mean	0.1497		Mean	0.1200
		Rel. std. dev.	±1.1%		Rel. std. dev.	±1.8%
Mol. wt. 151.12		Mol. wt. calcd.	151.42		Mol. wt. calcd.	151.12
		Rel. error	+0.2%		Rel. error	0.0%
Benzophenone	0.150		0.1510	0.120		0.1237
			0.1500			0.1225
			0.1510			0.1220
			0.1522			0.1180
			0.1507			0.1218
		Mean	0.1510		Mean	0.1216
		Rel. std. dev.	±1.5%		Rel. std. dev.	±1.3%
Mol. wt. 182.21		Mol. wt. calcd.	181.01		Mol. wt. calcd.	179.80
		Rel. error	−0.7%		Rel. error	−1.3%

Table II. Determination of the Molecular Weight of Some Substances in Ethyl Alcohol at Two Different Molarities

Standard reference substance: urea

Substance	Molarity Theor.	Molarity Found		Molarity Theor.	Molarity Found	
Methylurea	0.150		0.1495	0.120		0.1200
			0.1500			0.1190
			0.1485			0.1175
			0.1485			0.1175
			0.1475			0.1165
		Mean	0.1488		Mean	0.1181
		Rel. std. dev.	±1.1%		Rel. std. dev.	±3.0%
Mol. wt. 74.08		Mol. wt. calcd.	74.63		Mol. wt. calcd.	75.22
		Rel. error	+0.7%		Rel. error	+1.5%
Tartaric acid	0.150		0.1510	0.120		0.1172
			0.1520			0.1200
			0.1525			0.1220
			0.1525			0.1200
			0.1475			0.1205
		Mean	0.1511		Mean	0.1199
		Rel. std. dev.	±1.8%		Rel. std. dev.	±2.2%
Mol. wt. 150.09		Mol. wt. calcd.	148.99		Mol. wt. calcd.	150.09
		Rel. error	−0.7%		Rel. error	0.0%
Benzophenone	0.150		0.1490	0.120		0.1210
			0.1500			0.1225
			0.1475			0.1165
			0.1490			0.1200
			0.1485			0.1170
		Mean	0.1488		Mean	0.1194
		Rel. std. dev.	±3.0%		Rel. std. dev.	±2.3%
Mol. wt. 182.21		Mol. wt. calcd.	183.67		Mol. wt. calcd.	183.12
		Rel. error	+0.8%		Rel. error	+0.5%

Table III. Accuracy Data in the Determination of Molecular Weights of Some Substances in Eight Different Solvents

Solvent	Standard substance	Solute	Molecular weight Theoretical	Molecular weight Found	Relative error, %
Water	Urea	Methyl urea	74.08	76.4	+3.1
		Tartaric acid	150.09	160.1	+6.7
		Glucose	180.15	174.9	−2.9
Butyl alcohol	Urea	Methyl urea	74.08	74.5	+0.5
		Benzil	210.22	205.5	−2.2
Methyl acetate	Phenanthrene	Benzoic acid	122.12	122.7	+0.5
		p-Nitrobenzaldehyde	151.12	155.2	+2.7
		Azobenzene	182.22	184.1	+1.0
		Benzil	210.22	216.1	+2.8
Ethyl acetate	Phenanthrene	*p*-Nitrobenzaldehyde	151.12	155.9	+3.2
		Benzophenone	182.21	183.7	+0.8
		Benzil	210.22	211.2	+0.5
Acetone	Phenanthrene	Benzoic acid	122.12	121.8	−0.3
		p-Nitrobenzaldehyde	151.12	156.4	+3.5
		Benzil	210.22	205.8	−2.1
Carbon disulfide	Phenanthrene	Azobenzene	182.22	188.4	+3.4
		Benzophenone	182.21	189.8	+4.2
		Benzil	210.22	218.1	+3.7
Chloroform	Phenanthrene	*p*-Nitrobenzaldehyde	151.12	153.2	+1.4
		Benzophenone	182.21	184.9	+1.5
Benzene	Benzophenone	Phenanthrene	178.22	181.6	+1.9
		Benzil	210.22	212.7	+1.2

approximately 15 to 20 cal. per °C.; with the most unfavorable solvent such as water, the quantity of condensate—6 disks of 2-cm. diameter and 0.5 micron or less of thickness—is 1 25 mg., and the heat exchanged in the distillation is ≤ 0.75 cal.

For an accurate determination, the cooling of the glass must be carefully controlled; over-cooling leads to the formation of drops while, if cooling is poor, condensation could not happen. For an accurate measure of the temperature difference between the cells-bearing block and the cooling disk, a system of thin differential thermocouples is used. They are connected to an indicating instrument via a chopper amplifier and a lock-in detector which readily indicates temperature changes of the order of 0.05° C. The temperature difference between the copper block and the cooling disk has been standardized for the various solvents.

The condensation and evaporation of thin films of liquid on a solid surface depend principally upon the nature of previous treatments of the surface. Cleanliness is extremely important and in the absence of this condition, the measurements give abnormal results.

The ground glass must be in good contact with the block. This provides a hermetic closure and ensures that the temperature distribution over the glass during the thermal cycle is such that the solvent halo gradually and regularly decreases in diameter and disappears (Figure 2).

The measurements can be easily reproduced on the same solutions as many times as desired and all the solutions can be recovered unaltered at the end of the experiment.

The method has been applied to the determinations in the range of molecular weights below 500. No experiments have been carried out for high molecular weight substances, but the range of concentrations used seems to indicate a limitation.

ACKNOWLEDGMENT

The authors thank G. G. Gallo for helpful discussions and Sergio Terni for technical assistance.

LITERATURE CITED

(1) Bonnar, R. U., Dimbat, M., Stross, F. H., "Number-Average Molecular Weights," Interscience, New York, 1958.
(2) Dimbat, M., Stross, F. H., ANAL. CHEM. 29, 1517 (1957).
(3) Knight, A., Wilknis, B., Davies, D. K., Sicilio, F., *Anal. Chim. Acta* 25, 317 (1961).
(4) Müller, R. H., Stolten, H. J., ANAL. CHEM. 25, 1103 (1953).
(5) Newmayer, J. J., *Anal. Chim. Acta* 20, 519 (1959).
(6) Simons, E. L., ANAL CHEM. 30, 979 (1958).
(7) Wilson, A., Bini, L., Hofstader, R., *Ibid.*, 33, 135 (1961).

RECEIVED for review January 23, 1963. Accepted April 12, 1963.

The Use of Perchloric Acid in Propellants Analysis

J. B. MACORKINDALE and J. J. LAMOND

Chemical Inspectorate, Royal Arsenal, Woolwich, London, S.E. 18, England

▷ The uses of perchloric acid in the propellants laboratory are described. Simple, rapid, and precise determinations of lead, aluminum, copper, and potassium can be made on the resulting solutions and the estimation of sulfate in nitrocellulose is similarly expedited. Long experience has shown the procedure described to be without special hazard.

IN THE MANUFACTURE of propellants based on nitrocellulose, inorganic salts, metallic powders, and metallo-organic compounds are being used increasingly to obtain the desired ballistic characteristics. Usually such constituents are present in the propellant in minor proportions and their determination is rendered difficult by the preponderance of organic matter present. There are three common procedures for achieving separation of the inorganic matter: dissolution of the organic matter in a suitable organic solvent, wet oxidation of the organic matter with nitric-sulfuric acid, and controlled ashing of the propellant.

Of these methods, the first is unsuitable for metallo-organic compounds and, in addition, may be time consuming. Up to 24 hours may be required to accomplish solution, depending on the nature of the propellant and the solvent used. The second method requires several hours for complete oxidation and, if evaporation to dryness and ignition are necessary, errors due to volatilization and mechanical loss are liable to occur. In addition, if lead or barium salts are present the formation of insoluble sulfates may be undesirable. The third method takes about the same time as the second and, again, errors due to volatilization and mechanical loss are possible.

A new procedure described below, involving the oxidation of the propellant with hot perchloric acid, offers advantages over each of these methods. It is rapid, and complete oxidation is achieved in approximately 1 hour. The temperature of the reaction is controlled by the formation of the perchloric acid azeotrope (72.5%) which boils at 203° C.; thus, errors due to volatilization are minimized. For the determinations described, evaporation to dryness is unnecessary and errors due to mechanical loss are much less likely.

Although perchloric acid has long been known as a powerful oxidant under suitable conditions, its application has been restricted because of the hazards associated with its use. However G. F. Smith in several papers (*2*, *4*, *5*) has reported on the safe use of the acid as an oxidant in analytical chemistry. In addition, a report of the Analytical Methods Committee of the Society for Analytical Chemistry on the properties and precautions for use of the acid has been published (*1*).

The initial attraction of using perchloric acid as an oxidant was its suitability as a base electrolyte in the polarographic determination of lead. Preliminary tests showed that single- and double-base propellants could be safely oxidized with a 60% (w./w.) perchloric acid solution, the presence of nitric esters apparently assisting the oxidation process. The water-clear solutions obtained are suitable for the determination of several inorganic constituents in addition to lead, and various applications of the oxidation procedure are summarized below.

EXPERIMENTAL

Oxidation of Propellant. Both single-base (nitrocellulose only) and double-base (nitrocellulose and nitroglycerine) propellants can be dealt with satisfactorily by this procedure.

The quantity of propellant used depends on the concentration of the constituent to be determined, but amounts up to 10 grams of sample, either ground or chopped into pieces about 0.1-inch on a side, have been destroyed. Volumes of 60% (w./w.) perchloric acid solution suitable for the oxidation of various weights of propellant are as follows:

Wt. of sample, g.	Vol. of acid, ml.
1	10
2	15
5	20
10	50

The oxidation can be carried out in any suitable glass vessel, and conical flasks closed with filter funnels as splash traps, or beakers closed with clock-glasses have been used successfully. To carry out the oxidation, transfer the weighed quantity of sample to the vessel, add the requisite volume of 60% (w./w.) perchloric acid solution, and close the mouth of the vessel with a filter funnel or clock-glass. Place the vessel on a hot plate and heat until the initial reaction is about to start—i.e., the first traces of nitrous fume appear. At this point the sample, if ground, is almost completely in solution or, if chopped, is visibly reacting with the acid. Remove the vessel from the hot plate until the vigorous reaction has subsided, then replace it and allow the solution to boil briskly until it clears and is fuming strongly (20 to 30 minutes). In the destruction of 5- and 10-gram samples, considerable charring occurs and prolonged boiling is required to oxidize the charred matter. Under these conditions, the oxidation of the charred matter can be considerably hastened by the addition of 5 to 10 ml. of concentrated nitric acid before replacing the vessel on the hot plate. Allow the solution to cool, wash down the cover and sides of the vessel with water and reboil the solution for 2 minutes to remove any free chlorine formed during the oxidation reaction. Allow the diluted solution to cool when it is ready for use in the following determinations:

Lead. The lead content may be determined either by polarography or by complexometric titration with EDTA. For the polarographic determination, it is only necessary to dilute the perchloric acid solution to a known volume, transfer a portion of the solution to a cell, de-gas by passing nitrogen through the solution and reduce between −0.3 volt and −1.1 volts. In the complexometric titration, a measured excess of 0.02*M* EDTA is added, the acid solution is neutralized with strong sodium hydroxide solution (40%) using bromothymol blue as indicator, and buffered to pH5. The excess EDTA is titrated with a 0.02*M* lead nitrate solution with xylenol orange as indicator.

Lead and Aluminum Mixtures. In these mixtures, aluminum does not interfere in the polarographic determination of lead and the complexometric titration described above may be used to determine the lead plus aluminum content of the solution. Alternatively, the lead content can be determined separately by EDTA titration, the aluminum being complexed with acetyl acetone (*3*) before direct titration of the lead with standard EDTA solution, using xylenol orange as indicator.

Lead and Copper. Both of these metals can be determined polarographically. After carefully neutral-

Table I. Recovery of Lead from Propellant

Pb, mg. Added	Pb, mg. Recovered	Recovery, %
30.0	30.1	100.3
30.0	30.7	102.3
30.0	29.5	98.3
30.0	30.1	100.3
	Mean =	100.3

sample solution (usually about 0.5 ml. of 60% (w./w.) perchloric acid in 100 ml.). If the potassium salt is present in relatively high concentration, it may be determined as the perchlorate in the usual way.

Alternatively, the sodium tetraphenylboron method may be used after suitable dilution of the acid solution.

Sulfate. The sulfate content may be determined by precipitation as barium sulfate from the perchloric acid solution. After oxidation, the acid solution is evaporated, if necessary, to about 10 ml. and then diluted to about 300 ml. Hot barium chloride solution is added to the boiling solution to precipitate the sulfate. The determination is completed in the standard manner.

The sulfate content of ungelatinized nitrocellulose may also be determined in this way after destruction of the organic matter with perchloric acid, but as a consequence of the large surface area of the fibers the reaction with 60% acid is excessively rapid and 30% acid is therefore used. Perchloric acid, 30% (w./w.) strength (40 ml.), is added to the sample (5 grams) and the mixture heated on the hot plate. After an initial charring, a further reaction takes place with considerable frothing. When this reaction has ceased, the solution is boiled gently until it is clear. It is allowed to cool slightly, then is diluted with water and the sulfate precipitated as barium sulfate, as described above. The perchloric acid remaining in the solution does not interfere with the gravimetric determination of the barium sulfate.

Note. All of the above procedures have been widely used in the U.K. for several years without incident. No hazard is associated with this use of perchloric acid, providing that certain precautions are taken. These precautions include the following, which summarize the relevant points in the references (*1*, *2*, *4*, *5*):

Wear a face shield when using the acid in laboratory procedures. Store the acid in glass-stoppered bottles standing in dishes of some nonflammable and nonabsorbent material—e.g., glass or porcelain. Dilute spilled acid with water and wipe up with swabs of nonflammable material, such as wool waste. Thoroughly rinse the swabs after use. Do not use cotton wool or other cellulose materials. Dilute with water any acid that has become discolored and wash down the drain with plenty of water. Carry out reactions using this acid in a well ventilated fume cupboard free from accumulations of dirt and dust. Examine the woodwork of the fume cupboard occasionally. A splinter placed on a hot plate will indicate whether or not the wood has become unduly flammable. Readily oxidizable cements, such as those made from litharge and glycerine, must not be used to seal cracks in fume cupboards. Pastes of Alundum cement and sodium silicate, or similar materials, are satisfactory.

Table II. Determination of the Lead Content of Propellant

Method	Sample	No. of replicates	Pb, mean %	Standard deviation
Polarographic	*A*	9	1.78	±0.028
	C	6	0.42	±0.030
Volumetric	*B*	6	1.49	±0.006
Gravimetric	*B*	6	1.48	±0.006
	C	6	0.48	±0.020

Table III. Volumetric Determination of Lead and Aluminum in Propellant

	Lead			Aluminum		
Sample	No. of replicates	Mean %	Standard deviation	No. of replicates	Mean %	Standard deviation
D	6	1.74	±0.008	7	2.82	±0.018
E	9	2.46	±0.020	4	2.72	±0.017
F	3	2.31	±0.017	6	7.00	±0.016

izing the acid solution with sodium hydroxide, the solution is made up to a known volume. After de-gassing, copper is determined by reducing between −0.1 volt and −0.9 volt. Lead can be determined in the same portion of solution after compensating for the copper wave and polarographing between −0.6 and −1.2 volts.

Potassium. The potassium content of the propellant may be determined by flame photometry after suitable dilution of the perchloric acid solution. In this procedure, the instrument should be calibrated against standard solutions of the same acidity as the

Table IV. Polarographic Determination of Lead and Copper

Sample	Pb, %	Cu, %
G	0.40, 0.39	1.49, 1.49
H	0.43, 0.44	1.59, 1.58

Table V. Determination of Potassium in Propellant

Sample	Method	No. of replicates	KNO_3, mean %	Standard deviation
I	Standard method	6	1.40	±0.096
I	Flame photometry	6	1.32	±0.020

DISCUSSION AND RESULTS

The method described above for the polarographic determination of lead proved to be very rapid, taking 60 to 90 minutes to complete compared with the 6 to 7 hours required for the standard gravimetric method in which the propellant is destroyed with nitric-sulfuric acid and the lead determined gravimetrically as the sulfate. The results in Table I indicate the accuracy of the polarographic method.

The volumetric determination of lead using EDTA was later adopted in place of the polarographic method and takes about the same time to complete. A comparison of the precision of these methods is shown in Table II.

The precision of the EDTA method used for mixtures of lead and aluminum in propellant is shown in Table III.

Table VI. Gravimetric Determination of Sulfate in Nitrocellulose

Method	No. of replicates	H_2SO_4, mean %	Standard deviation
Nitric acid	6	0.12	±0.017
Perchloric acid	6	0.12	±0.000

The use of lead and copper salts in propellant compositions is fairly new and only a limited amount of work has been carried out. The polarographic procedure described can be carried out in 2 to 2½ hours and seems particularly applicable because of the small amount of lead present. Typical results are shown in Table IV.

In the most frequently used standard method for the determination of potassium, a pyridine solution of the propellant is ashed under controlled conditions and an aqueous extract of the sulfated residue is reduced. The time taken for this procedure is 10 to 12 hours compared with about 3 hours for perchloric acid oxidation and the flame photometric method. A comparison of the results by the two methods is made in Table V.

It takes some 4 hours to obtain a solution suitable for the precipitation of barium sulfate when the standard method for the determination of sulfate in nitrocellulose is employed. The sample is destroyed by oxidation of the sample with nitric acid and sodium chlorate, after which the nitric acid is removed by evaporation. The use of perchloric acid reduces this time to 1 hour, the results obtained by both methods being shown in Table VI.

LITERATURE CITED

(1) *Analyst* 84, 214 (1959).
(2) Diehl, H., Smith, G. F., *Talanta* 2, 209 (1959).
(3) Jablonski, W. Z., Johnson, E. A., *Analyst* 85, 297 (1960).
(4) Smith, G. F., *Anal. Chim. Acta* 8, 397 (1953).
(5) Smith, G. F., *Analyst* 80, 16 (1955).

RECEIVED for review December 3, 1962. Accepted April 11, 1963.

Rapid Titrimetric Determination of Orthophosphate with Cerous Ion

Applications to Technical Grade Inorganic Phosphates

T. A. TAULLI and R. R. IRANI

Research Department, Inorganic Chemicals Division, Monsanto Chemical Co., St. Louis, Mo.

▷ A sensitive and rapid volumetric titration procedure is described for the determination of macro and semimicro amounts of orthophosphate. Orthophosphate titration with cerous ion in a buffered medium at pH 7.0 to 9.5, using Eriochrome Black T indicator affords a visual colorimetric endpoint. Concentrations as low as 0.4 μg. per ml. of phosphorus have been measured. Accuracy at the 95% confidence limits of ±0.38% phosphorus (absolute) for pure and industrial grade orthophosphates containing 8 to 26% phosphorus has been obtained; corresponding precision was found to be ±0.24%. Interference studies with typical ions were conducted. Excluding polyphosphate anions, cation interference, especially ferric ion, was more serious than anion interferences.

PRIOR to analysis, the phosphorus in chemicals is normally converted to orthophosphate. For example, in analyzing a polyphosphate mixture, the individual polyphosphate species are separated using paper chromatography (*2*) or ion exchange (*1*, *7*). After separation, the polyphosphates are hydrolyzed to the ortho form and analyzed. Literature affords numerous methods for analyzing the orthophosphate ion. Gravimetrically, the following precipitation agents have been reported: magnesia mixture, iron chloride, and ammonium acetate (*9*, *16*), zirconyl chloride (*17*), ammonium molybdate (*18*), and quinoline molybdate (*10*, *19*, *20*). In most cases, the precipitates can be weighed and/or dissolved and titrated to give a measure of the phosphate content. The solutions of yellow molybdovanado and blue molybdenum complexes with orthophosphate have been measured spectrophotometrically (*5*, *6*). Each technique offers its own unique advantage, but, in all cases, none can be performed in less than 15 minutes. A more rapid method with at least comparable accuracy for direct phosphate determinations would indeed be advantageous.

The basic principle of a volumetric determination of orthophosphate via the precipitation of the orthophosphate by cerous(III) ion in a weakly alkaline medium was originated and reported by Püschel and coworkers (*11*, *12*). However, few details were available from this brief abstract concerning the procedure, foreign ion interferences, accuracy and precision.

Our work was initiated to gain quantitative data of the characteristics of the method. Specifically, the present study was designed to include the quantitative effects of possible interferences of common occurring impurities, examine the accuracy at various sensitivity levels, and test the application to industrial grade inorganic phosphates.

EXPERIMENTAL

Reagents. Analytical grade chemicals, as received, were used in the preparation of reagent solutions. Doubly distilled water was used for all reagents and sample dilutions.

Buffer Solution. Dissolve 67.5 grams of ammonium chloride in 300 ml. of water, add 570 ml. of concentrated ammonium hydroxide, and dilute to a liter. Store in a polyethylene bottle.

Eriochrome Black T Indicator. Commercially prepared solution (Fisher Scientific Co., St. Louis, Mo.).

Potassium Phosphate (Monobasic). Primary standard reagent.

Hydroxylamine Hydrochloride. Reagent grade, crystals.

Cerrous(III) Solution, 0.05*M*. Dissolve 27.5 grams of purified cerium(IV) ammonium nitrate in approximately 400 ml. of water containing 2 ml. of concentrated nitric acid. Add hydroxylamine hydrochloride until the yellow solution becomes colorless. Add 4 to 5 grams in excess. Dilute with water to a liter. Filter the solution and standardize by the procedure recommended herein, using potassium phosphate, monobasic, primary standard reagent (oven dried at 110° C.).

Solution of Foreign Ions. For anion interference studies, weighed amounts of reagent grade salts were added to the phosphate solutions to be titrated to give an anion concentration of 0.1*M*. (In the case of sulfate study, proportionally lesser amounts were added as indicated.)

For the cation studies, the amount of salt solution added was equivalent to producing a 0.5 or 0.1 wt. % loading of cation based on the phosphate salt analyzed. (The lower level was used only for the ferric ion study.)

Apparatus. pH Meter. A Leeds & Northrup instrument with standard glass–calomel electrode assembly.

Semimicro Buret. 5 ml., 0.01-ml. subdivisions.

Magnetic Stirrer and Hot Plate. A combination stirrer hot plate can be conveniently used.

Procedure. The procedure described is applicable to aqueous solutions of orthophosphate.

Weigh a sample of appropriate size so that the subsequent solution will permit aliquots containing 5 to 15 mg. of phosphorus to be titrated with $5 \times 10^{-2}M$ cerous solution. For solutions initially containing less than 5 mg. of phosphorus, a proportionally diluted cerous solution should be used. Total titrations with either titrant are thus maintained at a 5- to 10-ml. level. Transfer the sample solution to a 100-ml. beaker, and dilute to 30 ml. with water and heat solution to boiling. Using a pH meter, adjust the pH of the solution with sufficient ammonium hydroxide buffer to maintain a pH range of 7.0 to 9.5 throughout the titration. For all samples analyzed in this laboratory, the addition of approximately 0.5 ml. of buffer to the solution being titrated was sufficient. If the pH of the sample solution is above 9.5, adjust accordingly with dilute nitric acid and then add the buffer solution.

Add 5 drops of Eriochrome Black T indicator solution to the heated sample. If the solution is within the proper pH range, the color of the solution will be blue. While the temperature is held between 60° to 90° C., the agitated, heated solution is titrated rapidly with the standardized cerous titrant, using a semimicro buret, until a permanent red solution color occurs. Prior to the end point, a transitory reddening of solution occurs; titration is continued until a permanent red color is observed.

A blank correction is necessary for optimum accuracy. This is obtained by titrating a 30-ml. portion of heated water, containing an identical amount of buffer and indicator solution. Appropriate calculations, depending on dilution factor and sample weight are used to express the phosphorus content of the sample.

RESULTS AND DISCUSSION

Volume and Temperature. All titrations were made in a maximum total solution volume of 30 ml. Minimizing the solution volume increased the magnitude of color change of the end point. Because a precipitate forms during the titration, sharper end points were observed when the titrations were conducted with heated and agitated solutions.

Effect of pH. During this investigation, it was found that proper solution pH was important for accurate results. The pH of the solution must be maintained between 7 to 9.5 throughout the titration. Above or below this level, a purplish color prevailed. Lowering the pH below 7, probably results in a breakdown of the Eriochrome Black T–cerium(III) chelate, and the reddish color of the indicator anion prevails. Above the upper pH level, hydrolysis of the chelate has been postulated (*13*) to occur as follows:

$$\text{Ce(III) Erio } T_n + 3H_2O \rightarrow \text{Ce(OH)}_3 + 3H^+ + n \text{ Erio T} \quad (1)$$

In an alkaline medium, $Ce(OH)_3$ is immediately oxidized by air to $Ce(OH)_4$. The latter oxidizes the dye to a red color which is almost irreversible.

Within proper pH limits of 7.0 to 9.5, the addition of only a slight excess of cerium(III) solution causes the (blue) Eriochrome Black T anion to form a chelate with the cerium(III) and cause a change from a blue to a permanent red color. Our use of a buffer and a pH meter serves to maintain the proper pH level and eliminate possible errors in misinterpreting the end point. Without continuous observance of pH, as described above, a red colored solution could be interpreted as an end point instead of an improper solution pH level.

Indicator and Blank Correction. Various forms of Eriochrome Black T indicator are available. Some advocate the use of dry mixes (*4*), others, liquid forms (*3*) to obtain increased sharpness of an end point or from the standpoint of indicator stability itself. Püschel (*15*) used a solids mixture of Eriochrome Black T–hexamethylene tetramine, 1:200 parts, respectively.

In effect, the hexamethylene tetramine in this mixture was used as a solid diluent for the indicator dye, to afford the use of a dry indicator. In Püschel's work, the solutions to be titrated were buffered by the addition of varying amounts of the same indicator diluent substance—i.e., hexamethylene tetramine. Since some excess cerium(III) is required to react with the indicator, thereby necessitating a blank correction, we found it more convenient to use the indicator in a solution form and to add a liquid, ammonium chloride–ammonium hydroxide, buffer. Accordingly, reproduction of the exact amounts of indicator and buffer used in the blank titration could be more readily accomplished.

Results. In Table I are given the results obtained by this method on reagent and industrial grade inorganic phosphates. Precision at the 95% confidence level for substances containing 8 to 26% phosphorus was found to be ±0.24% absolute; the agreement at the 95% confidence level with known values of pure salts, as well as results obtained independently by conventional methods, was found to be ±0.38% absolute for these same phosphorus levels.

Table I. Accuracy and Precision of Orthophosphate Method

Using $4.8 \times 10^{-2}M$ Ce^{+3} solution

Sample	P (known), %	P (analyzed),[a] %	Av. % P. analyzed − % P known
KH_2PO_4	22.71	22.55, 22.93, 22.88 22.81, 22.68	+0.06
KH_2PO_4[b]	22.71	23.13, 22.83, 22.84 22.70, 22.62	+0.11
KH_2PO_4[c]	22.39	22.54, 22.45	+0.10
K_2HPO_4	17.75	18.00, 17.88	+0.19
K_3PO_4	14.01	13.73, 13.81	−0.24
Na_2HPO_4	21.82	22.23, 21.99, 21.90	+0.22
NaH_2PO_4[c]	25.81	25.65, 25.90	−0.04
Na_3PO_4[c]	8.03	8.23, 8.29	+0.23
$(NH_4)_2HPO_4$[c]	23%	22.88, 22.79	−0.16

[a] Precision at 95% confidence level = ±0.24%.
[b] Using $4.8 \times 10^{-4}M$ Ce^{+3} solution.
[c] Industrial grades containing approximately 0.5% impurities. Values given in known column is obtained by volumetric ammonium molybdate precipitation method (*18*).

Table II. Sensitivity of Orthophosphate Method[a]

P, mg.			
Present[b]	Found	Deviation	Rel. error, %
13.1325	13.1454	+0.0129	+0.10
10.8743	10.9669	+0.0926	+0.85
0.1230	0.1233	+0.0003	+0.25
0.0615	0.0623	+0.0008	+1.30
0.0123	0.0129	+0.0006	+4.88

[a] Total volume of solution, 30 ml.
[b] Stock solution prepared with KH_2PO_4, primary standard reagent grade, oven dried, 100° C., from which aliquots were taken.

Data shown in Table II demonstrate the capability and accuracy of this volumetric method as applied to macro and semimicro amounts of orthophosphate. As little as 12 μg. of phosphorus was determined within a 5% relative error level; accuracy at the macro phosphorus levels was better than 1.0% relative. Titrant strengths of $5 \times 10^{-2}M$ were used in the 5- to 15-mg. phosphorus region, whereas $5 \times 10^{-4}M$ cerous solutions were used below the 5-mg. region.

The attractiveness of this cerous titration method, because of its combination of rapidity and accuracy, is further exemplified by its comparison with several conventional methods as shown in Table III. Conventional methods dictate the orthophosphate be isolated by a precipitating agent and subsequently determined either gravimetrically or the precipitate be dissolved and then titrated. In contrast, the cerous method affords a direct titration of the orthophosphate solution, requiring no isolation steps.

Table III. Comparison of Methods

Absolute Standard Deviation, % P

Method	Precision	Accuracy	Time of analysis, min.[a]
Cerous titration	±0.12	0.19	5
Molybdate precipitation/volumetric[b]	±0.20	0.3	25
Quinolium precipitation/volumetric[c]	±0.17	...	25
Quinolium precipitation/gravimetric[c]	±0.13	...	60

[a] Based on comparative time required for analysis after sample has been dissolved and/or converted to orthophosphate and appropriate dilution made.
[b] By method of Wilson (*18*).
[c] By methods of Perrin and Wilson (*10, 19, 20*).

Interference Studies. The diverse cations examined included ferric, aluminum, magnesium, and calcium. The concentration level chosen, 0.5% by weight cation of phosphate compound, was felt to represent the maximum amount that would be encountered in industrial grade orthophosphate salts. The amount of cations actually present in the aliquot titrated would be proportionately less depending on the dilution performed with the original phosphate compound. Data in Table IV show that only solutions containing iron(III) at this level gave values outside the experimental error. The maximum tolerable iron (III) level was found to be at about the 0.1% by weight iron(III) of the phosphate compound. In addition, it was noted that with solutions containing iron(III) and aluminum(III), additional indicator had to be added, due to the oxidizing effect of the iron(III) ion on the indicator and the preferential chelation of the aluminum(III) over the cerous phosphate ions. The presence of the iron(III) and aluminum(III) ions caused a less distinct end point. An appropriately larger blank correction was applied because of the additional indicator added. Likewise, the presence of the designated amounts of calcium ion caused the phosphate solutions to be initially red, instead of blue. However, as soon as some cerous phosphate precipitate was formed during the titration, the color of the solution reverted to the normal blue color prior to the red end point. Despite this occurrence, no appreciable error was observed.

The effect of the several anions when present as salts in concentrations as high as $0.1M$ in the solutions to be titrated is shown in Table IV. These levels correspond to a molar ratio of anion to orthophosphate ion of 10:1. Of the anions examined, only sulfate was found to interfere adversely at this high level. However, the sulfate ion could be tolerated where its molar ratio to orthophosphate ion was 1:1. The positive sulfate interference could possibly be due to the formation of relatively stable cerium(III)–sulfate complex.

One disadvantage of the present method is that polyphosphates interfere. Thus, if pure polyphosphate salts are analyzed, without a hydrolysis step, the per cent phosphorus content was found to be only 20 to 60% of the true value. Therefore, it can be concluded that with the present method, the polyphosphate level in orthophosphate gives corresponding errors in the analysis. Indeed, Mayer and Schwartz (*8*) have reported that cerous ion associates with other phosphates as well as with the orthophosphate ion.

From the interference studies reported here, it could be generally postulated that any cation or anion which would complex or oxidize the indicator, or precipitate as the phosphate at the defined pH range would cause some degree of interference to the procedure. Likewise, diverse colored ions are undesirable. However, interfering ions, especially di- and trivalent metals, could be removed by ion exchange techniques (*14*). The method, as described, was evaluated with several inorganic orthophosphate compounds. However, the method, no doubt, could be extended to many other phosphorus-bearing materials providing the proper preliminary steps of ortho conversion and critical examination of possible interferences are applied.

Thus, in the phosphate industry, the cerous method should be useful in analyzing for total phosphorus content in inorganic as well as organic phosphorus compounds. In the analysis of mixtures of polyphosphates, the cerous method is recommended in analyzing the ion exchange or paper chromatographic phosphate fractions.

Table IV. Effect of Foreign Ions on Cerous Orthophosphate Method[a]

Foreign salt	P, mg. Added	Present	Found	Deviation	Rel. error, %
		Anion interference[b]			
NaCl	175	12.71	12.57	−0.14	−1.10
$NaNO_3$	255	12.71	12.61	−0.11	−0.86
$NaC_2H_3O_2$	246	12.71	12.67	−0.04	−0.31
Na_2SO_4 (anhyd.)	426	12.71	13.63	+0.92	+7.24
	213	12.71	13.49	+0.78	+6.14
	43	12.71	12.94	+0.23	+1.81
NaF	57	11.61	11.74	+0.13	+1.12
$Na_2HAsO_4 \cdot 7H_2O$	28	12.71	12.60	−0.11	−0.86
Na_4SiO_4	26	11.68	11.86	+0.18	+1.54
		Cation interference[c]			
$FeCl_3 \cdot 6H_2O$	1.3	12.16	11.50	−0.66	−5.43
	0.2[d]	10.24	9.89	−0.35	−3.42
$AlCl_3 \cdot 6H_2O$	2.3	12.04	11.78	−0.26	−2.16
$Mg(C_2H_3O_2)_2 \cdot 4H_2O$	2.6	13.10	12.79	−0.31	−2.37
$Ca(NO_3)_2 \cdot 4H_2O$	1.5	11.61	11.74	+0.13	+1.12

[a] Total volume of solution, 30 cc.; stock solutions prepared with KH_2PO_4, primary standard reagent, oven dried 110° C.
[b] Foreign salts added equivalent to $0.1M$ in anion concentration in solution during titration. Successively lower concentrations of 0.05 to $0.01M$, respectively, used for sulfate study.
[c] Equivalent to 0.5% by weight cation of phosphorus compound in stock solution.
[d] Equivalent to 0.1% by weight ferric ion of phosphorus compound in stock solution.

LITERATURE CITED

(1) Beukenkamp, J., Rieman, W., III, Lindenbaum, S., ANAL. CHEM. 26, 505 (1954).
(2) Crowther, J., *Ibid.*, p. 1383; see also E. Karl-Kroupa, 28, 1091 (1956).

(3) Diskant, E. M., *Ibid.*, **24**, 1856 (1952).
(4) Flaschka, H., Schöniger, W., *Z. Anal. Chem.* **133**, 321 (1951).
(5) Hill, U. T., ANAL. CHEM. **21**, 589 (1949).
(6) Hirata, A. A., Appleton, D., *Ibid.*, **31**, 2097 (1959).
(7) Kolloff, R. H., *Ibid.*, **33**, 373 (1961).
(8) Mayer, S. W., Schwartz, S. D., *J. Am. Chem. Soc.* **72**, 5106 (1950).
(9) Mohr, F., *Z. Anal. Chem.* **2**, 250 (1863).
(10) Perrin, C. H., *J. Assoc. Offic. Agr. Chemists* **42**, 567 (1959).
(11) Püschel, R., *Angew. Chem.* **73**, 76 (1961).
(12) Püschel, R., *Mikrochim. Acta* (Vienna), **1960**, 352.
(13) Püschel, R., University of Graz, Austria, private communication, 1962.
(14) Püschel, R., Lassner, E., *Z. Anal. Chem.* **174**, 1 (1960).
(15) Püschel, R., Wittman, H., *Mikrochim. Acta* (5–6), 670 (1960).
(16) Raewsky, V., *Compt. Rend.* **224**, 681 (1947).
(17) Stumper, R., Mettlelock, P., *Ibid.*, p. 122.
(18) Wilson, C. L., Wilson, D. W., "Comprehensive Analytical Chemistry," Vol. 1, 608, Elsevier, New York, 1960.
(19) Wilson, N. H., *Analyst* **76**, 65 (1951).
(20) *Ibid.*, **79**, 535 (1954).

RECEIVED for review September 28, 1962. Accepted April 29, 1963.

Assay of Aziridinyl Compounds

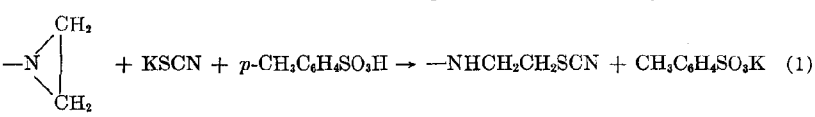
R. C. SCHLITT

Methods Development Section, Chemical and Materials Laboratory, Aerojet-General Corp., Sacramento, Calif.

▶ **Methanol-soluble aziridinyl compounds can be assayed by reacting with excess thiocyanic acid, generated in situ from potassium thiocyanate and *p*-toluene sulfonic acid, and back-titrating with methanolic potassium hydroxide. This procedure is fast, easily performed, and does away with the heterogeneous reaction between water-insoluble aziridinyl compounds and aqueous reagents. A precision of 0.065 was attained.**

WITH A GROWING INTEREST in aziridinyl compounds for the production of resins and polymers, there is a need for better methods to assay these starting materials. The literature describes procedures for the analyses of aziridines; however, limitations are encountered with each method. The kinetics of reactions of ethylenimines with thiophenol (*3*) and with substituted benzoic acids (*4*) were followed by infrared spectrometry and conductometric titrations. These reactions are slow and not useful in determining the purity of ethylenimines. Two colorimetric methods were developed (*2*, *5*) to determine the amounts of substituted ethylenimines. Ethylenimine derivatives were also assayed (*1*) by treatment with sodium thiosulfate in acid solution and back-titrating with base. The latter methods have the disadvantage of being time consuming, and many aziridinyl compounds are only slightly soluble in water which complicates their analysis with aqueous reagents.

To overcome these disadvantages a new method was developed that employs a methanol solvent, and a potassium thiocyanate–*p*-toluene sulfonic acid solution to open the aziridinyl ring. The reaction is:



$$\text{—N(CH}_2\text{CH}_2\text{)}_2 + \text{KSCN} + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} \rightarrow \text{—NHCH}_2\text{CH}_2\text{SCN} + \text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{K} \quad (1)$$

where one equivalent of acid is used to open one ring. The remaining acid is back-titrated with methanolic potassium hydroxide. This method is an improvement over the sodium thiosulfate method in that the methanol solvent dissolves both the organic and inorganic materials and the reaction is faster. The amount of excess acid added is not critical for thiocyanate ion, although it is with thiosulfate ion, which is decomposed by strong acids.

The procedure described in the experimental section, is a general method that can be applied to assay a number of aziridinyl compounds. Table I shows the results of the analysis of various compounds. Tris-1-(2-methyl)-aziridinylphosphine oxide is soluble in water, and the analysis was also determined by the thiosulfate method so a comparison of methods could be made. The other compounds are not water-soluble, therefore were not assayed by the thiosulfate procedure. The data show the precision of the determinations.

EXPERIMENTAL

Reagents. Potassium hydroxide, dissolved in ACS grade methanol, 0.1*N*, standardized against potassium acid phthalate.

Potassium thiocyanate solution, 160 grams dissolved in enough ACS grade methanol to make 1 liter.

p-Toluene sulfonic acid reagent, 73.2 grams of the monohydrate in 50 ml. of distilled water and enough methanol to make 1 liter. The water was added to suppress the formation of methyl sulfonate.

The indicators that were found to be satisfactory in the analysis of compounds in Table I are: bromothymol blue, potassium salt of phenol red, and a mixed indicator made by mixing equal portions of bromothymol blue and phenol red solutions. These indicators were made up as 0.1% solutions in methanol.

Apparatus. The ring-opening reaction and titration were conducted in a 250-ml. Erlenmeyer flask equipped with a magnetic stirrer. A 2-hole cork, holding a nitrogen purging tube, was fitted in the flask so the 50-ml. buret tip could easily pass into the flask.

Procedure. A 2.5-meq. sample, weighed to the nearest 0.1 mg., was dissolved in a solution of 50 ml. of potassium thiocyanate and 10.00 ml. of *p*-toluene sulfonic acid. The mixture was stirred for a moment under a nitrogen purge, 6 drops of the proper indicator added, and the mixture back-titrated with standard methanolic potassium hydroxide. The indicator, for each compound, was selected by doing the determination potentiometrically, and choosing the one that changes color with the potentiometric break.

A blank was determined by the procedure above with the omission of the sample.

DISCUSSION AND RESULTS

Potentiometric titrations of the blanks frequently show two potentiometric breaks. As the *p*-toluene sulfonic acid reagent ages, the two breaks become more noticeable. Also, upon increasing the water to methanol ratio for the reagent, the number of milliliters of base consumed between the first and second break becomes smaller. These observations were interpreted to mean that: methyl *p*-toluene sulfonate is being formed by the reaction of *p*-toluene sulfonic acid with the methanol solvent. The use of fresh or old reagent has little effect on the determination of aziridines. The only difference noted, when using old reagent, was that the color change of the indicator at the equivalence point was not as pronounced as with fresh reagent.

Some grades of *p*-toluene sulfonic acid contain trace amounts of iron. This

Table I. Assay of Aziridinyl Compounds

Compounds	Method	Indicator	Assay	Average	Std. dev.
Tris-1-(2-methyl)aziridinyl-phosphine oxide	Thiosulfate	Potentiometric	96.79 97.49 96.98 97.32 97.35	97.18	±0.290
Tris-1-(2-methyl)aziridinyl-phosphine oxide	Thiocyanate	Bromothymol blue	96.20 96.17 96.18 96.15 96.09	96.15	±0.042
Phenyl-bis-1-(2-methyl)-aziridinylphosphine oxide	Thiocyanate	Mixed	91.68 91.82 91.35 91.62 91.53	91.60	±0.175
Trimesoyl-1-(2-ethyl)-aziridine	Thiocyanate	Phenol red	84.72 85.05 84.94 85.23 85.30	85.04	±0.232
Tris(2-methyl)aziridinyl-triazine	Thiocyanate	Bromothymol blue	87.72 87.77 87.55 87.81 87.71	87.71	±0.099

gives a pink color when added to the potassium thiocyanate solution. The color causes no difficulty in the determination and actually helps to anticipate the end point. When a pink color develops, the procedure is changed so that the mixture is titrated without the indicator until near the end point, where the pink color begins to fade. The indicator is then added and the titration continued.

For the samples assayed, the only reaction time necessary before back-titrating with base is a short mixing period of approximately 20 seconds.

Frequently a precipitate of potassium *p*-toluene sulfonate will form upon the addition of *p*-toluene sulfonic acid to potassium thiocyanate; however, the salt does not interfere with the determination.

The average value for the analysis of tris-1-(2-methyl)aziridinylphosphine oxide is higher when analyzed by the thiosulfate method than when analyzed by the thiocyanate method. An explanation for the difference is that thiosulfate is decomposed in acid solution with the loss of hydrogen ion, as a result of hydrogen sulfide evolution. With the loss of hydrogen ion, a higher assay is obtained.

Table I shows the results of the determinations and expresses the precision as standard deviation.

ACKNOWLEDGMENT

The author thanks the Aerojet-General Corp. for permission to publish this work and to P. Stanley Gisler for his suggestions and assistance in the determinations.

LITERATURE CITED

(1) Allen, E., Seaman, W., ANAL. CHEM. **27**, 540 (1955).
(2) Epstein, J., Rosenthal, R. W., Ess, R. J., *Ibid.*, **27**, 1435 (1955).
(3) Meguerian, G., Clapp, L. B., *J. Am. Chem. Soc.* **73**, 2121 (1951).
(4) Powers, D. H., Jr., Schatz, V. B., Clapp, L. B., *Ibid.*, **78**, 907 (1956).
(5) Rosenblatt, D. H., Hlikka, P., Epstein, J., ANAL. CHEM. **27**, 1290 (1955).

RECEIVED for review February 15, 1963. Accepted April 15, 1963.

Elimination of Chloride Interference in the Chemical Oxygen Demand Test

RICHARD A. DOBBS and ROBERT T. WILLIAMS

Robert A. Taft Sanitary Engineering Center, 4676 Columbia Parkway, Cincinnati 26, Ohio

▷ A method is described for measuring the chemical oxygen demand (COD) of waste water that eliminates the necessity for a chloride correction. The method involves the addition of mercuric sulfate to the sample forming a soluble mercuric chloride complex that completely resists oxidation under the conditions of the COD test. The mercuric sulfate modification of the COD determination permits more rapid testing, is more accurate, and extends the usefulness of the test. Test results are reported on pure organic solutions and various sewage effluents containing known additions of chloride.

THE RECOMMENDED procedure (*1*) for determination of chemical oxygen demand has definite limitations. The values obtained reflect the oxidation of both organic and oxidizable inorganic materials contained in the sample. It is necessary to apply a theoretical correction for the presence of chlorides.

Moore, Kroner, and Ruchhoft (*4*) have reported quantitative oxidation of chlorides over the range 250 to 20,000 mg. per liter when 50% by volume of sulfuric acid was used with 0.25*N* potassium dichromate. The authors have obtained identical results up to 4000 mg. per liter of chloride. It should be emphasized, however, that quantitative oxidation of chlorides in a pure system does not have as a corollary a quantitative effect in the presence of organic matter. This aspect will be discussed in more detail in a later section.

Moore and Walker (*6*) later found that chloride oxidation varied from 92 to 102% in synthetic samples containing 8 to 350 mg. per liter of chloride. In the presence of silver sulfate, approximately 40 mg. per liter was oxidized at the same chloride levels. These results were obtained using 0.025*N* potassium dichromate.

The extent to which chlorides are oxidized when 0.25*N* potassium dichromate is used and when silver sulfate is added immediately has been determined by the authors. The results are shown graphically in Figure 1. In contrast to the limiting 40 mg. per liter oxidized with 0.025*N* potassium dichromate reported by Moore (*6*), the amount of chloride oxidized increases continuously as the chloride concentration increases.

Thus, the addition of silver sulfate, at the start of the digestion in the conventional procedure on samples containing more than 100 mg. per liter of chloride,

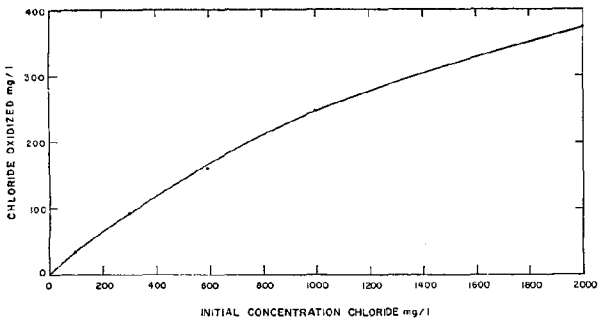


Figure 1. Oxidation of chlorides by 0.25N potassium dichromate when precipitated with silver sulfate

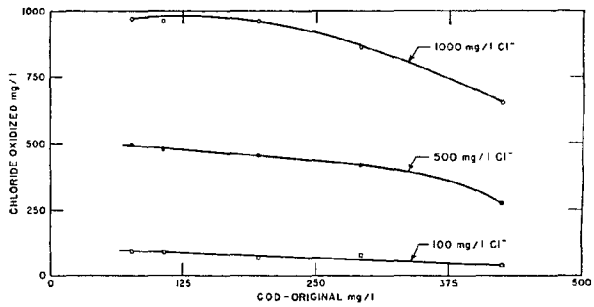


Figure 2. Oxidation of added chloride at various COD levels

will lead to error, since the amount of chloride oxidation is variable. In addition to the unknown degree of chloride oxidation when silver sulfate is added immediately, the following disadvantages are encountered: the loss of silver ion by precipitation results in less catalytic activity; and the resultant turbidity can cause some difficulty in determining the end point.

To avoid these difficulties, the usual procedure has been to oxidize the chlorides by digesting the sample for 45 minutes without silver sulfate; then the catalyst is added and the required digestion period is completed. Under these conditions a separate chloride analysis must be performed and a quantitative chloride correction applied. The current investigation resulted from data showing that a quantitative correction for chloride content has yielded negative COD values for some waste water samples.

The effect of chloride on the COD measurement was investigated. The COD values for a number of sewage effluents were measured. Chloride was added to increase the concentration by 100, 500, and 1000 mg. per liter and the COD was again measured. The results are shown graphically in Figure 2, where the milligrams per liter of chloride oxidized was plotted against the original COD value of the effluents. The milligrams per liter of chloride oxidized was calculated as follows:

$$\frac{\text{COD original} + \text{Cl}^- - \text{COD original}}{0.226}$$

These results indicate that significant errors can occur in the COD test when 100 mg. per liter or more of chlorides are present. Errors are particularly pronounced when high-chloride low-COD samples are tested and when high-chloride high-COD samples are analyzed.

The data shown in Figure 2 were subjected to a statistical analysis. The best mathematical representation of the data is a straight line whose equation, by the method of least squares, is:

$$y = 13.0 + 0.907x; \quad \sigma = \pm 21 \qquad (1)$$

where y = COD measured, mg./liter
$x = x_1 + 0.226x_2$, mg./liter
x_1 = COD original, mg./liter
x_2 = Cl^- added, mg./liter

The significant information gained from the statistical analysis is that the coefficient of x is less than one (0.907) and a positive bias is present (13.0). The statistical equation differs appreciably from the conventional equation

$$y = x_1 + 0.226x_2 \qquad (2)$$

These differences reflect an interaction between the organic matter and chloride content of the sample when oxidized in the standard procedure for COD determination.

When a preliminary digestion to oxidize chlorides is used, another difficulty is encountered. In the presence of chlorides and high concentration of ammonia, organic amine, or nitrogenous matter, a continuous reduction of dichromate occurs. The mechanism for this reduction is thought to involve a series of cyclic changes from chlorine to chloride through the formation of chloramines. The magnitude of this effect is illustrated in Table I, using glycine and urea as a source of nitrogen. The increased consumption of dichromate can only be explained on the basis of the chloramine cycle.

Another objection to a preliminary digestion for the oxidation of chlorides is the possibility that the gaseous chlorine may react with organic components in a waste water sample. As a result of this interaction the physical and chemical properties of the components are altered. The extent to which particular components are oxidized can be significantly affected. Moore, Ludzack, and Ruchhoft (*5*) have reported that benzene is 8% oxidized while chlorobenzene is over 40% oxidized. Hence, chlorine liberated from chlorides could conceivably chlorinate a benzene-containing sample to chlorobenzene and alter the COD results.

To overcome the difficulties presented by chlorides, it was theorized that a complexing technique would eliminate chloride from reaction. If chloride reactions could be prevented, a simpler and more accurate assessment of organic COD would be possible.

Table I. Effect of Chloramine Cycle on Measurements of COD

Sample identity	COD mg./liter Theoretical	COD mg./liter Measured	Deviation, %
Glycine	300	298	0.7
Glycine + 500 mg./liter Cl^-	413	532	29
Glycine + 1000 mg./liter Cl^-	526	611	16
Glycine + 2000 mg./liter Cl^-	752	858	14
Urea	0	21.5	...
Urea + 100 mg./liter Cl^-[a]	43.8	273	523
Urea + 200 mg./liter Cl^-[a]	66.1	315	377

[a] Theoretical is taken as measured blank of solution plus COD of chloride.

Medalia (*3*) reported that the suppressing action of chloride in the iron-peroxide procedure for trace amounts of organics in water could be prevented by adding mercuric nitrate. The chloride ion is tied up as a soluble mercuric chloride complex that eliminates it from further reactions.

Gleu (*2*) has reported that chloride interference in the titration of Ce(IV) and As(III) could be eliminated by complexation of the chloride with mercuric perchlorate.

EXPERIMENTAL

Apparatus and Procedure. The digestion apparatus consisted of a 300-ml., round-bottom flask with a ground-glass neck, 24/40, connected to a Friedrichs reflux condenser.

The standard procedure (*1*) was followed in all control determinations to compare the conventional technique with the suggested modification. Unless otherwise specified, all data were obtained by using a 50% by volume sulfuric acid reflux mixture and 0.25N

Table II. Chemical Oxygen Demand of Organic Compounds

Oxidation conditions—0.25N potassium dichromate and 50% sulfuric acid plus:

Compound	Without catalyst	Ag_2SO_4	$HgSO_4$	Ag_2SO_4 and $HgSO_4$	1000 mg./liter, Cl^-, $HgSO_4$ and Ag_2SO_4	Theoretical, mg./liter
Acetic acid, 1.049 gram/liter	97	1104	152	1105	1114	1118
% Theoretical	8.7	98.7	13.6	98.8	99.7	
Acetone 0.792 gram/liter	1102	1656	1173	1684	1695	1748
% Theoretical	63.1	94.8	67.1	96.4	97.0	
ABS, (sodium salt) 1.000 gram/liter	1849	2245	1930	2251	2255	2345
% Theoretical	78.8	95.7	82.3	96.0	96.2	
Benzene, 0.879 gram/liter (cooled)	985	1152	923	1116	1165	2700
% Theoretical	36.5	42.7	34.2	41.3	43.2	
Ethyl alcohol, 1 ml. 95%/liter	580	1530	739	1496	1498	1568
% Theoretical	37.0	97.5	47.1	95.4	95.6	
D-Glucose, 1.0088 gram/liter	1048	1020	1058	1037	1064	1075
% Theoretical	97.5	94.9	98.4	96.4	98.9	
Glycine, 1.000 gram/liter	632	635	637	636	643	640
% Theoretical	98.7	99.2	99.6	99.4	100.5	
Pyridine, 0.982 gram/liter	16.1	25.0	34.8	25.9	43.7	2185
% Theoretical	0.74	1.1	1.6	1.2	2.0	

Table III. Application of Mercuric Sulfate Modification of Chemical Oxygen Demand to Waste Water Samples

Sample Identity	COD mg./liter: Initial Cl^- mg./liter	Regular procedure: Ag_2SO_4 after 45 min.	Regular procedure: Cl^- corrected	Modified procedure: Chloride added mg./liter with $HgSO_4$ 500	1000	1600	2000
Little Miami primary	86	323	303	300	300	301	302
Loveland primary	224	298	248	239	237	238	243
Eastern Ave. raw sewage	106	523	499	481	484	488	489
Loveland[a] primary	112	53.0	27.7	26.6	27.8	29.7	29.5

[a] 0.025N Potassium dichromate used.

potassium dichromate. All samples were run in triplicate with duplicate distilled water blanks.

The new modification involves changing the standard procedure as follows. To a 50-ml. sample, or an aliquot diluted to 50 ml. with distilled water, add 1 gram of mercuric sulfate (A.R.). Add 5 ml. of concentrated sulfuric acid to dissolve the mercuric salt. Add 25.0 ml. of standard potassium dichromate followed by 70 ml. of concentrated sulfuric acid. Add 0.75 gram of silver sulfate and digest for 2 hours. Cool, transfer to a 500-ml. Erlenmeyer flask, and dilute to 300 ml. Titrate the excess potassium dichromate with ferrous ammonium sulfate using 1,10-phenanthroline ferrous sulfate (ferroin) as internal indicator.

To employ successfully the principle of complexing chlorides with a mercuric salt, several conditions had to be met. The complexing agent must not interfere with the basic COD procedure and must quantitatively inhibit chloride oxidation, while not adversely affecting the extent to which organic compounds are oxidized. The principle must also be applicable to a wide variety of waste water samples of complex composition.

COD Procedure Interference. Mercuric nitrate was tried initially in accordance with Medalia's (*3*) work, but the dichromate titration end point was not definitive. The difficulty was attributed to the nitrate ion since an identical effect was observed when potassium nitrate was used to spike samples. The nitrate ion oxidized the reduced form of the indicator, thereby shifting the end point of the titration beyond the equivalence point. To overcome this effect, mercuric sulfate was substituted since large quantities of sulfate ion were already present in the digestion mixture. Fortunately, the choice was most satisfactory and no other interferences with the COD procedure were encountered.

Inhibition of Chloride Oxidation. To determine whether mercuric sulfate completely prevents chloride oxidation, samples of distilled water containing 100 to 2000 mg. per liter of chloride, complexed with 1 gram of mercuric sulfate, were analyzed for COD. The maximum deviation in titration volumes between the blanks and chloride-complexed samples, in the range studied, was 0.05 ml. The results demonstrated complete inhibition of chloride oxidation.

It was necessary to determine the experimental excess of mercuric ion required to prevent oxidation of chloride at any concentration. Samples containing 500 and 1000 mg. of chloride were complexed with varying amounts of mercuric sulfate. The ratios of mercuric to chloride ion used were 3:1, 4:1, and 5:1. When analyzed for COD, the deviation in titration volumes between blanks and chloride-complexed samples were 1.33, 0.25, and 0.22 ml., respectively. The results indicate that a 4:1 ratio is sufficient to prevent chloride oxidation in a pure system. The 5:1 ratio is preferable since mercuric ion is known to form complexes with certain other anions found in waste waters.

RESULTS

Oxidation of Organic Compounds. The results obtained with eight different organic compounds are shown in Table II. The compounds selected represent different classes of organic substances that may be found in waste water samples. No attempt was made to repurify these compounds.

Approximately 1 gram of the organic compound to be tested was dissolved in distilled water and diluted to 1 liter. The sample size was based on the theoretical COD. The values for COD were measured under the oxidation conditions shown in Table II. It should be emphasized that, although mercuric sulfate had no adverse effect on the oxidation of the organic compounds tested, the use of silver sulfate remains essential for improved oxidation of certain organic compounds. Oxidation of the added chloride was prevented in all the solutions tested.

Application to Waste Water Samples. The most practical aspect of the study was evaluation of the principle as applied to the analysis for COD of various waste waters. Results obtained with waste water samples from three different sewage treatment plants are shown in Table III. Increments of chloride from 500 to 2000 mg. per liter were added to each of the effluents tested. The maximum variation in COD within a series containing mercuric sulfate and 0.25N potassium dichromate was only 1.7%. The per cent variation using 0.025N potassium dichromate was somewhat greater, but was not considered significant at the low level of COD involved.

CONCLUSIONS

With the modification the test can be applied to samples with high chloride concentrations that could not be meas-

ured by the regular procedure. The use of mercuric sulfate eliminates the chloramine cycle and the preliminary digestion for chloride oxidation. Since chloride reactions are eliminated, a separate chloride analysis is not necessary.

The quantitative inhibition of chloride oxidation in all the systems considered has demonstrated the usefulness of the mercuric sulfate modification in obtaining a more realistic evaluation of the organic content of waste water samples.

ACKNOWLEDGMENT

The authors are indebted to K. A. Busch and Gerald Stern for the statistical evaluation of the data in Figure 1, and to B. A. McDonald for her assistance in the early stages of the investigation.

LITERATURE CITED

(1) Am. Public Health Assoc., "Standard Methods for the Examination of Water and Waste Water; 11th ed. p. 399, New York, 1960.
(2) Gleu, K., *Z. Anal. Chem.* **95**, 305 (1933).
(3) Medalia, A. E., ANAL. CHEM. **23**, 1318–20 (1951).
(4) Moore, W. A., Kroner, R. C., Ruchhoft, C. C., *Ibid.*, **21**, 953–7 (1949).
(5) Moore, W. A., Ludzack, F. J., Ruchhoft, C. C., *Ibid.*, **23**, 1297 (1951).
(6) Moore, W. A., Walker, W. W., *Ibid.*, **28**, 164–7 (1956).

RECEIVED for review March 12, 1963. Accepted April 22, 1963. Division of Water and Waste Chemistry, 143rd Meeting, ACS, Cincinnati, Ohio, January 1963.

Determination of Surface Areas of Phosphates from Adsorption Measurements in Nonaqueous Media

R. E. MESMER and R. R. IRANI

Research Department, Inorganic Chemicals Division, Monsanto Chemical Co., St. Louis, Mo.

▶ **A method for the determination of surface areas of powders in acetic acid–toluene solutions has been developed and applied to various phosphates with surface areas between 1.3 and 71 sq. meters per gram. On powders with surface areas below 8 sq. meters per gram, duplicates agree within 0.2 sq. meter per gram and are in agreement with values determined by the conventional BET method. The method is based on the Langmuir equation for adsorption and it utilizes only common laboratory reagents and equipment. It is especially useful for measuring small surface areas, and for use with materials that are reactive in aqueous solutions.**

THE measurement of surface areas has long been of concern in applications of powders where reactivity or absorptivity is important. Numerous methods for acquiring these data have been reported in the literature. The most important and widely used is that of Brunauer, Emmett, and Teller (BET) (*2*). In the BET method, the amount of gas adsorbed as a function of gas pressure is measured in a vacuum system, and the surface area is calculated according to the BET equation.

More recently, continuous gas flow methods have been used by Innes (*4*) and Nelsen and Eggertsen (*8*). Other approaches have been described, such as gas permeability (*6*), microscopic examination, x-ray scattering, and others which are listed by Adamson (*1*) and the National Bureau of Standards (*7*).

The determination of surface areas by adsorption from solution has also been investigated. Dyes (*5*) and fatty acids (*3*, *9*, *12*) have been used most commonly, since these materials form monolayers on the adsorbent, and therefore, approach a saturation limit on the adsorbent.

Acetic acid forms multilayers at concentrations higher than 0.25*M*, and this fact has probably concealed its usefulness in determining surface areas. We have found that the adsorption of acetic acid from toluene on inorganic phosphates obeys the Langmuir isotherm in dilute solutions. With careful performance of titrations, greater precision than that achieved by the conventional BET method was obtained on surfaces that are affected by the sample preparation procedures required with the BET method.

EXPERIMENTAL

Materials. The calcium phosphates were prepared by reaction of lime with phosphoric acid under various conditions (*13*). The sodium polyphosphate sample was a commercial grade material. The toluene and acetic acid were reagent grade quality.

Procedure. Handle and transfer all solutions as described below.

Weigh about 10 grams of the adsorbent for each of three 100-ml. glass-stoppered volumetric flasks. For surface areas below 5 sq. meters per gram, it is advantageous to keep the solid-to-liquid ratio as large as possible yet permitting the removal of an aliquot after settling.

Add by pipet 25 ml. of the toluene–acetic acid solution. Three different concentrations in the range of 0.05*M* to 0.2*M* should be used for precise work—*M* refers to concentration in moles per kilogram of solution. Record the weights of these solutions to 0.5%.

Shake the flasks on a wrist-action Burrell shaker for 1 hour at room temperature. (Equilibrium is known to occur in this period, because there is no increase in the quantity of acetic acid adsorbed between 1 and 3 hours.) Allow 15 minutes for the solids to settle before withdrawing a 5-ml. aliquot. Add this aliquot to a 125-ml. Erlenmeyer flask containing 25 ml. of distilled water (CO_2-free) and 5 drops of phenophthalein solution. Record the weight of the aliquot and proceed with the titration, described later, using 30 to 50 ml. of 0.01*M* to 0.02*M* standard base.

Handling of Solutions. Several precautions in the handling of these solutions are necessitated by their high volatility. Stock solutions must be transferred to the reaction flasks and from reaction flasks to the titration vessel by pipets which are filled by the application of pressure instead of suction, as is the customary procedure. This can be accomplished by using a wash-bottle-type apparatus with glass tubing and rubber stoppers or tubing for making the connections. Pipets are allowed to drain into a receiver in the usual manner without loss due to volatility. Care must also be taken that the vessels are kept well stoppered during the shaking and weighing steps.

It is necessary to adjust the solid-to-liquid ratio in the reaction flask so that after settling there is sufficient clear supernatant solution for the withdrawal of an aliquot for analysis. A filter pipet (*11*) can be employed for this purpose, but the ordinary pipet is usually adequate.

Titrations. The critical part of this method is the care and accuracy

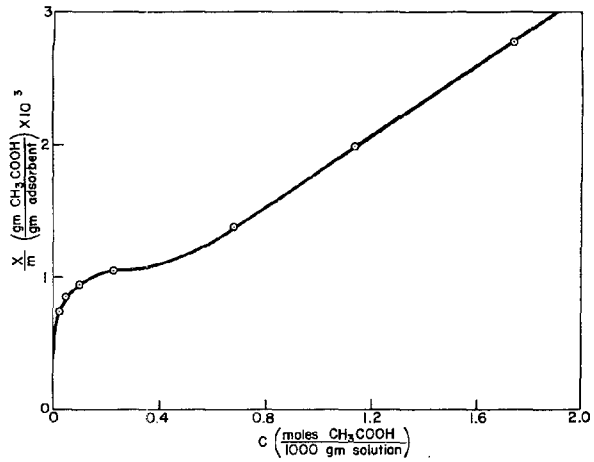


Figure 1. Adsorption of acetic acid from toluene on $CaHPO_4 \cdot 2H_2O$

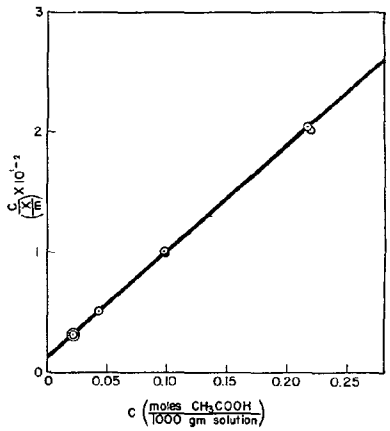


Figure 2. Langmuir absorption isotherm for acetic acid on $CaHPO_4 \cdot 2H_2O$

with which the titration is made. Standard base solutions with concentrations of $0.01M$ and $0.02M$ are prepared from carbonate-free sodium hydroxide. The titration is carried out to the phenolphthalein end point, using a 50-ml. weight buret. The use of weight burets eliminates the need to calibrate glassware when performing precise titrations.

Because the toluene–acetic acid solutions are immiscible with water, about 25 ml. of water is added to the flask before the aliquot (ca. 5 grams) is added for titration. The acetic acid is rapidly extracted into the aqueous phase when this mixture is agitated with a magnetic stirrer. Near the end point it is necessary to swirl the flask vigorously to make certain a false end point is not reached. With this procedure and the precautions described in handling the solutions, the titrations can be carried out with a precision of 1 or 2 parts per thousand, while the normal volumetric procedures lead to errors of 1% or greater. Since the change in concentration due to adsorption is normally of the order of a few per cent, errors in titration larger than 0.2% cannot be tolerated.

Calculations of Surface Area. The surface areas are calculated using the Langmuir equation for adsorption, since the systems studied followed this relationship in dilute solutions. The Langmuir equation

$$C \Big/ \left(\frac{x}{m}\right) = \frac{1}{ab} + \frac{C}{a} \qquad (1)$$

implies a linear plot of C *vs.* $C/(x/m)$ for monolayer adsorption where x/m denotes the amount of acetic acid adsorbed per gram of adsorbent, C is the concentration of acetic acid in moles per 1000 grams of solution, a is a measure of surface area, and b is a measure of the intensity of the adsorption. Limited evaluation of the dependence of b on temperature for some of the phosphates gave heats of adsorption of the order of 1 ± 1 kcal. per mole, indicating straightforward physical adsorption of the acetic acid.

In calculating x/m from the experimental data, a correction is included for the change in weight of the solution due to the removal of adsorbed acetic acid. Therefore, x/m is calculated from the data in the following way:

$$x/m = \frac{W(\Delta F)}{1 - F} \qquad (2)$$

where W is the total weight of the solution used per gram of solid, and F and ΔF are the weight fraction and change in weight fraction of acetic acid in toluene.

The slope of the Langmuir isotherm (Figure 2) is the reciprocal of the constant a (in units of grams of acetic acid per gram of solid). The surface area becomes:

$$\text{Surface area} = (2.056 \times 10^3)a \qquad (3)$$

in units of square meters per gram. This relationship is based upon 20.5 sq. A. as the molecular area of an acetic acid molecule (*1*).

DISCUSSION

The measurement of surface areas by adsorption from solution requires less apparatus and less time than most conventional methods. However, dye adsorption is usually complicated by the question of how the large molecule lies on the adsorbent and, therefore, raises the question of the molecular area to be used in calculations. Good results have been obtained using fatty acids with chain lengths of between 10 and 22 carbon atoms. These molecules give monolayer coverage on some materials, as is shown by the fact that a limiting value is approached with increasing acid concentration. This method is less desirable than the acetic acid method for several reasons: acetic acid is readily available, its purity is much greater than that of long-chain acids, and its analysis is much simpler. The reported procedures for analysis in the fatty acid method were either to evaporate the solvent and determine the change in weight of acid present or do a lengthy conductometric titration of the acid.

The quantity of acetic acid adsorbed by solid $CaHPO_4 \cdot 2H_2O$ is shown in Figure 1, over a wide range in acetic acid concentration. These data show that the Langmuir-type adsorption is not followed at higher concentrations, because no limiting value is approached. However, Figure 2 shows a good correspondence with the Langmuir equation at acetic acid concentrations up to $0.2M$. The other phosphates described in Table I also showed similar behavior in this concentration range. The surface areas have been calculated from data in this concentration region.

For measuring areas less than about 20 sq. meters per gram, acetic acid concentrations up to about $0.2M$ in the starting solutions are suitable; however,

Table I. Surface Areas

(Sq. meters per gram)

	Acetic acid	BET (N_2)
$Na_5P_3O_{10}$	1.7, 1.8	...
$CaHPO_4$ I	1.7, 1.8	...
$CaHPO_4$ II	7.6, 7.5	8.0, 10.8
$CaHPO_4 \cdot 2H_2O$ I	3.1, 3.0	2.0, 4.6
$CaHPO_4 \cdot 2H_2O$ II	1.8, 1.7	...
$CaHPO_4 \cdot 2H_2O$ III	2.5, 2.4	...
Calcium hydroxylapatite	72.8, 70.8	72.4, 71.6 73.5
$Ca(H_2PO_4)_2 \cdot H_2O$	1.3, 1.3	...

because materials with large surface areas absorb larger quantities of absorbate, the concentrations of the starting materials should be adjusted so that equilibrium concentrations between 0.05*M* and 0.2*M* are used in constructing the isotherm. Likewise, the solid-to-liquid ratio may be diminished when measuring larger areas.

At least three points on the isotherm should be determined for precise work, but a value for the surface area can be calculated from a single point if the isotherm is drawn through the origin. If this is constructed from a point at about 0.2*M* concentration, an error of from a few to 20% results, depending on the material and the accuracy of the single determination. When using this simplification, it is necessary to establish the accuracy, by first constructing a more complete isotherm. The average working time required for the performance of one of these single-point measurements is 45 minutes; the lapsed time is about 2 hours.

It was not found necessary to outgas the material before use in the cases of dry, precipitated $CaHPO_4$ and calcium hydroxylapatite. Outgassing is known to change the surface area of hydrates. Also, an effect of outgassing has been reported for the adsorption of acids from toluene onto silica gel (*10*). Therefore, powders should normally be dried or outgassed prior to surface area measurements, unless evidence shows this to be unnecessary.

RESULTS

Table I lists the surface areas of various phosphates which have been determined by the acetic acid and the conventional BET methods. The precision of the acetic acid adsorption data is 0.2 sq. meter per gram for duplicates up to 8 sq. meters per gram. In this range, the data are more precise than the BET data and are at least as precise at the 70 sq. meters per gram region. The poor agreement between duplicates by the BET method for $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$ may be due to the sensitivity of the surface area to the degree of surface hydration. Nonreproducible changes could have taken place during the preparation of these two samples for the BET measurements.

The acetic acid adsorption method is not useful for surface area measurements on very basic materials such as lime, which reacts completely with the acid. Results obtained on less polar materials such as silica show surface areas much less than those determined by nitrogen adsorption. This effect can be attributed to the less polar nature of the adsorbent, which would enhance the competitive adsorption of the acid and solvent. Materials which chemically sorb acetic acid might also give complex results when studied by this method.

No solvents other than toluene were studied. However, the choice of solvents is limited by several requirements. The solvent must be miscible with acetic acid, inert chemically toward it and toward the adsorbent, and nonpolar and nonpolarizable, in order that the adsorption of the solvent on a polar adsorbent does not compete with the acetic acid. Systems where binary adsorption occurs are too complex for routine surface area measurements.

LITERATURE CITED

(1) Adamson, A. W., "Physical Chemistry of Surfaces," Interscience, New York, 1960.
(2) Brunauer, S., Emmett, P. H., Teller, E., *J. Am. Chem. Soc.* **60**, 309 (1938).
(3) Harkins, W. D., Gans, D. M., *Ibid.*, **53**, 2804 (1931).
(4) Innes, W. B., ANAL. CHEM. **23**, 759 (1951).
(5) Kolthoff, I. M., MacNevin, W. M., *J. Am. Chem. Soc.* **59**, 1639 (1937).
(6) Kozeny, J., *Sitzber. Akad. Wiss. Wien Math. naturw. Kl., Abt. IIa*, 136, 271 (1927).
(7) Natl. Bur. Standards, "Bibliography of Solid Adsorbents," Circ. 566 (1956).
(8) Nelsen, F. M., Eggertsen, F. T., ANAL. CHEM. **30**, 1387 (1958).
(9) Orr, C., Jr., Bankston, P. T., *J. Am. Ceram. Soc.* **35**, 58 (1952).
(10) Puri, B. R., Sud, R. K., Lakhanpal, M. L., *J. Indian Chem. Soc.* **31**, 612 (1954).
(11) Rapaport, M., Hancock, C. K., *J. Chem. Educ.* **39**, 98 (1962).
(12) Smith, H. A., Fuzek, J. F., *J. Am. Chem. Soc.* **68**, 229 (1946).
(13) Van Wazer, J. R., "Phosphorus and Its Compounds," Vol. I, Interscience, New York, 1958.

RECEIVED for review September 27, 1962. Accepted April 22, 1963.

Spectropolarimetry

Acid-Base Titrimetry with Asymmetric Indicators and Determination of Metal Ions and Asymmetric Substances

STANLEY KIRSCHNER and DINESH C. BHATNAGAR

Wayne State University, Detroit, Mich.

▶ Because of the recent development of high-precision photoelectric spectropolarimeters, it is possible to purchase or construct instruments which will permit the rapid determination of optical rotation at many different wavelengths. A method is presented, utilizing such an instrument, which allows for the titration of acids or bases using optically active substances as indicators. The titration curves resemble those of conductometric titrations. The method also provides for the determination of metal ions and asymmetric coordinating agents, and permits the determination of the ligand-metal ion ratio in coordination compounds, as well.

BECAUSE of the limitations inherent in making determinations with a visual polarimeter, the instrument is not readily adaptable for titrimetry and, in analysis, has found its prime use in the comparison of optical rotation of samples with that of standards. Mattock (*6*), Freegard (*4*), and others have also used the visual polarimeter in continuous variation studies of metal complexes with asymmetric ligands in the determination of ligand-metal ion ratios.

In recent years versatile spectrophotometers of high quality, light sources of high intensity in both the visible and ultraviolet regions, and polarizing prisms with appropriate cements allowing transmission into the ultraviolet have become commercially available. Some individual investigators have also constructed similar instruments in their own laboratories (*2*). This has allowed construction of spectrophotometric photoelectric polarimeters which utilize phototubes in place of the human eye as a detector, monochromators in place of special lamp and filter combinations for producing monochromatic light of different wavelengths, and intense light sources for determining the optical rotation of solutions which are also strongly absorbing (*3*, *5*). Several such polarimeters are commercially available (*5*), and some can fairly readily be adapted for use in titrimetry—e.g., photoelectric polarimeter, Carl Zeiss,

Inc., 485 Fifth Ave., New York 17, N. Y.; Standard-Keston polarimetric attachment, Standard Polarimeter Co., 6 Banta Place, Hackensack, N. J.—but they are limited to a few wavelengths or to a narrow frequency range in the visible region.

The authors and their coworkers (*1*) have designed a relatively simple spectrophotometric polarimeter for use in the region 2600 to 10,000 A., which utilizes a Beckman Model DU spectrophotometer with a 10-cm. tube compartment, and which was constructed at a relatively low cost compared with that of commercial instruments of comparable versatility, wavelength range, and precision. In addition, determinations of optical rotation are extremely rapid because they consist of absorbance measurements and because the optically active sample in its solvent and cell acts as its own blank, for both colored and "colorless" solutions. The instrument is particularly applicable to spectropolarimetric titrations of the types described below because (*a*) the relatively large sample compartment allows for easy handling of suitably large volumes of solution, (*b*) a multiplier phototube is used to measure light intensities in place of the human eye for the comparison of visual fields, thus avoiding the eye's attendant limitations, (*c*) a monochromator permits selection of suitable wavelengths in the visible and ultraviolet regions without the problems of special lamps and filters, (*d*) intense light sources allow the use of relatively optically dense solutions, (*e*) no solvent blanks are necessary during the determinations, and (*f*) the optical rotation is determined as a function of the measured optical absorbance difference of the solution between two positions of the analyzer prism (*1*), which also helps to make for simple, rapid determinations.

PRINCIPLES AND PROCEDURES

Acid-Base Spectropolarimetric Titrimetry with Asymmetric Indicators. Indicator Selection. For the titration of strong acids and bases, it is necessary to use as an indicator an optically active substance which exhibits a marked change in its optical rotation at the titration end point. For the titration of a strong acid with a strong base, *d*-(or *l*-) tartaric acid is such a substance. It undergoes a marked optical rotation change upon conversion to the monohydrogen salt and undergoes a further marked change upon conversion to the disodium salt, which, in this case, allows determination of the quantity of indicator added to the system. This is also indicative of the potential of this method for titrimetric determination of weak acids, a matter which is now under study.

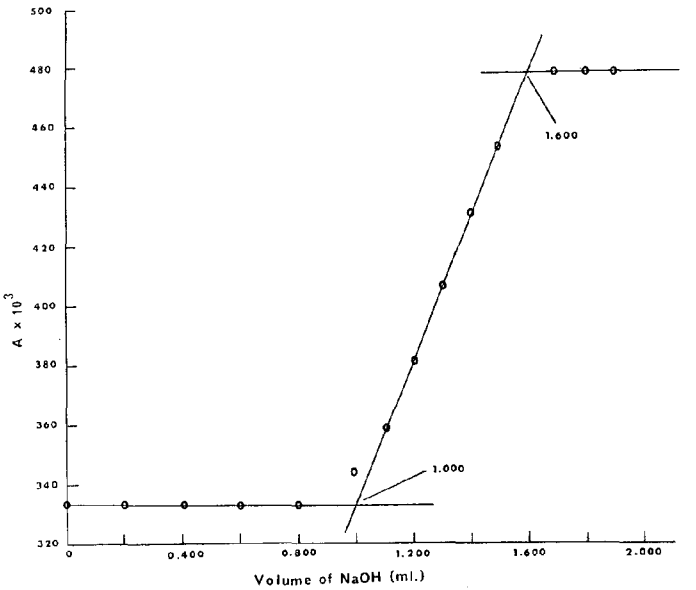


Figure 1. Spectropolarimetric titration of HCl and *d*-tartaric acid with standard NaOH

λ = 4000 A.

Titrimetric Procedure. If a relatively large volume (>50 ml.) of a relatively dilute (ca. 0.1 *N*) acid of known or unknown concentration, containing an added optically active indicator whose optical rotation changes markedly on going from an acidic to a basic solution —e.g., *d*-tartaric acid—is titrated with a relatively concentrated (ca. 5*N*) base of unknown or known concentration, respectively, using a microburet which is readable to 0.001 ml., measurement of the optical rotation of the system at a few points before and after the end point permits a relatively simple determination of the end point by graphical procedures (Figure 1). The titration resembles a conductometric titration in that it is necessary to obtain only a relatively few points (optical rotation or absorbance difference *vs.* volume of titrant) before and after the end point, to plot the resulting straight lines on graph paper of appropriate size, and then to determine the volume of titrant at the point where the lines cross. It is also possible to determine the concentration of the added asymmetric indicator, if it reacts with the base and undergoes a further appropriate optical rotation change in so doing (Figure 1).

The volume relationship described above is chosen so as to minimize dilution effects. As is often true in conductometric titrations, equilibrium conditions near the end point are relatively unfavorable, and titration points should therefore not be determined too near the end point (see Figure 1). Another factor which may also affect the points in the vicinity of the end point is the acid dissociation constant(s) of the asymmetric indicator. This question is also under study and will be reported on in a later publication. It is sometimes useful to determine the optical rotatory dispersion of the indicator substance to aid in the selection of the wavelength giving the most appropriate rotation change and transmittance combination for the reaction under study.

Spectropolarimetric Titrimetry of Metal Ions and Asymmetric Substances. Indicator Selection. For the titration of metal ions by this technique, it is necessary to select as an indicator an optically active substance that rapidly forms a complex of the metal ion having an optical rotation which is markedly different from that of the indicator alone. An example is copper(II)-*l*-(+)-histidine monohydrochloride, which forms 1:1 and 1:2 complexes, both of which have rotations sufficiently different from that of the ligand alone to allow determination by a spectropolarimetric procedure. For the titration of optically active substances by metal ions, a metal ion must be chosen which rapidly forms a complex with the optically active compound with an optical rotation markedly different from that of the compound.

Titrimetric Procedure. As in the previous case, a relatively large volume of a relatively dilute asymmetric coordinating agent—e.g., *l*-(+)-histidine monohydrochloride—of known or unknown concentration may be titrated with a relatively concentrated solution of a metal ion—e.g., copper(II) cation—of unknown or known concentration, respectively, with which it forms a complex (Figure 2.) Excellent use of the

optical rotatory dispersion of the complex can also be made here in the selection of the wavelength and transmittance giving the greatest observable change per unit volume of titrant.

Complexes involving various ratios of ligand to metal ion can be used in these titrations. In fact, it is often possible to determine the ligand-metal ion ratio in compounds by this technique. Figure 2 shows two end points in the titration. The first represents the 2:1 ligand-metal complex, and the second, the 1:1, although, in this case, the lines form too obtuse an angle for an accurate determination of the second end point. As the angle between the two intersecting lines increases, the degree of precision of the end-point determinations decreases, so that system components should be selected to provide as large an optical rotation difference as possible, in order to achieve the smallest possible angle of intersection. Even in Figure 2 the first end point shows so obtuse an angle that it can reasonably be read to only two significant figures. This phenomenon is also being studied further and will be reported later.

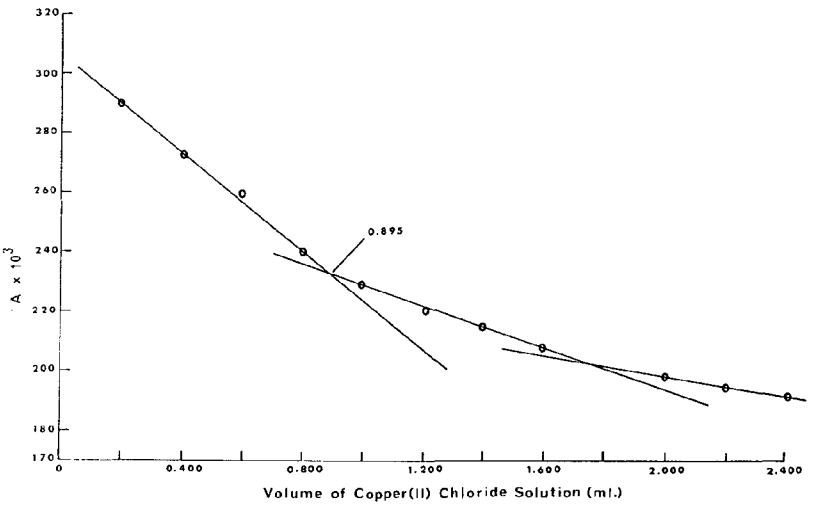


Figure 2. Spectropolarimetric titration of *l*-(+)-histidine monohydrochloride with copper(II) chloride

λ = 4000 A.

RESULTS

The spectropolarimetric titration of 50-ml. of 0.1*M* hydrochloric acid containing 1 ml. of 2*M* *d*-tartaric acid required a volume of approximately 5*M* sodium hydroxide which differed from the calculated volume by 0.32% for three determinations (average). The determination of the concentration of the added *d*-tartaric acid required a volume of standard sodium hydroxide which differed from the calculated volume by an average of 0.41% for three determinations. Both titrations were carried out at 4000 A.

The spectropolarimetric titration of *l*-(+)-histidine monohydrochloride with 1.5*M* copper(II) chloride at 4000 A. required a volume of the copper chloride solution which differed from the calculated volume by an average of 0.33% for three determinations using only the first end point (Figure 2), that for the 2:1 ligand-metal complex.

INSTRUMENTAL OPERATIONS

The operation of the instrument itself consists of placing a sample in an appropriate absorption cell (constructed of optically inactive glass, quartz, or other suitable transparent, inactive material, 5 cm. long, 2.5 cm. wide, and 6 cm. high and used in place of a polarimeter tube), adding small known increments (ca. 0.2 ml.) of the concentrated titrant, stirring, allowing the turbulence to cease, and then reading the absorbance of the solution twice—once with the analyzer prism in one of its two possible positions (*1*) (where its transmittance is made to read a certain preselected value each time—e.g., 100% or 50%—by appropriate changes in the sensitivity controls of the instrument), and once with the analyzer prism in its other position. The absorbance difference (or absorbance, with the analyzer in its second position) is plotted against titrant volume and the next increment of titrant is added. Four such points obtained both before and after the end point are usually sufficient for an adequate plot. An average titration takes about 30 minutes.

Selection of the most appropriate wavelength is usually not very critical. It can be determined by examination of the absorption spectrum and optical rotatory dispersion of the product (and/or reactants) of the reaction. The wavelength giving the largest rotation change with maximu m transmittance will usually be the most appropriate.

CONCLUSIONS

The application of spectropolarimetry to titrimetric procedures for certain systems provides a simple, rapid means for the determination of unknown components of those systems. In particular the method has been applied successfully to the titrimetric determination of strong acids and strong bases utilizing an asymmetric indicator and a spectropolarimeter as an end-point detector. In addition, the method has been used to determine a weak optically active acid by direct titration with a strong base. It has also been used to determine metal ions and optically active coordinating agents which react with each other to produce complexes having optical rotations different from those of the ligands.

Studies are under way to determine whether weak acids and bases may be determined by this procedure, using other optically active indicators which are pH-sensitive. In addition, this method should be applicable to determinations of ligand-metal ratios in complex inorganic compounds, as well as of metals and optically inactive coordinating agents using asymmetric substances which are weak coordinating agents as indicators. Studies on these systems are also under way and will be reported in a later paper.

ACKNOWLEDGMENT

The authors express their sincere appreciation to the National Science Foundation for a fellowship grant without which this work could not have been undertaken.

LITERATURE CITED

(1) Albinak, M. J., Bhatnagar, D. C., Kirschner, S., Sonnessa, A., "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, ed., pp. 154 ff, Macmillan, New York, 1961.
(2) Carroll, B., Tillem, H., Freeman, E., ANAL. CHEM. **30**, 1099 (1958).
(3) Djerassi, D., "Optical Rotatory Dispersion," McGraw-Hill, New York, 1960.
(4) Freegard, N., *Chem. Ind. (London)* **1957**, 984.
(5) Heller, W., Fitts, D. D., "Polarimetry," in "Physical Methods of Organic Chemistry," A. Weissberger, ed., 3rd ed., Vol. 1, Part 3, Chap. 33, Interscience, New York, 1960.
(6) Mattock, G., *J. Chem. Soc.* **1954**, 989.

RECEIVED April 9, 1962. Accepted May 6, 1963. Division of Analytical Chemistry, 138th Meeting, ACS, New York, N. Y., September 1960.

Radioactivation Analysis of Sodium by Counting Photoneutrons

SAADIA AMIEL and MAX PEISACH

Israel Atomic Energy Commission, Soreq Research Establishment, P.O.B. 527, Rehovoth, Israel

▷ A method is described for a nondestructive radioactivation analysis of sodium in complex matrices, in which Na^{24} is assayed by counting photoneutrons emitted from deuterium by the 2.75-m.e.v. gamma ray, in an assembly consisting of D_2O and neutron detectors. This principle offers efficient discrimination against large amounts of radioactivities with energies below 2.23 m.e.v., the threshold for the photodisintegration of deuterium. The photoneutron activity was proportional to the Na^{24} content in the sample, and microgram quantities of sodium were analyzed with a precision of 2%. Sensitivities better than 0.1 μg. are indicated. Interference from other radionuclides is discussed. Possible extension for the analysis of elements other than sodium is discussed as well.

Because of the widespread occurrence of sodium and its importance in many fields, accurate methods for its analysis have been developed. Flame photometry is mainly used when high sensitivity is required, but this sensitivity can be affected by the presence of other components which frequently occur together with sodium (*2*). Nuclear methods of analysis utilizing characteristic nuclear properties indicate a more specific method of analysis with a greater sensitivity (*6*).

Radioactivation analysis of sodium is generally based on the formation of sodium-24 by neutron capture. This isotope decays with a half life of 15.0 hours and can be measured either by its 2.75-m.e.v. gamma ray or by the coincidence measurement of the cascade of this gamma ray and the one of 1.37 m.e.v. In most cases it is sufficient to discriminate against gamma rays of less than 2 to $2^1/_2$ m.e.v. (*11*) and to measure the gross activity of radiation above this level. Further differentiation between sodium-24 and other activities in the same energy range is made by following the half life.

When sodium occurs in a complex matrix, sodium-24 activity frequently forms only a small part of the gross activity of a highly active sample, and analysis by radioactivation without chemical processing is then hindered by overloading the detector, paralyzing it for most of the counting time. Electronic discrimination at a preset energy level then becomes difficult, if not altogether impossible. In such cases there is a decrease in accuracy and sensitivity, and hence the need arises either for chemical separations or, if nondestructive analysis is essential, for a detector insensitive to gamma radiation below about 2 m.e.v. The photodisintegration of deuterium and the emission of photoneutrons require gamma ray energies greater than 2.23 m.e.v. This suggests that a detecting system based on counting the emission of photoneutrons from deuterium would be naturally biased and would be entirely insensitive to energy quanta below the photoneutron threshold of 2.23 m.e.v. Such a detector would have an additional advantage because the emitted neutrons can be counted without interference from other radiations and may be detected against any beta- or gamma-ray background.

The number of radionuclides which emit gamma rays of energy greater than 2.23 m.e.v. is relatively small and their number is still further reduced when only those with half lives within a factor of about 10 of that of sodium-24, say 1 to 100 hours, are considered as possible sources of photoneutron emission from deuterium. Thus the counting of photoneutrons emitted from the interaction between the high energy gamma rays of sodium-24 and deuterium can form the basis for the assay of sodium-24 and the determination of sodium by neutron radioactivation. The emission of photoneutrons from deuterium was used for the analysis of deuterium in water samples (*4*, *9*) when their neutron activities were compared with those of standards placed as targets around an intense source of sodium-24. The present method for sodium analysis is the same in principle, but has the roles of source and target interchanged. That is, whereas for deuterium analysis the source is constant and the target is the unknown, here the source is unknown and the target constant.

The Sample. It is clear that the form of the sample is immaterial. For optimal conditions it is undesirable that the sample should contain large quantities of neutron absorbers, or should contain material which could lead directly to neutron emission. It would also be inconvenient if the sample contained relatively large amounts of material which on neutron radioactivation would emit high-energy gamma rays.

Sample components which could lead to a higher neutron count are nuclides undergoing spontaneous fission and alpha-particle emitters inducing (α,n) reactions on light elements in the sample and container. Direct interference by delayed neutrons is not serious since all delayed neutron emitters have half lives less than about 1 minute and they may be allowed to decay. Samples which contain beryllium would certainly lead to high results due to the production of photoneutrons by gamma rays above 1.67 m.e.v., the threshold for photoneutron emission from beryllium. The extent of interference from the above sources can be checked experimentally and will be discussed later.

High-energy gamma-ray emitters with short half lives of, say, less than 1 hour, can be left to decay without losing too much activity of sodium-24, while those with half lives longer than 100 hours would add a nearly constant count rate during the period of measurement and this can be treated as part of the background. Radionuclides falling between these groups, such as 2.6-hour manganese-56 and 40-hour lanthanum-140, can have their presence corrected for by following the decay of photoneutron emission. The only serious source of interference appears to be from gallium-72 which emits high-energy gamma rays and decays with a half life very close to that of sodium-24. It would appear that the accuracy of the method for sodium analysis would be affected if gallium is present in the sample. Interference from the presence of fission products in the sample during measurement is expected but can be checked experimentally.

Irradiation Conditions. Besides being produced by neutron capture in sodium, for which the thermal neutron, cross section is 536 mb. (*5*), sodium-24 can be produced with fast neutrons by an (n,α) reaction on aluminium or an (n,p) reaction on

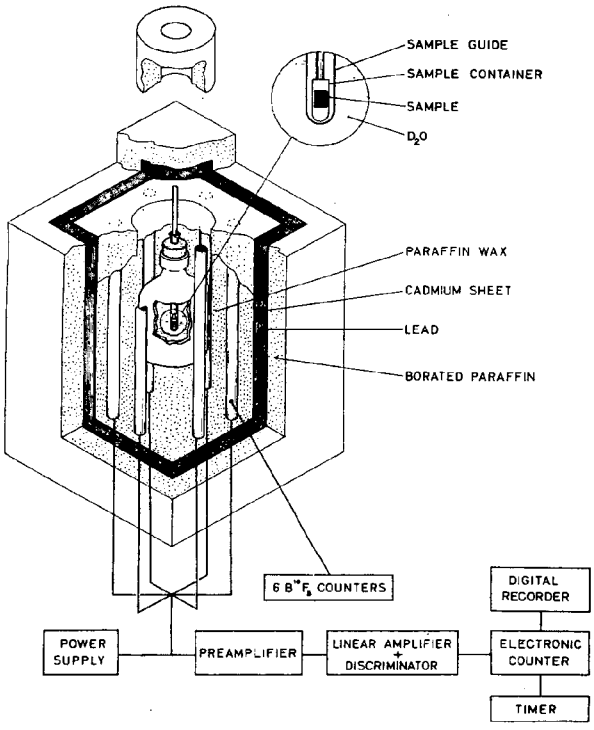


Figure 1. Photoneutron measurement assembly and block diagram of electronic circuit

magnesium. The effective cross sections for these reactions with fission spectrum neutrons are 0.6 and 1.2 mb., respectively (*10*). Because the production rate of sodium-24 from these elements in a mixed neutron flux normally available in a reactor (partially thermalized fission spectrum neutron flux) is lower by two or more orders of magnitude than that of the (n,γ) reaction on sodium, mixed fluxes can be used for the analysis of sodium, except where the method is used at its ultimate sensitivity in samples where the aluminium or magnesium content far exceeds the sodium content.

The duration of the irradiation is best adjusted to the approximate sodium content of the sample. However, irradiations lasting longer than about a day do not add significantly to the sensitivity or accuracy of the method

Neutron Detection. To obtain the maximum output of photoneutrons from a source of sodium-24 it is necessary to surround the source with a sufficiently thick layer of deuterium. Since light hydrogen has an appreciable cross section for neutron capture, 0.3 barn, it is desirable to keep its concentration as low as possible. An efficient way to detect neutrons is to count them after they have been thermalized by a moderator such as heavy water, paraffin, graphite, or ordinary water. Ideally, the counters could be immersed in a bath of heavy water, but for economy paraffin wax or graphite could be used as moderator surrounding a volume of heavy water in which the neutrons are produced. A 4-π arrangement of enriched $B^{10}F_3$ proportional neutron counters placed in the moderator around the photoneutron source provides an efficient detection system of very low sensitivity to gamma radiation.

Counting Conditions. The duration of counting depends on the activity of the sample and the precision required. The delay between irradiation and counting is determined by the absence or presence of other activities in the sample and the nature of the radiations they emit, and those interfering activities also determine for how long the sodium-24 decay should be followed. To be able to correct for longlived interferences it is required that the counting equipment be stable over a long period of time. It is desirable that the counting equipment be constructed from materials with low neutron absorption.

EXPERIMENTAL

Samples for analysis were weighed out into polyethylene vials and were irradiated in the Israel Research Reactor No. 1 where thermal fluxes of up to 5×10^{13} neutrons/cm.^{2}-second were available. Because of radiation damage to the vials, the irradiation did not exceed 1 hour. The irradiated sample was dropped into the counting assembly (Figure 1) so as to lie at the center of a flask of 1 liter of heavy water containing more than 99% deuterium. Neutrons generated from this container were counted with a ring of six $B^{10}F_3$ proportional neutron counters connected in parallel to a scaler and supplied from a common high voltage source. The entire assembly was embedded in a block of paraffin wax 40 × 40 × 50 cm. which served as a moderator to thermalize the fast neutrons. Screening from external neutron sources was provided by a structure of bricks of borated paraffin and sheets of cadmium metal, and radiation from extraneous gamma sources was shielded off by a wall of lead bricks on the outside. Pulses from the counters were fed to a recording scaler, the counting period of which was controlled by an electric timer.

The stability of the apparatus was regularly checked with a radioactive neutron source placed in the counting position and the lack of response to gamma rays was checked with a 10-mc. cobalt-60 source which gave no rise in the background count rate [very high cobalt-60 activities gave the expected rise over background due to the 2.5-m.e.v. gamma ray of 4×10^{-5}% abundance (*8*)]. It was incidentally observed that the efficiency of the counters was 6.7% with standard Pu-Be neutron source placed in the sample position.

Although the counters were biased to discriminate against gamma radiation, it was still possible that under intense gamma radiation some spurious counts could be obtained. To remove this source of error the heavy water container was replaced by an identical one filled with natural water, and a measurement was again taken. The difference between the count rate obtained with heavy water and that with natural water gave the photoneutrons' count rate of the source. Since natural water itself contains 0.015% deuterium it was expected that for perfect discrimination against gamma rays, the ratio of the counts obtained with the two waters could be the ratio of their deuterium contents, in this case about 1.5×10^{-4}. The values obtained were in good agreement with this value showing that the counters were sufficiently well biased against gamma rays.

The possible interference from sample materials which themselves could lead to neutron emission was checked and determined in the same way. Thus, samples in which (α,n) reactions or fission could occur, leading to neutron counts not arising from deuterium, were detected and counted with natural water around the sample. The same was true for photoneutron emission from beryllium when that element was present in the sample. In all these cases the photoneutron emission from sodium was given by the differences between the count rates with the heavy water and natural water placed around the sample.

RESULTS

Irradiated samples of pure sodium compounds were counted over long periods of time to check the stability of the apparatus by following the decay of sodium-24. In all cases no deviation

from the 15.0-hour half life was observed. Counting was continued for periods over a week during which time the activity decayed by more than a factor of 2000.

Absolute calibration of the apparatus was carried out by observing the count rate of photoneutron emission from standardized sodium-24 sources. In the experimental apparatus described above, sodium-24 gave one photoneutron count for every 2.45×10^4 disintegrations (Table I).

Samples of known sodium content were irradiated in various fluxes for varying amounts of time, and their photoneutron emission rates were determined in order to calibrate the apparatus and to determine the precision of the method. To obtain sufficiently high counting rates, relatively large amounts of sodium were used for these tests. Table II shows results obtained from such standards, some of which were irradiated simultaneously and others in quick succession in order to obviate errors due to long-term drifts in the reactor flux. The normalized count rates refer to the number of counts per minute obtained per μg. of Na irradiated at a flux of 10^{13} neutrons/cm.^{2}-second for 1 hour. The counts from which the results in Table II were calculated, had a relative standard deviation of about 0.6% whereas the relative standard deviation of the results in the Table is about 1.8% which shows that the counting errors played little part in the result and that the observed precision is the precision of the method, under the prevailing experimental conditions.

The accuracy of the method was checked on a large number of samples of known sodium content ranging from 2 mg. down to 0.3 μg. Some results of these tests are given in Table III.

Table I. Absolute Efficiency of Photoneutron Counting

Sample number	Neutron count rate (min.$^{-1}$)	Activity, d.p.m.	Ratio disintegrations per neutron count
8A	1661	4.042×10^7	2.433×10^4
8B	1674		2.414
9A	1909	4.742	2.484
9B	1955		2.425
10A	2400	5.957	2.482
10B	2452		2.429
11A	2891	6.968	2.410
11B	2834		2.459
12A	3195	7.862	2.461
12B	3233		2.431
13A	3504	8.626	2.462
13B	3548		2.431
14A	3896	9.627	2.471
14B	3912		2.461
			Mean 2.447×10^4
			Std. dev. ±247 (1%)

Table II. Calibration of Photoneutron Count Rate for Sodium Analysis

Weight sodium (mg.)	Irradiation: Duration (min.)	Irradiation: Flux, neutrons/cm.^{2}-sec.	Observed count rate per min. per mg.	Normalized[a] count rate per min. per μg.
3.11	2	7.1×10^{12}	3.792×10^3	15.63
3.29	60	3.2×10^{13}	5.066×10^4	15.83
3.95	2	6.7×10^{12}	3.461×10^3	15.14
4.78	60	3.2×10^{13}	4.912×10^4	15.35
5.21	60	3.2×10^{13}	4.966×10^4	15.52
7.08	2	6.7×10^{12}	3.503×10^3	15.32
12.25	2	6.7×10^{12}	3.635×10^3	15.90
28.48	1	2.4×10^{12}	6.449×10^1	15.75
32.03	2	7.1×10^{12}	3.867×10^3	15.96
			Mean	15.60
			Std. dev.	±0.29 (1.86%)

[a] Normalized to an irradiation of 1 hour at a flux of 10^{13} neutrons/cm.^{2}-sec.

Table III. Some Results of Sodium Determinations

Range	Sodium content (μg.) Present	Found	Error μg.	Error %
10 to 2200	2175.7	2204.0	+28.3	+1.30
	1271.0	1270.1	−0.9	−0.07
	841.8	836.2	−5.6	−0.67
	74.40	74.97	+0.57	+0.77
	20.61	21.00	+0.39	+1.89
	18.16	18.09	−0.07	−0.39
1 to 10	7.34	7.21	−0.13	−1.77
	2.960	2.849	−0.111	−3.75
	2.282	2.281	−0.001	−0.04
	2.010	2.031	+0.021	+1.04
	1.883	1.916	+0.033	+1.75
	1.024	1.088	+0.064	+6.25
<1	0.923	0.896	−0.027	−2.93
	0.712	0.727	+0.015	+2.11
	0.326	0.307	−0.019	−5.83

DISCUSSION

Precision and Sensitivity. The sources of error that affect the precision of the method arise at three stages—the preparation of the sample, its irradiation, and its counting. Because sample preparation requires simple operations the errors inherent in them are considered to be small and of the same order as similar procedures in other analytical methods. For this reason this source of error is not discussed here.

Errors that may arise at the irradiation stage are errors arising from reactor flux variations and difference between irradiation fluxes through the sample and the standard with which it is compared. Relative errors occurring at this stage do not depend on the weight of sodium in the sample as the amount of sodium-24 activity built up in the sample varies linearly with the weight of sodium it contains and with the neutron irradiation flux to which it is exposed. As a result, the values given in Table II can be used as an indication of the precision of the method as a whole since errors due to counting those results do not play an important role, and sampling errors there are assumed to be constant and small.

When the over-all precision for the analysis of small amounts of sodium has to be determined, the additional errors of counting should also be taken into account. These errors arise from the statistical errors normally involved in counting random events, errors due to background activity, and errors due to the presence of other components in the sample that could yield neutron counts.

For a gross sample count of S and a background, B, the standard deviation of the net sample count, $\Delta = S - B$, is given by σ_Δ where

$$\sigma_\Delta = \pm\sqrt{S + B} = \pm\sqrt{2B + \Delta}$$

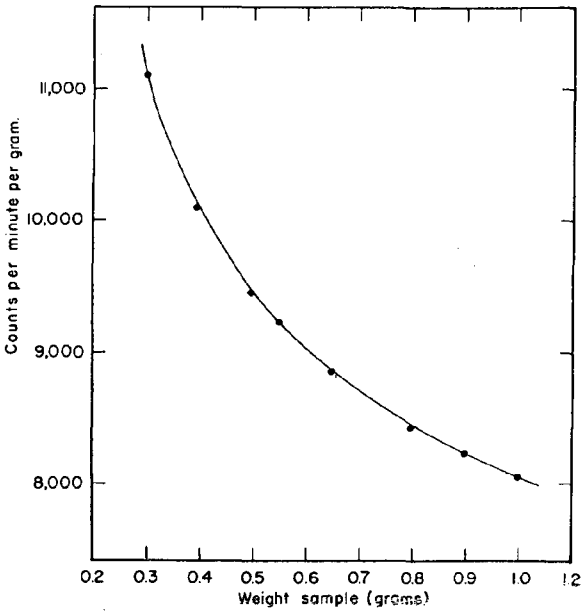


Figure 2. Variation of count rate with sample size, of sample containing high concentration of strongly neutron-absorbing material

Sample contained 0.188% Na and 39.4% w./w. Cd. Curve calcd. for self-absorption of cadmium and points are experimental

With a background of about 12 counts per minute, as measured in this investigation, a precision of ±10% (relative standard deviation) can be obtained for a sample containing 0.34 μg. of sodium which is irradiated for 1 hour at a flux of 10^{13} neutrons per cm.^{2}-second and is counted for about 2 hours. The sensitivity of the method can be much improved by longer irradiations at higher fluxes. A flux of 5×10^{13} n/cm.^{2}-second can be obtained readily. For practical considerations irradiations should not extend much more than a day, say 30 hours or two half lives, when the activity would be about 16 times greater than for the same sample irradiated for 1 hour at the same flux. Hence the sensitivity of the method for the same ±10% precision can be improved to about 0.004 μg. Conversely, it can be shown that the minimum weight which can be determined with a precision of say, 2% (the relative standard deviation of the results under the experimental conditions of irradiation), is about 2 μg., but with the longer irradiation and the higher flux it reduces to about 0.025 μg.

When samples are to be analyzed for sodium in the presence of elements which can cause (α,n) reactions or undergo fission, or in the presence of beryllium which would yield photoneutrons as well, the additional activity can be measured with natural water in place of D_2O in the counting assembly (as was described above). This extra activity is then treated as an added background.

Accuracy. The results in Table III give a clear indication of the accuracy of the method. However, because of the sensitivity of the method, careless handling of the samples can lead to systematically-high results especially when small weights of sodium are analyzed. This was shown by a series of aluminum samples that were irradiated to determine the extent of sodium-24 formation by the reaction $Al^{27}(n,\alpha)Na^{24}$. Irradiation of vials handled only with pincers and tongs gave consistent results (see value in Table IV), but samples handled with gloves showed contamination of about 40% (due to about 0.5 μg. of sodium from the talc used with the gloves). Samples touched with bare hands showed nearly three times as much activity as in the clean vials (equivalent to about 4 μg. of Na).

Systematically-low results were obtained from samples containing appreciable amounts of strongly neutron-absorbing material. Figure 2 shows the decrease of count rate per unit weight sample for a material containing 0.188% sodium and 39.4% cadmium. In the figure the experimental points are shown against the curve calculated for self-absorption of cadmium (*3*) and normalized for the known sodium content of the sample. The addition of a known amount of sodium as internal standard (spike) enables the correct sodium content to be computed.

Interference from Other Elements. The most common elements that occur together with sodium do not interfere with the analysis by photoneutron emission. Potassium-42 emits a γ-ray of 2.44 m.e.v. but only with an abundance of 0.04% of its disintegrations; the amount of potassium would have to be 500 times higher than the sodium content of the sample to introduce an error of 2% to equal the experimental error (precision) of this method. Calcium does not yield any interfering isotope on neutron irradiation while magnesium interferes only in so far as it produces sodium-24 by the reaction $Mg^{24}(n,p)Na^{24}$ with fast neutrons, which is discussed below. Most elements which occur in the anions usually associated with sodium do not interfere because of the absence of gamma rays over 2.23 m.e.v. emitted in their decay, so that sodium can be analyzed in any chemical form.

The main elements which can interfere because of the high-energy gamma rays they emit after neutron irradiation are listed in Table IV. In the same table are listed the calculated and observed photoneutron emission from 1 μg. of element irradiated for 1 hour at a

Table IV. Calculated and Observed Photoneutron Count Rates for Common Elements Likely to Interfere in Sodium Analysis, Compared with Count Rate for Sodium

Element	Isotope	Half life (hours)	Activity[a] Calcd.	Activity[a] Observed	Sodium[b] equivalent, μg.
Sodium	Na^{24}	15.0	14.84	14.90	1
Manganese	Mn^{56}	2.58	12.65	11.99	1.24
Gallium	Ga^{72}	14.1	3.28	3.04	4.90
Lanthanum	La^{140}	40.2	0.515	0.50	2.98×10^1
Magnesium	Na^{24}	15.0	0.00247[c]	0.003[c]	4.97×10^3
Aluminum	Na^{24}	15.0	0.00142[c]	0.0017[c]	8.76×10^3
Potassium	K^{42}	12.4	0.00059	0.00058[d]	2.53×10^4

[a] Normalized counts per minute for 1 μg. of metal irradiated for 1 hour at a thermal neutron flux of 10^{13} n/cm.^{2}-sec. and counted 1 hour after irradiation.

[b] Wt. element in micrograms yielding a neutron count rate equivalent to 1 μg. of Na 1 hour after the end of irradiation.

[c] For a fission-spectrum neutron flux of 10^{12} n/cm.^{2}-sec. Assuming a thermal to fission flux ratio of 10:1.

[d] Measured for "Analar" grade $KHCO_3$ containing approximately 0.03% Na and corrected for the sodium-24 contribution.

thermal neutron flux of 10^{13} neutrons/-cm.^{2}-second, and counted 1 hour after the end of irradiation. The calculated values were obtained from the measured efficiency for sodium-24 gamma rays of 2.75 m.e.v. corrected for the cross section of the deuterium (γ,n) reaction (7) for the energy of the gamma ray concerned. The observed results are in very good agreement with the calculated values. Column 6 of Table IV gives the weight of element in micrograms necessary to produce a photoneutron count rate equivalent to that of 1 μg. of sodium, both being irradiated for 1 hour at a thermal flux of 10^{13} neutrons/cm.^{2}-second and counted 1 hour after irradiation. From these values it is clear that the determination of sodium offers some difficulties in samples where the manganese or lanthanum concentration is high and is almost impossible in samples containing gallium as long as the gallium-72 is not removed before counting. Naturally, the shorter-lived interference from manganese-56 can be reduced by waiting for a longer time before counting.

Depending on the nature of the interfering element, it is frequently possible to alter irradiation conditions to improve the ratio of sample to interference count rates. Thus, the photoneutron count rate of a sample containing equal weights of sodium and manganese irradiated for 1 hour will, according to the values in Table IV, consist of almost equal contributions from the two components, at the start of counting. If, however, the same sample is irradiated for a longer time, say 10 hours, even at a lower flux, the relative contribution of sodium at the start of counting is doubled. On the other hand, if the sample is rich in lanthanum, short high-flux irradiations are preferable because long irradiations will favor the relatively higher yield of the longer-lived nuclide.

Aluminum and magnesium which produce sodium-24 by fast neutron reactions obviously interfere in the analysis for sodium. From Table IV it can be seen that an aluminum content about 175 times that of sodium and a magnesium content of about 100 times that of sodium, would only add about 2% to the photoneutron count rate. However, the values given in Table IV do not reflect how little the true extent of interference is, since both aluminum and magnesium results have been normalized to a fission spectrum neutron flux of 10^{12} neutrons/cm.^{2}-second, and compared with that for a thermal neutron flux of 10^{13} for sodium. In an actual irradiation with a mixed flux (partially moderated fission spectrum neutron flux), the interference from these two elements is still further decreased when the ratio of thermal to fast neutrons is more than 10. Sodium analysis in large concentrations of aluminum and magnesium can still be carried out if the samples are irradiated first unshielded and then shielded with cadmium. The cadmium ratio for sodium was measured and found to be 45.8 ± 0.8. (This result was obtained for an irradiation flux consisting of fast and thermal neutrons in the unusually high ratio of about 1:3.) As the sodium-24 production from Al or Mg is unaffected by the cadmium screen, the difference between the two results enables the sodium content to be calculated.

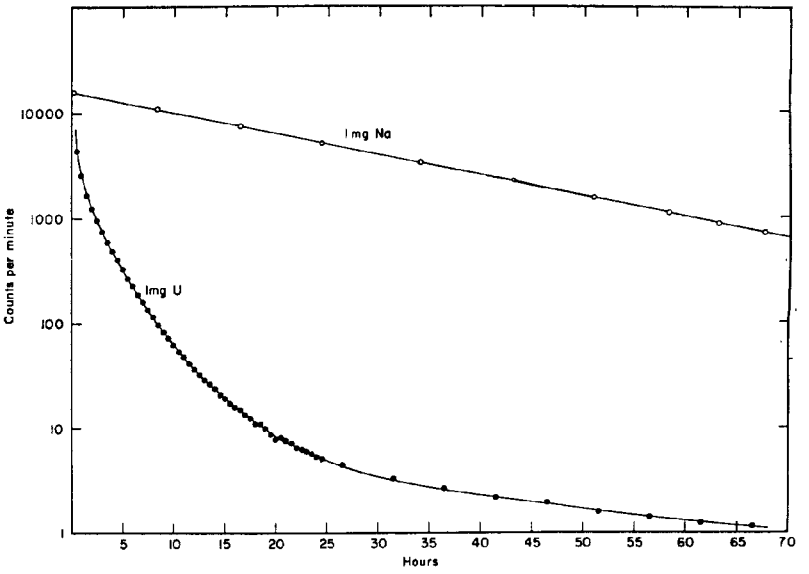


Figure 3. Comparison of photoneutron count rate from 1 mg. of sodium and 1 mg. of natural uranium after irradiation for 1 hour at flux of 10^{13}n/cm.^{2}-sec.

When samples contain uranium, the formation of fission products on neutron irradiation could lead to higher photoneutron emission. The count rates obtained from 1 mg. of natural uranium and from 1 mg. of sodium both irradiated for 1 hour at a neutron flux of 10^{13} neutrons/cm.^{2}-second are compared in Figure 3. Although shortly after irradiation the count rates are comparable, the fission product decay is so much faster than that of sodium, that 15 to 20 hours later, the count rate of sodium is about 400 to 800 times greater. So even if uranium and sodium are present in equal proportions in the sample to be analyzed, it is sufficient to wait for about one half life (15 hours) to eliminate the interference altogether. The small amounts of uranium normally present in samples assayed for sodium obviously do not interfere. The determination of sodium in the presence of high concentrations of uranium is still possible for uranium concentrations up to 10 times that of sodium, at which concentration the mixed fission products would contribute a little more than 1% to the sodium count rate, 20 hours after irradiation. If the ratio of uranium to sodium (by weight) exceeds 10, the error due to the presence of fission products becomes large, and nondestructive analysis by this method is then possible only if an accurate analysis of uranium is made and its presence corrected for. Such analysis can be carried out nondestructively as well (1) using essentially the same experimental apparatus and counting delayed neutrons.

ACKNOWLEDGMENT

Thanks are due to the operating crew of IRR-1 who attended to the irradiations, to Yoram Gurfinkel and Amos Nutes who helped with the construction of the apparatus, and to Vili Carbunaru for his assistance with the experiments.

LITERATURE CITED

(1) Amiel, S., ANAL. CHEM. 34, 1683 (1962).
(2) Dean, J. A., "Flame Photometry," p. 163, McGraw-Hill, New York, 1960.
(3) Gilat, J., Gurfinkel, Y., Israel Atomic Energy Comm. *Rept.* IA-756 (1962).
(4) Haigh, C. P., "Second Radioisotope Conference Oxford 1954," Vol. II Butterworth, London, 1954.
(5) Hughes, D. J., Schwartz, R. B., "Neutron Cross Sections," 2nd ed., Brookhaven National Laboratory, Upton, N. Y., 1958.
(6) Koch, R. C., "Activation Analysis Handbook," p. 44, Academic Press, New York, 1960.
(7) Marion, J. B., Fowler, J. L., "Fast Neutron Physics Part I," p. 28, Interscience, New York, 1960.
(8) Morinaga, H., Takahashi, K., *J. Phys. Soc. Japan* 14, 1460 (1959).
(9) Odeblad, E., *Clin. Chim. Acta* 1, 67 (1956).
(10) Roy, J. C., Hawton, J. J., Atomic Energy of Canada *Rept.* AECL-1181 (1960).
(11) Schroeder, G. L., Winchester, J. W., ANAL. CHEM. 34, 96 (1962).

RECEIVED for review February 11, 1963. Accepted April 29, 1963.

Diffuse Reflectance Spectra of Potassium Iodate and Some Mercuric Iodide Complexes

T. R. GRIFFITHS[1]

North East Essex Technical College, Colchester, England

▶ **In an earlier publication the potential of diffuse reflectance spectroscopy in the ultraviolet was assessed. Using this technique, further experiments with KIO_3 variously diluted with an inactive diluent, LiF, have been carried out to examine the possibility of its use as an analytical tool. With certain precautions, results of a semiquantitative nature can be obtained at wavelengths down to 220 mμ. The spectra obtained from powdered solid K_2HgI_4 and $K_2HgI_3 \cdot H_2O$ give evidence as to their structure.**

One of the analyst's most valuable tools is that of the visible and ultraviolet spectra of solutions. Such spectra give highly accurate evaluations of the concentration of different species in solution. However, there are times when certain compounds are not readily soluble, or, if they are, a change may take place, often undetected, on dissolution. X-ray crystallography is, of course, the accurate method of establishing the structure of solid materials prior to dissolution, but a single crystal is often essential. When this is not available, much useful information can still be obtained from the Von Laue powder method.

The purpose of this study was twofold: to see if this technique could be used in an analytical manner and to ascertain the structure of solid $KHgI_3 \cdot H_2O$ and K_2HgI_4 and compare the results obtained with solution spectra, thereby demonstrating usefulness similar to the Von Laue method. Allied regions of these topics have been studied by other workers (*1*, *7*, *12*, *14–23*, *26*, *29*, *31*, *34–36*).

EXPERIMENTAL

When monochromatic light is diffusely reflected by a powdered surface, it is split into two components, diffuse and regular reflectance. This latter effect plays the major role when the powder particles are large (*15*). This regular reflectance is not required since it causes band broadening and it can be removed essentially by placing crossed polarization prisms between the reflecting sample and standard surfaces and the detector (*20*). Alternatively, if the powder particles are submicron in diameter, and thus approximate to the dimension of the wavelength (*19*) of the incident light, the effect of regular reflectance is almost completely negated. Its additive effect is, of course, further diminished upon dilution with a material which is also used as the reference standard. Thus, for pure diffuse reflectance spectra of materials containing allowed transitions, particle size is not critical when concentrations are in the region of 10^{-2} mole per liter or less (*15*). This work, being concerned largely with potassium iodate which shows a forbidden band in its diffuse reflectance spectrum (*10*), involved concentrations in the order of 5 moles per liter—i.e., approximately twice as much diluent as iodate by weight—thus necessitating careful grinding and thorough homogeneous mixing to eliminate the effect of regular reflectance.

The apparatus used in the spectral measurements was that described earlier (*10*), except that a recently redesigned S.Z.G. 500 photomultiplier attachment was employed.

The problem of obtaining reproducible flat surfaces (*10*) was resolved by using a Plexiglas tamper (*29*) or a flat, polished steel tamper, the latter being slightly better because its weight made for firmer packing. Surfaces could thus be obtained with a reproducibility in absorbance values of ±0.025. Further, to keep this error low, spectra were normally taken against a Whatman No. 4 filter paper as standard (*36*), and from the results were subtracted the spectra of pure lithium fluoride against filter paper. Figure 1 shows typical diffuse reflectance spectra of potassium iodate and mercuric iodide.

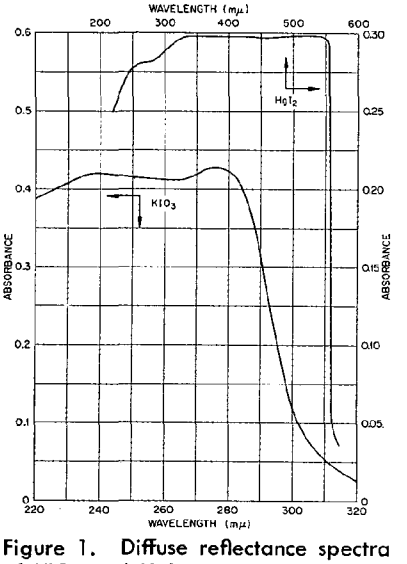


Figure 1. Diffuse reflectance spectra of KIO_3 and HgI_2

LiF as diluent and reference

All compounds used were the purest obtainable from British Drug Houses, Poole, Dorset, and were thoroughly dried, prior to grinding, in a Townsen and Mercer micro drying pistol under high vacuum over P_2O_5 at 80° C. Grinding was carried out to submicron size in an M.270 analytical mixer mill, obtainable from Glencreston, Stanmore, Middx., using an M.274 hardened stainless steel grinding cylinder with hemispherical end caps and containing one steel ball pestle. In certain instances submicron size was deliberately not reached for potassium iodate. Diluent and sample were weighed into an M.262 polystyrene mixing vial and shaken with two Plexiglas ball pestles until thoroughly mixed (2 minutes). The materials used were not avidly hygroscopic, but water adsorption was kept to a minimum by exposing the materials to the air as little as possible and by keeping the bottom of the specimen tray covered with silica gel (*10*).

In this work the term "dilution" is used rather than "adsorption" (*15*), as it more adequately describes the processes taking place when ionic materials are used.

RESULTS AND DISCUSSION

The results depicted in Figure 2 show that there is a linear nature in the relationship between the concentration of potassium iodate diluted with lithium fluoride and the absorbance recorded at wavelengths down to 220 mμ. Conformity to Beer's law is thus inferred. Further, from these results, because of the appropriate choice of potassium iodate, it has been possible to deduce the experimental limitations of this method. First, when particle size and the wavelength of the incident light are not comparable, there is no correlation between absorbance and concentration (Figure 2). Secondly, results taken on the steeply rising absorption edge are less accurate because of the wider slit

[1] Present address, Metals & Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

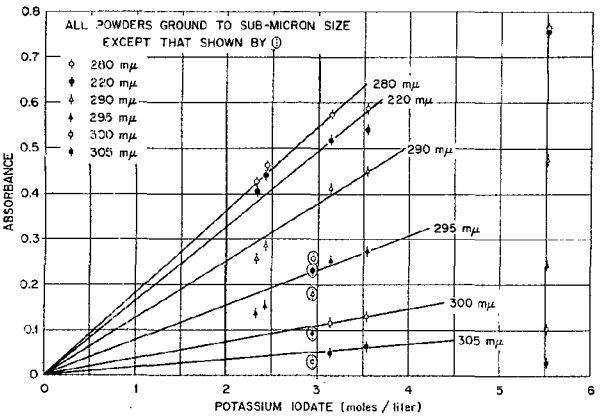


Figure 2. Plot of absorbance of KIO_3 against concentration in moles per liter at different wavelengths with LiF as diluent

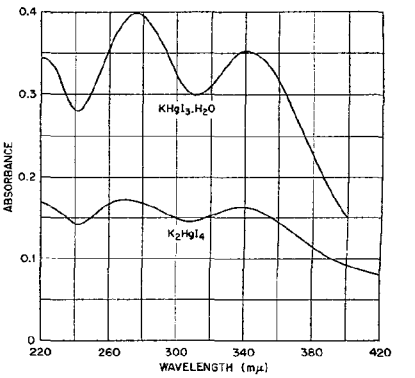


Figure 3. Diffuse reflectance spectra of K_2HgI_4 and $KHgI_3 \cdot H_2O$

LiF as diluent and reference

widths that must be used; very low absorbance values are also not so precise because of lack of instrumental precision. Thirdly, with relatively uniform particle size, deviations from linearity are observed when the absorbance of the peak is greater than 0.6 (*10*). This may be due in part to the fact that the observed transition in iodate is a forbidden one (*10, 28*) and thus in the higher concentration range (see Figure 2) the iodate particles in the surface may be absorbing some of the emitted rays from neighboring particles, thereby lowering the intensity of the light collected from the surface. It is therefore to be expected that this factor will not be observed when the spectra of compounds containing allowed transitions in this spectral range are quantitatively measured. Evidence for this may be deduced from recent work by Kortüm (*15*). If it is assumed that his powders contain submicron particles, as may be inferred from his paper, then an approximately straight-line relationship can be calculated for the reflectance spectrum of mercuric iodide in a concentration range of 10^{-2} to 10^{-4} mole per liter.

Since Zeitlin and coworkers have shown (*1, 7, 34*) that the diluent used in reflectance studies can affect the spectra obtained, some comments on the above system are appropriate. The highly ionic fluorides are accepted as inactive diluents (*1, 10, 15*). Also, the spectra of potassium iodate and mercuric iodide (Figure 1) when diluted with lithium fluoride showed no variation with time, and it is recommended that this check be always employed. Kortüm (*15*) further remarks upon the absence of chemisorption of mercuric iodide upon sodium fluoride. Finally, it is concluded that this study of the forbidden transition in iodate has enabled the various factors that must be taken into consideration in the application of diffuse reflectance spectroscopy to be ascertained in an analytical manner.

The results depicted in Figure 3 show that the spectrum obtained from the compounds $KHgI_3 \cdot H_2O$ and K_2HgI_4 are essentially identical and they can be considered to arise from related tetrahedral structures from the following. The tetrahedral (*4, 32*) complex ion, HgI_4^{-2}, when in solution, gives rise to a doublet, the peak positions being reported at 320 to 340 mμ and 265 to 275 mμ (*6, 8, 9, 11*), dependent upon solvent. Until recently, Raman spectroscopic evidence for the existence of the HgX_3^- ion was inconclusive (*4, 27, 33*). Recent ultraviolet (*9, 11*) and Raman spectroscopic work (*13*) have now established its definite, but sensitive, existence. The first transition for HgI_3^- appears at ca. 305 mμ (*11*). [Association constants derived from these ultraviolet spectroscopic data will be published shortly (*9*).] This band was not observed when $KHgI_3 \cdot H_2O$ or K_2HgI_4 was dissolved in water; only a slightly modified spectrum of linear (*4, 6, 11, 33*) HgI_2 was recorded.

The presence of tetrahedral ions and molecules has been demonstrated in Cs_2ZnCl_4 (*3*) and $ZnCl_2(NH_3)_2$ (*25*), respectively. The coordination of the ammonia ligands in the latter is obviously through the lone pair electrons on nitrogen. Since tetrahedral mercuric halide complexes containing dative bonds are known—e.g., $[(C_4H_9)_3As]_2[HgBr_2]_2$ (*4*)—it is probable that in $KHgI_3 \cdot H_2O$ the water molecule is coordinated to mercury through oxygen, thereby giving a slightly distorted tetrahedral configuration about mercury. The evidence does not support a planar structure in the solid state similar to that proposed for $HgCl_3^-$ in solution (*13*). Thus this technique should prove useful to workers interested in solid state structures.

The reflectance spectrum of red mercuric iodide diluted with lithium fluoride (Figure 1) is essentially that found by Kortüm using sodium fluoride (*15*), and first reported by Zeitlin and Goya (*34*). When red mercuric iodide is ground with magnesium oxide, K. obtains evidence for a doublet with peaks at ca. 320 and 277 mμ. When it is ground with potassium iodide, peaks are obtained at ca. 320 and 272 mμ. Although this latter spectrum is compared with that of mercuric iodide in 10*N* potassium iodide solution, no assignment for these bands is given. Since red mercuric iodide consists of a layer structure built up of HgI_4 tetrahedra sharing corners with other tetrahedra (*30*), it is now suggested that the doublets obtained in this work and those of Kortüm (*15*) are due to a tetrahedral arrangement of ligands about mercury. This result is not surprising when it is remembered that both mercurous and mercuric iodide may be prepared by triturating the elements together in the correct proportions.

So far, the lowest energy transitions of HgI_4^{-2} have not been assigned. Various workers have, however, laid down general schemes (*2, 24, 32*). Probably the most useful is the LCAO-MO approach by Wolfsberg and Helmholtz (*32*), in which the *nd*, $(n + 1)s$ and $(n + 1)p$ orbitals on the central metal atom and the *p* orbitals on the ligand are used. There are two available, unfilled orbitals into which electrons may be promoted, but until calculations have been made to determine which of these levels is lowest in energy and which of the filled levels is highest in energy, no authoritative pronouncement on the precise transition that occurs can be made.

ACKNOWLEDGMENT

The author thanks M. C. R. Symons for encouragement and D. W. James and G. P. Smith for valuable discussion. The provision of the spectrometer and photomultiplier attachment by the Department of Scientific and Industrial Research is gratefully acknowledged. Technical assistance was also received from A. K. Griffiths and Brian Foster.

Thanks are due to the Education De-

partment of the Essex County Council for supplying the monies necessary for carrying out this program.

LITERATURE CITED

(1) Anthony, P., Zeitlin, H., *Nature* **187,** 936 (1960).
(2) Ballhausen, C. J., "Introduction to Ligand Field Theory," p. 171, McGraw-Hill, New York, 1962.
(3) Brehler, B., *Z. Krist.* **109,** 68 (1957).
(4) Delwaulle, M., *Bull. Soc. Chim. France* **1955,** 1294.
(5) Evans, R. C., Mann, F. G., Peiser, M. S., Purdie, D., *J. Chem. Soc.* **1940,** 1209.
(6) Fromherz, H., Lih, K., *Z. physik. Chem. (Leipzig)* **A 167,** 103 (1933).
(7) Goya, H., Waugh, J. L. T., Zeitlin, H., *J. Phys. Chem.* **66,** 1206 (1962).
(8) Griffiths, T. R., Ph.D. thesis, Southampton University, England, 1960.
(9) Griffiths, T. R., Colchester, England, unpublished results, 1962.
(10) Griffiths, T. R., Lott, K. A. K., Symons, M. C. R., ANAL. CHEM. **31,** 1338 (1959).
(11) Griffiths, T. R., Symons, M. C. R., *Trans. Faraday Soc.* **56,** 1752.
(12) Jahoda, F. C., *Phys. Rev.* **107,** 1261 (1957).
(13) Janz, G. J., James, D. W., *J. Chem. Phys.* **38,** 905 (1963).
(14) Kortüm, G., *Spectrochim. Acta Suppl.* **1957,** 534.
(15) Kortüm, G., *Trans. Faraday Soc.* **58,** 1624 (1962).
(16) Kortüm, G., Braun, W., *Z. physik. Chem. (Frankfurt)* **18,** 242 (1958).
(17) Kortüm, G., Kortüm-Seiler, M., *Z. Naturforsch.* **2a,** 652 (1947).
(18) Kortüm, G., Schlotter, H., *Z. Elektrochem.* **57,** 353 (1953).
(19) Kortüm, G., Vogel, J., *Z. physik. Chem. (Frankfurt)* **18,** 110 (1958).
(20) *Ibid.*, p. 230.
(21) Kortüm, G., Vogel, J., Braun, W., *Angew. Chem.* **70,** 651 (1958).
(22) Kubelka, P., Munk, F., *Z. tech. Physik* **12,** 513 (1931); *J. Opt. Soc. Am.* **38,** 448 (1948).
(23) Lermond, C. A., Rogers, L. B., ANAL. CHEM. **27,** 340 (1955).
(24) Liehr, A. D., *J. Chem. Educ.* **39,** 135 (1962).
(25) MacGillavry, C. H., Bijvoet, J. M., *Z. Krist.* **94,** 249 (1936).
(26) Naughton, J. J., Frodyma, M. M., Zeitlin, H., *Science* **125,** 121 (1957).
(27) Rolfe, J. A., Sheppard, D. E., Woodward, L. A., *Trans. Faraday Soc.* **50,** 1275 (1954).
(28) Smith, M., Ph.D. thesis, Southampton University, England, 1958.
(29) Symons, M. C. R., Trevalion, P., *Spectrovision* **10,** 8 (1961).
(30) Wells, A. F., "Structural Inorganic Chemistry," p. 345, Oxford University Press, London, 1962.
(31) Wendlandt, W. W., Franke, P. H., Smith, J. P., ANAL. CHEM. **35,** 105 (1963).
(32) Wolfsberg, M., Helmholtz, L., *J. Chem. Phys.* **20,** 837 (1952).
(33) Woodward, L. A., *Quart. Rev.* **10,** 185 (1956).
(34) Zeitlin, H., Goya, H., *Nature* **183,** 1041 (1959).
(35) Zeitlin, H., Niimoto, A., ANAL. CHEM. **31,** 1167 (1959).
(36) Zeitlin, H., Niimoto, A., *Nature* **181,** 616 (1958).

RECEIVED for review March 1, 1963. Accepted May 2, 1963.

Anion Exchange Separation of Magnesium and Calcium with Alcohol–Nitric Acid

JAMES S. FRITZ and HIROHIKO WAKI

Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa

▶ Magnesium and calcium are separated by anion exchange, using dilute nitric acid in a medium containing a high proportion of a water-miscible alcohol. A "column separation factor" is proposed and used in selecting the best eluting medium. A solution of 0.5M nitric acid in 90% isopropyl alcohol is the eluent. Amberlyst XN-1002 resin is recommended for the separation.

A NUMBER of papers have been published on the ion exchange separation of magnesium and calcium. This separation has been done on a cation exchange resin merely by eluting with hydrogen ions (*1, 10*), although the difference in affinity for the resin is not very large. To enhance the separability, complex-forming agents such as ammonium acetate (*6*), ammonium formate (*13*), and ethylene (dinitrilo) tetraacetic acid (EDTA) (*14*) under proper pH conditions, have been used. An anion exchange separation was also made (*11*).

All of these complexing agents used in Mg-Ca separation are salts of organic acids. Common inorganic acids seem more convenient as the eluents, because the treatment and analysis of the effluent containing the metal after elution are easier in most cases. In anion exchange which depends only on complexability of a metal, however, alkaline earth metals have always been classified in a nonsorbable group, because neither element forms any complex anions in these aqueous acids or even in the resin phase. On the other hand, the addition of a water-miscible organic solvent to a metal-complex system makes the complex formation more effective. This sometimes leads to larger separability of metals in anion exchange (*2–4, 7, 8, 12, 15*) as well as in cation exchange (*5*). Recently the Ca-Sr-Ba anion exchange separation, which is impossible using aqueous nitric acid, was done by Fritz and Garralda (*3*) using an isopropyl alcohol–nitric acid mixture.

In the present work, an anion exchange separation of magnesium and calcium is studied under various conditions using dilute nitric acid in aqueous-alcohol media. The best separation is accomplished using 0.5*M* nitric acid –90% isopropyl alcohol.

EXPERIMENTAL

Resins. The anion exchange resin Amberlyst XN-1002 (Rohm & Haas Co.) was ground into smaller particle sizes; 40 to 60 mesh was used for bath experiments and 60 to 100 mesh for column experiments. The resin was converted to the nitrate form with nitric acid. Used resin was regenerated by washing the sorbed metals with extremely dilute nitric acid or pure water. Nitrate resin was stored in a dark place. Dowex 1-X8, 100 to 200 mesh, anion exchange resin was also used in nitrate form for comparison. Although resins for batch experiments were roughly air-dried under suction, complete dryness was not attained.

Reagents. Nitric acid, alcohols, EDTA, and other reagents were all reagent grade and were used without purification. Stock solutions of calcium, magnesium, nickel, manganese, aluminum, iron, zinc, cobalt, copper, and cadmium were prepared by dissolving their nitrates in pure water or dilute nitric acid. Impurities in these reagents were generally negligible. Solutions of magnesium, calcium, nickel, manganese, aluminum, and iron were sometimes purified by the ion exchange method or a small correction was made from a blank when it was necessary in the recovery experiments.

Mixed Solutions. The eluent for the separation of magnesium and calcium is prepared by mixing 100 ml. of 5*M* nitric acid and 900 ml. of isopropyl alcohol in a 1-liter volumetric flask and diluting the solution to volume with water. The sample solution added to the column is usually 10 ml. of the same solvent composition as the eluent. The metal

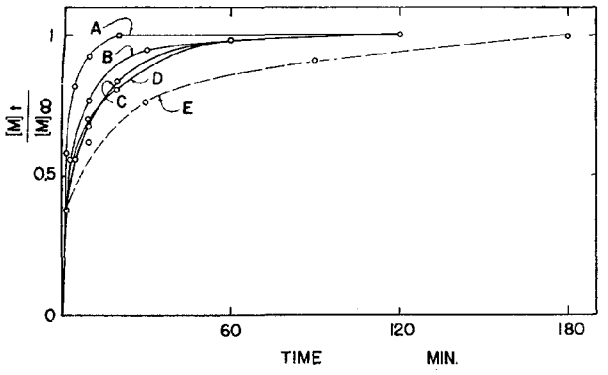


Figure 1. Sorption rate measurement:

$[M]_t$. Sorbed amount of metal at time t
$[M]_\infty$. Sorbed amount of metal at equilibrium
A. 0.25 mmole Mg, swollen Amberlyst XN-1002, *tert*-butyl alcohol
B. 0.25 mmole Ca, air-dried Amberlyst XN-1002, isopropyl alcohol
C. 0.25 mmole Ca, swollen Amberlyst XN-1002, *tert*-butyl alcohol
D. 0.5 mmole Ca, air-dried Amberlyst XN-1002, *tert*-butyl alcohol
E. 0.25 mmole Ca, air-dried Dowex 1-X8, *tert*-butyl alcohol

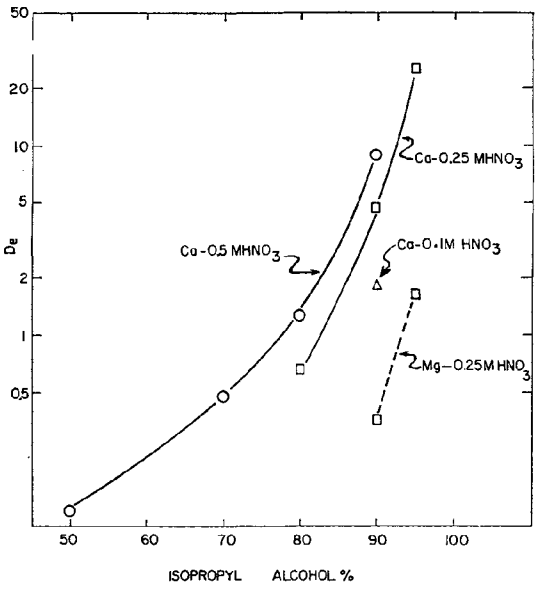


Figure 2. Variation of D_e with nitric acid and isopropyl alcohol contents

solutions used for batch experiments are prepared in the same manner.

Determination of Metal Ions. For the determination of all elements, standard EDTA titration methods are used. The concentration of EDTA titrant is 0.001 to 0.05M, depending on the amount of metal ion titrated. Details of titration procedure are described below.

Sorption Rate Measurement. To 1 gram of air-dried resin put in each stoppered glass vessel, 0.5M nitric acid–90% alcohol (*tert*-butyl alcohol or isopropyl alcohol) solution containing 0.25 or 0.5 mmole of metal (Mg or Ca) is added and shaken mechanically. After a definite time (2 to 180 minutes), an aliquot of the solution phase is withdrawn and analyzed titrimetrically with EDTA. The sorbed amount of metal is calculated from the difference between total metal taken and the amount remaining in the solution phase. Some experiments were done with resin which was immersed in the same acid-alcohol mixture for about 30 minutes before addition of the metal.

Distribution Coefficient Measurement in Various Alcohol–Nitric Acid Media. Twenty milliliters of 0.1 to 0.5M HNO_3 containing 50 to 90% alcohol and 0.25 mmole of each metal ion is added to 1 gram of resin. After shaking for 3 hours an aliquot of solution is taken and analyzed. All equilibrations are done at 24° ± 1° C. The distribution coefficient, D_e, is calculated as follows:

$$D_e = \frac{\text{mmole of metal ion per milliequivalent of resin}}{\text{mmole of metal ion per milliliter of solution}}$$

In order to know the exchange capacity of resin taken, another 0.5 gram is transferred into a small glass column at the time the resin is weighed for the batch process. The resin in the column is converted to the chloride form, and the exchange capacity is determined by release of chloride ions with sodium nitrate, followed by Mohr's titration.

For small D_e values of magnesium, the calculation by column technique is applied as follows:

$$D_e = D_v f = \frac{V_{max} - i}{c}$$

where D_v = volume distribution coefficient
f = conversion factor between ml. and meq.
V_{max} = effluent volume, ml., at maximum concentration of eluted metal
i = interstitial volume of column, ml.
c = column exchange capacity

Loading Experiment. Conditions for batch equilibration are almost the same as above, except that the metal amount is varied and 2 grams of resin is used for low loads of magnesium.

In making elution curves for column separations using various loads of magnesium and calcium, the sample solution is added to the Amberlyst column, and the elution with the same eluent is continued until a maximum concentration of calcium in the effluent is obtained. Five-milliliter fractions of the effluent are collected and analyzed for magnesium or calcium. Details of the column procedure are almost the same as described below.

Procedure for Separation and Determination. A 10-ml. column (i.d. 1.1 to 1.2 cm.) is carefully prepared and 40 ml. of the fresh eluent is passed through it. The occurrence of bubbles in the resin bed is avoided. A 10-ml. sample solution which contains no more than 0.25 mmole of calcium and is 0.5M in nitric acid and 90% (v./v.) isopropyl alcohol is added to the column. Collection of effluent from the column in a graduated cylinder is begun. The sample solution is passed through the column at a flow rate of about 0.3 ml. per minute. When no liquid is left above the resin bed, 1 ml. of eluent is added to wash the inside wall. Then the elution is carried out continuously by dropwise addition of 0.5M nitric acid–90% isopropyl alcohol from a separatory funnel. The flow rate is maintained at 0.5 to 0.6 ml. per minute. The first effluent equivalent to the interstitial volume is discarded, since it contains no metal ions. The next 40 ml. of effluent is taken for the Mg determination. A few 5-ml. fractions may be checked to confirm quantitative elution of magnesium. Then the eluent is changed and calcium is stripped with 30 to 40 ml. of 0.02M aqueous HNO_3 at a flow rate of ~2 ml. per minute.

Determination. The effluent for magnesium is diluted to 200 to 300 ml. and titrated with 0.05M EDTA, using Eriochrome Black T indicator after adjusting the pH to 10 with ammonia, or an aliquot of the effluent is taken and titrated with more dilute EDTA. If the amount of magnesium is small (less than 0.05 mmole), magnesium is titrated with 0.01M EDTA, after the excess nitric acid and alcohol have been evaporated off carefully. Or preferably, the following technique is used for small amounts of magnesium. The effluent is made pH 7 to 8 with ammonium and passed through a 5-ml. column of the ammonium form cation exchanger Dowex 50W-X8. The column is washed with a small amount of water and magnesium is stripped with 10 ml. of pH-buffered solution containing a known amount of EDTA. After the column is washed with water, the excess EDTA is back-titrated with dilute $ZnCl_2$ solution.

The calcium fraction is adjusted to pH 10 with ammonia and standard EDTA solution is added in excess. The excess EDTA is back-titrated with zinc chloride, using Eriochrome Black T indicator.

RESULTS AND DISCUSSION

Sorption Rate. The sorption rate for magnesium and calcium was compared using Amberlyst XN-1002 and Dowex 1-X8 resins. *tert*-Butyl alcohol was chosen to determine the equilibration time for the measurement of distribution coefficients because it is the most viscous of the alcohols used. The amount of metal ion sorbed is plotted against equilibration time in Figure 1. With the Amberlyst resin, calcium attains equilibrium in *tert*-butyl alcohol in about 2 hours. The rate of sorption is somewhat faster in isopropyl alcohol. The shape of the sorption curve seems not to depend on the amount of metal ion taken or on whether the resin was preswollen in the nitric acid–alcohol mixture. In the case of magnesium, equilibrium is reached in a very short time in *tert*-butyl alcohol. On the other hand, 3 hours is still not sufficient for equilibration using Dowex 1-X8, despite the fact that this resin is of smaller particle size than Amberlyst XN-1002 resin. We therefore conclude that Amberlyst XN-1002 is better for anion exchange separations in nonaqueous medium.

Distribution Coefficients in Various Media. Three important factors may be varied in seeking the optimum condition for the ion exchange separation of magnesium and calcium in nitric acid–alcohol systems: the kind of alcohol present, the percentage of alcohol, and the concentration of nitric acid used.

First, a series of alcohols from methanol to *tert*-amyl alcohol was studied using 0.5*M* nitric acid containing 90% alcohol. Higher alcohols were not used because of their immiscibility with aqueous nitric acid. Distribution coefficients are shown in Table I. The change of D_e value with the variation of alcohol has almost the same tendency with both elements and both resins. However, the D_e of calcium and magnesium with Dowex 1-X8 is always higher than with Amberlyst. Among the lower alcohols D_e increases with decreasing dielectric constant of solvent, but among C_4 or higher alcohols this becomes irregular. The solubility of organic solvents in water seems also to be related to the sorbability of metal ion. Although many factors should affect a nonaqueous metal-anion exchange process, knowledge of the complex form of the metal ion and of the solvent composition in the resin phase might help to explain this behavior.

The ratio of distribution coefficients is often called the "separation factor." From this, methanol or ethanol may be chosen as the best solvent for separation. However, a separation factor should be a measure of the ability for column separation, because a separation by a batch technique is generally impossible. Therefore, the separation factor must be as follows:

$$S = \frac{V_{\max(M2)}}{V_{\max(M1)}}$$

where $V_{\max(M)}$ indicates the effluent volumes from the beginning of the sample addition to the maximum concentration of metals M_1 and M_2 in the effluent. When the D value is large and constant for each metal,

$$\frac{V_{\max(M2)}}{V_{\max(M1)}} \approx \frac{D_{M2}}{D_{M1}}$$

However, at low D values the interstitial volume of the resin bed cannot be neglected. In this case S becomes

$$S = \frac{D_{v(M2)} + i}{D_{v(M1)} + i}$$

or

$$S = \frac{D_{e(M2)} + i_e}{D_{e(M1)} + i_e}$$

where D_v = volume distribution coefficient $D_2 > D_1$, i = column interstitial volume fraction, i_e = column interstitial volume, ml. per resin meq.

The separation factor is not constant and may change as each D value changes with the loading.

In Table I S values were calculated for the separation of calcium and magnesium. The value of $i_e = 0.32$, which was used in the calculation, was considered to be a fairly constant value under the column separation conditions. Using S, separability was in the order: isopropyl alcohol > ethyl alcohol > *n*-propyl alcohol > *tert*-butyl alcohol. Any of these four solvents may be effective for magnesium-calcium separations when 0.5*M* nitric acid is used. However, the isopropyl alcohol–aqueous nitric acid system using Amberlyst XN-1002 was chosen for further studies.

A few experiments were done in which the nitric acid concentration or the organic solvent content was varied (Figure 2). The distribution coefficient of both elements increases with increased acid concentration and an increasing alcohol content. A nitric acid or isopropyl alcohol content higher than 0.5*M* nitric acid–90% isopropyl alcohol seemed more effective theoretically for Mg-Ca separation. However, a high nitric acid content tends to react with organic solvent. The combination of a lower nitric acid content and a higher organic content results in poor solubility of metal ions, and the distribution coefficients change inconveniently with small changes in composition of the solvent system. For these reasons, 0.5*M* nitric acid containing 90% isopropyl alcohol was selected.

Effect of Loading on Distribution Coefficient and Elution Curves. The distribution coefficient of a metal ion changes with loading. Therefore the elution position from a column depends on the amount of metal taken. For separations on a macro scale, it is necessary to know the relation between the sample load and distribution coeffi-

Table I. Results from Batch Experiments Using Various Alcohols

Alcohol	Dielectric constant[a]	Solubility in water[b]	Dowex 1-X8 $D_{e(Mg)}$	Dowex 1-X8 $D_{e(Ca)}$	Dowex 1-X8 $D_{e(Ca)}/D_{e(Mg)}$	Amberlyst XN-1002 $D_{e(Mg)}$	Amberlyst XN-1002 $D_{e(Ca)}$	Amberlyst XN-1002 $D_{e(Ca)}/D_{e(Mg)}$	Amberlyst XN-1002 $S_{(Ca/Mg)}$[c]
H_2O	80	∞	~0	~0		~0	~0		~1
Methyl	32.6	∞				0.05[d]	0.8	16	3
Ethyl	24.3	∞	0.3	5.3	18	0.21[d]	4.0	19	8.1
n-Propyl	20.1	∞				0.71	7.0	10	7.2
Isopropyl	18.3	∞	1.7	13.6	7.8	0.71	8.8	12	8.9
n-Butyl	17.1	7.9				1.2	6.0	5.0	4.2
Isobutyl	17.7	9.5[18° C.]	5.8	34	5.9	4.8	12.7	2.7	2.5
sec-Butyl	15.8	12.5				1.6	10.7	6.7	5.7
tert-Butyl	10.9[30° C.]	∞	3.0	17.2	5.7	1.1	9.0	8.4	6.7
tert-Amyl	5.8	12.5				2.0	10.2	5.1	4.5

[a] At 25° C.
[b] At 20° C.
[c] Separation factor calculated from $S = \frac{D_{e(Ca)} + 0.32}{D_{e(Mg)} + 0.32}$.
[b] Data from column technique.

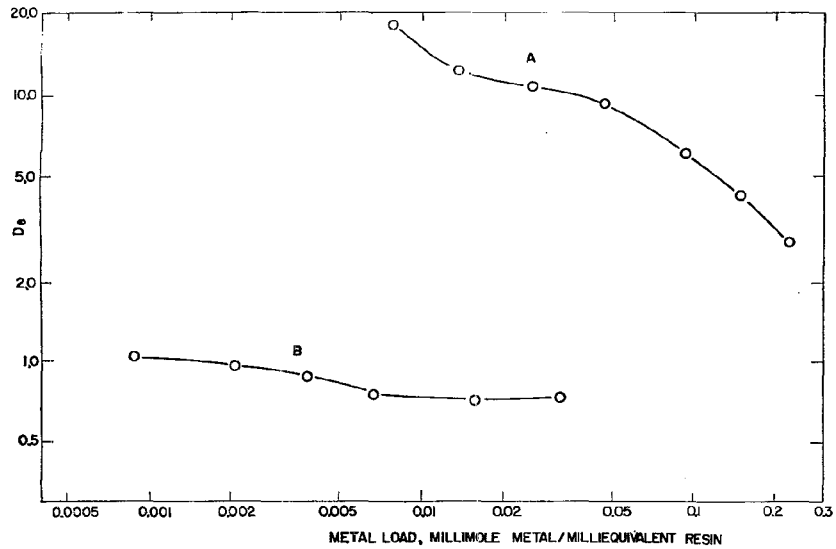


Figure 3. Variation of distribution coefficients with load

A. Ca, batch experiment
B. Mg, batch experiment

cient or the elution behavior. As can be seen in Figure 3, D_e of calcium depends considerably on its load, while D_e of magnesium is less affected. This means that magnesium elution shows no long tailing and a beautiful separation may be expected.

In Figure 4, elution curves using various amounts of metal ions are shown. Magnesium is quantitatively eluted within 4.5 column volumes in every case where the initial sample solution is 1 column volume or less. The elution position of calcium is affected only by the amount of calcium, but not by the amount of magnesium. The calcium limit for a good separation seems to be about 0.25 mmole when a 10-ml. column is used. However, more calcium can be handled in a larger column. A quantitative separation of 0.5 mmole of calcium from 0.5 mmole of magnesium was accomplished within the same time as before, using a column having the same length but twice the bed volume (20 ml. instead of 10 ml.). The volume flow rate from the 20-ml. column was twice that of the smaller column. The elution curves from the 10-ml. and the 20-ml. column were almost identical in shape. Thus, if the elution is carried out so that the number of theoretical plates of the column is not varied, an extension to larger amounts

Table II. Quantitative Separations of Calcium from Magnesium and Other Metals

Metal	Taken, mmole	Found, mmole	% error	Collected effluent fraction, ml.	Notes
Mg	0.1765	0.1770	+0.3	45	
Ca	0.2027	0.2020	−0.3		
Mg	0.0392	0.0392	0.0	55	Flow 0.8 ~ 1 ml./ min.
Ca	0.0389	0.0389	0.0		
Mg	0.414	0.411	−0.7	55	Sample volume 15 ml.
Ca	0.0389	0.0390	+0.3		
Mg	0.371	0.370	−0.2	55	Flow 0.7 ~ 0.8 ml./ min.
Ca	0.0374	0.0374	0.0		
Mg	0.741	0.742	+0.1	45	Sample volume 15 ml. Flow 0.5 ~ 0.7/ min.
Ca	0.0374	0.0375	+0.3		
Mg	0.0264	0.0266	+0.8	47	
Ca	0.2478	0.2487	+0.3		
Mg	0.0264	0.0264	0.0	42	
Ca	0.2478	0.2487	+0.4		
Mg	0.1231	0.1234	+0.2		
Ni	0.1035	0.1038	+0.3	60	
Ca	0.0761	0.0762	+0.1		
Mg + Mn	0.436	0.436	0.0	60	
Ca	0.0950	0.0948	−0.2		
Mg(Al, Fe)	0.2520	0.2522	+0.1	45	
Ca	0.1052	0.1054	+0.2		

Table III. Distribution Coefficients of Other Metals in 0.5M HNO_3–90% Isopropyl Alcohol

Metal	D_e
(Ca)	(8.8)
Cd	3.2
Cu	2.0
Co	1.4
Ni	1.2
Mn	0.9
(Mg)	(0.71)
Fe	0.6
Al	0.2

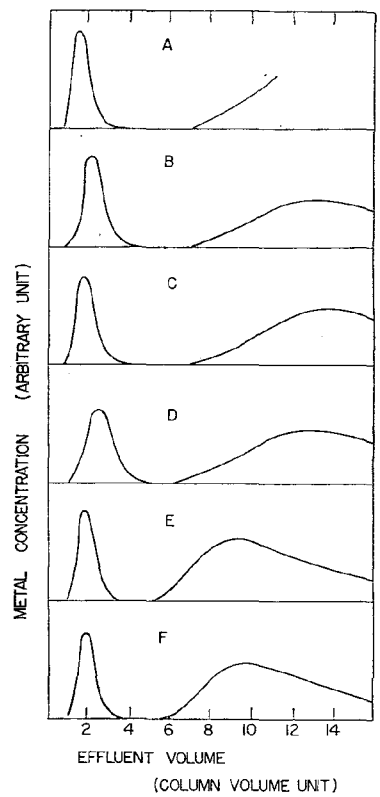


Figure 4. Elution curves with various loads

Curve	Metal, mmole	Sample vol., ml.	Column dimension, sq. cm. × cm.	Flow rate, ml./ min.
A	Mg = 0.05 Ca = 0.05	1	1.03 × 9.7	≈0.5
B	Mg = 0.05 Ca = 0.05	10	1.03 × 9.7	≈0.5
C	Mg = 0.5 Ca = 0.05	10	1.03 × 9.7	≈0.5
D	Ni = 0.05 Ca = 0.1	10	1.03 × 9.7	≈0.5
E	Mg = 0.25 Ca = 0.25	10	1.03 × 9.7	≈0.5
F	Mg = 0.5 Ca = 0.5	20	2.14 × 9.5	≈1.0

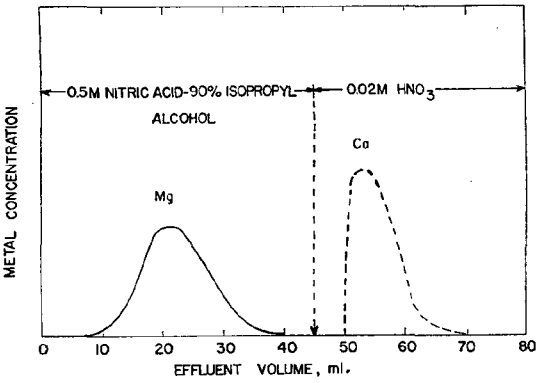


Figure 5. Typical elution curves

Column (1.03 sq. cm. × 9.7 cm.) 10 ml.
Mg, Ca = each 0.05 mmole

of calcium will be possible without taking any longer time, provided that the resin bed is carefully prepared.

In practice it is convenient to collect magnesium in one fraction of effluent. Magnesium is usually eluted quantitatively (>99.9%) in 45 ml. of the first eluent and there is a significant volume of no metal flow before a breakthrough of calcium occurs. Therefore if the separation is carried out under the same conditions as in the loading experiments, testing of the intervening effluent is unnecessary. A typical separation curve is shown in Figure 5. Testing will be desired for changed conditions of elution or for a sample of extremely different Ca-Mg ratio.

Table II presents quantitative analytical data for various amounts and ratios of calcium and magnesium. The results were satisfactory even under varying conditions such as an increased flow rate and an increased volume of initial sample solution.

Distribution coefficients of other metal ions were measured by the same batch condition as for calcium and magnesium (Table III). The metals which have lower D_v values than that of nickel can be separated from calcium. Nickel seems to be a limiting element for the complete separation (Figure 4). Cadmium, copper, and cobalt ought to be eluted between magnesium and calcium and enter both fractions. However these elements can very easily be separated beforehand by Kraus' method (*9*), as can zinc, iron, and manganese.

The separation data for foreign ions in various combinations with calcium and magnesium are also given in Table II. Calcium was quantitatively separated from nickel and manganese, and the separation and determination of magnesium and calcium were successful in the presence of nickel, iron, and aluminum.

LITERATURE CITED

(1) Campbell, D. N., Kenner, C. T., ANAL. CHEM. **26**, 560 (1954).
(2) Faris, J. P., Warton, J. W., *Ibid.*, **34**, 1077 (1962).
(3) Fritz, J. S., Garralda, B. B., unpublished data.
(4) Fritz, J. S., Pietrzyk, D. J., *Talanta* **8**, 143 (1961).
(5) Fritz, J. S., Rettig, T. A., ANAL. CHEM. **34**, 1562 (1962).
(6) Honda, M., *Bunseki Kagaku* **3**, 132 (1954).
(7) Kojima, M., *Ibid.*, **7**, 177 (1958).
(8) Korkisch, J., Tera, F., ANAL. CHEM. **33**, 1265 (1961).
(9) Kraus, K. A., Moore, G. E., *J. Am. Chem. Soc.* **75**, 1460 (1953).
(10) Lure'e, Yu. Yu., Stefanovich, S. N., *Zavodsk. Lab.* **13**, 660 (1947); *C. A.* **42**, 7464 (1948).
(11) Nelson, F., Kraus, K. A., *J. Am. Chem. Soc.* **77**, 801 (1955).
(12) Tera, F., Korkisch, J., Hecht, F., *J. Inorg. Nucl. Chem.* **16**, 345 (1961).
(13) Tsubota, H., Kitano, Y., *Bull. Chem. Soc. Japan* **33**, 770 (1960).
(14) Wünsch, L., *Chem. Listy* **51**, 376 (1957).
(15) Yoshino, Y., Kurimura, Y., *Bull. Chem. Soc. Japan* **30**, 563 (1957).

RECEIVED for review January 18, 1963. Accepted May 6, 1963. Contribution 1252. Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

Quantitative Immunofluorescein Titration of Human and Bovine Gamma Globulins

SIR: Earlier attempts for quantification of the fluorescent antibody (FAb) technique were restricted to the relative intensity measurement of FAb-stained tissue preparations using microfluorometers mounted on a microscope (*3, 8*). Recently Halikis and Arquilla (*5*), and Fox (*2*) used a standard photofluorometric technique to measure fluorescent labeled proteins quantitatively, but in relative terms. The rapid progress both in the technique of fluorescence measurement (*10*) and in the preparation of stable and specific fluorescent antibodies (*4, 9*) make possible a truly quantitative precipitin titration by means of photofluorometric measurements in solutions.

The method described here is based on the measurement of the excess FAb in the supernatant of the precipitin reaction mixture. The results were compared with those obtained by the classical quantitative precipitin titration, using the Folin-Ciocalteu method for protein determination.

EXPERIMENTAL

Materials and Methods. The systems studied were human gamma globulin (HGG)–fluorescent rabbit anti human gamma globulin (FRAHGG), and bovine gamma globulin (BGG)–fluorescent rabbit anti bovine gamma globulin (FRABGG). HGG and BGG, fractions II, were obtained from Sigma Chem. Co., St. Louis, Mo. Fluorescein isothiocyanate was purchased from Nutritional Biochemicals Co., Cleveland, Ohio. FRAHGG was obtained from Microbiological Associates, Bethesda, Md. Antiserum against BGG was prepared by immunizing male rabbits and collecting the antiserum. The gamma globulin fraction of the antiserum was obtained by use of the cold alcohol precipitation method of Cohn, *et al.* (*1*). The gamma globulin fraction was conjugated with fluorescein isothiocyanate and purified by a Sephadex—G 25 gel filtration technique described elsewhere (*4*). The commercial FRAHGG was also passed through Sephadex—G 25. After this treatment FRAHGG and FRABGG did not contain unconjugated dye. The degree of conjugation, obtained by Nairn's method (*9*), was 4.2 for the FRABGG and 3.8 for the FRAHGG preparation. Since the over-all gamma globulin precipitin reactions were studied, no further attempts were made to characterize the FAb reagents against specific antigenic components of the gamma globulins.

The precipitin reactions were carried out at 4° C. for 16 hours in 0.2-ml. volumes. The precipitates were centrifuged at 8000 g. and washed with buffered saline, pH 7.2. An aliquot of the clear supernatant was diluted 1:20 with 0.01*M* borate buffer, pH 8.5, and the fluorescence of this solution was measured in a Turner M. 110 fluorometer.

Since the supernatant also contained, beside the active FAb, a considerable amount of fluorescein-conjugated, nonantibody gamma globulin, all fluorescence measurements were made against a fluorescent reaction blank, prepared by precipitating all active FAb from the FRAHGG and FRABGG reagents with excess HGG or BGG, respectively. The residual fluorescence of the FRABGG preparation was 72% of the total fluorescence; that of the FRAHGG was 69%. By this treatment, the method is essentially a differential fluorometric measurement, the difference between two readings being equal to the amount of FAb reacted with antigen (Ag). Therefore, the method is practically independent of the amount of fluorescent nonantibody materials present in the system.

To achieve optimal fluorescence intensity and selectivity for the fluorescein label, primary filters with a 436-mμ sharp peak and a secondary filter to pass wavelengths >510 mμ were used.

Protein determinations of the antibody/antigen (Ab/Ag) complex and of the FAb were made with the Folin-Ciocalteu method, as modified by Lowry, *et al.* (*7*).

A fluorescence calibration curve was prepared with pure FRAHGG and FRABGG in 0.01*M* borate buffer, pH 8.5. The fluorescence measured in the Turner fluorometer was plotted against the protein concentration of the conjugates as obtained by the Folin-Ciocalteu method (Figure 1). In the precipitin reaction the FAb protein values were obtained directly from this curve, assuming that the specific and nonspecific globulins in the FRAHGG and FRABGG reagents fluoresce in equal measure.

RESULTS

The results of the experiment are shown in Tables I and II. In the tables all data were corrected for the residual fluorescence; therefore, the values refer

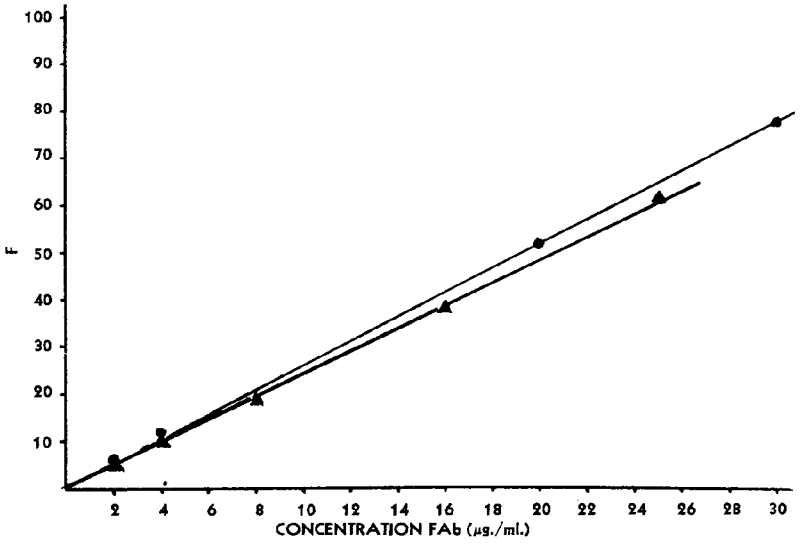


Figure 1. Fluorescence–FAb protein calibration curve in 0.01*M* borate buffer, pH 8.5

▲ = FRAHGG
● = FRABGG

F = fluorescence in arbitrary units

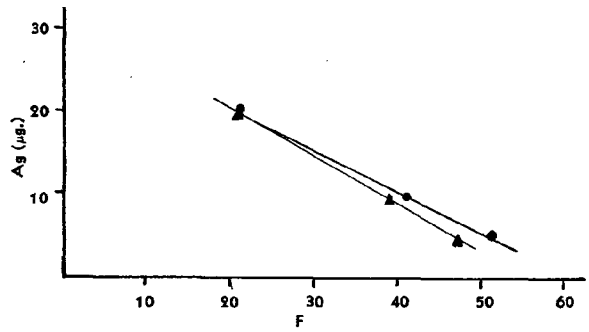


Figure 2. Correlation between fluorescence of excess FAb and Ag content in precipitin reactions
▲ = FRAHGG
● = FRABGG

F = fluorescence in arbitrary units in the diluted supernatant
Reaction volume: 0.2 ml.

to active FAb. The amount of FRAHGG or FRABGG reagent added was adjusted fluorometrically in each reaction mixture to give uniformly 100 μg. of active FAb. The fluorescent measurement gives an immediate check for the presence of excess Ab in the supernatant, a condition which is indispensable for the quantitative precipitin titration. The data presented in Tables I and II are mean values taken from three separate runs, each run representing 3 parallel titrations. The relative errors were calculated from the total number of data both for the fluorescence measurement and for the Folin-Ciocalteu protein determinations.

When the amount of Ag was plotted against the corrected fluorescence of the supernatant, a straight line was obtained for Ag values ranging from 5 to 22 μg. (Figure 2). In the large Ab excess zone (< 5 μg. of Ag) the relationship is not linear, and near the equivalence point (> 22 μg. of Ag) of the Ag–Ab reaction the fluorescence measurement is not sufficiently accurate. Since the range of determination depends primarily on the amount of excess Ab present, the range of applicability can be extended by properly choosing the dilution of the FAb reagent.

The relative sensitivity of the method in the above test series was 1.6 scale divisions on the Turner fluorometer at 10 × sensitivity setting for every 1 μg. of HGG or BGG added. The absolute sensitivity depends on the reacting proportions of Ag and Ab. In the slight Ab excess zone, using highly diluted FAb (70 μg. per ml. protein content), 2 μg. per ml. HGG or BGG gave well-measurable change in fluorescence.

DISCUSSION

The data of Table I and Table II and Figure 2 clearly show that the quantitative measurement of the fluorescence of the Ab excess in the supernatant of the precipitin reaction mixture can be used for accurate determination of HGG or BGG. The close agreement in the amounts of Ab precipitated, calculated from protein assay and from fluorometric measurement, indicate that simple and rapid optical measurements can replace N_2 or protein measurements, required by the classical quantitative precipitin method, without sacrificing accuracy. An even greater advantage of the quantitative immunofluorescein method is that it obviates the necessity of checking for excess Ab or Ag in the reaction mixture, since the fluorescence, measured in the way described above, indicates the Ab excess. The quantitative determination of unknown Ag, using the experimental curve of Figure 2, is sufficiently accurate for most measurements. The close agreement between Ab/Ag ratios, obtained by the classical and fluorometric methods, also permits the use of the classical precipitin equation of Heidelberger and Kendall (*6*) in the following form:

$$\frac{\text{FAb pptd.}}{\text{Ag pptd.}} = a - b\,(\text{Ag pptd.})$$

where a and b are empirical constants, FAb pptd. (precipitated) = FAb added − FAb excess. Once a and b are established from a calibration curve, a single fluorometric measurement is sufficient to satisfy the equation.

The sensitivity of the reaction can be further increased if more specific antibodies can be prepared having lower residual fluorescence; also, if the FAb is used in the maximal dilution which still permits precipitation. The empirical constants of the precipitin equation may be determined with higher ac-

Table I. Comparison of Precipitin Titration Results by Protein Assay and by Fluorescence Measurement in HGG–FRAHGG System

Reaction volume: 0.2 ml.
FAb added: active FAb, corrected for residual fluorescence
F = fluorescence in arbitrary units in 1:20 diluted supernatant corrected for residual fluorescence

HGG added, μg.	FAb added, μg.	Total protein in ppt., μg.	F	Ab excess, μg.	Ab in ppt.[a] μg.	Ab in ppt.[b] μg.	Rel. error, % [c]	Rel. error, % [d]
5	100	28	47	78	22	23	8.2	4.8
10	100	50	39	65	35	40	5.7	4.7
20	100	86	21	34	66	66	5.2	4.9
40	100	140	2	..	100	100	6.8	4.9

[a] From fluorescence measurement: FAb pptd. = FAb added-FAb excess.
[b] Calculated from difference between total protein pptd. and HGG added.
[c] Fluorescence measurement.
[d] Protein determination.

Table II. Comparison of Precipitin Titration Results by Protein Assay and by Fluorescence Measurement in BGG–FRABGG System

Reaction volume: 0.2 ml.
FAb added: active FAb, corrected for residual fluorescence
F = fluorescence in arbitrary units in 1:20 diluted supernatant corrected for residual fluorescence

BGG added, μg.	FAb added, μg.	Total protein in ppt., μg.	F	Ab excess, μg.	Ab ppt.,[a] μg.	Ab in ppt.,[b] μg.	Rel. error, % [c]	Rel. error, % [d]
5	100	25	51.5	80	20	20	7.5	4.8
10	100	48	40	62	38	38	5.8	4.8
20	100	90	21.5	33	67	70	5.3	4.9
40	100	140	2	..	96	100	6.0	4.8

[a] From fluorescence measurement: FAb pptd. = FAb added − FAb excess.
[b] Calculated from difference between total protein pptd. and BGG added.
[c] Fluorescence measurement.
[d] Protein determination.

curacy from a direct Ab/Ag ratio measurement using I^{131} or another fluorescent dye as the second label.

ACKNOWLEDGMENT

The advice and help of J. R. Collier and F. X. Gassner of Colorado State University is gratefully acknowledged.

LITERATURE CITED

(1) Cohn, E. J., Strong, L. E., Hughes, W. L., Jr., Mulford, D. I., Ashworth, J. N., Melin, M., Taylor, H. L., *J. Am. Chem. Soc.* 68, 459 (1946).
(2) Fox, E. M., *Proc. Soc. Exptl. Biol. Med.* 109, 577 (1962).
(3) Goldman, M., *Exptl. Parasitol.* 9, 25 (1960).
(4) Gordon, M. A., Edwards, M. A., Tompkins, V. N., *Proc. Soc. Exptl. Biol. Med.* 109, 96 (1962).
(5) Halikis, D. N., Arquilla, E. R., *Diabetes* 10, 142 (1961).
(6) Heidelberger, M., Kendall, F. E., *J. Exper. Med.* 62, 697 (1935).
(7) Lowry, C. H., Rosenbrough, N. J., Farr, A. L., Randall, R. J., *J. Biol. Chem.* 193, 265 (1951).
(8) Mellors, R. C., Siegel, M., Pressman, D., *Lab. Invest.* 4, 69 (1955).
(9) Nairn, R. C. (Ed.) "Fluorescent Protein Tracing," E. & S. Livingstone, Edinburgh, 1962.
(10) Udenfriend, S., "Fluorescence Assay in Biology and Medicine," Academic Press, New York, 1962.

ROBERT P. TENGERDY

Department of Pathology
and Microbiology
Colorado State University
Fort Collins, Colo.

RECEIVED for review March 11, 1963. Accepted May 22, 1963. This work was supported in part by the Faculty Improvement Grant 3820-103.

Voltammetry and Electron Paramagnetic Resonance Spectra of Halonitrobenzene Anion Radicals

SIR: The recently-developed technique of electrochemically generating free radical ions provides a new tool in the study of complex electrode reactions, many of which are of analytical significance (*1, 3–7*). Armed with the electron paramagnetic resonance (EPR) information, it is often a simple matter to backtrack and devise electroanalytical techniques which give a better picture of the electrode process. During a study of the EPR spectra of halonitrobenzene anion radicals, we encountered unusual results which illustrate these points very well.

The reduction of *ortho*-bromonitrobenzene in dimethylformamide (DMF) containing 0.1*M* tetraethylammonium perchlorate (TEAP) as supporting electrolyte gives rise to two peaks at a hanging mercury-drop electrode (HDE). The half-peak potentials, $E_{p/2}$, are at −1.15 and −1.77 volts *vs.* S.C.E. (aqueous). Using an applied potential of −1.3 to −1.5 volts *vs.* S.C.E., *ortho*-bromonitrobenzene does not give an EPR spectrum corresponding to the bromonitrobenzene anion radical. Instead, the EPR spectrum is, without question, that of the unsubstituted nitrobenzene anion. A complete study of the halonitrobenzenes was made. The results are summarized in Table I. Unsubstituted nitrobenzene is included for comparisons.

Table I shows clearly that the three iodonitrobenzenes lose their iodine to give the nitrobenzene anion radical as a stable intermediate in the reduction process. For the bromo isomers only the *ortho* derivative readily loses the bromine. (If the reduction of *p*-bromonitrobenzene is carried out in DMF with tetrabutylammonium iodide as supporting electrolyte, the EPR spectrum is a mixture of that for nitrobenzene anion and the *p*-bromonitrobenzene anion.) In the chloro series, the chlorine is retained in all three isomers. We found that the *ortho*-fluoro derivative retains the fluorine in DMF, and the *p*-fluoronitrobenzene anion radical (fluorine retained) was observed by Maki and Geske in acetonitrile (*4*). The *meta*-fluoronitrobenzene was not examined but there is little reason to expect elimination. The reduction of these various halonitrobenzenes has been studied by a variety of workers but such elimination reactions have apparently not been noted. In a very recent report, Holleck and Becher noted intermediate waves in the reduction of *p*-iodo- and *p*-bromonitrobenzene in DMF with tetraethylammonium iodide as background electrolyte (*2*). These intermediate waves did not correspond to any known reduction product. In the case of the *p*-iodo compound, this is very likely the "extra" wave for iodide elimination (see Table I). While the present results are unexpected, they are consistent with the known ease of cleavage of carbon–halogen bonds (*8*) and, in the case of the *o*-bromonitrobenzene, with the steric effects of bulky *ortho* groups.

Knowing the EPR results, it is easy

Table I. Electrochemical and EPR Data for Halonitrobenzenes[a]

Substituent	$E_{p/2}$ (volts *vs.* S.C.E.)	Hyperfine lines in EPR spectra: Expected	Observed[b]	a_N	a_1	a_2	a_3
-H	−1.18, −1.98	54	54	9.79	4.06	3.38	1.09
Ortho-Cl	−1.14, −1.69	36[c]	31	9.06	4.28(*d*)	3.18(*d*)	1.13(*t*)
Meta-Cl	−1.08, −1.95	36	26	8.75	4.14(*t*)	3.36(*d*)	0.97(*d*)
Para-Cl	−1.08, −1.72	27[d]	25	9.16	3.44(*t*)	...	1.12(*t*)
Ortho-Br	−1.15, −1.77	36	54	9.78	4.05	3.38	1.08
Meta-Br	−1.15, −1.73	36	26	8.83	4.16(*t*)	3.40(*d*)	0.93(*d*)
Para-Br	−1.15, −1.75	27	25	9.04	3.42(*t*)	...	1.12(*t*)
Ortho-I	−1.10, −1.26, −1.78	36	54	9.73	4.02	3.38	1.10
Meta-I	−1.10, −1.25, −1.75	36	54	9.83	3.98	3.38	1.07
Para-I	−1.09, −1.23, −1.77	27	54	9.83	4.02	3.38	1.06

[a] In DMF, 0.1*M* TEAP; $E_{applied}$, −1.3 to −1.5 volts *vs.* S.C.E.
[b] a_N is N^{14} coupling constants; a_1, a_2, and a_3 are proton coupling constants. In nitrobenzene anion, a_1 has been assigned as a doublet splitting from *para* H; a_2 is a triplet from the *ortho* H's; and, a_3 is a triplet from the *meta* H's. (ref. *5*). Coupling constants are believed precise to ±0.08 gauss.
[c] In the *ortho* and *meta* substituted nitrobenzenes where the halogen is retained, the spectra are best represented by couplings with 2 nonequivalent protons and a pair of equivalent protons. Assuming no overlapping lines, a total of 36 is expected. No unequivocal assignments are possible from our spectra. The (*d*) and (*t*) after the coupling constants indicate doublet or triplet splitting. The *a* values are listed in the order shown merely to suggest similarity to nitrobenzene anion splittings.
[d] For a *para* substitution, where halogen retention occurs, 2 pairs of equivalent protons are present. With no overlaps, 27 lines are expected. The couplings of *p*-Cl and *p*-Br nitrobenzene anions are such that 2 lines overlap and the 25 lines observed are entirely consistent with the predicted spectra.

to carry out experiments at the HDE designed to show electrochemically that I^- or Br^- is eliminated from the above compounds. Thus, if one reduces at −1.3 volts for 2 minutes and then carries out an anodic-going, cyclic polarogram, peak polarograms for the formation and subsequent dissolution of mercury iodide and bromide films are readily obtained.

In the case of the iodo compounds, where the extra wave is obtained, it is possible to test if elimination occurs first or after initial formation of a 1-electron adduct. The following two pieces of information indicate the iodide is first eliminated, then nitrobenzene anion radical is formed. First, by applying only −1.1 volts to *p*-iodonitrobenzene (see Table I) for two minutes and then scanning anodically, a mercury iodide film pattern is obtained—indicating iodide ion has been generated. Secondly, at this same potential, no EPR signal can be observed. The latter is readily obtained at the potential of the second peak. Thus, it appears that the first peak is a 2*e* reduction eliminating iodide, the second peak is the formation of the nitrobenzene anion radical, and the third represents further reduction of the nitro function. Since the *ortho*-bromonitrobenzene does not give a distinct "extra" first peak, this technique cannot be applied here. Further details of the electrochemistry and EPR spectra will be presented later.

LITERATURE CITED

(1) Geske, D. H., Maki, A. H., *J. Am. Chem. Soc.* **82**, 2671 (1960).
(2) Holleck, L., Becher, D., *J. Electroanal. Chem.* **4**, 321 (1962).
(3) Lee, H. Y., Adams, R. N., ANAL. CHEM. **34**, 1587 (1962).
(4) Maki, A. H., Geske, D. H., *J. Am. Chem. Soc.* **83**, 1852 (1961).
(5) Maki, A. H., Geske, D. H., *J. Chem. Phys.* **30**, 1356 (1959).
(6) *Ibid.*, **33**, 825 (1960).
(7) Piette, L. H., Ludwig, P., Adams, R. N., ANAL. CHEM. **34**, 916 (1962).
(8) Rosenthal, I., Albright, C. H., Elving, P. J., *J. Electrochem. Soc.* **99**, 227 (1952).

TOYOKICHI KITAGAWA[1]
THOMAS P. LAYLOFF
RALPH N. ADAMS

Department of Chemistry
The University of Kansas
Lawrence, Kan.

RECEIVED for review March 11, 1963. Accepted May 6, 1963. This work was supported by the Atomic Energy Commission through contract AT(11-1)-686 and the Air Force through the Air Force Office of Scientific Research.

[1] On leave from Osaka City University, Osaka, Japan.

Preparation and Isolation of Isomeric Ketones by the Girard Reaction

SIR: The wide scope of the Girard reaction was thoroughly reviewed by Wheeler (*9*), and the chemistry and application of the classical reagents were likewise discussed in detail (*8*). Experiments carried out recently in our laboratory on essential oils and their carbonyl constituents showed that certain isomeric ketones may be conveniently prepared, as well as efficiently separated, by this reaction.

Conversion of Menthone to Isomenthone. *l*-Menthone, with $[\alpha]_D^{25} = -25.1°$ and composed of 92.6% menthone and 7.4% isomenthone, was obtained by fractional distillation of oil of peppermint. It was treated with Girard T reagent following the method described by Teitelbaum (*7*), and the recovered carbonyl fraction (82%) was examined by gas liquid partition chromatography (*5*). Infrared analysis of the eluate (*4*) showed admixture of the ketone with considerable amounts of isomenthone. The retention times were: menthone, 9.1 minutes; isomenthone, 9.9 minutes. The substrate was Ucon Polar (20%) on Chromosorb W at a temperature of 170° C. Quantitative evaluation of chromatograms by the sigma method (*1*, *5*) revealed that 65% of the ketone was isomerized during the reaction. Interconversion failed to take place in the absence of the reagent.

Isolation of the ketones from binary mixtures is difficult—b.p. 211 (±1) ° C. —and involves tedious and time consuming manipulations (*2*). Their resolution was accomplished by treating the reaction mixture at progressively-prolonged time intervals with small volumes of formalin and extracting thereafter with diethyl ether. Gas chromatographic examination of extracts thus prepared showed that menthone was more rapidly generated than isomenthone, and fractions containing more than 95% of either ketone were readily recovered from the binary mixture. Similar results were obtained when *dl*-menthone was used as starting material.

Optical rotation measurements made on recovered fractions proved that *l*-menthone was largely converted to *d*-isomenthone during the process—unreacted product $[\alpha]_D^{25} = -21.3°$, (menthone 87.2%, isomenthone 12.8%); reacted product $[\alpha]_D^{25} = +49.8°$, (*l*-menthone 35.3%, *d*-isomenthone 64.7%). In agreement with these results, genuine peppermint oils displaying strong laevo-rotations (*l*-menthone 9 to 32%) (*5*) were found to yield distinctly dextro-rotatory carbonyl fractions following treatment with Girard T reagent. Only optically inactive isomenthone was formed from *dl*-menthone.

Isolation of α- and β-Vetivone. Following treatment with Girard T reagent and separation of nonketonic constituents, oil of vetiver yields a mixture composed largely of α- and β-vetivone. The difficulties of purifying and isolating the isomers have been cited (*3*). Controlled hydrolysis of the reaction products with small successive portions of formalin permitted distinct separations—the α-isomer generates more rapidly than the β-isomer—and the recovery of fractions consisting almost entirely of either configuration. Similar processing of isolates thus enriched afforded the preparation of gas chromatographically pure compounds. Retention time: α-vetivone, 21.6 minutes; β-vetivone, 18.9 minutes. The substrate was Reoplex 400 (20%) on Chromosorb W. and the temperature was 220° C. Product recovery was 93%.

Selective regeneration of the carbonyls from their Girard T hydrazones failed or was drastically curtailed when dilute hydrochloric acid or excess aqueous formaldehyde was used as hydrolyzing agent.

Resolution of Carvone and Carvomenthone. Carvone and carvomenthone, two constituents of spearmint oil (*6*) were likewise separated by means of such stepwise hydrolysis. Product recovery was 81%. Only unreacted carvomenthone was isolated from the reaction mixture prior to hydrolysis. Retention time: carvomenthone, 11.3 minutes; carvone 17.7 minutes. The substrate was SAIB (20%) on Chromosorb W and the temperature was 170° C.

The technique described is being applied successfully in our laboratory to the isolation of carbonyl compounds which occur in essential oils and are difficult to resolve by conventional procedures. Variables which markedly affect the efficiency of the purification process include the relative carbonyl concentrations present, the formalin concentration of the system at any given time, and the rate at which

the regenerated products are extracted. For the experiments reported, 1 part of aqueous formalin was added to 10 parts of the solution of the Girard T derivatives after 5-minute, 20-minute, 1-, 2-, 4-, 8-, 16-, and 32-hour intervals.

The observations made serve to illustrate that isomeric configurations may be generated by means of the Girard reaction from properly constituted ketones, and that pure carbonyl compounds may conveniently be recovered from mixtures by staggered formalin hydrolysis under controlled conditions. The classical method should thus be applied with some caution to the examination of complex preparations containing labile carbonyls, and the possible introduction of compositional artifacts should not be overlooked. The experimental findings reported should also prove of value for the reappraisal of literature data on carbonyl compounds occurring in natural products, when the data are based exclusively on the Girard T reaction.

ACKNOWLEDGMENT

The authors are indebted to F. J. Cramer, A. M. Todd Co., Kalamazoo, Mich., for courteously providing a genuine sample of *l*- menthone and to J. M. Derfer, the Glidden Co., Jacksonville, Fla., for kindly supplying an authenticated specimen of *dl*-menthone for this study. We also thank Dorothy Smith of this laboratory for carrying out the optical rotation measurements.

LITERATURE CITED

(1) Bartlet, J. C., Smith, D. M., *Can. J. Chem.* **38**, 2057 (1960).
(2) Guenther, E., "The Essential Oils," Vol. **II**, p. 391, Van Nostrand, New York, 1949.
(3) Nigam, I. C., Levi, L., *Can. J. Chem.* **40**, 2083 (1962).
(4) Nigam, I. C., Sahasrabudhe, M., McConnell Davis, T. W., Bartlet, J. C., Levi, L., *Perfumery Essent. Oil Record* **53**, 614 (1962).
(5) Smith, D. M., Levi, L., *J. Agr. Food Chem.* **9**, 230 (1961).
(6) Smith, D. M., Skakum, W., Levi, L., *Ibid.*, **11**, 268 (1963).
(7) Teitelbaum, C. L., *J. Org. Chem.* **23**, 646 (1958).
(8) Walker, G. T., *Am. Perfumer Cosmet.* **77** (12), 37 (1962).
(9) Wheeler, O. H., *Chem. Rev.* **62**, 205 (1962).

ISHWAR C. NIGAM[1]
LEO LEVI

Food and Drug Directorate
Department of National Health and Welfare
Ottawa, Canada

RECEIVED for review April 1, 1963. Accepted April 18, 1963.

[1] National Research Council of Canada Postdoctorate Fellow, 1962–63.

Mercury-Coated Platinum Electrodes

SIR: There has been a great deal of interest in various forms of a mercury-coated platinum electrode. Stationary, mercury-coated electrodes have been used in voltammetry (*6*, *7*), and a rotating mercury-coated electrode has been used in stripping analysis (*2*). Hanging mercury drop electrodes, often supported by a mercury-wetted platinum microelectrode, have been used in electrode kinetic studies (*1*, *4*), voltammetry (*8*), and studies of amalgams (*5*).

Three methods have been used to coat a platinum electrode with mercury. The platinum has been plated with an amalgam-forming metal, such as gold, and then covered with mercury (*1*, *4*). Mercury has been electrolytically plated onto the platinum surface from an acidic mercuric nitrate solution (*2*, *3*, *5*, *6*, *8*). Most recently, platinum has been covered with mercury by abrading the platinum surface under mercury (*7*). Successful coating by abrading or mercury plating has been reported only for the preparation of small electrodes.

When mercury directly wets the platinum surface, as in the latter two methods, the need for a clean surface free of any oxides has been demonstrated. Surface platinum oxides can be electrolytically reduced by holding the potential of the platinum electrode at or near the potential of a hydrogen electrode for a short period of time. Experiments performed in this laboratory demonstrate that electrodes cleaned in this manner and dipped into mercury are found, on removal, to be coated with mercury.

EXPERIMENTAL

Reagents and Apparatus. Perchloric acid solutions were prepared from doubly-distilled, lead-free, 70% perchloric acid and distilled water. The mercury used was washed well with dilute nitric acid and distilled.

A typical electrode was prepared for coating by sealing a short piece of 13-mil diameter platinum wire in soft glass and spot-welding to it a 1-mil, platinum-foil square, 1 cm. on a side. Care was taken to make all platinum-to-glass seals smooth and convex in shape so that all exposed platinum would be covered with mercury on immersion.

A potentiostat, which could be programmed for constant potential or linear potential sweep, was employed in reductions done at controlled potential. A three-electrode system, consisting of a platinum foil counter electrode, the platinum electrode to be coated, and a hydrogen reference electrode, was used in conjunction with the potentiostat. A circuit consisting simply of a 3-volt battery, the electrode to be coated, and a platinum foil counter electrode was used for reduction in some experiments. No precautions were taken to remove dissolved gases from solutions during the reduction of the surface oxides. All current–voltage curves were run in oxygen-free solutions using the three electrode system and potentiostat programmed for linear potential sweep, and were recorded on a Leeds and Northrup Speedomax recorder.

Procedure. An electrode was first degreased in alcoholic potassium hydroxide solution and thoroughly cleaned in boiling nitric acid. Upon removal from the nitric acid, the electrode was immediately rinsed with distilled water and placed in a cell containing a 1*N* solution of perchloric acid and a mercury pool deep enough to completely cover the electrode when immersed. The mercury pool is only for wetting and is not electrically connected to any part of the system. In the case of controlled potential reduction, the electrode was held at a potential equal to or more cathodic than 0.1 volt (*vs.* NHE) for a period of 10 minutes. The electrode was then dipped into the mercury pool momentarily without disconnecting the current and removed with its coating of mercury.

The results of the potentiostatic work indicated that mercury coating could be done successfully without the necessity of precisely-controlled potential. Evolving hydrogen on an electrode for a period of several minutes and immersing it in the mercury pool was sufficient to obtain a good coating. Apparently, any source of current, such as a 3-volt battery, which is capable of maintaining hydrogen evolution at the platinum electrode would be satisfactory.

The electrodes were tested for complete coverage by running current–voltage curves to a potential at which hydrogen was being evolved and comparing them to similar curves run on mercury pools of the same area. If the first immersion did not completely cover the electrode, as was often the case, two or three immersions were usually all that was necessary to complete the coverage. The process of running a current–voltage curve to hydrogen evolution may be instrumental in preparing the remaining ex-

posed platinum surface for mercury wetting.

Occasionally an electrode could not be completely covered. Removing the partial coating with nitric acid, cleaning the electrode in boiling 70% perchloric acid (caution) and again in nitric acid, and repeating the coating procedure would yield a well covered electrode.

RESULTS AND DISCUSSION

The current–voltage curves run on completely covered electrodes showed little, if any, difference from those run on mercury pools of the same area. The residual current and hydrogen evolution wave were within the experimental deviation in the two cases. Thus, these electrodes would be expected to have the electrochemical surface properties of mercury. However, the small volume of mercury and/or the platinum–mercury interface may cause the behavior of these electrodes to differ from that of a mercury pool in certain applications—e.g., stripping analysis (*3*, *5*).

This method for coating a platinum electrode with mercury is rapid and simple. An electrode of any geometry can be covered. Coated foil electrodes, wire electrodes, and hanging mercury drop electrodes have been prepared in this laboratory by this method. Coated platinum foil electrodes offer the advantage of a large exposed mercury surface the area of which can be accurately determined and does not vary with time. A coated wire electrode can be made into a miniature reference electrode by dipping it into a slurry of an insoluble mercury salt.

Work is being continued in this laboratory to determine the range of conditions suitable for coating electrodes and the electrical and chemical characteristics of the electrodes. Various applications of these electrodes in voltammetry are being investigated.

LITERATURE CITED

(1) Berzins, T., Delahay, P., *J. Am. Chem. Soc.* **77**, 6448 (1955).
(2) Brukenstein, S., Nagai, T., ANAL. CHEM. **33**, 1201 (1961).
(3) Gardiner, K. W., Rogers, L. B., *Ibid.*, **25**, 1393 (1953).
(4) Gerischer, H., *Z. Physik. Chem. (Leipzig)* **202**, 302 (1953).
(5) Kemula, W., Galus, Z., Kublik, Z., *Bull. Acad. Polon. Sci. Ser. Sci. Chim. Geol. Geograph.* **7**, 723 (1959); *C. A.* **54**, 18135d (1960).
(6) Marple, T. L., Rogers, L. B., ANAL. CHEM. **25**, 1351 (1953).
(7) Moros, S. A., *Ibid.*, **34**, 1584 (1962).
(8) Ross, J. W., DeMars, R. D., Shain, I., *Ibid.*, **28**, 1768 (1956).

LOUIS RAMALEY
R. L. BRUBAKER
C. G. ENKE

Frick Chemical Laboratory
Princeton University
Princeton, N. J.

RECEIVED for review March 26, 1963. Accepted May 7, 1963. Work supported by Air Force Grant AF-AFOSR-151-63

CORRESPONDENCE

(Ethylene dinitrilo)tetraacetic Acid Titration of Lead(II) in the Presence of Orthophosphate and Alkaline Earths

SIR: Because of the insolubility of lead(II) orthophosphates, $H_2PO_4^-$, HPO_4^{-2}, and PO_4^{-3} interfere with many of the common methods of determining lead. Investigation of the EDTA titration of lead in the presence of alkaline earths using copper–PAN complex indicator as suggested by Flaschka (*1*) and Flaschka and Abdine (*2*, *3*) revealed that the method was effective for the determination of lead in the presence of phosphate.

Flaschka and Abdine (*3*) pointed out that this method, employing PAN indicator and a back titration with copper(II), was quite acceptable on a micro scale, but led to difficulties on a macro scale. When titrating an unknown amount of lead, a considerable excess of EDTA had to be added to assure total chelation, and therefore a large quantity of Cu(II) was required in back titrating. This large amount of back titrant gave rise to intensely blue-colored solutions of the Cu–EDTA complex which totally obscured the end point color. Thus, a direct titration was suggested using PAN and a Cu–EDTA solution.

In the titration of Pb(II) in the presence of phosphate, we find the opposite to be true. That is, a direct titration is not desirable since the end point is very poor because of a lead phosphate precipitate formed when the solution is buffered at pH 5 to prevent titration of the alkaline earths (*1*, *4*). However, a back titration proves to be very acceptable in that the dissolution of the precipitate serves as a guide to the quantity of EDTA required and therefore necessitates only a small volume of Cu(II). A sharp, reproducible end point is obtained.

EXPERIMENTAL

Reagents. Standard EDTA solution, 0.0100*M*, was prepared by dissolving 3.7225 grams of reagent grade disodium(ethylenedinitrilo)tetraacetate dihydrate (dried at 80° C. for 3 days) in water and diluting to exactly 1 liter.

Cupric sulfate solution, 0.01*M*, was prepared by dissolving 2.50 grams of reagent grade cupric sulfate pentahydrate in water and diluting to 1 liter.

PAN indicator solution, 0.05%, was prepared by dissolving 50 mg. of PAN in 100 ml. of ethanol.

Buffer solution, pH 5, was prepared by dissolving 13.6 grams of sodium acetate trihydrate in 0.055*M* acetic acid and diluting to 1 liter with acid.

Sodium hydroxide solution, 1.0*M*.

Procedure. The copper solution was standardized by titration of standard EDTA solution using PAN indicator. A volume of 10 to 20 ml. of standard EDTA solution was pipetted into a 250-ml. conical flask and diluted to about 50 ml. A volume of 50 ml. of ethanol was added to the flask, followed by 5 to 10 ml. of buffer, pH 5, and 10 drops of PAN solution. The solution was then titrated with Cu(II) solution. The color change was from yellow to green and, at the end point, from green to violet.

Enough of the lead(II) phosphate to provide about 25 mg. of lead was weighed out, dissolved in a few ml. of 6*N* nitric acid, and transferred to a 250-ml. conical flask. The solution was diluted to approximately 50 ml. and neutralized with 1.0*N* sodium hydroxide (pHydrion paper). Five to 10 ml. of buffer, pH 5, was added and the sample was titrated with standard EDTA until no precipitate remained. Then 50 ml. of ethanol and 10 drops of PAN were added, and the sample was back-titrated with standard Cu(II) solution from a canary-yellow color to a persistent violet. The back titrant was added very slowly so that a fading pink color was not mistaken for the end point. The ethanol served to

increase the solubility of PAN and its copper complex.

RESULTS AND DISCUSSION

Examples of some typical results obtained by this method are given in Table I.

The accuracy of this method compares favorably with that of other methods for Pb(II) analysis, and no problems due to the low solubility of $PbHPO_4$, $Pb_3(PO_4)_2$, or $Pb_{10}(PO_4)_6(OH)_2$ are encountered.

At pH 5, the titration can be carried out without interference from the alkaline earths and can be performed at a pH as low as 3.5 (*3*, *4*). However, many metal ions will interfere. Some of these

Table I. Sample Lead(II) Analyses

Sample	Theoretical, %	Found, %
$PbHPO_4$	68.4	68.6
$Pb_2P_2O_7$	70.4	69.8
$Pb_{10}(PO_4)_6(OH)_2$	77.4	77.2
$PbCl_2$	74.5	74.4

are: Cu(II), Ni(II), Hg(II), Fe(III), Cd(II), Zn(II), and Al(III).

This principle of using the dissolution point of an insoluble phosphate as a guide for the amount of EDTA required for titration has also been applied in this laboratory to the titration of calcium in the presence of orthophosphate. This analysis consists of the titration of calcium with EDTA at pH 10 using [1-(1-hydroxy-4-methyl-2-phenylazo) - 2 - naphthol - 4 - sulfonic acid, Calmagite] or murexide as an indicator and Mg(II) as a back titrant.

LITERATURE CITED

(1) Flaschka, H. A., "EDTA Titrations," pp. 90–1, Pergamon Press, New York, 1959.
(2) Flaschka, H., Abdine, H., *Chemist Analyst* **45**, 58–61 (1956).
(3) Flaschka, H., Abdine, H., "The EDTA Titration," pp. 25–7, J. T. Baker Chemical Co., Phillipsburg, N. J., 1957.
(4) Reilley, C. N., Schmid, R. W., ANAL. CHEM. **30**, 947 (1958).

FRANKLIN H. BLOOD
WILLIAM H. NEBERGALL

Department of Chemistry
Indiana University
Bloomington, Ind.

The Use of Raney Nickel in the Rapid Determination of Small Concentrations of Nitric Acid in Sulfuric Acid

SIR: Many industrial processes require sulfuric acid of known and low nitric acid content. Allen's modification (*1*) of Devarda's method for determination of nitric acid uses Devarda's alloy, consisting of 45 parts aluminum, 50 parts copper, and 5 parts zinc, to reduce nitric acid to ammonia in alkaline solution, with subsequent Kjeldahl distillation and titration of the ammonia. Devarda's alloy did not work well for low concentrations of nitric acid and neither did aluminum. Therefore, a Raney nickel alloy catalyst was tried to determine whether rapid and quantitative reaction at lower levels of nitric acid was possible.

EXPERIMENTAL

Reagents. Methyl purple indicator solution, Fleisher's, available from Fisher Scientific Co.

Raney Nickel Alloy, No. 2813 Raney Catalyst Powder, Raney Catalyst Co., Inc., Chattanooga, Tenn.

Procedure. Weigh an appropriate amount of sample to the nearest milligram (Table I) into an 800-ml. Kjeldahl flask. Add 200 ml. of deionized water. Cool the mixture to about room temperature. Add 20 ml. of 50% sodium hydroxide by tilting the flask and pouring in a manner to minimize mixing of the sodium hydroxide and the diluted sample.

Table I. Sample Weight and Normality of Acid Recommended for Various HNO_3 Concentrations

HNO_3 in sample, %	Sample weight, grams	Raney Ni, grams	N, H_2SO_4 Titrant
0.005 to 0.1	10	1 ± 0.01	0.005
0.1 to 1.0	10	3 ± 0.01	0.1
1.0 to 10	1	3 ± 0.01	0.1

Without delay add the appropriate amount (Table I) of Raney nickel catalyst and connect the Kjeldahl flask to the Kjeldahl distillation apparatus. Place 25 ml. of saturated boric acid in the Kjeldahl apparatus receiver (a 500-ml. Erlenmeyer flask). While the Kjeldahl flask is connected, swirl the contents to cause mixing. Heat gently and intermittently to maintain a steady and rapid formation of fine bubbles until no further bubbles form (about 30 to 45 minutes). Increase the heat to cause 100 ml. of the solution in the Kjeldahl flask to distill and be collected in such a manner that the condensate passes directly into the boric acid in the Kjeldahl receiver.

Remove the receiver, add 3 to 6 drops of methyl purple indicator solution, and titrate with the appropriate sulfuric acid solution (Table I). The color change of the indicator is from green to grey to purple, and the first detectable purple color is the end point. Some analysts may prefer to use a reference solution during titration as a matter of preference. The authors did not use it in the work reported.

Determine a reagent blank, following exactly the same procedure as specified above for the analysis of an actual sample. A blank shall be run with every set of samples. Samples containing ammonium salts require separate distillation of a sample for ammonia which is prepared as above except that the Raney nickel alloy is omitted. The ammonia found is deducted from the total nitrogen found.

Table II. Recovery of HNO_3 in 70% Sulfuric Acid by Reduction with Raney Nickel Alloy Catalyst and Kjeldahl Distillation

HNO_3 %	HNO_3 added, mg.	HNO_3 found, mg.
0.005	0.58	0.59
0.010	1.00	1.05
...	...	0.99
0.05	5.02	4.99
...	...	4.84
0.10	10.0	9.8
...	...	10.2
1.0	95	92.4
...	...	92.9
10.0	95	90.1
...	...	91.8

RESULTS

Synthetic blends of known composition were prepared and analyzed as shown in Table II.

LITERATURE CITED

(1) Furman, N. H., "Standard Methods of Chemical Analysis," Vol. 1, 6th ed., p. 748, Van Nostrand, New York, 1962.

CHARLES WANKAT
D. A. KEYWORTH
V. A. BRAND

Universal Oil Products Co.
Des Plaines, Ill.

Quantitative Study of Gas Chromatographic Analysis of Head Space Gas of Dilute Aqueous Solutions

SIR: Weurman (*2*) in studying enzymatic formation of volatile materials in raspberries reported linear relationships when chromatographic peak heights from head space vapor analyses were plotted against concentrations for isopropanol, ethyl acetate, propionaldehyde, and acetone at 0.001 to 0.025% (10 to 250 p.p.m.) in water. By modifying conventional head space sampling methods, Bassette, Özeris, and Whitnah (*1*) were able to analyze some volatile organic compounds at concentrations in the range of 0.01 to 1.0 p.p.m. The research reported here was undertaken to establish the quantitative aspects of this modified technique.

EXPERIMENTAL

Apparatus. The apparatus, operating conditions, and head-space gas-sampling procedure were identical to those reported (*1*) except that a 9.5-ft. commercially prepared, $^1/_8$-inch stainless steel column packed with 20% Carbowax 20 M on 60- to 80-mesh, acid-washed Chromosorb W was employed.

Chemicals. Aqueous sample solutions containing by volume: 1.0, 0.1, and 0.01 p.p.m.—propanal, *n*-butanal, *n*-pentanal, 2-butanone, 2-pentanone, 2-hexanone, methyl formate, ethyl formate, ethyl acetate, ethyl propionate, allyl sulfide, and diethyl sulfide.

10.0, 5.0, and 1.0 p.p.m.—methanol.

10.0, 1.0, and 0.1 p.p.m.—ethanol, *n*-propanol, and *n*-butanol.

1.0, 0.8, 0.6, 0.4, 0.2, 0.1, and 0.01 p.p.m.—acetone.

Procedure. Each of the dilute aqueous solutions was analyzed in duplicate as head-space vapor by the proposed method.

RESULTS AND DISCUSSION

Standard curves showing chromatographic peak heights plotted against p.p.m. concentration of the chemical compounds studied are shown in Figure 1. All of the lines in the figure are defined by three different concentrations except the one for acetone; seven concentrations of acetone were analyzed. Each point in the figure represents the average peak height in duplicate analyses. Duplicates varied no more than 5%. As can be seen from Figure 1, linear relationships existed between chromatographic peak heights and concentration. Within each homologous series, slopes of the standard curves varied considerably.

Differences in slopes of curves in Figure 1 draw attention to some interesting relationships between the analytical procedures and the type of organic compounds studied. Alcohols could not be detected at below 0.1 p.p.m. In fact, the lower limits for the determination of methanol was 1.0 p.p.m. All of the other compounds could be determined at 0.01 p.p.m. In contrast with alcohols, diethyl sulfide produced a higher peak, for a concentration, than any of the other compounds. Within each class, lower molecular weight homologs generally yielded shorter peaks. Two exceptions were the five-carbon aldehyde (*n*-pentanal) and the six-carbon ketone (2-hexanone), each of which produced less response than the respective shorter chain homologs.

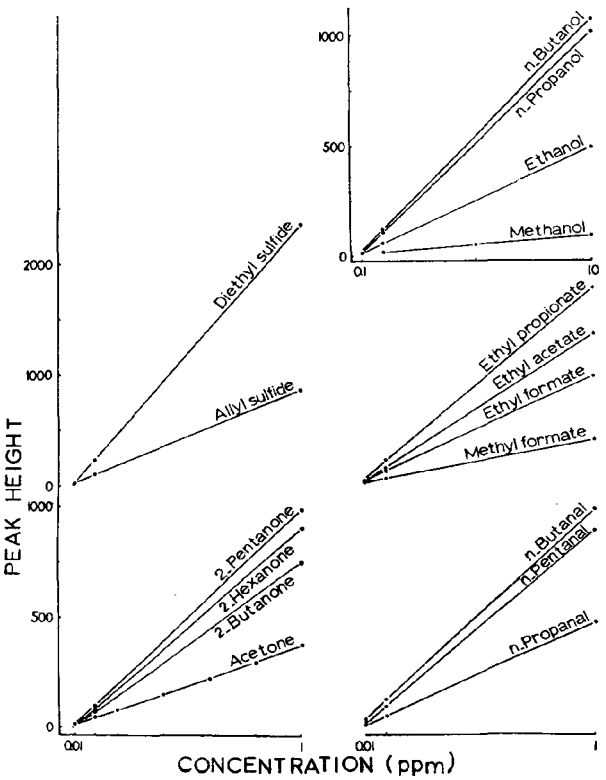


Figure 1. Relationship between peak heights (% full scale deflection × attenuation factor) and concentration of organic compounds analyzed

Some differences in peak heights observed in this study undoubtedly can be attributed to the chromatographic phase of the analysis *per se*. Other differences probably result from the sampling procedure. The concentration of material drawn into the head space and injected into the instrument varies in relation to the characteristics of the material being analyzed. Interrelations between factors influencing the relative peak heights would make interpretation of these differences highly speculative and beyond the scope of this correspondence.

Development of standard curves utilizing head-space gas analysis in the analyst's laboratory should provide a basis for quantitative analysis of trace organic chemical compounds at and below the p.p.m. level.

LITERATURE CITED

(1) Bassette, R., Özeris, S., Whitnah, C. H., ANAL. CHEM. 34, 1540 (1962).
(2) Weurman, C., *Food Technol.* 15, 531 (1961).

SÜHEYLA ÖZERIS
RICHARD BASSETTE

Dept. of Dairy Science
Kansas State University
Manhattan, Kan.

Contribution No. 313, Department of Dairy Science, Kansas Agricultural Experiment Station, Manhattan, Kan.

A Polarographic Study of the Copper(II) Complexes of Mono-, Di-, and Triethanolamine

SIR: The data of Fisher and Hall (*1*) have been examined and analyzed by the application of Leden's equations (*2*) as modified and applied to the polarography of mixed complexes by Watters and coworkers (*3–6*).

For these systems and experimental conditions

$$F_0 = \text{antilog}\,[0.4342\,(-\Delta E_{1/2})\,nF/RT] = \text{antilog}\,[33.251\,(-\Delta E_{1/2})] =$$

$$\sum_{x=0}^{N}\sum_{y=0}^{N} K_{xy}[\mathrm{A}]^x(\mathrm{OH}^-)^y \quad (1)$$

where $\Delta E_{1/2}$, X, Y, and [A] are used as defined by Fisher and Hall. The symbol (OH^-) is used to denote the activity of the hydroxide ion which is calculated from pH data using 13.83 as pK_w instead of 14.00 as was used in reference (*1*). Equation 1 is valid only if polynuclear complexes are absent.

Values of the various constants are calculated as follows. Equation 1 is written in an expanded form assuming only the more likely complexes. For example at pH = 13 in the monoethanolamine system, the following complexes might be expected: Cu(MEA)(OH), $Cu(MEA)_2(OH^-)$, $Cu(MEA)(OH^-)_2$, and $Cu(MEA)_2(OH^-)_2$. The equation would then be

$$F_0 = K_{11}[\mathrm{A}](\mathrm{OH}^-) + K_{21}[\mathrm{A}]^2(\mathrm{OH}^-) + K_{12}[\mathrm{A}](\mathrm{OH}^-)^2 + K_{22}[\mathrm{A}]^2(\mathrm{OH}^-)^2 \quad (2)$$

Experimental values of F_0, [A], and (OH^-) are inserted and the equations solved by determinants for the constants. If one or more of the predicted complexes does not exist, or is present in concentrations less than 0.1% of the total copper concentration, no value is usually obtained for the constant. As a check, these calculated constants can be used to calculate a predicted $\Delta E_{1/2}$ for each experimental point which is then compared to the experimental $\Delta E_{1/2}$.

Monoethanolamine. The observed potential shifts at pH = 13 and 11 can be accurately (±2 mv.) predicted on the basis of the following complexes and calculated constants: $Cu(MEA)_2[OH^-]_2$, log K_{22} = 19.60; $Cu(MEA)_2[OH^-]$, log K_{21} = 16.67. The legend of Figure 2, curve *B*, in reference (*1*) is in error and should read "pH = 13, add 0.08 volt."

The situation at pH = 9 is more complicated. As stated by Fisher and Hall, the data indicate a complex of two ethanolamines to one copper(I) and also a complex of two ethanolamines to one copper(II), with evidence of a complex of three ethanolamines to one copper(II) at higher [A] values. However, it is impossible to determine the number of hydroxides in these complexes at a constant pH and the potentials obtained at $[A] = 10^{-2}$ between pH = 9 and pH = 11 are probably mixed potentials and unreliable as a basis for calculations. Thus the formulas and constants for these species remain undetermined.

The formula and structure of the copper(I) complex would be of special interest because, in general, copper(I) is stabilized by monodentate ligands while bidentate ligands stabilize copper(II) in preference to copper(I). It seems unlikely that the protonated form of monoethanolamine could act as a ligand, but this species is present in high concentration at pH = 9 and the data clearly indicate a complex of two ethanolamines to one copper(I). If the complexed ethanolamines were capable of acting as bidentate ligands it would be expected that copper(II) would be stabilized and no copper(I) complex would be evident.

Diethanolamine. The observed potential shifts at pH 13, 11, and 9 can be predicted (±2 mv. for 75% of the points) on the basis of the following complexes and calculated constants: $Cu(DEA)[OH^-]_3$, log K_{13} = 18.97; $Cu(DEA)_2[OH^-]$, log K_{21} = 14.10; $Cu(DEA)_2[OH^-]_2$, log K_{22} = 19.28. The value of log K_{21} is the least certain since the concentration of this complex never exceeds one third of the total copper concentration.

The data at $[A] = 10^{-2}$ seem to be unreliable since discrepancies of 5 to 10 mv. are found at this concentration between the data of Figure 1, curve *B* and Figure 3 of reference (*1*). Perhaps more consistent results would have been obtained if the measurements at constant [A] had been performed at a higher value of [A].

Triethanolamine. The observed potential shifts at pH 13, 11, and 7 can accurately be predicted (±2 mv.) on the basis of the following complexes and calculated constants: $Cu(TEA)[OH^-]_3$, log K_{13} = 20.18; $Cu(TEA)_2[OH^-]_2$, log K_{12} = 18.02; $Cu(TEA)[OH^-]$, log K_{11} = 11.83; $Cu(TEA)_2[OH^-]_2$, log K_{22} = 19.00. The value of log K_{22} is the least certain since the concentration of this complex never exceeds one half of the total copper concentration.

The fit between experimental and calculated $\Delta E_{1/2}$ values becomes poor as pH = 9 is approached from either direction at $[A] = 10^{-2}$. This may be caused by neglecting the complex, $Cu(TEA)_2[OH^-]$, which was not found at pH = 7, 11, or 13. Of course, the presence of this complex cannot be verified with no data for pH = 9 available.

A planar structure with three chelate rings for $Cu(TEA)[OH^-]_3$ is prohibited by steric considerations, and therefore only two chelate rings are possible for the complex. If the hydroxides in $Cu(TEA)[OH^-]$ and $Cu(TEA)[OH^-]_2$ represent ionization of the chelated alcohol groups, the third hydroxide in $Cu(TEA)[OH^-]_3$ must represent either the ionization of the third, unchelated, alcohol group or the ionization of a bound water molecule (or its replacement by a hydroxide ion). The difference in kind between the second and third hydroxides may explain the fact that $(pK_{12} - pK_{11}) = 6.19$ while $(pK_{13} - pK_{12}) = 2.16$.

In Figure 4, curve *A*, of reference (*1*) the −log [A] values are in error and should be corrected by subtracting 0.1 from the published values.

LITERATURE CITED

(1) Fisher, J. F., Hall, J. L., ANAL. CHEM. **34**, 1094 (1962).
(2) Leden, I., *Z. Physik. Chem.* **188A**, 160 (1941).
(3) Schupp, O. E., III, Youness, T., Watters, J. I., *J. Am. Chem. Soc.* **84**, 505 (1962).
(4) Sturrock, P. E., Loughran, E. D., Watters, J. E., *Inorg. Chem.* **1**, 457 (1962).
(5) Watters, J. I., Mason, J. G., *J. Am. Chem. Soc.* **78**, 285 (1956).
(6) Watters, J. I., Mason, J. G., Schupp, O. E., III, *Ibid.*, p. 5782.

PETER E. STURROCK
School of Chemistry
Georgia Institute of Technology
Atlanta, Ga.

Determination of Nitrogen Impurity as Uranium Nitrides in Fused Uranium Dioxide (UO_2)

SIR: Lathouse, Huber, and Chase (*4*) reported that nitrogen content in UN and U_2N_3 was measured acceptably when these compounds were dissolved in a digestion mixture of 1 to 1 HCl with additions of copper selenate and hydrofluosilicic acid. They then transferred the digested solution into a still with an addition of a NaOH solution, completed a distillation into a boric acid solution containing a mixed indicator, and titrated the collected ammonia with a standard acid.

In our laboratories, fused UO_2 is one of several candidate fuel materials used in fuel fabrication development studies (*1*). Since these studies as well as in-reactor test studies of UO_2 fuel elements can be abruptly terminated by cladding failures caused by internal gas pressures, an accurate analysis is required of fixed and sorbed gases (*1*) present in fuel materials before fabrication. The bulk of gases present in fused UO_2 was found to be nitrogen in the form of uranium nitrides (*2, 3*).

Vacuum extraction and Kjeldahl techniques are used in our laboratories to analyze for fixed or sorbed gas content in UO_2 samples. Past efforts to correlate nitrogen values obtained by these two analytical techniques with calculated values of prepared UO_2 samples containing known amounts of UN and $UN_2(U_2N_3)$ were not successful. Nitrogen values for samples of commercially fused UO_2 also have represented areas of disagreement between vendor and our laboratories. Because of these several findings, an investigation was made to apply the Lathouse (*4*) digestion mixture to the determination of nitrogen impurity as uranium nitrides (UN, U_2N_3, UN_2) in fused UO_2.

The objectives of the study were to extend the method to the determination of nitrogen impurities as uranium nitrides in a UO_2 matrix, and to lower the range of the method to the 50- to 1000-p.p.m. level.

The digestion mixture was successfully used. It was necessary to use a new boric acid mixed indicator for the required increase in sensitivity. A reductant, Devarda's alloy, was also necessary.

EXPERIMENTAL

Reagents. Reagent grade chemicals and double-distilled water were used. An NaOH solution was prepared by dissolving 680 grams of sodium hydroxide in 2 liters of double-distilled water. Devarda's alloy, 0.5 gram, was then added and the solution was boiled until the volume was reduced to 1.8 liters (*6*).

Boric Acid Indicator. A boric acid mixed indicator for nitrogen was used. A solution was prepared by dissolving 20 grams of boric acid in double-distilled hot water. Then 7.5 ml. of 0.1% bromcresol green (*5*) in alcohol and 4 ml. of 0.1% methyl red in alcohol were added. The solution was then diluted with double-distilled water to 1-liter volume. If the mixed indicator boric acid solution turned yellowish instead of pink in color, the entire solution was discarded. A new boric acid mixed indicator solution was prepared, but a new supply of methyl red in alcohol indicator was used. The methyl red indicator was used to increase the sensitivity of the end point detection in the titration determination.

Apparatus. Conventional Kjeldahl equipment, laboratory glassware, and titration equipment were used.

Procedure. Weigh out about 200 mg. of −100-mesh UO_2 sample into a 50-ml. Erlenmeyer flask. Record the actual weight. Then add 25 ml. of 1:1 HCl and 2 ml. of H_2SiF_6. Heat just below boiling for about 30 minutes. Add about 200 mg. of cupric selenate. Digest until solution is complete.

Transfer the cooled sample solution to Kjeldahl distillation equipment and add 25 ml. of the NaOH solution. Distill and collect the condensate in a 50-ml. Erlenmeyer flask containing 5 ml. of the boric acid mixed indicator solution. Adjust the heat input so that about 20 ml. of condensate will be collected in 5 minutes. The boric acid solution need not be accurately measured (*6*).

Titrate the collected ammonia (ammonium borate) with a standard acid near 0.005*N*. Make a blank determination by using the same amount of reagents and solutions as used in the sample determination. At times, high blank determinations are a result of ammonia present in the laboratory air. A special laboratory hood or ammonia-free work area is necessary for parts per million nitrogen determinations.

Calculate nitrogen content by the conventional titration formula.

Table I. Determination of Nitrogen as Uranium Nitrides in Fused UO_2

(Values are average of at least four determinations)

Sample	Nitrogen (p.p.m.) 1	2	3	Theoretical	4
UN (in UO_2)	690	890	1310	1340	250
UN_2 (in UO_2)[a]	540	1450	1220	1250	690

Digestion methods (Kjeldahl techniques)

1. Hydrochloric acid
2. Perchloric acid and hydrogen peroxide
3. 1:1 HCl with additions of cupric selenate and hydrofluosilicic acid

Vacuum extraction technique

4. Vacuum extraction at 1000° C. with mass spectrometric analysis of gases

[a] Some U_2N_3 possible in sample

Table II. Determination of Nitrogen as Uranium Nitrides in Fused UO_2 with Reductant in NaOH Solution

Sample	Nitrogen (p.p.m.) Reductant (Devarda's alloy) Added to NaOH	Not added to NaOH	Theoretical
UN (in UO_2)	972	888	1000
UN_2 (in UO_2)[a]	1083	908	1100

Rel. std. dev. on samples with reductant added, 1.5 to 2.5%; without reductant added to NaOH solution, 11 to 15%.

[a] Some U_2N_3 possible in sample.

DISCUSSION AND RESULTS

The preliminary work was performed on two samples consisting of UN in UO_2 and UN_2 in UO_2. Table I shows that of the several digestion techniques available for analyzing nitrogen as uranium nitrides in UO_2, only the recommended method gave complete recovery of the nitrogen.

An important feature of this digestion technique is the essential action of the selenate ion, described by Lathouse, Huber, and Chase (*4*). An important consideration in our work was the action of the Devarda's alloy. In our early experimental work we found that it was necessary to add Devarda's alloy to the NaOH solution. The addition of the reductant gave values with better precision and accuracy on prepared UO_2 samples. Table II shows

analyses of samples with and without the addition of Devarda's alloy.

Precision of the method was established by analyzing both prepared samples and vendor-supplied fused UO_2. The values are average of at least 4 determinations by two analysts using the recommended method. The relative standard deviation is 2.5%.

Accuracy was determined by analyzing synthetic mixtures of UN and UN_2 in UO_2 and by addition of ammonium chloride. The relative error is about 3% in the 50- to 1000-p.p.m. range. This range is typical of the nitrogen content normally found in fused UO_2.

EXTENSION OF METHOD

Previously it was mentioned that past efforts to correlate nitrogen values as obtained by other dissolution techniques and including the present method with values as obtained by vacuum extraction techniques were not successful on either commercial samples or prepared samples containing known amounts of UN and UN_2 in UO_2. Our data (Table I) indicate that the vacuum extraction at 1000° C. gave fair results for UN_2 and U_2N_3 in UO_2, but low results for UN in UO_2. The later value appears reasonable since UN is reportedly stable in vacuum to about 1700° C.

Vacuum extraction techniques, of course, remain quite useful for measurement of sorbed gases that are released from UO_2 at the 1000° C. temperature. But for fused UO_2 that contains UN, or other high temperature stable compounds, a new, high temperature–vacuum technique is needed. We have made preliminary modifications to our vacuum fusion equipment to permit operating temperatures to 2000° C. A study of this modified system is planned.

ACKNOWLEDGMENT

The authors thank Mrs. I. S. Paret and H. J. Pierce for performing many developmental analyses. The authors are indebted to D. W. Brite, D. R. de Halas, and W. E. Roake for their helpful suggestions and criticisms during the course of this work.

LITERATURE CITED

(1) Anderson, H. J., Anicetti, R. J., "Specification for High Density Uranium Dioxide (Nuclear Grade)," **HW-74204**, July 11, 1962.
(2) Cadwell, J. J., "Quarterly Progress Report," Fuels Development Operation, **HW-72346**; October, November, December, 1961 (Classified).
(3) *Ibid.*, **HW-74377**; April, May, June, 1962 (Classified).
(4) Lathouse, Joan, Huber, F. E., Jr., Chase, B. L., ANAL. CHEM. **31**, 1606–7 (1959).
(5) Pierce, W. C., Haenisch, E. L., "Quantitative Analysis," 2nd ed., 123, Wiley, New York, 1940.
(6) Winkler, L. W., *Z. Angew. Chem.* **26**, 231 (1913).

HARLAN J. ANDERSON
JAMES C. LANGFORD
General Electric Co.
Hanford Laboratories
Richland, Wash.

Work performed for the U. S. Atomic Energy Commission under Contract AT-(45-1)-1350.

Determination of Rhodium in Rhodium–Uranium Alloys by Precipitation with Hydrogen Sulfide

SIR: In a series of metallurgical studies involving phase diagrams of binary systems of uranium with different elements, the rhodium–uranium system was investigated. A method of determination of rhodium in the binary alloys which could be adapted to the determination of from 2 to 56% of rhodium was sought. Several methods which might be utilized have been reported in the literature. Two of these which were given primary consideration were precipitation of rhodium with hydrogen sulfide, recommended by Gilchrist (*2*), and reduction of rhodium to the metal with hydrazine hydrochloride (*6*). Since it had been reported that the precipitation of rhodium sulfide is sometimes incomplete (*5, 8*), the latter method was first investigated. The rhodium is precipitated with sodium tartrate and reduced to the metallic state by prolonged boiling with hydrazine hydrochloride and an excess of sodium carbonate or sodium hydroxide. It was expected that the addition of sufficient sodium carbonate, prior to the rhodium precipitation, would prevent the precipitation of uranium. Preliminary experiments showed that this could indeed be done, but that rhodium was not always quantitatively recovered owing to possible incomplete reduction to the metal and hydrolysis of the precipitate during filtration.

Table I. Effect of Digestion on Rhodium Recovery

Added, mg. U	Added, mg. Rh	Sulfide digestion time	Rh found, mg.
200	20.5	1 hour	19.3
200	20.5	3 hours	19.8
200	25.6	overnight	25.8
200	25.6	overnight	25.8

The precipitation of rhodium as the sulfide proved to be complete and selective under conditions developed below. However, for complete rhodium recovery, overnight digestion of the sulfide precipitate was desirable as shown in Table I. This gave a rhodium sulfide precipitate which was well coagulated and readily filtered. Any uranium which may have coprecipitated was removed by leaching the metallic rhodium precipitates with dilute nitric acid as described by Richmond, Baldwin, and Maienthal (*4*) for the analysis of platinum–uranium alloys.

The method of solution of the alloys was dependent on the rhodium content. If it was less than 35%, the samples were dissolved in hydrochloric acid and hydrogen peroxide; those of higher rhodium content were taken into solution by the sealed tube method (*3, 7*) The completeness of the sulfide precipitation and the insolubility of rhodium in the nitric acid leachings was verified by checking the combined filtrates by the colorimetric procedure of Gardner and Hues (*1*) which uses stannous chloride at an acidity at which the red rhodium complex is developed.

EXPERIMENTAL

Dissolve the sample over low heat with concentrated hydrochloric acid and the dropwise addition of hydrogen peroxide, or by solution in 15 ml. of concentrated hydrochloric acid and 0.3 ml. of concentrated perchloric acid in a sealed tube at 300° C. Evaporate the solution to about 10 ml., dilute to 100 ml. with water, filter, and wash well with 2% hydrochloric acid (v./v.). Add 10 ml. of concentrated hydrochloric acid to the filtrate, dilute to 400 ml. with water, heat to boiling, and gas with hydrogen sulfide for 1 hour while keeping the temperature of the solution just under boiling. Remove from the heat and continue gassing with hydrogen sulfide for $^1/_2$ to 1 hour while the solution is cooling. Let stand overnight, filter, wash well with 2% hydrochloric acid (v./v.) saturated with hydrogen sulfide, and reserve the filtrate. Dry and ignite the precipitate to 600° C. in a porcelain crucible and reduce in hydrogen over a burner, using a Rose crucible

lid and delivery tube. Leach in 5 ml. of 50% nitric acid (v./v.) at about 80° C. for 30 minutes with frequent stirring. Add 5 ml. of 20% nitric acid (v./v.), filter, wash well with 1% nitric acid (v./v.), and reserve the filtrate. Dry and ignite the precipitate to 600° C. in a weighed porcelain crucible, reduce in hydrogen as before, cool, and weigh. To confirm the completeness of the sulfide precipitation, combine the reserved filtrates, evaporate to a low volume to remove nitric acid, and check for the presence of rhodium colorimetrically by method of Gardner and Hues (*1*).

RESULTS AND DISCUSSION

Results on the binary alloys are shown in Table II. The agreement of those samples which were done in duplicate was within 0.1 to 0.3% of the amount of rhodium present. The sample weight was determined by the amount of alloy available; duplicates were taken when sufficient sample could be obtained. The optimum rhodium content for analysis probably ranges from 25 to 100 mg., although smaller amounts could certainly be handled with ease. The rhodium recovered from the colorimetric determination of the combined filtrates ranged from 0.00 to 0.04 mg., which was not a weighable amount, showing that this recovery may be omitted in all but the most accurate work.

Table II. Results on Rhodium–Uranium Alloys

Sample No.	Sample weight, grams	Rh found, % By sulfide precipitation	Rh found, % In combined filtrates
Rh 4	0.94	2.90	0.00
Rh 5	1.26	5.85	0.00
Rh 9	0.17	40.95[a]	0.02
	0.20	41.06	0.02
Rh 13	0.33	18.35	0.00
Rh 22	0.25	32.11	0.02
	0.25	32.07	0.02
Rh 23	0.27	23.39	0.00
	0.27	23.35	0.00
Rh 25	0.19	56.60	0.02

[a] Bulk of sample dissolved in HCl + H_2O_2 and rhodium determined as sulfide. Residue remaining taken into solution in a sealed tube, rhodium determined colorimetrically and added to gravimetric results.

ACKNOWLEDGMENT

This work was done in connection with studies of the rhodium–uranium system by J. J. Park. The author thanks C. L. Gordon for taking some of the samples into solution by the sealed tube method.

LITERATURE CITED

(1) Gardner, R. D., Hues, A. D., ANAL. CHEM. 31, 1488 (1959).
(2) Gilchrist, R., "The Platinum Metals and Gold," Chap. 20, p. 381, in "Applied Inorganic Analysis," by Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., Hoffman, J. I., 2nd ed., Wiley, New York.
(3) Gordon, C. L., Schlecht, W. G., Wichers, E., *J. Res. Natl. Bur. Std.* **33**, 457 (1944).
(4) Richmond, M. S., Baldwin, J. R. Maienthal, E. J., U. S. Atomic Energy Comm., *Rept.* NBS-4555, p. 3, 1956.
(5) Schoeller, W. R., Powell, A. R., "The Analysis of Minerals and Ores of the Rarer Elements," 3rd ed., p. 332, Harper, New York.
(6) *Ibid.*, p. 354.
(7) Wichers, E., Schlecht, W. G., Gordon, C. L., *J. Res. Natl. Bur. Std.* **33**, 363 (1944).
(8) Wilson, C. L., Wilson, D. W., "Comprehensive Analytical Chemistry, Classical Analysis," Vol. Ic, pp. 682–4, Elsevier, Amsterdam.

E. JUNE MAIENTHAL

National Bureau of Standards
Washington, D. C.

WORK supported in part by the U. S. Atomic Energy Commission.

Rapid Extraction and Spectrophotometric Determination of Vanadium(V) with 2-Thenoyltrifluoroacetone

SIR: The study of spectrophotometric reactions with 2-thenoyltrifluoroacetone, TTA, (*4*) has been extended to vanadium(V). The red color of the vanadium(V)–TTA complex in *n*-butyl alcohol forms the basis of a new rapid method for the determination of vanadium(V) at the milligram level. The color reaction is fairly selective and sensitive.

EXPERIMENTAL

Apparatus and Reagents. The apparatus has been described previously (*4*).

TTA (Columbia Organic Chemicals Co., Columbia, S. C.) solutions in *n*-butyl alcohol (0.3*M*) were used.

A stock solution of vanadium(V) chloride was prepared by dissolving about 5 grams of ammonium *meta*-vanadate (Merck and Co., Inc., Rahway, N. J.) in 40 ml. of concentrated hydrochloric acid and diluting to 500 ml. with water. The lemon-yellow solution contained $VOCl_3$. An aliquot of this solution was treated with a known volume of standard Mohr's salt solution, the excess of which was determined by back titration with potassium dichromate solution (*1*). The test solutions (200 μg. of vanadium per ml.) were prepared by suitable dilution of the stock solution.

Buffer solutions (1*M*) of different pH were prepared by standard procedures: potassium chloride–hydrochloric acid (pH 2.3), and phthalate buffers (pH 3.4, 4.0, 6.02).

Procedure. The experimental outline was similar to that reported in earlier papers of this series (*4*).

A suitable aliquot (0.5 to 1.5 ml.) of vanadium chloride solution containing 200 μg. of vanadium per ml. was mixed with 10 ml. of buffer solution of desired pH in a 250-ml. separatory funnel and extracted for 5 minutes with 10 ml. of TTA solution in *n*-butyl alcohol. The red-colored organic layer (*n*-butyl alcohol) was measured at 420 mμ against a reagent blank.

RESULTS AND DISCUSSION

The absorption spectrum of a solution of vanadium(V)–TTA chelate (vanadium = $1.57 \times 10^{-4}M$), extracted at pH 2.5, shows maximum absorption at 410 mμ after which the absorbance gradually drops and becomes negligible beyond 600 mμ. All the absorbance measurements were performed at 420 mμ. The absorptivity at 420 mμ is 3563.5 ± 36.

The extraction starts at pH lower

Table I. Diverse Ions

[Vanadium(V) = 200 μg]

Foreign ion	Source	Tolerance limit, μg.
Zn^{+2}	$ZnSO_4.7\ H_2O$	10,000
Ca^{+2}	$Ca(NO_3)_2$	10,000
Sr^{+2}	$Sr(NO_3)_2$	10,000
Cu^{+2}	$CuSO_4.5\ H_2O$	1,000
Co^{+2}	$CoSO_4.7\ H_2O$	500[a]
Ni^{+2}	$NiSO_4.7\ H_2O$	1,000[a]
Al^{+3}	$Al_2(SO_4)_3.18\ H_2O$	10,000
Fe^{+3}	$FeCl_3.6\ H_2O$	1,000[b]
Cr^{+3}	$Cr_2(SO_4)_3.18\ H_2O$	500
Ti^{+4}	$Ti(SO_4)_2$	1,000
Ce^{+4}	$Ce(NO_3)_4$	500
As^{+5}	As_2O_5 (dissolved in HCl)	5,000
Sb^{+5}	Sb_2O_5 (dissolved in HCl)	500
Nb^{+5}	Nb_2O_5 (fused with $KHSO_4$, dissolved in citric acid)	250
Cl^-	NaCl	10,000
F^-	NaF	1,000
SO_4^{-2}	$(NH_4)_2SO_4$	10,000
MoO_4^{-2}	$(NH_4)_2MoO_4$	1,000
PO_4^{-3}	$(NH_4)_2HPO_4$	1,000
$Tart^{-4}$	Tartaric acid	10,000

[a] Foreign ion first removed by extraction at pH 8.6.
[b] Foreign ion removed by extraction from 10*M* nitric acid.

than 0.1, gradually increases, becomes 100% from pH 2.5 to pH 4.1, and thereafter it sharply decreases. A pH range of 2.5 to 4.1 is recommended for quantitative extraction. Phthalate buffers were chosen for extraction purposes at pH 3.4 and up.

The vanadium–TTA system follows Beer's law at 420 mμ over the range of 0.8 to 11 μg. of vanadium per ml. The color is quite stable up to 3 hours, after which fading slowly occurs. The tolerance limit (*4*) for 20 representative ions is recorded in Table I. In addition, uranium and manganese give color reactions and interfere. Tungsten, tin, and EDTA interfere seriously by inhibiting the formation of color. Tolerance limits for ions of mercury, bismuth, zirconium, thorium, citric acid, and boric acid are the same as those recorded for manganese (*4*). Interferences due to large amounts of nickel (*4*), copper (*2*), and cobalt (*3*) can be eliminated by preliminary extraction at pH 8.6 with TTA. At this pH, the extraction of vanadium is practically nil.

The extraction of vanadium in mixtures with iron(III), chromium(III), titanium(IV), zirconium(IV), arsenic(V), cobalt(II), nickel, niobium(V), cerium(IV), and molybdate(VI) is a notable feature of the method since the latter are commonly associated with vanadium in actual analytical samples. Furthermore, the lack of interferences from complex-forming anions like chloride, sulfate, fluoride, and phosphate is interesting.

From 10 runs with 200 μg. of vanadium(V), the absorbance measured was 0.560 ± 0.006 so that the relative standard deviation was ±1%. The sensitivity is 0.016 μg. per ml. On this basis, the method is comparable to the existing standard methods for vanadium (*5*).

LITERATURE CITED

(1) Charlot, G., Bezier, D., "Quantitative Inorganic Analysis," p. 623, Wiley, New York, 1957.
(2) De, A. K., Khopkar, S. M., *Z. Anal. Chem.* **171**, 4 (1959).
(3) De, A. K., Majumdar, S. K., *Anal. Chim. Acta* **27**, 153 (1962).
(4) De, A. K., Rahaman, M. S., ANAL. CHEM. **35**, 159 (1963); *Anal. Chim. Acta* **27**, 591 (1962).
(5) Sandell, E. B., "Colorimetric Determination of Traces of Metals," p. 925, Interscience, New York, 1957.

ANIL K. DE
MD. SYEDUR RAHAMAN

Department of Chemistry
Jadavpur University
Calcutta 32, India

An Improvement of the Amperometric Titration of Thiols at the Rotating Platinum Electrode

SIR: The commonly described amperometric titration of thiols consists of successive additions of the cation used—e.g., Ag^+ or Hg^{+2}—to a buffered solution of the thiol (*4*). The current through the solution is read at some fixed time after each addition. The potential applied to the rotating platinum electrode is such that cations in excess of the quantity bound by the —SH groups are discharged. As the amount of thiol to be determined decreases, the time spent on the titration increases. The reason is the great number of current readings required (about 10), and the sluggishness and instability of the electrode which are more disturbing with a more sensitive galvanometer circuit. Thus the determination of 1.5 μmoles —SH requires about 12 minutes (*2*). This amount of —SH seems to approach the lower limit for convenient determination by the conventional amperometric method, although exact information on this limit is difficult to find.

We have introduced a modification of the amperometric method which permits 0.04 μmole —SH to be determined with good reproducibility in less than 3 minutes. This has been achieved simply by an interchange of the order in which Ag^+ and —SH are introduced into the titration vessel. With the exception of this change and some minor practical alterations, we have used the amperometric argentimetric method as described by Benesch, Lardy, and Benesch (*1*).

Our procedure is as follows: The electrode and the bridge are immersed into the titration vessel which contains 20 to 30 ml. of "tris," pH 7.4. Usually the current is stabilized at zero within 30 seconds. One milliliter of a solution of $AgNO_3$ ($2.5 \cdot 10^{-4}M$) is then added to the vessel. The sensitivity of the galvanometer circuit is such that about maximal deflection results from this operation. An accurately known volume of the thiol solution is now introduced (10 to 200 μl. in our experiments) and the corresponding decrease of the current is read almost immediately. To secure maximum exactitude, the latter current reading should amount to between two thirds and one third of the value attained by the addition of $AgNO_3$. The volume of thiol solution which would just reduce the current to zero (the end point), is now easily computed on the assumption that the galvanometer deflection is a linear function of the quantity of thiol added. Hence the normality of the thiol solution is obtained from three rapid current readings only. Our apparatus is somewhat simplified relative to the conventional setup since the $AgNO_3$ can be delivered from a pipet instead of a buret.

With rapidly reacting —SH groups—like those contained in glutathione, cysteine, and cysteamine—a stable current reading is attained within 10 seconds after the addition of thiol.

Table I. Reproducibility and Stoichiometry Obtained in 10 Titrations of Each of the Thiols Glutathione, Cysteine, and Cysteamine (2-Mercapto ethylamine)

30 ml. of Tris buffer [Tris(hydroxymethyl)aminomethane, 0.15*M*, KCl, 0.01*M*, gelatin 0.01% w./v., at pH 7.4] and 30 to 50 μl. of thiol solution ($2\text{–}3 \cdot 10^{-3}M$ —SH) were used in each determination.

Titration no.	Glutathione end point, μl.	Cysteine end point, μl.	Cysteamine end point, μl.
1	98.5	72.7	68.2
2	96.4	73.0	67.8
3	96.4	72.7	66.8
4	96.2	71.1	67.0
5	96.0	73.0	67.0
6	96.5	71.7	67.2
7	95.9	71.5	66.2
8	95.8	72.0	66.0
9	96.8	72.8	67.5
10	96.7	72.5	66.6
Mean	96.52	72.30	67.03
Std. dev.	±0.770	±0.677	±0.684
Rel. std. dev.	0.798%	0.936%	1.020%
Stoichiometry: Number of Ag^+ ions consumed by each thiol molecule	1.07	1.45	1.3

The kinetics of the reaction between Ag^+ and the —SH groups of hemoglobin can easily be followed as expressed in the curve relating current to time after the introduction of hemoglobin into the vessel. Figure 1 shows that there is a linear relationship between the current and the amount of thiol added down to about one third of the maximal current. The deviation from linearity indicates dissociation of the silver mercaptides.

In Table I are shown the results of titrations of about 0.1 μmole of the 3 substituted thiols—glutathione, cysteine, and cysteamine. The relative standard deviations are about 1% of the mean. This reproducibility appears to be better than the one obtained by Burton (*2*) in his conventional titrations, in spite of the fact that the amounts of thiols determined in his titrations were about 10 times greater than the quantities measured by us. The average time spent on the titrations reported in Table I was 2.7 minutes. This figure includes the preparation of the apparatus for each titration. The stoichiometric relationships are similar to those reported for conventional amperometric titrations (*3*). The last row of Table I shows that more than one Ag^+ is apparently consumed per —SH group, presumably because the silver mercaptides (RSAg) bind some of the excess silver (*3*). In this respect our method consequently does not represent any advantage.

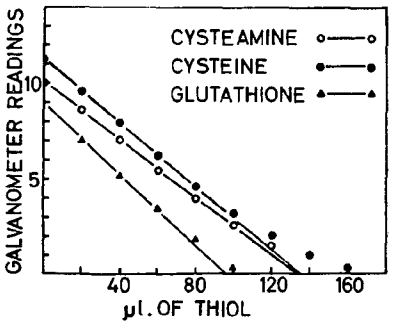


Figure 1. Demonstration of linear dependence of current on amount of thiol added

Initial concn. of $AgNO_3$ was $0.9 \cdot 10^{-5}M$, in 30 ml. of Tris, pH 7.4. Below about one third of initial current reading, linear relationship is no longer obeyed, indicating dissociation of silver mercaptides

In our modified titration procedure the concentration of Ag^+ exceeds that of the thiol during the entire titration.

Consequently, errors due to spontaneous oxidation of the thiol in the titration vessel are ruled out. Thus it was unnecessary to remove oxygen from the solution by bubbling nitrogen through it. Furthermore, one is free to choose a pH higher than 7.4 in the buffer, since a low pH is no longer needed to counteract the spontaneous oxidation. Sluggishness and instability of the silver-coated platinum electrode due to "intoxicating effects" of the thiols are reduced or eliminated in our system. The excess of silver counteracts the dissociation of the silver mercaptides. At the end point, however, this excess is abolished and the dissociation is considerable (see Figure 1). In contrast to the conventional method, the sharpness of the calculated end point of our modified method is not affected by such a dissociation, since the calculation is not based upon the actual attainment of the end point during the titration.

LITERATURE CITED

(1) Benesch, R. E., Lardy, H. A., Benesch, R., *J. Biol. Chem.* **216**, 663 (1955).
(2) Burton, H., *Biochim. Biophys. Acta* **29**, 193 (1958).
(3) Kolthoff, I. M., Eisenstädter, J., *Anal. Chim. Acta* **24**, 83 (1961).
(4) Kolthoff, I. M., Harris, W. E., IND. ENG. CHEM., ANAL. ED. **18**, 161 (1946).

HANS CHR. BØRRESEN[1]

Institute of Clinical Biochemistry
Rikshospitalet, University of Oslo
Oslo, Norway

[1] Fellow of The Norwegian Cancer Society.

The Quantitative Recovery of Germanium by Distillation from Hydrochloric Acid in the Presence of Sodium Chloride

SIR: In Cluley's well-known analytical procedure, germanium is brought into solution by fusion with sodium carbonate, and separated as the tetrachloride by distillation from hydrochloric acid of approximately constant-boiling composition. The constant-boiling acid is produced by adding to the neutralized germanium solution an equal volume of concentrated acid. The specific gravity of standard reagent grades of concentrated hydrochloric acid varies be tween 1.18 and 1.19; Cluley stipulates the use of 1.18 sp. gr. acid, whereas Sandell states only that the mixture should be $6M$ in hydrochloric acid (*2*, *3*). The mixture will be approximately $5.8M$ in HCl when concentrated acid of sp. gr. 1.18 is used, and approximately $6.2M$ in HCl in the case of acid of 1.19 sp. gr.

It is the purpose of this note to show that in the presence of sodium chloride, these slight variations in the initial concentration of the acid in the mixture undergoing distillation may exert a profound effect on the recovery of the germanium.

RESULTS

In the presence of 2.2 grams of sodium chloride—which is necessarily produced as a result of the sodium carbonate (2.0 grams) fusion and subsequent neutralization procedure—distillation of a germanium solution $6.2M$ in HCl resulted in a slight escape of fumes for a few moments immediately prior to the appearance of the first drop of distillate, and in a very severe loss of germanium. No significant loss occurred if the solution was only $5.8M$ in HCl, or in either case in the absence of sodium chloride. This loss was obviated by employing a long delivery tube, which initially dipped into a few milliliters of water in the receiver, and subsequently was maintained just below the surface of the distillate.

Typical experimental results are illustrated in Table I.

DISCUSSION

Almásy and Barcánfalvi found that the vapor–liquid equilibrium of the $GeCl_4/HCl/H_2O$ system is shifted in

Table I. Effect of HCl/NaCl Concentration on Ge Recovery

Sp. gr., concd. HCl	Molarity, diluted HCl	NaCl (grams)	Delivery tube	Fumes apparent before distillate	Ge recovery (μg) from: 50 μg. Ge	500 μg. Ge
1.18	5.8	0	Short	No	50.5	509
1.19	6.2	0	Short	No	49.1	494
1.18	5.8	2.2	Short	No	48.3	489
1.19	6.2	2.2	Short	Slight	14.0	153
1.19	6.2	2.2	Long	...	49.9	495

favor of an increase of $GeCl_4$ (and presumably HCl also) in the vapor phase by the presence of calcium chloride in the liquid phase (*1*). Sodium chloride evidently produces a similar effect, and germanium may therefore be lost easily in the vapor initially evolved from boiling solutions containing sodium chloride, which escapes condensation when the HCl concentration in the liquid phase is as high as 6.1*M* (the constant-boiling concentration for the HCl/H_2O system in the absence of sodium chloride). Loss probably also occurs at lower HCl concentrations, depending upon the concentration of the sodium chloride present.

LITERATURE CITED

(1) Almásy, A., Barcánfalvi, F., *Nehézvegyip. Kut. Int. Közlemén.* 1, 293–301 (1959); *C.A.* 54, 6236*f* (1960).
(2) Cluley, H. J., *Analyst* 76, 523–35 (1951).
(3) Sandell, E. B., "Colorimetric Determination of Traces of Metals," 3rd ed., pp. 482–93, Interscience, New York, 1959.

HUGH B. RAYNER

British Columbia Research Council,
at the University of British Columbia,
Vancouver 8, British Columbia,
Canada.

Determination of Aluminum in Organo-Aluminum Compounds by X-Ray Fluorescence

SIR: We have developed an x-ray fluorescence method for the determination of aluminum in organo-aluminum compounds. The method is applicable over the range from 0.05 to 10% and possibly even higher. The method has been developed especially for aluminum analysis of highly reactive pyrophoric compounds. Recent publications (*1*, *3*) point up the application of x-ray fluorescence to aluminum concentration determination. However, our method differs significantly from any previously reported, since it applies to liquid systems which are highly reactive and require special handling techniques and equipment.

EXPERIMENTAL

We used a General Electric XRD-3 x-ray instrument for this work. The original heat exchanger and line voltage stabilizer were replaced to make the instrument essentially equivalent to the XRD-5. The integral components of the instrument were: a General Electric No. 2SPG power supply, a Hamner Model SX-R proportional counter preamplifier, a Hamner Model N302 nonoverload amplifier and pulse height discriminator, a General Electric No. 4SPG counter tube and helium tunnel assembly, a General Electric SPG electronic time register, a General Electric No. 2SPG scaler, a General Electric No. 2SPG rate meter, and a Machlett AEG-50-S chromium target x-ray tube.

Table I. Comparison of Aluminum Analysis Data from X-Ray Fluorescence and Chemical Methods

Sample No.	Aluminum, % X-ray	Aluminum, % Chemical method
A	4.70	4.68
B	11.56	11.33
C	22.47	22.98
D	4.88	4.85
E	4.71	4.75
	Mean error	±0.16
	Relative error	±1.64%

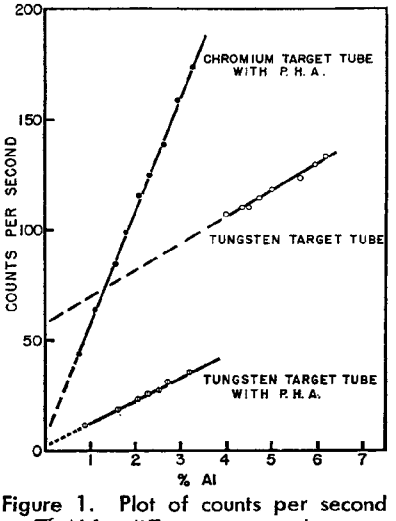


Figure 1. Plot of counts per second vs. % Al for different target tubes

The procedure followed in setting the pulse height discriminator is that outlined by Miller (*2*). The electronic components were left on constantly. However, the x-ray source was usually turned off overnight. We found that a 30-minute warm-up period was advisable each morning before checking the pulse height discriminator settings.

We have made a modification to the sample chamber of the XRD-3 which should be mentioned because it has certain advantages. The wall of the sample chamber adjacent to the x-ray tube was converted into a cooling panel. Small holes were drilled through the wall forming a water passage around the point of contact of the tube with the sample chamber. Tubing was connected to both ends of this passage. With this arrangement, tap water is circulated through the passageway at all times so that the only heat to which the sample is exposed is that generated by the x-ray beam.

The sample cells we used were made out of nylon by the Instrument Shop in our Research and Development Dept. After two years of operation we have seen no adverse effect of the x-ray beam on the nylon of the sample cell.

The general analytical procedure for determination of aluminum in organo-aluminum compounds may be described as follows: prepare a stock solution containing approximately 60% triethylamine and 40% Stoddard solvent (dried over sodium). Place 20 ml. of this solution in a 50-ml. glass-stoppered graduated cylinder. Inject argon into the graduated cylinder through one hole of a two-hole rubber stopper. Purge a syringe with argon and then fill with the organo-aluminum compound to be analyzed, cap with a silicone rubber plug, and weigh. Transfer the sample from the syringe to the graduated cylinder containing the triethylamine solution. Recap the empty syringe and place the glass stopper on the graduated cylinder. Weigh the empty syringe and the graduated cylinder. The size of the sample is determined by the estimated aluminum content in the sample. For pure aluminum triethyl, the best sample size is approximately 4 ml. After thorough mixing, transfer the sample to the x-ray sample cell for analysis. Allow 1 minute after placing the sample cell into the x-ray beam for the helium atmosphere to reach pressure equilibrium. Register counts over a 400-second time period. For such counting intervals, the count level will usually be in excess of 50,000, giving a σ value of less than 1.5% resulting from counting error. Total instrument time per sample is approximately 8 minutes. Considering calculation time, a sample may be analyzed for aluminum over wide concentration range in approximately 15 minutes. The accuracy of the method is shown by the data in Table I.

DISCUSSION

The principal factors responsible for the successful application of x-ray fluorescence to the determination of low-level aluminum in pyrophoric organic systems were the availability of a chromium x-ray target tube, the modification of the sample chamber to provide sample cooling, and the use of sample cells fabricated out of nylon. Our first work on aluminum analysis was done with a tungsten target tube and without a pulse height discriminator. The background

count was very high and the net count extremely low.

After installation of the pulse height discriminator into the system, we were successful in reducing the background count to a much lower level, but the sensitivity under these conditions was low. Fortunately, at this time the first chromium x-ray target tubes designed for use with General Electric equipment became available. Using this tube, we observed a 400% increase in aluminum sensitivity over that observed when using the tungsten target tube. By using the pulse height discriminator, we were able to hold the background count low and take advantage of this tremendous increase in sensitivity. Figure 1 emphasizes the great benefit gained by the combination of the pulse height discriminator and the chromium x-ray target tube for the determination of aluminum.

Because of the nature of low molecular weight organo-aluminum compounds, we offer certain suggestions concerning their handling. Never expose the organo-aluminum compound to air or water. Always have an excess of complexing agent, in our case triethylamine, in the solution being analyzed by x-ray fluorescence. Otherwise, there will be enough free aluminum trialkyl present in the sample to cause immediate deterioration and rupture of the sample cell window.

LITERATURE CITED

(1) Balis, E. W., Bronk, L. B., Pfeiffer, H. G., Welbon, W. W., Winslow, E. H., Zemany, P. D., ANAL. CHEM. **34**, 1731–3 (1962).
(2) Miller, D. C., *Norelco Reptr.* **4**, *No. 2*, (1957).
(3) Smith, G. D., Maute, R. L., ANAL. CHEM. **34**, 1733–5 (1962).

H. F. SMITH
R. A. ROYER

Analytical Research Section
Research and Development Department
Continental Oil Co.
Ponca City, Okla.

Correction for Anomalous Fluorescence Peaks Caused by Grating Transmission Characteristics

SIR: In an earlier communication, the construction and calibration of a recording spectrofluorometer was described (*4*). During a study of fluorescence spectra using this instrument, an artifact appeared in some of the recorded spectra, the origin of which was traced to the grating of the analyzer monochromator. Because this type of behavior may be sufficiently general, when using high precision gratings, it was felt that it should be brought to the attention of other investigators in the field of analytical fluorescence.

During studies on the fluorescence of 2-hydroxy-3-naphthoic acid, monosodium salt (I) we were puzzled by a narrow band which appeared at about 540 mμ on the long wavelength side of the major fluorescent maximum of (I) as shown in Figure 1, curve *A*. Because the relative intensity of this band, compared to the main band, did not change with purification, an impurity could not account for its presence in the recorded spectrum. It was further puzzling to note that the wavelength maximum of this band did not show variations with solvent or pH as did other parts of the band. As a check, a variety of compounds having well characterized fluorescent spectra in this same region of the spectrum were run on the spectrofluorometer, and a similar shoulder at about 540 mμ appeared in the recorded fluorescence spectra of these compounds. This led to the conclusion that the 540-mμ band in (I) was caused by an instrumental anomaly, and was not a part of the fluorescence spectrum per se.

The anomalous fluorescence maximum has been attributed to a "Wood Anomaly" (*1*) of the high dispersion diffraction grating used in the monochromator (Bausch and Lomb, 500-mm. Monochromator, having a 1200-lines-per-mm. grating blazed for the near ultraviolet). The term "Wood Anomaly" is used to refer to an anomalous and abrupt change in intensity of the spectral transmission properties of a diffraction grating at a particular wavelength. This means that a monochromator containing such a grating will show an abrupt maximum or minimum in its efficiency at certain wavelengths. The description of such anomalies by Palmer seems to be consistent with our observations (*3*).

To compensate for the Wood Anomaly of the grating, the combined monochromator and photomultiplier system was calibrated with a National Bureau of Standards lamp, certified to conform to the spectral irradiance of ICI illuminant A (*2*, *5*).

The resultant recording represented the spectral response of the analyzing monochromator–photomultiplier combination when corrected for changes in intensity of the source as a function of wavelength. This type of curve should be used when correcting recorded fluorescence spectra. The spectral efficiency of the monochromator alone could be obtained from these data only by an independent calibration of the spectral response of the photomultiplier tube or by use of an integrating screen.

The procedure described above gave rise to the calibration curve shown in Figure 2. This curve represents the

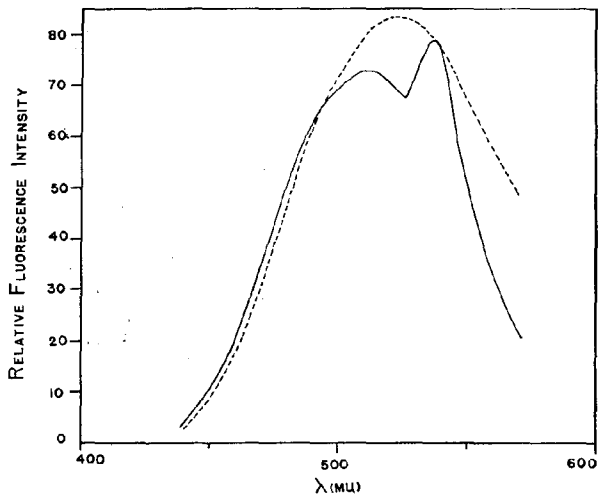


Figure 1. Fluorescence spectra of 10^{-3}M 2-hydroxy-3-naphthoic acid, monosodium salt in 10% alcohol, 90% water

(Fluorescence intensity plotted in arbitrary units)
A. Spectrum as recorded without correction: ————
B. Spectrum corrected for instrument response (using data from Figure 2 — — — — —

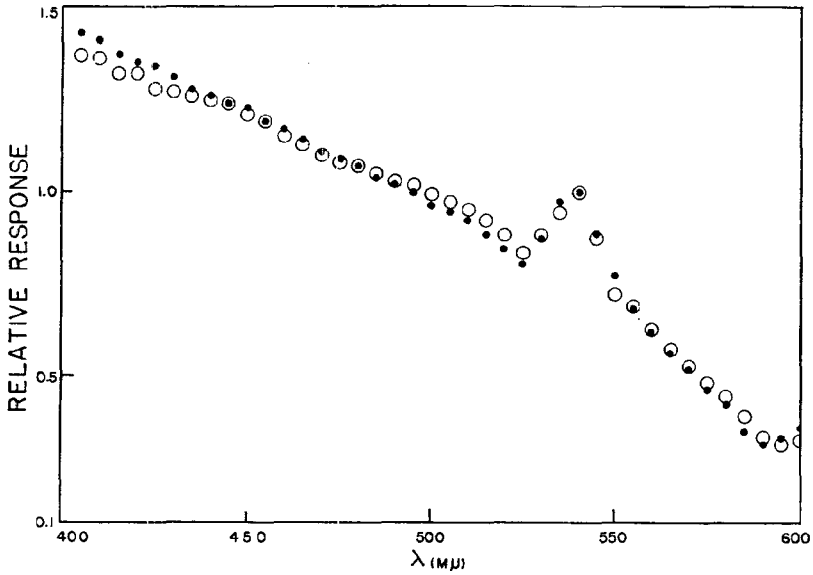


Figure 2. Relative response of spectrofluorometer to equal flux of incident radiation, normalized to 1.00 at 540 mμ

●—monochromator slit width = 2.00 mm.
○—monochromator slit width = 0.10 mm.

relative response of the monochromator-photomultiplier system to equal flux of radiation incident on the entrance slit of the monochromator. It is evident that the curve is essentially independent of slit width except at short wavelengths. The efficiency of this combination goes through abrupt maxima at 540 mμ corresponding to the maximum of the anomalous band observed in the spectrum of (I). Whenever the correction curve of Figure 2 was applied to the recorded curve of (I) the corrected spectrum, shown in Figure 1, curve *B*, was obtained. The difference between curves 1*A* and 1*B* is striking. Not only does the apparent fluorescence curve show two peaks, but it gives the impression that the center of the main band system lies at ca. 510 mμ, rather than at ca. 525 mμ as determined from the corrected curve. This behavior serves to illustrate, once again, that one must exercise extreme caution when recording absolute emission spectra.

LITERATURE CITED

(1) Chisholm, J. C., Bausch and Lomb Optical Co., Rochester, N. Y., private communication, 1962.
(2) National Bureau of Standards Circular #NBS-478, page 53, 1950.
(3) Palmer, C. H., Jr., *J. Opt. Soc. Am.* **42**, 269 (1952).
(4) Rehwolt, R. E., King, R. M., Hercules, D. M., ANAL. CHEM. **33**, 1362 (1961).
(5) White, C. E., Ho, M., Weimer, E. Q., *Ibid.*, **32**, 438 (1960).

RICHARD M. KING

Department of Chemistry
Lehigh University
Bethlehem, Pa.

DAVID M. HERCULES

Department of Chemistry
Juniata College
Huntingdon, Pa.

WORK supported by National Science Foundation Grant No. NSF G5271.

Chronopotentiometric Investigation of the Adsorption of Iodine at Platinum Electrodes

SIR: There has been an interest in the determination of adsorption of potential-determining ions at electrodes. Methods which determine the number of coulombs due to the reaction of adsorbed reactant have been employed. Chronopotentiometry has been used by Lorenz to study adsorbed iodine on platinum electrodes and the usefulness of the method has been indicated (*5*, *6*). Anson has suggested that some of the deviations from linearity of $iT^{1/2}$ plots observed by Bard during the oxidation of iodide might be due to the adsorption of iodide at platinum electrodes (*1*, *3*). Integration of singlesweep oscillopolarograms has recently been applied to the determination of adsorption in iodine–iodide solutions at platinum electrodes; the results indicated that iodine was extensively adsorbed on the electrode but that iodide was not (*8*, *9*). The adsorption of iodine and bromine has also been studied by Balashova and Obrucheva, but by methods which do not involve electrochemical determination of adsorbed coulombs (*2*, *7*). The present correspondence concerns observations made as part of a study of the iodine–iodide system.

Solutions used were 1*F* in sulfuric acid, with varying amounts of potassium iodide added to the deaerated solution. Chronopotentiograms were run conventionally, using a John Fluke constant current source, a Keithley Electrometer to monitor the reference–indicator potential difference, and a Moseley X-Y recorder connected to the output of the Keithley to record the chronopotentiogram. A three-compartment cell was used and the indicator electrode was a piece of platinum foil about 1.6 sq. cm. in area, spot-welded to a platinum wire lead; a Beckman calomel electrode served as reference. The third electrode was a piece of platinum gauze. In some experiments a Beckman platinum button electrode was used with results essentially the same as those with the platinum flag electrode. The flag electrode was not sealed into glass but was immersed in solution so the flag was completely covered. In some of the experiments the flag electrode was anodized in the iodide solution, washed, and transferred to a second three-compartment cell, also 1*F* in sulfuric acid but free of iodide.

Figure 1 shows forward and reverse chronopotentiograms for a 1m*M* solution of potassium iodide at a 1.6-sq.-cm. platinum electrode and a current of 250 μa., with current reversal at progressively increasing points along the potential halt. The ratio of t_f/T_r, where t_f is the time anodic current is passed and T_r is the reverse transition time, increases from 1.3 for reversal at the head of the potential halt to 2.0 for the last reversal shown in the vicinity of the forward, anodic transition time, T_f. Similar results were obtained for various current densities in that in all instances t_f/T_r increased as t_f approached T_f. Table I lists values of t_f/T_r at various currents for a 1m*M* iodide solution; t_f in this instance is

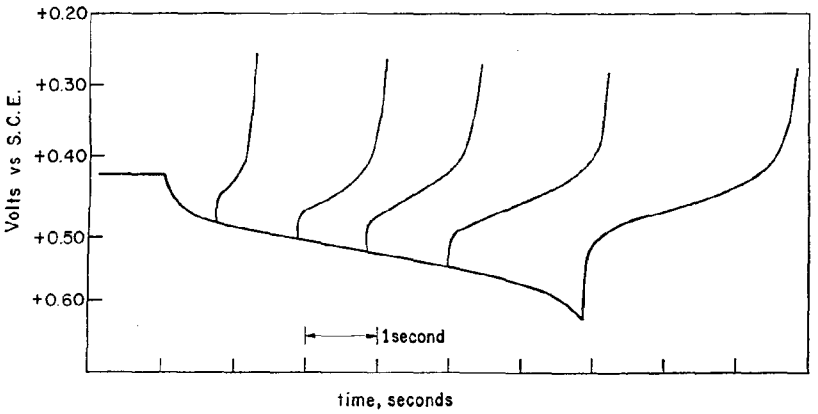


Figure 1. Effect of current reversal at various points along iodide oxidation chronopotentiogram

very close to the forward, anodic transition time, T_f. The ratio t_f/T_r is seen to increase with decreasing current.

When argon was bubbled vigorously through the solution during the course of anodic and cathodic chronopotentiograms, anodic transition times were not obtained—i.e., stirring was sufficient to prevent concentration polarization and a transition time. However, cathodic breaks in the potential-time curves on current reversal were always obtained. A typical curve is given in Figure 2; 15 seconds of anodization at 250 μa. was followed by current reversal in the gas-stirred solution 0, 5, and 10 seconds after current cessation prior to current reversal.

Figure 3 indicates chronopotentiograms at 50 μa. after the platinum electrode had been immersed in the iodide cell, treated as will be indicated, washed by dipping for at least 5 seconds in a vigorously bubbling sulfuric acid solution, transferred to a 1*F* sulfuric acid, iodide-free cell where chronopotentiograms were run. Curves *A* and *B* in Figure 3 show anodic and cathodic chronopotentiograms after the platinum flag had been dipped in a 1m*M* KI solution for 15 seconds, washed, and transferred. The transfer solution was not stirred. Curve *C* shows the chronopotentiogram, initially cathodic then reversed anodic, after the flag electrode had first been anodized at 50 μa. in the 1m*M* KI solution cell. Curve *D* is similar to *C*, except that the solution in the transfer cell was stirred with argon during the recording of the chronopotentiograms.

The results clearly indicate that a considerable amount of iodine, but not iodide, is strongly adsorbed at the surface of the electrode. The data in Table I are consistent with iodine adsorption; more coulombs are delivered on current reversal (iodine reduction) than would be the case if diffusion processes were solely responsible for mass transport (*4*). As the number of coulombs passed in the forward process is increased (in Figure 1 by increasing the point along the chronopotentiogram where reversal is made and in Table I by considering decreasing currents) the ratio of the forward to the reverse transition time increases. This is understood if a given number of coulombs were adsorbed on the electrode; with the passage of a larger number of coulombs the coulombs due to adsorbed reactant (I_2) becomes a smaller fraction of the total and consequently the ratio of the times must approach three. As the current increases, thereby decreasing the number of coulombs passed, the ratio tends to unity, which would be the limiting case if all the iodine evolved on anodization adsorbed on the electrode surface. Figure 2 indicates that vigorous argon bubbling does not eliminate the cathodic step, as would be the case for a freely-diffusing species. A delay after anodization but prior to current reversal results in a shorter cathodic halt, presumably as a result of a slow desorption of the adsorbed iodine.

Table I. t_f/T_r[a] as Function of *i*

ca. 1m*M* iodide; electrode area 1.6 sq. cm.

i, μa.	t_f, seconds	t_f/T_r
60	97	3.2
80	48.5	2.6
100	28.5	2.2
200	6.8	1.9
300	3.0	1.8
400	1.5	1.6
500	1.0	1.4

[a] t_f is very close to the transition time for the iodide oxidation.

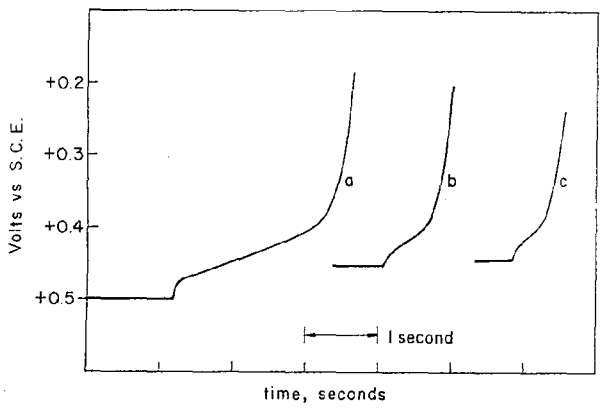


Figure 2. Cathodic chronopotentiogram in argon-stirred solution

After 15-seconds iodide oxidation; *a* = 0, *b* = 5, *c* = 10, seconds delay prior to current reversal

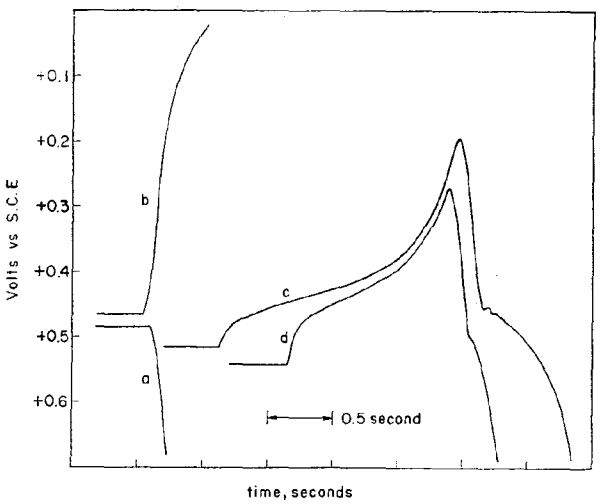


Figure 3. Chronopotentiograms after transfer

a = Anodic, *b* = cathodic, *c* = cathodic, after oxidation in iodide solution, *d* = cathodic after oxidation in iodide solution; transfer solution is argon-stirred iodide solution

The results of the transfer experiments indicate that, within the sensitivity of the method, iodine is adsorbed but iodide is not; anodic halts are not obtained in the transfer cell on the platinum flag which had been dipped in an iodide solution (curve *A*, Figure 3). This is contrary to results reported by Anson under essentially similar conditions (*1*). Curves *C* and *D* in Figure 3 show that reduction of the adsorbed iodine yields iodide free to diffuse away from the electrode, as indicated by the removal of the reverse, iodide oxidation step in the argon stirred solution.

When bromide was oxidized at a platinum electrode, the cathodic reverse transition time was one third that of the forward anodic wave, regardless of when the reversal was made. Further, when argon was bubbled through a bromide-containing solution, cathodic currentreversal after anodization did not yield a cathodic transition time, as in the iodide system. Thus, under the conditions of this experiment, bromine is not adsorbed to the same extent as iodine.

LITERATURE CITED

(1) Anson, F. C., ANAL. CHEM. **33**, 1123 (1961).
(2) Balashova, N., *Zh. Fiz. Khim.* **32**, 2266 (1958).
(3) Bard, A., ANAL. CHEM. **33**, 11 (1961).
(4) Delahay, P., "New Instrumental Methods in Electrochemistry," p. 195, Interscience, N. Y., 1954.
(5) Laitinen, H. A., ANAL. CHEM. **33**, 1458 (1961).
(6) Lorenz, W., Muhlberg, H., *Z. Elektrochem.* **59**, 736 (1955).
(7) Obrucheva, A., *Zh. Fiz. Khim.* **32**, 2155 (1958).
(8) Osteryoung, R., Lauer, G., Anson, F. C., ANAL. CHEM. **34**, 1833 (1962).
(9) Osteryoung, R., Lauer, G., Anson, F. C., *J. Electrochem. Soc.* **110**, in press (1963).

ROBERT A. OSTERYOUNG

North American Aviation Science Center
Canoga Park, Calif.

Gravimetric Determination of Silica as Quinolinium Molybdosilicate in Phosphate Rock

SIR: Brabson and coworkers (*1*) described a gravimetric method for the determination of silica in the presence of fluorine and phosphorus in which boron was added to complex fluorine, and the silicon and phosphorus were precipitated as the 8-quinolinolium salts of molybdosilicic and molybdophosphoric acids. The precipitate was washed with a saturated solution of the silicon salt and weighed. Phosphorus was determined separately and silicon was determined by difference.

The procedure has been useful in the analysis of fluorine-bearing materials contaminated with phosphates, even in the analysis of phosphate rock in which the ratio of phosphoric oxide to silica is as high as four. The National Bureau of Standards issued a sample of Florida phosphate rock (NBS 120a) for collaborative analysis in which the ratio of phosphoric oxide to silica is about 7. The precision of the results obtained on this sample by the by-difference method (*1*) was unsatisfactory, and improvements in the method were sought.

Wilson's work with the quinolinium salts of phosphorus $(C_9H_7N)_3 \cdot H_3PMo_{12}O_{40}$ (*6*, *7*), and silicon, $(C_9H_7N)_4 \cdot H_4SiMo_{12}O_{40}$ (*5*), indicated that these salts are better suited for volumetric procedures than are their 8-quinolinolium analogs. Perrin (*4*), using Wilson's volumetric method (*7*) as a basis, developed a very accurate gravimetric method for phosphorus. A by-difference gravimetric method for silicon, based on the separation of the combined quinolinium salts, appeared to have advantages over the 8-quinolinolium procedure (*1*).

EXPERIMENTAL

Reagents. Sodium Molybdate Solution. Dissolve 11 grams of sodium hydroxide pellets in 100 ml. of water in a platinum dish. Add 54 grams of molybdenum trioxide, MoO_3, and heat on a hot plate, stirring with a Teflon rod until the solution is clear. Cool to room temperature, dilute to 250 ml., and filter. Dilute to 1000 ml. and store in a polyethylene bottle.

Quinoline Solution. Prepare according to Perrin (*4*).

Thymol Blue Indicator Solution. Prepare according to Brabson *et al.* (*1*).

Saturated Wash Solution. Dilute a mixture of 36 ml. of glacial acetic acid and 447 ml. of concentrated hydrochloric acid to 6 liters. Fuse a 0.25-gram sample of quartz with sodium hydroxide. Proceed as described for decomposition of sample, but do not add boric acid. Precipitate the silica from eight 50-ml. aliquots (about 25 mg. of silica in each) and filter. Transfer each precipitate to a 1-liter round-bottomed flask and add about 750 ml. of the acid solution. Boil for 10 minutes under a reflux condenser. Cool to room temperature, allow to stand overnight, and filter just before use.

Procedure. Decomposition of Sample. Proceed as described by Brabson *et al.* (*1*).

Precipitation of Silica. Proceed as in (*1*), but use 25 ml. of sodium molybdate solution and 25 ml. of quinoline solution. Cover the dish with a watch glass and set it in boiling water for 1 hour. Stir frequently.

Cool to room temperature in a water bath, allow the precipitate to settle, and filter through a weighed porcelain filtering crucible. Transfer all the liquid before washing is begun. Wash twice by decantation. For the first wash use 30 ml. of water and for the second use 30 ml. of saturated wash solution. Transfer the precipitate to the crucible and police the dish thoroughly with the wash solution. Wash the precipitate 5 times with the wash solution after the transfer has been completed. Wash once with 5 ml. of water. After the precipitate has been transferred to the crucible, do not allow the pad of precipitate to suck dry and crack between washings. Each increment of wash solution should be added just before the previous increment disappears. Dry the precipitate for 2 hours at 160° C.

Cool in an evacuated desiccator over Dehydrite. Weigh and heat an additional hour at 160° C. to ensure drying to constant weight. Subtract a blank obtained by carrying equal quantities of all the reagents through the steps of the procedure.

Determine phosphorus on a separate sample by precipitating and weighing as quinolinium molybdophosphate (*3*).

Calculations.

Net weight of precipitate $-$

$$\frac{\text{weight of } P_2O_5 \text{ in sample}}{0.032074} =$$

weight of quinolinium molybdosilicate

Weight of quinolinium molybdosilicate $\times$ 0.02568 = weight of SiO_2.

DEVELOPMENT OF THE METHOD

Molybdosilicic acid forms in a fairly narrow pH range, but molybdophosphoric acid forms over a wider pH range. Conditions suitable for formation of molybdosilicic acid (*1*, *5*) were chosen for this work. Conditions recommended by Wilson (*5*) for the precipita-

tion and washing of quinolinium molybdosilicate were used in the first studies of the method. The quinolinium molybdosilicate was dried to constant weight at 160° C., the temperature recommended by Fennell and Webb (*2*) for quinolinium molybdophosphate.

In initial tests, the results were low when the theoretical percentage of silica in the molybdosilicate was used in the calculations. Wilson (*5*) recognized that the precipitate is slightly soluble in water and used an experimentally-determined factor to compensate for this solubility. This type of correction did not appear to be practicable, however, with samples containing relatively small amounts of silicon and large amounts of phosphorus. A saturated solution of the silicon salt was prepared in a mixture of hydrochloric and acetic acids of the same concentration as the precipitation medium. Theoretical weights of precipitate were obtained when this solution was used to wash the precipitate.

To prevent the formation of extraneous precipitates, such as quinoline–molybdenum compounds, solutions of molybdosilicic and molybdophosphoric acids must be made strongly acid before quinoline is added. In strongly acid solution, molybdophosphoric acid is stable indefinitely but molybdosilicic acid decomposes slowly. Progressively lower results were obtained when acidified solutions of molybdosilicic acid were allowed to stand for increasing lengths of time before quinoline was added. No difficulty was encountered when the quinoline was added immediately after the solution was acidified.

Quantitative recoveries of silicon and phosphorus were obtained when standard solutions of the two elements were assayed separately. Unexpectedly low results were obtained when the samples contained significantly more phosphorus than silicon. The explanation for this phenomenon apparently lies in the widely different solubilities of the phosphorus and silicon precipitates. The phosphorus precipitate begins to form as soon as a few drops of the quinoline solution are added, whereas the silicon precipitate does not persist until about 3 ml. of the quinoline solution have been added. Since the phosphorus compound forms so rapidly, it probably occludes molybdosilicic acid and prevents it from reacting with quinoline.

Dropwise addition of the quinoline was considered as a means of preventing occlusion of molybdosilicic acid, but any benefit from this change in procedure was nullified by decomposition of molybdosilicic acid in the strongly acid medium. The best compromise found was to add the quinoline rapidly to the mixed molybdo-acids at room temperature and then to heat the mixture in boiling water for 1 hour. The silicon compound then recrystallized and was very easy to filter and wash. Improvement in the properties of the phosphorus compound was less marked, but the mixed precipitate had satisfactory physical properties.

Table I. Accuracy of Quinolinium Method in Determination of Silica in Phosphate Rock

NBS sample no.	NBS value for SiO_2, %	SiO_2 Found, % 8-Quinolinolium method (*1*) No. of detns.	Av.	Std. dev.	Quinolinium method No. of detns.	Av.	Std. dev.
56a	11.02[a]	9	10.91	±0.26	6	10.92	±0.08
120	7.70[b]	10	7.81	±0.18	5	7.75	±0.08
120a	..[c]	..	...	...	10	4.71	±0.12

[a] The average result by four cooperating laboratories was 11.01.
[b] The average result by three cooperating laboratories was 7.40.
[c] Not yet certified.

RESULTS

Two analysts determined SiO_2 in three NBS samples of phosphate rock. The results in Table I are compared with analyses obtained earlier by the 8-quinolinolium procedure (*1*). The NBS recommended value for P_2O_5 was used in the calculations. Results obtained by the National Bureau of Standards (*3*) by a modified Berzelius method for SiO_2 are included also.

LITERATURE CITED

(1) Brabson, J. A., Mattraw, H. C., Maxwell, G. E., Darrow, A., Needham, M. F., ANAL. CHEM. 20, 504 (1948).
(2) Fennell, T. R. F. W., Webb, J. R., *Talanta* 2, 105 (1959).
(3) Hoffman, J. I., Lundell, G. E. F., *J. Res. Natl. Bur. Std.* 20, 607 (1938).
(4) Perrin, C. H., *J. Assoc. Offic. Agr. Chemists* 41, 758 (1958).
(5) Wilson, H. N., *Analyst* 74, 243 (1949).
(6) *Ibid.*, 76, 65 (1951).
(7) *Ibid.*, 79, 535 (1954).

J. A. BRABSON
R. D. DUNCAN
INEZ J. MURPHY

Division of Chemical Development
Tennessee Valley Authority
Wilson Dam, Ala.

Spot Test for Beryllium Based on Color Reaction with Eriochrome Cyanine R

SIR: Difficulties were encountered in attempting the morin spot test for beryllium because impure reagent gave rise to strong fluorescence of the blank. To avoid this difficulty a color reaction spot test for beryllium has been devised based upon the reaction with Eriochrome Cyanine R used by Hill (*1*) for the spectrophotometric determination of beryllium. This reaction has also been applied in a ring oven determination of beryllium (*2*). By modification of Hill's masking system, it was possible to obtain a test with a limit of identification of 0.1 μg. of Be in the test drop. Of 67 ions tested, none interfered when 50 μg. were present in the test drop with 1 μg of Be.

EXPERIMENTAL

To perform the test the following reagent solutions are required.

Buffer Solution. Prepare a solution which is 4*M* in ammonia and 4*M* in ammonium chloride and adjust the pH with hydrochloric acid or ammonia to 9.6 as established with a pH meter.

Reagent Solution. Prepare an approximately 0.1% solution of Eriochrome Cyanine R (Dry Stain, Matheson Coleman & Bell) in buffer solution. This solution must be prepared fresh daily.

Masking Solution. Mix equal volumes of a 20% solution of sodium potassium tartrate and a saturated solution of disodium (ethylenedinitrilo)tetraacetate (EDTA) in 1 to 5 ammonia solution.

The test is performed on a spot plate by adding, in order, one drop of the unknown, one drop of masking solution, and one drop of reagent solution. If beryllium is present, a pink-orange coloration is formed. In the absence of beryllium, the color is yellow or yellowish-brown. Small amounts of beryllium will give an orange test, while large amounts will give a violet test. It is helpful, but not essential, to run simultaneously a blank and a control test.

The following ions did not interfere when 500 μg. were compared to 1 μg. of Be:

Li^+, Na^+, K^+, NH_4^+, Rb^+, Cs^+, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Ti^{+4}, Zr^{+4}, VO_3^-, MoO_4^{-2}, WO_4^{-2}, Mn^{+2}, ReO_4^-, Ru^{+3}, Ir^{+4}, Ag^+, Au^{+3}, Zn^{+2}, Cd^{+2}, BO_2^-, Tl^+, CO_3^{-2}, Sn^{+4}, Pb^{+2}, NO_3^-, PO_4^{-3}, Bi^{+3}, $S_2O_3^{-2}$, SO_4^{-2}, SO_3^{-2}, SeO_3^{-2}, SeO_4^{-2}, TeO_3^{-2}, TeO_4^{-2}, Cl^-, ClO_3^-, Br^-, BrO_3^-, I^-, IO_3^-, Ce^{+3}, and Ce^{+4}.

Compared to 1 μg. of Be, the following ions interfered at 500 μg. but did not interfere with the test at 50 μg.:

VO_2^{+2}, MnO_4^-, Fe^{+3}, Co^{+2}, Ni^{+2}, Pd^{+2}, Cu^{+2}, Hg^+, Al^{+3}, Ge^{+4}, As^{+3}, S^{-2}, F^-, Th^{+4}, and UO_2^{+2}.

At the 50-μg. level the following four ions slightly distorted the color of the test for 1 μg. of Be but did not prevent the test: Cr^{+3}, CrO_4^{-2}, Rh^{+3}, and Sb^{+3}.

DISCUSSION

The strength of the reagent solution did not influence the sensitivity of the test, although a concentration in the vicinity of 0.1% is most convenient for ease of observation of the results.

Although Eriochrome Cyanine R reacts with a number of ions, the combined masking effects of tartrate and EDTA make this test highly selective for beryllium. The use of a buffer in the reagent solution is required to control the pH to obtain the neutral color of the reagent. In acidic or strongly basic media, the reagent color is sufficiently similar to the color of the reaction product with beryllium to make the reaction useless for identification purposes.

LITERATURE CITED

(1) Hill, U. T., ANAL. CHEM. **30**, 521–4 (1958).
(2) West, P. W., Mohilner, P. R., ANAL. CHEM. **34**, 558–60 (1962).

PATRICIA R. MOHILNER[1]

Coates Chemical Laboratories
Louisiana State University
Baton Rouge 3, La.

WORK was supported by PHS research grant No. 7481 to Philip W. West from the National Institutes of Health, Public Health Service.

[1] Present address, Department of Chemistry, Chatham College, Pittsburgh 32, Pa.

AIDS FOR THE ANALYST

A New Automatic End Point Detector for Constant Current Coulometric Titrations

C. B. Roberts and H. A. Brejcha, The Dow Chemical Co., Midland, Mich.

A NEW AUTOMATIC end point device is designed to terminate coulometric titrations. In our laboratory it is used with a Sargent coulometric current source which provides the desired remote control and a wide range of currents. It makes use of both amperometric and potentiometric principles and is especially useful for the determination of unsaturated compounds by electrolytically-generated bromine and iodine. It has the advantages of simplicity of operation, a minimum of interaction between generating and detecting electrodes, and high sensitivity.

A 50-μa. meter relay terminates the generating current at, or slightly before, the end point, while another meter registers the relative solution potential at all times during the titration. The two meters are synchronized, but the relay meter no longer functions as an indicating device after it has been activated; thus, the second or monitoring meter indicates the end point of the titration. Two adjustments are required before a titration is carried out: a zero control adjusts the meters to zero before titrant has been generated, and a span control adjusts the monitoring meter to full scale after an excess of titrant has been generated. After these adjustments the titration is terminated at midpoint (25 μa.) on the monitoring meter when the current control on the source is on remote. The relay needle may be set at a reading slightly below the midpoint to allow for overshoot. If, after generation has been automatically terminated, the monitoring meter has not quite reached midpoint a few short increments of titrant may be added by the manual control on the current source until the midpoint reading is reached. If a fully automatic end point is desired, a few preliminary end points can usually determine the correct setting of the relay meter needle to compensate for overshoot and result in a midscale reading.

The instrument has been designed for slow reaction rates where solution potential may rise prematurely and shut off the titration. As titrant is consumed upon standing, the solution potential drops and current generation will start again to provide additional titrant. A delay circuit causes a lapse of a few seconds between the time the relay meter becomes deactivated and the current is turned on; this makes possible a much smoother end point.

The schematic is shown in Figure 1. The signal from the detecting electrodes is impressed across the grids of the 12AU7 tube. This results in a difference of potential across the plates of the tube, and causes a proportional amount of current to flow through the meters of M_1 and M_2. The current relay in the constant current source is controlled by a Model MR, 0- to 50-μa. Larson relay meter. When the contacts of the latter are open and the current control is on remote, titrant is generated; when they close, the titration stops. The delay circuit is controlled by the thyratron tube 2D21 and the RC circuit in its grid. A plug-in alarm circuit may be energized to signal the end of the titration.

A 50,000-ohm potentiometer (R_1) is placed across the detecting electrodes and is used as the span adjust. As titrant is generated and the voltage rises across the detecting electrodes, current is drawn and a voltage develops across the resistor. This distorts the true potentiometric curve obtained under no-load conditions, but it results in the electrodes reaching equilibrium very quickly; this is most desirable for automatic titrations. Figure 2 shows voltage–time curves for various values of resistors when bromine is generated at 193.0 ma. The value chosen still provides a sharp end point, but avoids the sluggishness of response which higher resistances produce. When excess bromine is present (yellow electrolyte), a portion of the voltage across the potentiometer (R_1) is used to provide a full-scale reading of the meters.

When bromine or iodine is used as titrant, the amount of current flowing through the electrode system depends upon the thickness of the diffusion layer surrounding the detecting electrode; thus the stirring rate should be kept constant for the blank and throughout the titration. A smooth magnetic stirring bar without a center rib has been found to be very satisfactory.

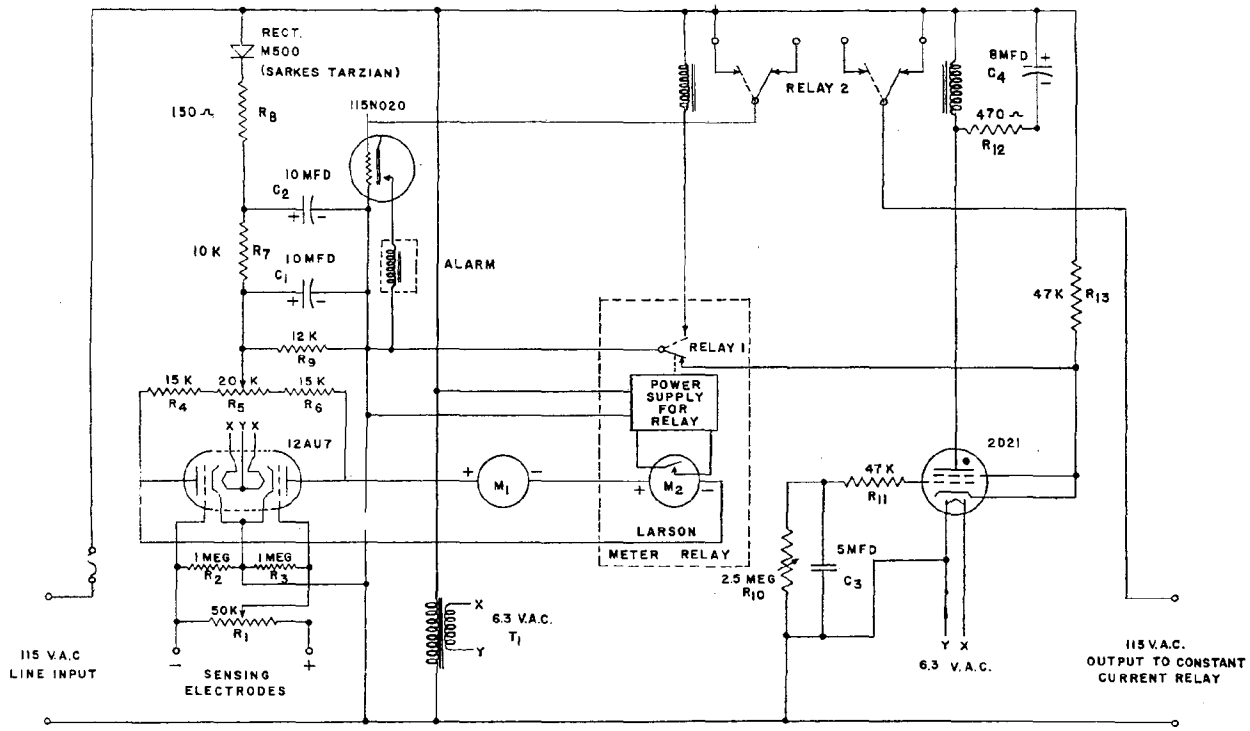


Figure 1. Circuit diagram of automatic end point detector

Zero adjust is provided by a 20K potentiometer (R_5) in the plate circuit of the triodes.

The detecting electrodes for bromine and iodine titration are of standard design. A small-diameter saturated calomel electrode (Sargent NS-30490) serves as reference. It should be placed opposite a half-inch platinum wire detecting electrode and turned so that its contact point with the solution is away from the field set up by the generating current. The kick which results when the generating current is turned on and off should not exceed 2 μa. This slight deflection will not interfere with the operation of the instrument.

The generating anode is a $1^1/_4$- by $^3/_4$-inch piece of platinum foil (0.008 inch thick). The generating cathode is designed for easy removal and addition of catholyte (*1*).

PROCEDURE

A blank is titrated by placing electrolyte in the cell and generating titrant manually for a few seconds until the monitoring meter reads midscale. The timer is set back to zero, the sample added, and the constant current control set to remote. As the contacts on the meter relay open, generating current starts and the titration proceeds until it is automatically terminated.

RESULTS AND DISCUSSION

Aliquots of sodium arsenite were titrated automatically with bromine at 193.0 ma. with a meter relay setting of 10 μa. This is a fast reaction, and the meter reading remained constant after the generating current was stopped. In 10 determinations the titration time ranged from 248.0 to 248.5 seconds with a relative standard deviation of $\pm 0.07\%$. Accuracy was of a comparable degree.

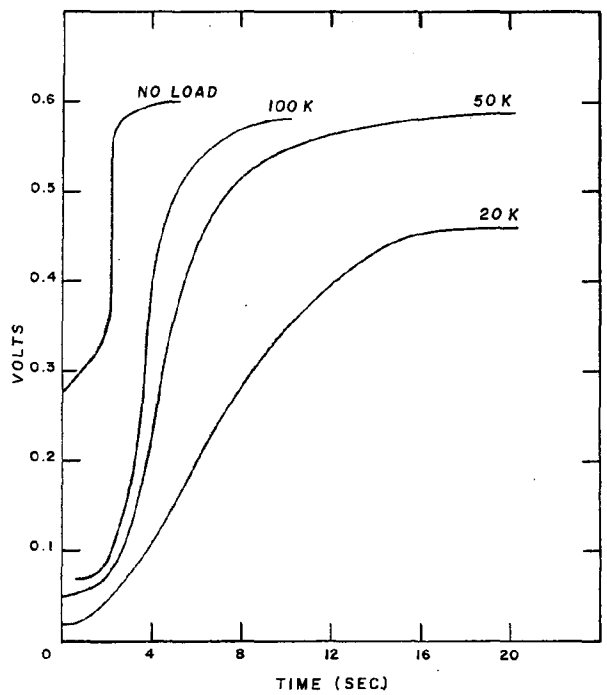


Figure 2. Voltage–time curves for various load resistors

Aliquots of 10-undecanoic acid were titrated with bromine automatically at 193.0 ma. with a meter relay setting

of 15 μa. In eight determinations the range was from 240.3 to 242.6 seconds with a relative standard deviation of ±0.3%. Three to five increments of titrant were automatically added before a constant potential was maintained. More precise results could have been obtained by manually adding the last few seconds of titrant.

The detector may be used with any constant current source provided with the necessary relays to control the current and the timer. It has a midscale sensitivity of approximately 15 nanoequivalents of double bond per microampere and thus is quite useful for microanalyses. By using higher currents (100 to 200 ma.), assay amounts can be determined with good precision and accuracy.

LITERATURE CITED

(1) Roberts, C. B., in "Titrimetric Methods," D. S. Jackson, ed., pp. 21–31, Plenum Press, N. Y., 1961.

Division of Analytical Chemistry, 144th Meeting, ACS, Los Angeles, Calif., April 1963.

A Simple, Inexpensive, Heated Infrared Gas Cell

Eugene A. Burns,[1] Propulsion Sciences Division, Stanford Research Institute, Menlo Park, Calif.

A SIMPLE, inexpensive, heated infrared gas cell has been designed and fabricated for the purpose of elucidating the infrared-active gases evolved on thermal decomposition of high energy compounds. A survey of leading manufacturers of infrared equipment at the inception of these studies revealed that there was no heated gas cell commercially available. Because of the potentially explosive nature of some of the high energy fuel additives which were to be examined, it was desirable to fabricate an inexpensive cell.

Several possible cell designs were considered and evaluated, and the best features of these were incorporated in the design shown in Figure 1. The chemical requirements imposed by the high energy compounds, in general, permit use of a glass container. The method of attaching the optical windows to the cell was best served by "O"-ring closures. A simple glass section was constructed with a stopcock connected to a male 9/18 ball joint attached in the center and two glass (size 15) "O"-ring joints at either end. The gas volume of the cell is approximately 15 ml. with an optical path of 8 cm. Vacuum seal is made between the optical plate and the glass section with a choice of Silicone, Neoprene, Viton A, or Teflon "O" rings. The optical plates are held in place with lead gaskets maintained by the furnace itself. The furnace is fabricated in two sections and the closure is ensured by adjusting the two sections until they are as close together as practical. Each section of the furnace is prepared from an aluminum block, machined, and wrapped with 30 inches of No. 20 insulated Nichrome wire. This wire is held in place and uniform heating is ensured by a coating of No. 6 Sauereisen. The Sauereisen is applied in a paste form and heated to a hard finish. Thermocouple and thermistor wells are drilled in the block for measurement and regulation of the temperature. When 115 volts are applied across the heater terminals, the cell temperature is 225° C. To use readily obtained inexpensive "O"-ring groove glass and optical windows, the size of the cell was relatively small and hence some of the energy from the source is lost. It is necessary to align the cell in the light path to give maximum energy, and then attenuate the reference side of the spectrometer. To obviate this difficulty, construction of a larger diameter cell would be required, which in turn would require a higher capacity furnace and a larger sample size. The disadvantages encountered with a larger furnace, larger windows (inefficient furnace and heat losses from the windows), and a larger sample size (when dealing with potentially explosive compounds the smaller the sample the better) offset the alternative attenuation requirement.

The furnace may be powered from a 115-volt variable transformer (Variac or equivalent with a maximum capacity of 7.5 amp.), with manual temperature control. For precise temperature control in the order of 0.02° C., a thermistor temperature regulator similar to that of Gray and VanDilla (*2*) was constructed. A Victory Engineering Co. Type 51A1 glass bead thermistor was used as the sensing device. Figure 2 shows the schematic of this device. By adjustment of the bridge balance with helipot R_1 and ratio arms R_3, R_4, and R_5 to a prescribed setting, regulation of the temperature is effected by the phase sensitive control system. This system (*2*) operates in the following manner:

The output of the bridge is fed directly to a 6 SL7-GT dual triode connected as a two-stage resistance-capacitance coupled amplifier. The amplifier output is coupled through C_6 and R_{11} to the grid of a 2050 Thyratron. The plate circuit of the thyratron is supplied with a.c. power through switch S_2 and the coil of the relay, so that contacts on the relay close when the thyratron conducts. If the bridge is unbalanced, an alternating voltage having a phase dependent on the direction of the imbalance is supplied to the grid of the thyratron. When the temperature of the thermistor is below the preset value on the balance resistor, the phase of the thyratron grid voltage is then a few degrees ahead of the alternating supply to the plate of the thyratron. Hence, when the plate voltage goes into its positive half cycle the grid voltage is already positive and the thyratron starts conduction at the beginning of

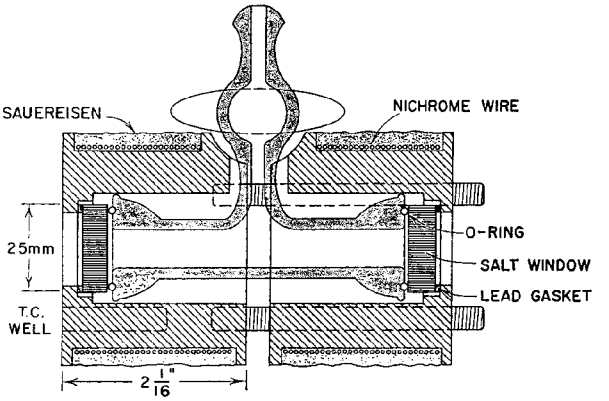


Figure 1. Cross-section diagram of heated infrared cell

[1] Present address, Space Technology Laboratories, Inc., One Space Park, Redondo Beach, Calif.

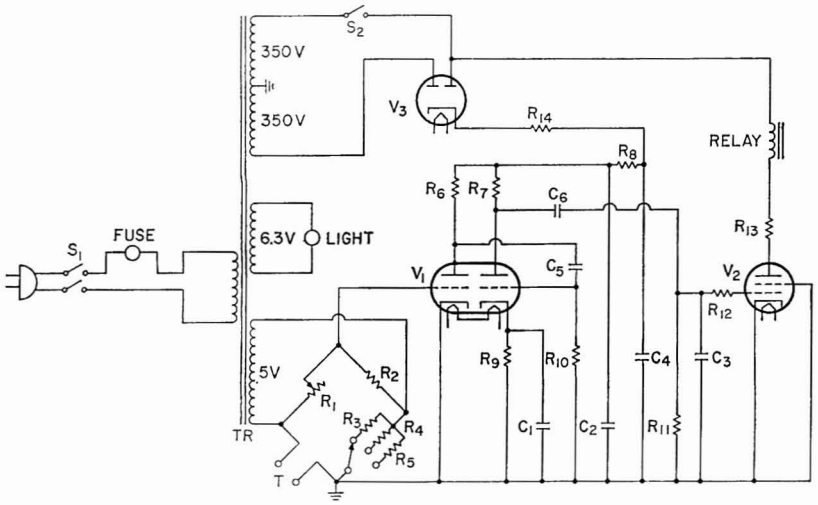


Figure 2. Schematic diagram of temperature regulator

R_1 = 1000-Ω ten-turn helipot; $R_2 = R_3$ = 500 Ω, 1% W.W.; R_4 = 5K, 1% W.W.; R_5 = 50K, 1% W.W.; $R_6 = R_7 = R_{10} = R_{11}$ = 500K, 1/2W; R_8 = 25K, 1/2W; $R_9 = R_{14}$ = 5K, 1/2W; R_{12} = 10K, 1/2W; R_{13} = 2.5K, W.W. 10W

C_1 = 10 μf. 50 volt; $C_2 = C_4$ = 8 μf., 450 volt; $C_3 = C_5$ = 0.01 μf., 600 volt; C_6 = 0.05 μf., 600 volt

V_1 = 6 SL7-GT; V_2 = 2050; V_3 = 6 X 5 GT; T = Victory 51A1 Thermistor

each positive half-cycle of plate voltage. As the temperature of the cell increases the amplitude of the bridge output and thyratron-grid voltages decreases, and finally reads zero when the preset temperature is attained because the bridge is then balanced. If the temperature continues to increase above the preset value, the bridge is again unbalanced but 180° out of phase. The grid is then positive during only the last few degrees of each positive cycle of plate voltage; hence, the conduction time of the thyratron is very short, and the average current through the relay coil is not sufficiently large to close the relay.

The calibration curve of the setting on the helipot and ratio arms as a function of temperature was determined and is shown in Figure 3. To set a prescribed temperature all that is necessary is to evaluate the resistance from this curve and set the value on the helipot and the ratio arms. It should be mentioned that although the temperature regulation is capable of ±0.02° C., and when the steady state equilibrium has been established, this regulation is attained, little is known concerning the precise heat loss in the vicinity of the salt windows. Hence, a small conical thermal gradient is expected at each end of the cell. The cell is designed to minimize this gradient; however, a reasonable estimate of the temperature at the inner surface of the salt window is low, −0.5% of the temperature of the cell. When the gradient is integrated over the volume of the cell at steady-state equilibrium, a reasonable estimate for the error in the temperature of the cell is −0.08%.

This gas cell is quite versatile for it can be used over all the infrared region from 2 microns to 50 microns with proper selection of optical windows and spectrometer capability. The temperature range utilized at the long wavelengths may be limited because some infrared materials coldflow at elevated temperatures. Any temperature-dependent phenomenon in the gas phase which concerns infrared active gases may be explored.

An example of a use of this cell is the infrared determination of the heat of vaporization of liquids. Specifically, 0.25 ml. of recently distilled nitrobenzene was placed in the gas cell. The cell was evacuated for 5 minutes, and then was filled to a total pressure of 760 mm. with dry nitrogen. The temperature of the cell was raised to specified values and at each temperature the total pressure of the cell was adjusted to 760 mm. After the temperature was in control, the infrared spectrum was obtained between 1750 and 1425 cm.$^{-1}$ From the combination of the relationship

$$\log p = -\frac{\Delta H}{2.3\,RT} + C \qquad (1)$$

where p is the vapor pressure of a component, ΔH is the latent heat of vaporization, R is the gas constant, and T is the absolute temperature and the Beer's Law

$$A = apl \qquad (2)$$

where A is the absorbance at a particular wavelength, a is the absorbancy index, p is the pressure of the absorbing species, and l is the optical path length, we find

$$\log A = -\frac{\Delta H}{2.3\,RT} + k \qquad (3)$$

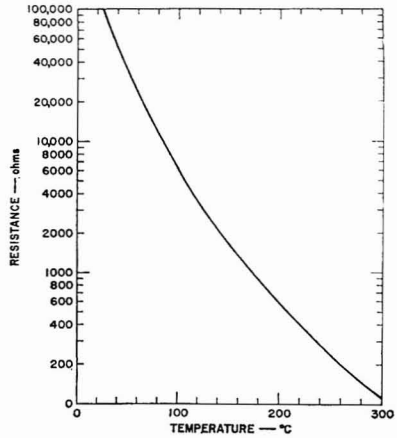


Figure 3. Resistance setting–temperature curve of temperature regulator

for constant path length. Plots of the base-line absorbance of the peak near 1540 cm.$^{-1}$ as a function of $1/T$ gave good straight lines. The average heat of vaporization of nitrobenzene calculated from Equation 3 is 11.36 kcal. per mole which compares favorably with that of 11.72 kcal. per mole reported by Brückner (*1*). This technique is not an inexpensive way to determine heats of vaporization. However, it has a major advantage over conventional manometric methods in that the sample need not be pure, provided the impurity does not absorb the same frequency, for by use of infrared discrimination only the component of interest will be observed. It is conceivable then, that the heat of vaporization of several compounds could be determined simultaneously by measurement at different wavelengths.

The heated infrared gas cell affords the opportunity to measure interactions and reaction kinetics in the gas phase. Results of thermal decomposition studies of ammonium perchlorate, hexanitroethane, and other high energy compounds will be presented elsewhere. Because of the small cell volume to path length ratio, this technique is quite sensitive; for example, the amount of ammonium perchlorate that decomposes to give rise to a quantitatively measurable hydrogen chloride spectrum is in the order of 100 μg.

LITERATURE CITED

(1) Brückner, A., *Z. Anorg. Allgem Chem.* **199**, 91–2 (1931).
(2) Gray, T. S., VanDilla, M., *Report No.* **180A**, Climatic Research Laboratory, Quartermaster Corps, Lawrence, Mass., October 10, 1945.

PRESENTED at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 9, 1962.

An Automatic Programmer for Chromatographic Eluents

S. R. Lerner, Radioisotope Service, Veterans Administration Hospital, and Biochemistry Department, Baylor University College of Medicine, Houston, Texas

THE VARYING INFLUENT buffer requirements for ion exchange chromatography lead to the development of the automatic apparatus described to set up elution schemes free of delays or human error in the buffer program. The flexibility of the appartus allows its use for simple buffer changes at predetermined times or the setting up of buffer gradients with changes in the inflowing buffer to provide for shaping the elution gradient. In contrast to other apparatus (*1*, *3–5*), this programmer allows flexibility in both the total volume and shape of the gradient sequence by simply controlling the time of inflow of each buffer into the stirred gradient vessel. As each asymptote of pH or salt concentration is approached in the gradient vessel, the timing card programs in a new buffer to increase the gradient slope. To prolong a gradient requires only the substitution of a fresh program card, notched at different times to delay the start of the new buffer. With adequate reservoirs of each buffer, there is no possibility of emptying the gradient vessel inadvertently, with consequent introduction of air into the column.

The apparatus consists essentially of a multi-inlet Teflon plug stopcock with a common outlet similar to the apparatus described by Hamilton and Anderson (*2*). The inlet–outlet pathway is selected by a timing mechanism which actuates a motor to rotate the stopcock to the next position in sequence; a most useful apparatus for liquid chromatography has four inlet ports.

CONSTRUCTION DETAILS

The apparatus, which is available from Adelco Labs., P.O. Box 592, Bellaire, Texas, may be constructed for self-contained mounting or for rack mounting as a component of a larger apparatus. All of the components are mounted on the front panel (Figure 1*a*). As shown in Figure 1*b*, the motor-driven stopcock arrangement is mounted on standoffs with a clevis (Figure 1*d*) to fit the motor shaft to the stopcock handle. A cam (Figure 1*c*), notched at appropriate points for the stopcock to be used, is mounted on the motor shaft, with a roller leaf-actuated, snap-action switch (Hetherington S2B6F1) mounted to bear on the cam. When the time clock actuates the pulse generator, the stopcock motor (W. W. Grainger, Inc., Chicago, Ill., Catalog No. 5K208, 7 r.p.m.) is energized for a period of about 0.5 second, which rotates the motor shaft enough to raise the switch arm from the cam notch and energizes the motor directly, allowing it to run until the next notch stops the motor by returning the switch to the first position. The motor magnetic brake stops the motor shaft promptly; coasting may lead to erratic results. A block diagram of the apparatus is shown in Figure 2.

The stopcock is a modified, four-way Teflon plug stopcock (similar to Scientific Glass Apparatus Co., Bloomfield, N. J., Catalog No. JS-4110/1mm.) with four 12/1 ball joints on the sidearms and a solid Teflon plug which is drilled

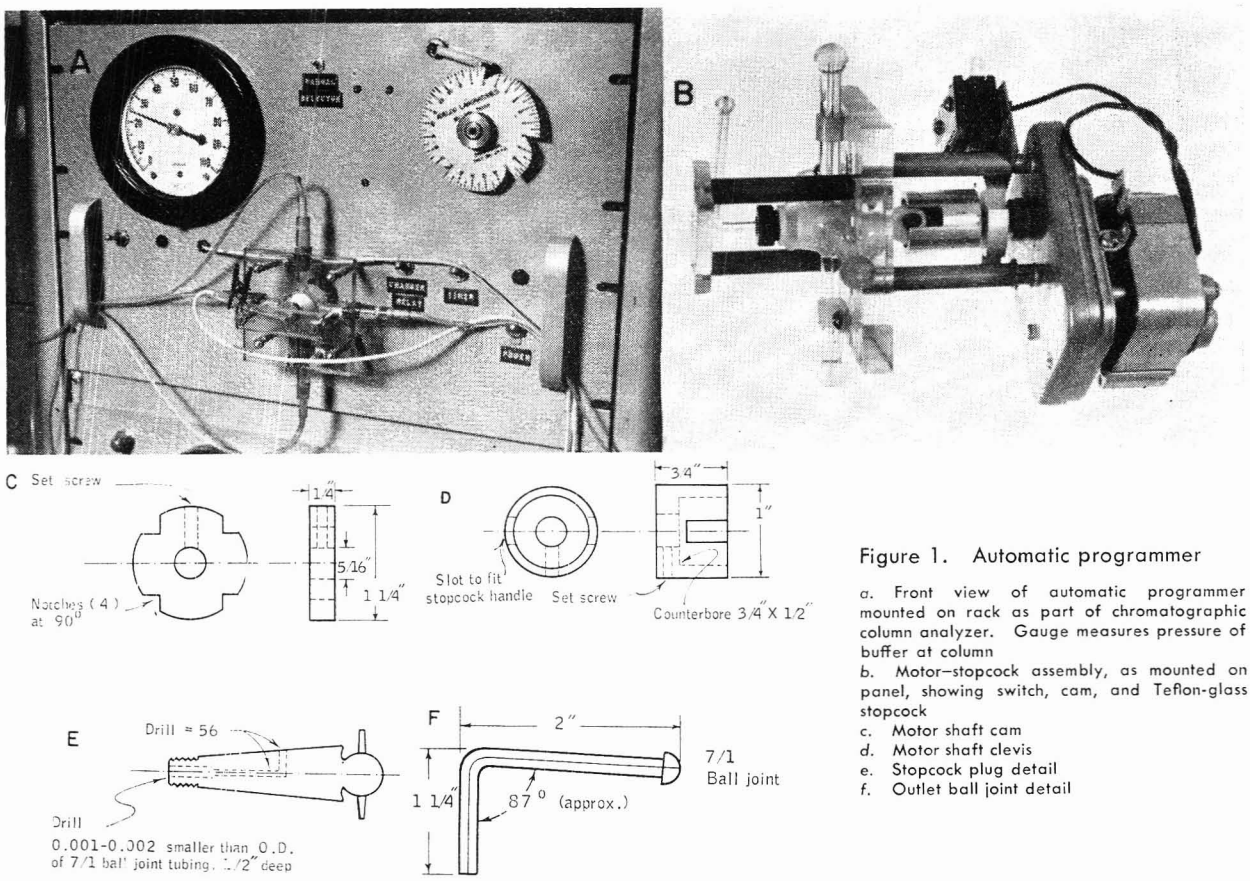


Figure 1. Automatic programmer

a. Front view of automatic programmer mounted on rack as part of chromatographic column analyzer. Gauge measures pressure of buffer at column
b. Motor–stopcock assembly, as mounted on panel, showing switch, cam, and Teflon-glass stopcock
c. Motor shaft cam
d. Motor shaft clevis
e. Stopcock plug detail
f. Outlet ball joint detail

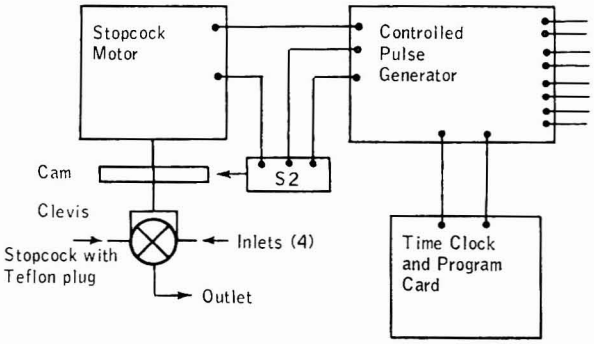


Figure 2. Block diagram of automatic programmer

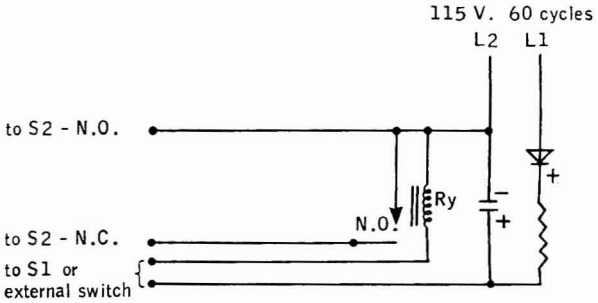


Figure 3. Circuit diagram for long pulse generator

D: Diode, Sarkes-Tarzian M-500 or equal
Ry: Relay, 10,000-ohm coil, Potter & Brumfield RS5D-10K or equal
R: Resistor, 100K, 1/2 W
C: Capacitor, 50 mf., 150 volts
S1: Switch, actuating, Switchcraft 2003L
S2: Switch, motor, Hetherington S2A6F1 or equal

as indicated in Figure 1*e*. A 7/1 ball joint is bent as shown in Figure 1*f* and inserted into the axial hole of the Teflon plug. The low coefficient of friction of the Teflon allows the stopcock to rotate with the 7/1 ball joint stationary, held in place by an end piece and a rotational stop as shown in Figure 1*b*.

The pulse generator circuit is required to close a relay to actuate the stopcock motor for about 0.5 second on closure of a switch for a prolonged period. This is achieved by the circuit shown in Figure 3. The alternating current input is rectified by diode *D* and furnished through a limiting resistor *R* to charge the electrolytic condenser *C*, and to maintain it charged. When the actuating switch *S1* is closed, the charge is dumped through the relay coil, closing the relay momentarily; the time constant is governed by the product of *C* and the resistance of the coil, as long as *R* is large enough to provide negligible recharging of *C* during the discharge period.

The timing clock consists of a standard one-revolution-per-day clock motor (Cramer Control Corp., Centerbrook, Conn., type 117P, 1 r.p.d.) driving a $3\frac{1}{2}$ inch diameter program card of heavy paperboard, calibrated by quarter hours. Notches are cut with scissors as indicated in Figure 4. In this example, a column started at 11:00 A.M. would elute with the starting buffer until 1:00 P.M., when the second buffer would be started, either into a gradient vessel or into the column.

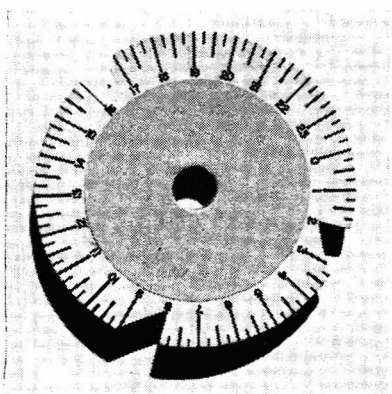


Figure 4. Program card

At 7:00 P.M., the third buffer would be connected, and at 3:00 A.M. the fourth buffer would be connected. If additional buffers or eluents are needed, the ball joint connections allow quick changing to additional reservoirs for the fifth, sixth, etc., eluents. This changing can usually be arranged to take place during normal working hours. The small amount of eluent trapped in the 1-mm. capillary of the stopcock can be flushed out with new eluent, if desired. Rubber or plastic washers are desirable for all the ball joint connections.

In the case of columns which are regenerated and reused, a fourth notch on the program card will return the stopcock to the first eluent at the end of the elution sequence, and the column would be ready to use again the next morning.

Additional indicators, switches, etc., can be added as desired. Features found useful have included a ready light (neon bulb across *S1* to indicate proper operation and full charge in capacitor *C*), a manual stopcock-positioning switch (pushbutton switch across relay contacts to operate stopcock motor manually), outlet plug (with contacts wired across stopcock motor leads to provide indicator signal to recorder to mark time of buffer change), input plug contacts (in parallel with actuating switch to permit operation of changing mechanism by closure of external switch by fraction collector, etc.), and timer motor switch.

A simulated ion exchange run was made as shown in Figure 5. The pH of the exit solution and the light transmission were recorded at a flow rate of 25 ml. per hour. The light transmission of methyl orange at its isosbestic point (470 mμ) is independent of the pH and was chosen to simulate a changing salt concentration. Initially, the flow of 0.1*N* acetic acid (28.0 ml. per hour) is recorded. At 2 hours, the first change starts a gradient (100 ml.) magnetically-stirred flask toward 0.1*N* sodium acetate, pH 5.0, 7.5 mg. per liter of methyl orange. At 8 hours, the buffer–methyl orange is applied directly to the column, bypassing the gradient vessel, and at 11 hours, a 0.2*N* sodium phosphate, pH 7.5, 30 mg. per liter methyl orange solution is automatically applied to the column. At 16 hours, the stopcock rotates back to the first position and the 0.1*N* acetic acid regenerates the simulated column. It is readily apparent that alteration of the pH, ionic strength, gradient vessel size, and time of each period can produce changes in the shape of the pH and/or ionic strength curves. This can be done with little manipulation beyond changing the time notch positions, buffers, or gradient vessel size. Once the optimal conditions have been selected, they can be repeated automatically.

DISCUSSION

This apparatus is a versatile controller of the flow of liquids or gases through any stopcock that can be mounted on the panel face. Three-way stopcocks may be used by changing the cam to one notched at 120° intervals. Flow may be directed from one pair of arms to another pair, as in the usual three or four-way stopcock. A gradient vessel may be used through a portion of the elution sequence, followed by stepwise changes in buffers

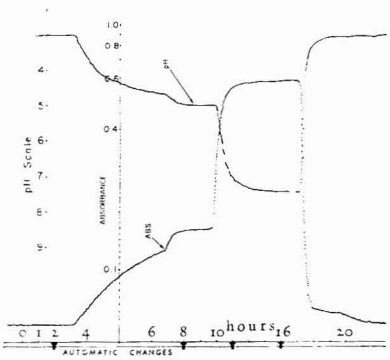


Figure 5. Recording of pH and absorbance of simulated eluent system vs. time

for later portions of the elution scheme. The programming of several buffers into a gradient vessel offers a finer control of the shape of the gradient than the use of a single concentrated, remote pH inflow. The flow of gases or samples for gas chromatography could be automatically programmed, for example, to repeatedly analyze a flowing stream by injecting into the chromatograph the constant volume sample trapped in the cross-drilled hole in the Teflon plug of a four-arm stopcock.

LITERATURE CITED

(1) Hale, D. K., "Ion Exchangers in Organic and Biochemistry," C. Calmon and T. R. R. Kressman, eds., pp. 160–2, Interscience, New York, 1957.
(2) Hamilton, P. B., Anderson, R. A., ANAL. CHEM. **31**, 1504 (1959).
(3) Kellie, A. E., Wade, A. P., *Biochem. J.* **66**, 199 (1957).
(4) Peterson, E. A., Sober, H. A., ANAL. CHEM. **31**, 857 (1959).
(5) Smith, Ivor, "Chromatographic Techniques," pp. 252–4, Interscience, New York, 1958.

Multiple Hydrogenation Insert

R. A. Eisenhauer and R. E. Beal, Northern Regional Research Laboratory, Peoria, Ill.

TO HYDROGENATE samples on a semimicro scale, a stainless-steel insert, which has a capacity of 10 ml., is available for use with an Aminco, 300-ml. reaction vessel. However, when many samples must be hydrogenated for analytical purposes, time becomes an important factor because only one sample can be hydrogenated at a time with the 10-ml. insert. Methods for hydrogenating several samples simultaneously were explored, and a new insert was designed that allows the hydrogenation of six samples concurrently.

EXPERIMENTAL

Fabrication. Individual sections of this insert were cut from solid stainless-steel rods of approximately $1^5/_8$ inch diameter. The inside of each section was bored to a depth of $1^5/_8$ inches, and the section was cut to approximate dimensions (Figure 1). The top of each section was threaded with 24 internal threads, the bottoms with 24 external threads, except for the bottom of the sixth section. All internal threads have a $^1/_{16}$-inch relief at the base of the threads. The bottom of one section forms the top of the next, except for the first and sixth sections. The first section has a $^5/_{16}$-inch threaded cap and the sixth, a flat bottom and no threads. Teflon gaskets, cut from a $^1/_{16}$-inch sheet, were used between each section. The gaskets fit between faced surfaces giving an excellent seal. A $^1/_4$-inch hole was drilled in the center of each section, and a piece of $^1/_4$-inch pressure tubing, $^3/_4$ inch long, was welded in each hole projecting into the section thus giving an opening for hydrogen. The inside diameter of the pressure tubing is $^3/_{32}$ inch. Without this tubing, leakage occurs and samples intermix.

Procedure. Materials to be hydrogenated are placed in each of the six sections of the insert and a suitable catalyst is added. The sections are fitted together with fingertip pressure. Knurled surfaces on each section prevent the fingers from slipping over the machined stainless steel. This pressure on the Teflon gaskets is sufficient to obtain an adequate seal to prevent leakage. Hydrogen inlet holes need not be aligned because the pressure tubing extends to the center of each section, and with approximately 1 to 5 grams in each section, no leakage occurs. When the insert is completely loaded and assembled, it is inserted into an Aminco $2^9/_{16}$-inch o.d. micro-series reactor. This reactor is bored from a solid forging and has an over-all length of $11^3/_4$ inches. The reactor containing the insert is then placed in a rocker assembly, which includes a heating jacket and means for introducing hydrogen. The pressure vessel tilts through an angle of 30° at 36 cycles per minute. This movement gives the material in each section ample agitation and catalyst contact.

The Northern Laboratory is a laboratory of the Northern Utilization Research and Development Division, Agricultural Service, U. S. Department of Agriculture. Mention of trade names is for identification only and does not imply endorsement by the Department.

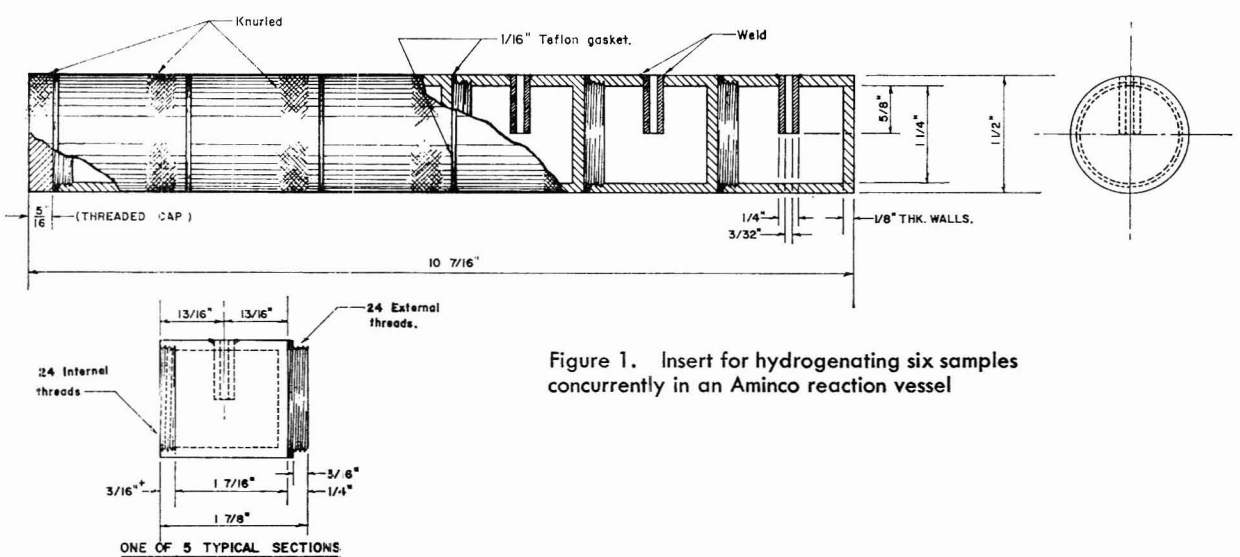


Figure 1. Insert for hydrogenating six samples concurrently in an Aminco reaction vessel

Safe, Simple Method of Opening Irradiated Silica Ampoules

Ray Porritt and Malcolm Thackray, Australian Atomic Energy Commission, Research Establishment, Lucas Heights, N. S. W., Australia

When performing irradiations in high-flux nuclear reactors, it is frequently necessary to seal samples in small silica tubes. Since the tubes and their contents become highly radioactive and often generate appreciable gas pressures, the safe opening of the tubes and the quantitative recovery of their contents often presents a difficult problem.

When the contents constitute a single liquid or solid phase, the ampoule can be crushed in a suitable metal or plastic beaker using a plastic rod and annular beaker cover. However, with semisolid biological samples (blood, butter, etc.), this technique often gives poor recovery and leads to very great difficulties when, as frequently happens, the next step is a perchloric acid oxidation of the organic matter. Moreover, the technique is not easily adaptable to remote operation from behind a lead shield.

While performing a series of activation analyses on butter and butterfat, we developed a very safe technique which gives quantitative recovery of the ampoule contents and can be easily operated from behind a 4-inch lead shield. Briefly, the method consists of crushing the ampoule in a vertical piece of flexible plastic tube.

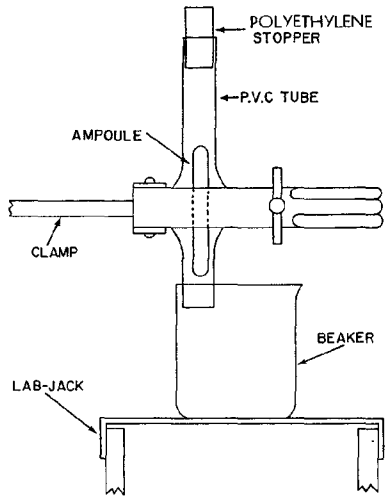


Figure 1. Apparatus for opening irradiated samples

The steps are as follows (see Figure 1.): Select a piece of clear plastic tubing (PVC or polythene) about 5 inches long and having an i.d. about twice the external diameter of the ampoule to be opened. Place a suitable polythene stopper in the lower end and loosely support the tube vertically in the V of a strong laboratory clamp. Clean the ampoule of all external contamination and drop it into the plastic tube. Move the plastic tube upward until the ampoule is opposite the clamp, and gently tighten the clamp onto the ampoule. Transfer the polyethylene stopper from the bottom of the tube to the top. By means of a laboratory jack, raise a beaker into position around the lower end of the plastic tube. Tighten the screw clamp until the ampoule breaks. Remove the polyethylene stopper, and slacken the clamp so that it only just supports the plastic tube. Rinse through with acetone or other suitable solvent, and boil off the acetone before beginning a perchloric acid oxidation.

Although this method was developed to deal with semisolid biological samples, we now find it the simplest way of opening any active ampoule.

A Partition Sampler for Vapor Analysis by Gas Chromatography

Ewan R. Colson, Research and Testing Department, Gas and Fuel Corp. of Victoria, 469 St. Kilda Rd., Melbourne, Victoria, Australia

Recently, we have had to determine quantitatively small amounts of comparatively high-boiling compounds such as naphthalene, in concentrations up to about 0.45 mg. per liter, and thiophane (tetrahydrothiophene), about 0.03 mg. per liter, present in manufactured gas from various sources. Conventional methods of sampling and gas chromatographic analysis proved unsuitable, probably because of sorption of the compound of interest on the walls and fittings of the glass gas-sampling tubes used for transport of samples from the plant or pipeline to the laboratory.

It is now believed that a suitable method of sampling gases prior to gas chromatographic analysis for naphthalene, thiophane, or other compounds has been developed which overcomes sorption difficulties with gas-sample tubes and enables easy transport of samples.

While the partition sampler described was developed for sampling directly from process pipelines, it should offer advantages over the gel adsorbers described by Widmark and Widmark (*1*) for their applications—chromatographic analysis of vapors in air, and quantitative collection and reinjection of compounds separated by gas chromatography.

EXPERIMENTAL

Procedure. The method comprises drawing a measured volume of the gas through a short metal tube which contains a suitable packing for quantitatively absorbing the compound of interest. The tube is then sealed and transported to the chromatograph. Here the carrier gas is temporarily shut off, and the sample tube is inserted between the carrier-gas supply and the column inlet. The tube is heated rapidly for about 5 seconds to change the equilibrium partition of absorbed substances between packing and vapor space, and the carrier-gas flow is restarted during the heating period. The compound of interest is separated and the peak is measured in the usual way.

From a consideration of the principles of chromatography, the sampling method described is quantitative providing the gas-sample volume does not exceed the initial retention volume of the compound of interest on the packing used (at the temperature and flow rate of sampling). Widmark and Widmark, in their technique for collection and reinjection of fractions from and into a gas chromatograph, have reported an average loss of 1.5% per collection–reinjection cycle for 1-μl. samples of substances not irreversibly sorbed by the silica gel packing used.

Sample Tube. After unsatisfactory experiences with activated charcoal and alumina, probably because of varying moisture contents, Silicone Oil (Embaphase, May and Baker) on Chromosorb P (30- to 60-mesh) has proved a suitable packing for the sampler. However, any stationary phase, liquid and stable over the necessary temperature range (in our case 20° to 150° C.), and any normal chromatographic support should be satisfactory for this purpose.

Stainless-steel tubing is particularly suitable for containing the packing as its high resistivity enables fast, direct resistance heating with simple equipment. As an example, for thiophane, samplers of stainless-steel tubing, 4.1-mm. i. d., containing 12.5 cm. of 30% Silicone Oil on Chromosorb P have proved suitable. The sample volume is

limited to 100 ml. for ambient temperatures up to 37° C. The rate of sampling is 50 ml. per minute. The tubing has a wall thickness of 0.74 mm. and is heated by passing a current of about 90 amp. at 1.3 volts for 5 seconds, whereby a temperature of 150° C. is attained in the center of the packing. This power can be obtained by parallel operation of two soldering-iron transformers with secondary windings intermittently rated (on 6 seconds, off 36 seconds) at 3.3 volts, 30 amp.

The above sampler, when used for naphthalene, would pass a gas sample volume about 25 times that for thiophane before slippage of naphthalene would occur. However, the sampling time may be inconveniently long and the sample unnecessarily large for a sensitive detector. Hence a sampler containing less packing could be substituted (or one with a lighter liquid loading), so that a 100-ml. sample volume may be used. An unnecessarily long partition sampler may quantitatively retain components of lesser retention volume than the component of interest, making unnecessary demands on the column used in the later analytical separation.

Calibration. The partition sampler offers a neat way of introducing calibration samples into the chromatograph. It obviates the necessity of using an accurately known liquid volume of 1 μl. or less for calibration of sensitive ionization detectors. Although large dilutions of the sample component in a solvent may be required, the sampler can eliminate the solvent peak from calibration runs.

An accurate dilution of the calibration substance is made in a pure solvent, so that a reasonable volume (10 or 20 μl.) of this calibration mixture will give a peak area approximating that of the samples.

The solvent is chosen so that its vapor will break through the partition sampler (at room temperature) during the passage of a volume of air which is insufficient to elute the vapor of the calibration solute. To avoid possible evaporation losses, a slow current of air is also drawn through the sampler while the liquid is being injected into one end from a microsyringe.

Then the partition sampler containing the calibration solute alone (and possible solvent impurities) is connected to the chromatograph and heated as described before.

CONCLUSIONS

The partition sampler provides an effective means of sampling naphthalene, thiophane, or other vapors in gases.

The use of the partition absorber instead of the silica gel adsorber of Widmark and Widmark should overcome their reported difficulties with water vapor, and should prevent decomposition of lower alcohols, esters, ethers, and ketones which is caused by heating these substances on the gel.

ACKNOWLEDGMENT

The author acknowledges the advice and assistance of G. M. Brown and other colleagues, and thanks the management of the Gas and Fuel Corp. of Victoria for permission to publish this paper.

LITERATURE CITED

(1) Widmark, K., Widmark, G., *Acta Chem. Scand.* 16, 575, (1962).

A Convenient Mass Reference Plate for Use in Spark Source Mass Spectrometry

F. Neil Hodgson, Monsanto Research Corp., Dayton, Ohio

Michel Desjardins, University of Cincinnati, Cincinnati, Ohio

William L. Baun, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio

ONE PROBLEM frequently encountered in spark source mass spectrometry is the accurate assignment of mass numbers to the lines observed on the photographic plate. Though mass reference plates which may be compared to the unknown plate are now available (*1*), setting the magnetic field to duplicate exactly the dispersion of the reference plate masses is tedious and can be accomplished only after some experimentation. Additionally, reference plates are available for only a limited number of mass ranges. Therefore, it may be necessary to sacrifice needed resolution for the convenience of having a ready-made mass reference plate.

A method of making a mass reference plate, which is sufficiently accurate for most line identification, has been developed as a result of spark source studies performed on polynuclear aromatic hydrocarbons (*2*). This type of compound, when introduced into the spark, gives lines representing masses up to the molecular weight. Using coronene, $C_{24}H_{12}$, for example, an exposure of approximately 10^{-9} coulomb yields lines at almost every mass unit up to mass 300. Since these lines arise, largely, from C^{12} (mass 12.000) and H^1 (mass 1.0078) combinations, the lines are arrayed at nominally whole mass number intervals. Lines at masses much greater than the molecular weight of the compound can be obtained by increasing the exposure. For example, the spectrum of anthracene recorded at 10^{-9} coulombs exposure showed lines up to the molecular weight, but the spectrum of anthracene, recorded at a coulomb exposure 20-fold greater, showed ions of masses up to the anthracene dimer. These additional lines can be used as mass references also.

PROCEDURE

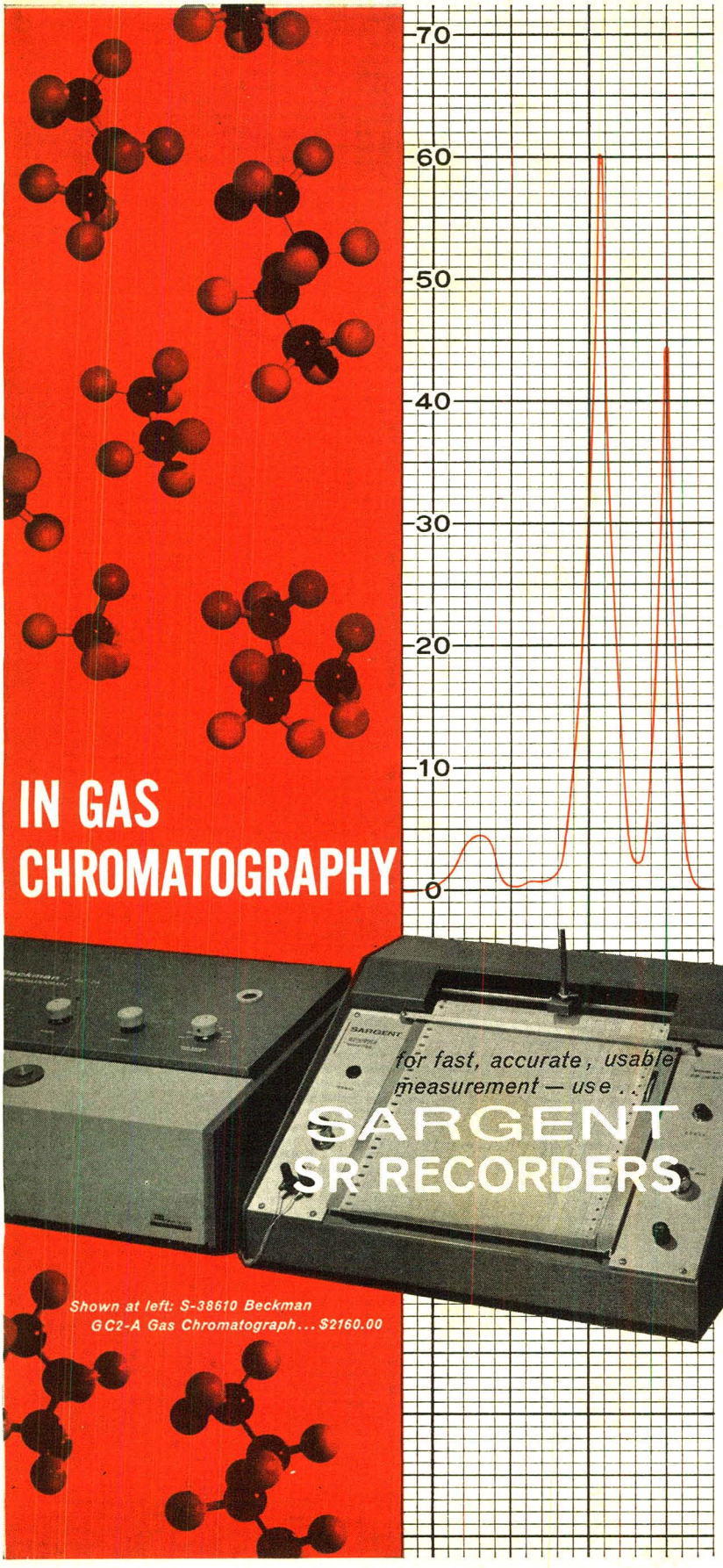
The technique for making the reference plate is quite simple. Electrodes, formed of high purity aluminum, are hollowed out and packed with a polynuclear aromatic hydrocarbon. Naphthalene is not satisfactory for this purpose because of its high vapor pressure, but anthracene, or any hydrocarbon of three or more fused rings, may be used. Exposures are made on a suitable photographic emulsion, using these electrodes to produce the spark. Either Ilford Q2 plates or Kodak SWR plates are satisfactory. After the plate is processed according to the recommended procedure and dried, it may be placed on a viewing box and every 5th or 10th mass number labeled with a soft lead pencil or a crow quill pen. The strongest lines will be in the low mass region and three outstanding lines will be recognized as due to carbon at mass 12 and to aluminum at masses 27 (Al^+) and 13.5 (Al^{+2}). Using these lines as guides, the other mass lines can be identified with little difficulty.

The great advantage of this approach to the identification of mass lines is its flexibility. A reference plate may be made to cover any mass range. The reference scale may be made as the last exposure of the plate on which the lines to be identified occur. Additionally, instrumental irregularities, which might cause a mismatch with a fixed mass reference, will be compensated, because the same instrument and conditions can be used for making the reference plate as for running the samples.

LITERATURE CITED

(1) Consolidated Electrodynamics Corp., Pasadena, Calif., 21-110 News Letter, Vol. 1, No. 1, Jan. 10, 1963.
(2) Hodgson, F. N., Desjardins, Michel, Baun, W. L., *J. Phys. Chem.* 67, 1250 (1963).

IN GAS CHROMATOGRAPHY



for fast, accurate, usable measurement — use . . .

SARGENT SR RECORDERS

Shown at left: S-38610 Beckman GC2-A Gas Chromatograph . . . $2160.00

Sargent SR Recorders have input circuits, ranges, charts, and other characteristics specifically engineered for application with Beckman GC Gas Chromatographs, Precision Chronofrac, and custom-made experimental chromatographs. They offer you these important advantages:

FAST PEN RESPONSE. Less than one second is required for full scale travel, ensuring faithful reproduction of the sharp slopes and peaks of the chromatogram.

SENSITIVITY. Four microvolts per millimeter (1 millivolt per full 240 mm scale) permits full realization of the potential of the gas chromatograph and chromatographic method.

REPRODUCIBILITY—to a fraction of a millimeter—ensures that the accuracy of analytical measurement is not limited by the measuring instrument, which is accurate to within 20 microvolts.

SPECIAL CHART. Wide 240 mm scale is graduated from 0 to 100 to simplify calculations. Zero point is offset from mechanical zero to show negative signals and simplify adjustment—and is at the right for a logical, conventional presentation of the chromatogram.

VERSATILITY. A variety of accessories permit selection of chart speeds, charts, voltage ranges, pens, etc. for other applications—with true potentiometric measuring (no input dividers to distort the measured circuit).

INTEGRATING UNIT is available, as a component part of the recorder or as an accessory unit, to provide continuous integration of chromatogram record for quantitative analysis.

Besides their use in gas chromatography, Sargent SR Recorders have vital applications in spectrophotometry . . . in pH titration—in recording measurements by any analytical device, from simple cells to the more complex instrument, that provides a D.C. voltage output.

PRICES

S-72180-20 RECORDER—Potentiometric, 1 mv, Gas Chromatograph, Sargent Model SR (Pat. No. 2,931,964). With input circuit adapted for optimum performance with gas chromatographs **$720.00**

S-72180-30 RECORDER—Potentiometric, 1 mv, Gas Chromatograph, Integrating, Sargent Model SR (Pat. No. 2,931,964). Identical with S-72180-20 but with S-72170 Disc integrator installed for continuous integration of chromatogram. **$1305.00**

For complete information on SR Recorders, write for Bulletin SR-GC.

SARGENT

Scientific Laboratory Instruments
Apparatus • Supplies • Chemicals

E. H. SARGENT & CO., 4647 W. FOSTER, CHICAGO 30, ILLINOIS
Detroit 4, Mich. • Dallas 35, Texas • Birmingham 4, Ala. • Springfield, N. J. • Anaheim, Calif.

Circle No. 81 on Readers' Service Card

HAVE YOU WRITTEN FOR YOUR COPY?

84

CATALOG "G"

get your copy

new complete

CATALOG AVAILABLE

This new catalog presents our complete line:

- Moisture Determination Balances
- Harvard Trip Balances
- Triple Beam Balances
- Cent-O-Gram Balances
- Dec-O-Gram Balances
- Hand Loading Scales
- Heavy Duty Laboratory Balance
- Industrial Balances
- Even Arm Solution Balances
- Highway Scale
- Heavy Duty Solution Balances
- Spring Scales
- Weights

CLIP THIS COUPON and SEND NOW

OHAUS

OHAUS SCALE CORPORATION
1050 COMMERCE AVENUE • UNION, NEW JERSEY
Dept. GA

Please send me my copy of the all new CATALOG "G", no obligation of course.

FIRM or INSTITUTION.....

NAME.....TITLE.....

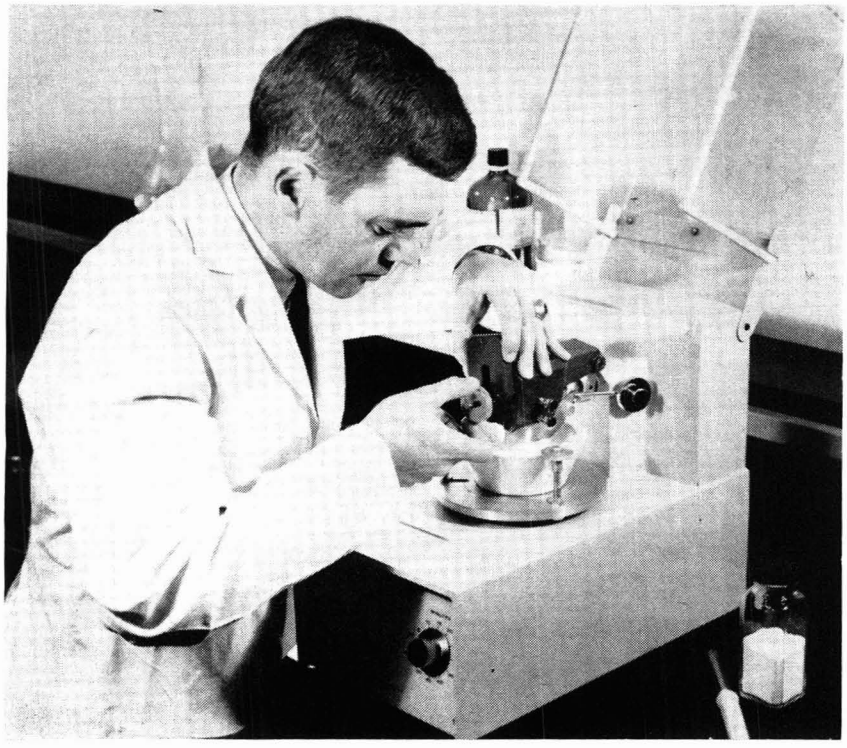
ADDRESS.....

CITY.....ZONE.....STATE.....

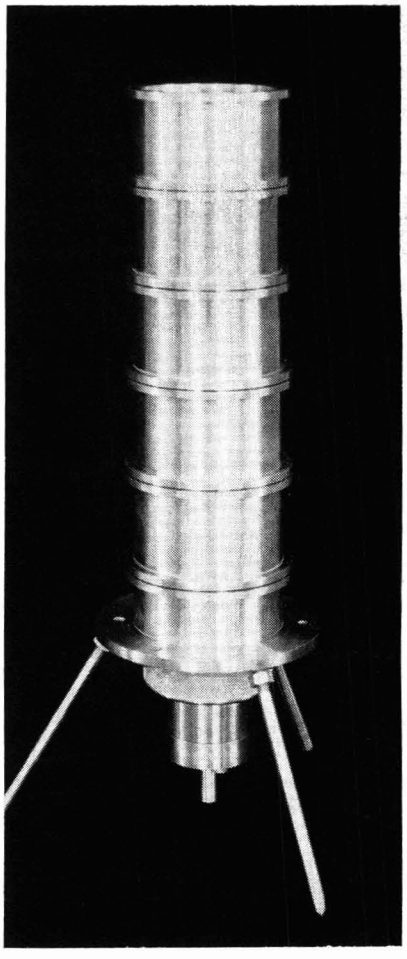
Circle No. 12 on Readers' Service Card

NEW PRODUCTS

EQUIPMENT APPARATUS INSTRUMENTS



The Model 155 automatic mortar-grinder is used to reduce samples to a fine uniform powder. The apparatus is supplied with scraper kit and two loading weights for the grinding head. A wide variety of mortars and pestles in various materials is available. Mortars from 80 to 135 mm. in diameter can be used. Fisher Scientific Co., 300 Fisher Bldg., Pittsburgh 19, Pa. **401**



The cascade impactor is used for particle size distribution analysis of aerosols. Constructed of a series of progressively smaller jets, each followed by an impaction slide, the device operates on the principle that particles in a moving air stream impact on a slide placed in their path when their momentum is sufficient to overcome the drag of the air stream as it moves around the slide. The impactor samples aerosols composed of particles smaller than 25 microns in diameter. Deposition of classified particles on slides permits detailed study and count through dyeing, gold shadowing, and other techniques. Scientific Advances, Inc., 1400 Holly Ave., Columbus 12, Ohio. **402**

THESE DAYS, WHERE CAN YOU GET PHARMACEUTICAL TESTING YOU CAN RELY ON?

Never before has it been so important to know that you can have your testing done by a firm with actual pharmaceutical "know-how":

Not only does Philadelphia Laboratories offer the reputation, the qualified personnel and the wide experience to handle the most exacting test procedures, but it has the industry's newest and most modern facilities.

Philadelphia Laboratories can handle every phase of testing for you:

(1) Chemical
(2) Animal Toxicity & Pyrogens
(3) Pharmacological
(4) Micro-Biological
(5) Anti-Biotic
(6) Pre-Clinical

What's more, they can carry out a new idea from development to finished product, even to designing and writing labels that meet all federal requirements. For further information, just mail the coupon below, or better still, call (215) HObart 4-8400 directly.

PHILADELPHIA LABORATORIES, INC.

ROOSEVELT BLVD. & BLUE GRASS RD.
PHILADELPHIA 15, PA.

Please send me more detailed information on the following testing procedures:

1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 ☐ 6 ☐

Other (please specify)_____

NAME_____

ADDRESS_____

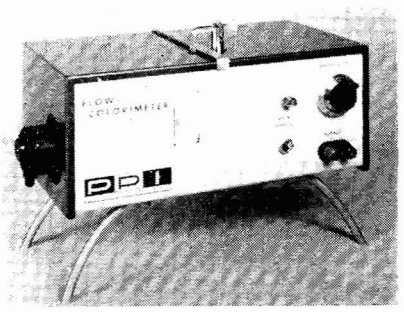
COMPANY_____

CITY_____ ZONE____ STATE_____

AC-1

Circle No. 94 on Readers' Service Card

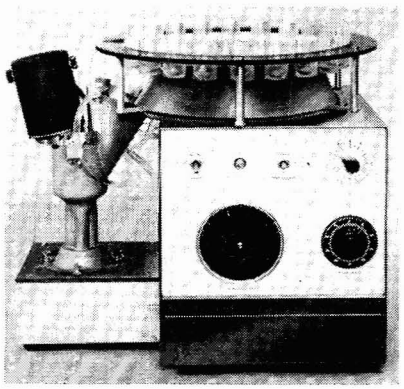
NEW PRODUCTS



This colorimeter was designed for monitoring column effluents in chromatographic applications. The Flow-Colorimeter Model 600 incorporates a voltage stabilizer, a filter turret for changing of monochromatic filters, a glass absorption cell, a cell positioning device, and a 570 mμ peak wavelength interference filter. The instrument can be used with most commercial indicating or recording devices. Phoenix Precision Instrument Co., 3803-05 N. Fifth St., Philadelphia 40, Pa. **403**

Color Monitor

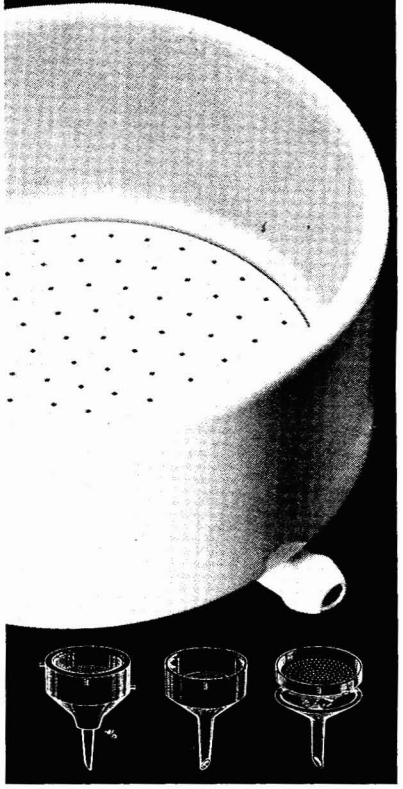
The Chromo-O-Scope monitors the color quality of any product or process by detecting minute changes in the ratio of two selected wavelength components. The instrument operates continuously and has an adjustable response speed. In addition, an adjustable field of view permits the focus to cover large areas or small targets. Milletron, Inc., Irwin, Pa. **404**



The "Solidprep" sampling device is used to prepare solid samples for wet chemical analysis. Samples are loaded into individual sample cups. At timed intervals, each of the cups is automatically tripped into the device where the sample is disintegrated, homogenized, and put into solution. An aliquot is automatically supplied to the analytical system. Technicon Controls, Inc., Chauncey, N. Y. **405**

LABORATORY

Filtration



Coors can help you with laboratory filtration by providing you with a complete range of filtration equipment in many sizes and styles, all immediately available through your local laboratory supply dealer. Coors filters come in 15 styles, with a total of 74 sizes matched to meet your exacting requirements. Coors filtering devices include the #220 and #221 Filter cones; #270, #290, #291. #300 Gooch crucibles; #765, #767, #769 Porous Bottom crucibles; #490 fixed plate Buchner funnels; #491 loose plate Buchner funnels. Special Buchner funnels include the double-wall #495, two-piece #496 and table type #497 and #498; #510 Hirsch funnel; #511 Conical funnel; #775 Emich micro-filtersticks and various porous cups, plates and cylinders. Write for Bulletin No. 498, showing filters.

INSIST THAT YOUR LABORATORY PORCELAIN WARE CARRY THIS MARK OF DEPENDABILITY

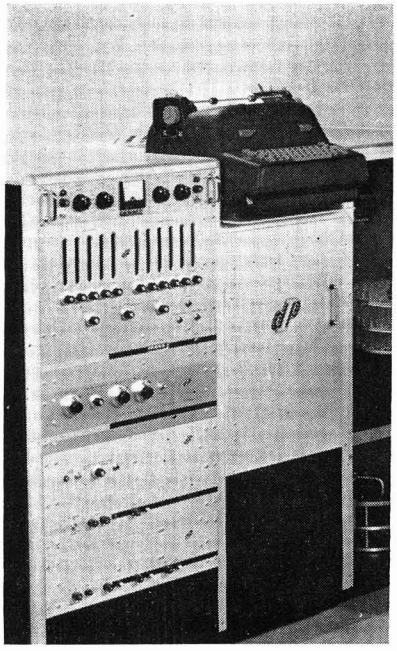
COORS U.S.A.

COORS PORCELAIN COMPANY, GOLDEN, COLORADO

Circle No. 36 on Readers' Service Card

Melting Point Tester

A new micro melting point tester has a projection microscope which permits easy observation. Polarized light may be used. The maximum melting temperature which can be determined is 480° C. and either a thermometer or thermoelement can be used. Epic, Inc., 150 Nassau St., New York 38, N. Y. **406**



The Gammamaster, an automatic gamma scintillation counting system, has reduced the contribution to background count of stored samples by placing them a minimum of 25 inches from the detector. Background count is further reduced by 4 inches of shielding around the crystal detector and additional shielding located in the radiation path between stored samples and detector. Instrument & Development Products Co., 355 W. 109th Place, Chicago 28, Ill. **407**

Power Supply

The HV-200 power supply is capable of delivering 0 to 2000 volts at 0 to 100 milliamperes and has an automatic safety control. This control is used when the power supply is operated for constant current; the power supply is turned off if the voltage exceeds a preset value. The instrument has 0.01% ripple, and operates at better than 0.5% regulation. Scientific Industries, 220-05 97th Ave., Queens Village 29, N. Y. **408**

NOW!
RECORD VOLTS, OHMS, MILLIAMPS
with ONE RECORDER
... NO EXTRAS!

ONLY $595 COMPLETE

New Bausch & Lomb V.O.M.-5 RECORDER

. . . an all-new, complete 5-inch strip-chart recorder that breaks all precedent in the field . . . brings you the finest features of potentiometric recorders for *one low* price. Compare these exclusive advantages, all these "extras" at no extra cost, with any other recorder in its class.

- Five voltage ranges, 10 millivolts to 500 volts D.C.—full scale deflection.
- Six linear ohms scales, 1-to-100,000 ohms full scale, with zener diode D.C. supply.
- Four D.C. current ranges—10 microamperes to 100 milliamperes.
- Off balance input impedance—over 10 megohms.
- Five chart speeds, 400-to-1 range.
- Event marker, with interchangeable pens.
- Function switch with mechanical pen letdown.
- Operates in flat, 30° tilt, or wall-mounted position.
- Compact—only 4¾" x 14½" x 11¾".
- Portable—only 16 lbs.

And more. Lots more! Mail the coupon now for the whole story on this new 5-speed recorder with versatility-plus!

BAUSCH & LOMB B&L

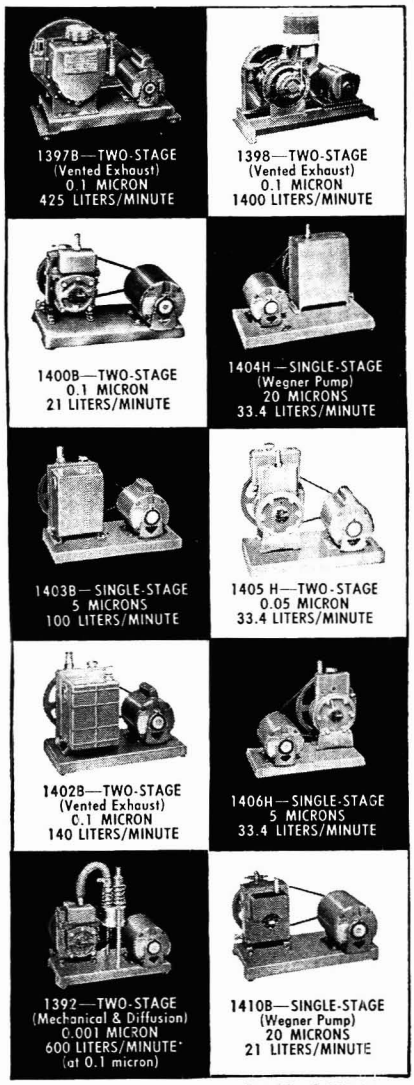
BAUSCH & LOMB INCORPORATED
60943 Bausch Street
Rochester 2, N. Y.

☐ Please demonstrate the V.O.M.-5 Recorder at my convenience.
☐ Send Recorder Catalog D-2032.

Name ..... *Title* .....
Company .....
Address .....
City ..... *Zone* ..... *State* .....

Circle No. 25 on Readers' Service Card

Pick the Vacuum Pump that Fits Your Needs!



Pat. No. 2,337,849

WELCH DUO-SEAL VACUUM PUMPS are designed to fit almost every application better and at less cost . . . in the laboratory, industry and school. Ten different models to choose from . . . capacities from 21 to 1400 liters per minute . . . ultimate pressures from 2×10^{-2} mm Hg down to 1×10^{-4} mm Hg and better . . . two-stage and single-stage mechanical pumps with vented exhaust, and mechanical and diffusion combination pumps.

Over the years, Welch Duo-Seal Pumps have built a world-wide reputation for best performance, greatest reliability and quietest operation. *When you use a Duo-Seal Pump, you're using the best!*

For complete specifications and prices, ask for Duo-Seal Catalog

SINCE 1880 **THE WELCH SCIENTIFIC COMPANY**

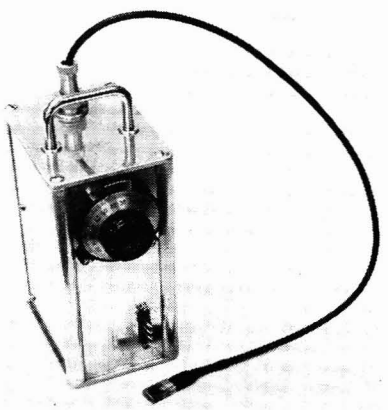
foremost manufacturers of scientific equipment

Circle No. 95 on Readers' Service Card

NEW PRODUCTS

Infrared Test Panel

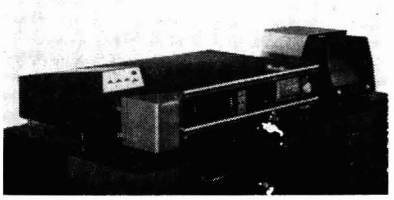
An infrared laboratory test panel can be supplied in three face temperatures: 1200°, 1000°, and 800° F. Formed resistance wire embedded in an insulating block brings a ceramic face up to the emission temperature. A grill under the panel can be adjusted for closeness to the panel. Size of heating panel is 1′ × 2′ × 6″; over-all dimensions with stand are 1′ × 2′ × $1\frac{1}{2}$′. The unit has many applications for laboratory use including testing of drying times in paints, coatings, etc., heat seal testing, and experimental determinations of heat process parameters. Infra-Red Systems Inc., Riverdale, N. J. **409**



The nuclear magnetic resonance instrument shown can be constructed from a kit containing all necessary parts except for connecting wire and glue. The instrument can be used to measure magnetic fields or, in conjunction with a relatively small magnet, can demonstrate NMR. Scientifica, 148 St. Dunstan's Ave., Acton, London, W. 3., England. **410**

Spectrometer

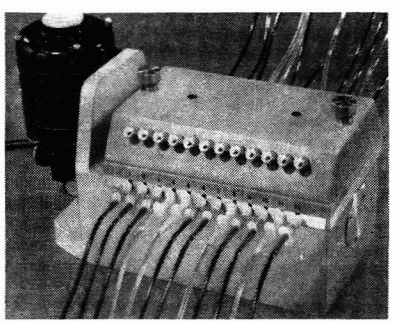
In the "Spectrovac," new automatic direct-reading spectrometer, the working elements are housed in a vacuum chamber. This increases the versatility of the instrument; carbon, sulfur, and phosphorous can be determined simultaneously with the metallic elements. Wavelength ranges from 1500 to 4300 A. are covered, with linear reciprocal dispersion of 2.76 A./mm. This instrument is said to permit the use of more sensitive lines, with higher resolution, than other apparatus of its type. Baird-Atomic, Inc., 33 University Rd., Cambridge 38, Mass. **411**



This low-cost spectrographic analyzer consists of a spectrograph, an ignited d.c. source unit, an excitation stand, and a viewer-comparator. The spectrograph has a modified Wadsworth mount with a focal length of 0.855 meter. A Bausch & Lomb grating of 960 lines per mm. gives wavelength coverage from 4500 to 9300 A. in the first order, and 2250 to 4650 A. in the second order. A dispersion of 6.08 A./mm. in the second order is provided. The instrument can be used for qualitative and quantitative analysis. Applied Research Laboratories, Inc., P. O. Box 1710, Glendale 5, Calif. **412**

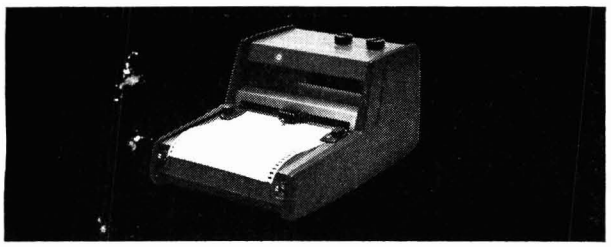
Multichannel Analyzers

Nuclear instrumentation manufactured under license from Intertechnique, S. A., France is now available. Analyzers of 400, 1024, and 4096 channels can be supplied. Also offered are complete analyzer accessories which permit multiple input capabilities, spectrum stripping facilities, and a selection of digital output devices. Packard Instrument Co., Inc., Box 428, La Grange, Ill. **413**



The 12-channel liquid pump provides flow rates from 0 to 4000 ml. per hour per channel. Each of the flow dials has a set of six nominal calibration marks for establishing preliminary flow rates. Applications include feeding liquids in continuous automated chemical analyses, continuous dialysis, or multiple chromatographic column separations. The liquid is entirely contained within plug-connected resilient tubing so that a wide range of chemicals can be handled. Durrum Instrument Corp., 841 Woodside Rd., Redwood City 2, Calif. **414**

VARIAN MAKES A GOOD RECORDER
(the G-14) EVEN BETTER (by adding an integrator)

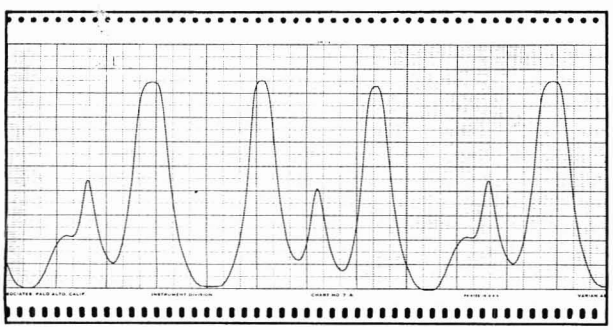


THIS IS THE GOOD RECORDER

Varian's newest graphic recorder, the G-14. It's a versatile, solid-state laboratory unit. It has some significant advancements covering a broad spectrum of recording applications: one-millivolt span, continuous electronic reference voltage, fully transistorized circuitry, excellent accuracy, fast pen speed, and freedom from effects of external transients.

Turn the G-14 on—it's ready to record. The chart may be manually advanced, instantly inspected, and easily marked and torn off. New chart rolls can be installed in 15 seconds. Unique pen design insures smooth performance at all writing speeds.

Dual chart speeds and four input ranges are standard. One full-scale width of true zero suppression is available in addition to the full-scale adjustment of the zero point. Optional equipment includes event markers and spare chart motor assemblies.



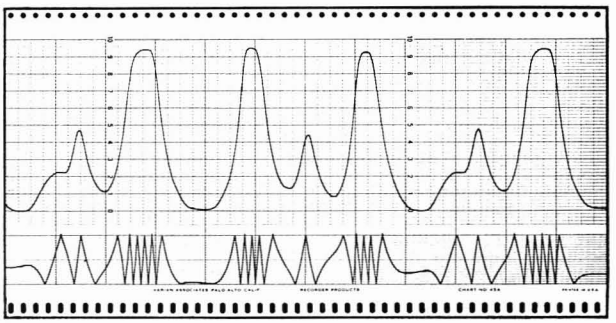
This is a sample of a standard five-inch chart from the G-14. Neat, clean, easy to read . . . tells the whole story. Accurately. Graphically. Varian's unique design and standard of excellence make the G-14 the most versatile solid-state recorder in the business. And that's very good.

G-14 SPECIFICATIONS	
Spans:	1, 10, 100 mv and 1v, instantly selectable
Accuracy:	1% on 1 mv span; ½% on other spans
Pen Speed:	0.6 seconds full scale
Chart Drive:	Dual speeds; 15 choices from 1″/hr to 16″/minute
Weight:	13 pounds; 15 pounds with integrator
Bench Space Required:	9⅜″ x 13½″; 13⅜″ x 13½″ with the integrator
INTEGRATOR SPECIFICATIONS	
Accuracy:	± 0.1% of full scale
Count Rate:	1 to 30,000 counts per minute

G-14 Recorder with Disc Model 214 Integrator . . . Base Price $1295.00
Disc Model 214 Integrator, factory-installed on G-14 Recorders now in service . . . Base Price . . . . . $ 660.00
G-14 Recorder alone . . . Base Price . . . . . $ 685.00

NOW FOR THE BETTER PART

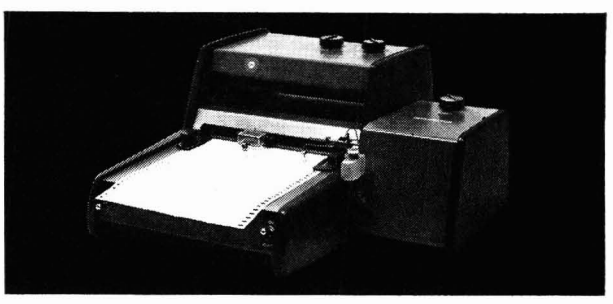
Look at this chart. It's different. It was made on the same model recorder equipped with a mechanical integrator made by Disc Instruments, Inc. and factory-installed by Varian. For accurately interpreting chart curves, this unit provides the important difference between a good close guess and the good measureable facts. With integrator, the G-14 automatically computes the area under a strip chart curve and presents this information continuously on the same chart. This means the G-14 can produce quantitative as well as qualitative records.



USEFUL APPLICATIONS: Gas Chromatography analysis • X-ray diffraction work • Flow measurement and integration • Temperature, sun radiation averaging • Averaging electric power • Weighing materials carried by conveyor belts • Measuring electrical charge (current integration) • Undoubtedly there are other applications unique to your laboratory's experimental work.

The G-14 is modified by externally mounting the integrating attachment on the right-hand side of the recorder. The attachment is housed in a metal cover which matches the G-14 case. The integrator readout pen covers 1″ of the chart width on the right-hand side, with 3.5″ of the chart available for a full-scale deflection of the main recording pen.

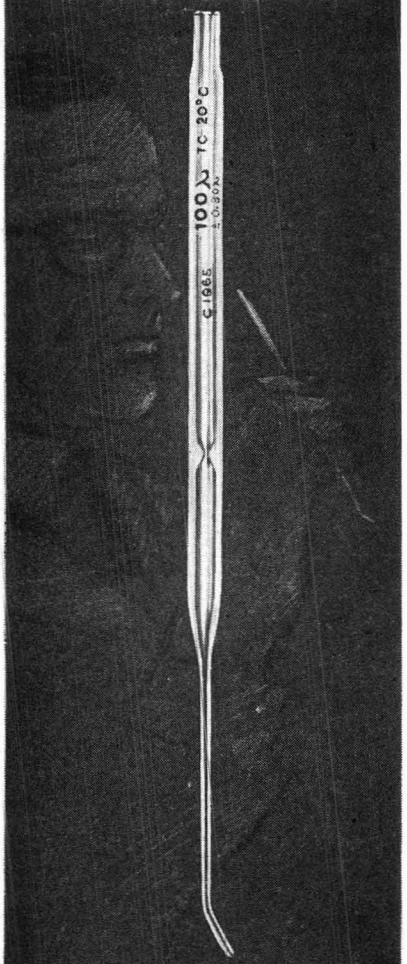
The integrator-equipped recorder meets all G-14 performance specifications with one exception: Pen travel is reduced from 5″ to approximately 3.5″ so that recorder range, zero adjustment, and pen response speeds apply to a 3.5″ full scale width. The Disc Model 214 Integrator may be factory-installed on G-14 Recorders now in service. Write Recorder Products for complete specifications.



VARIAN ASSOCIATES PALO ALTO 4, CALIFORNIA

Circle No. 132 on Readers' Service Card

DANISH TYPE
AMERICAN MADE
LAMBDAS



EASY SIZE IDENTIFICATION —— all markings, including serial numbers, size, tolerances, and company name, are permanently fused into each pipette.

ACCURATE calibrated twice to assure stated accuracy.

ECONOMICAL considerably less than comparable imported product.

For further information concerning prices and sizes, detach and return coupon below.

ROCHESTER SCIENTIFIC CO., INC.
735 Park Ave., Rochester 7, N. Y.

LAMBDA PIPETTES

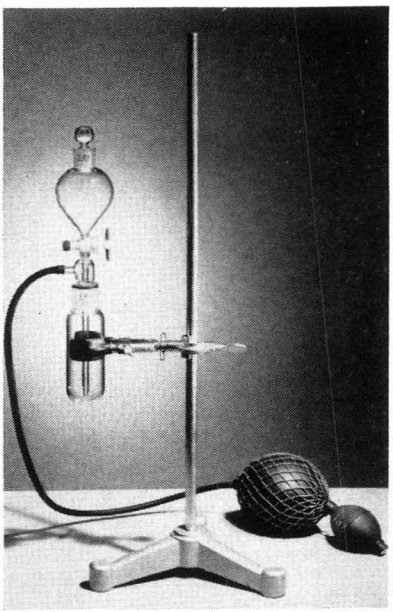
Name .....
Firm .....
Address .....
.....
Position .....

Circle No. 134 on Readers' Service Card

NEW PRODUCTS

TLC Materials

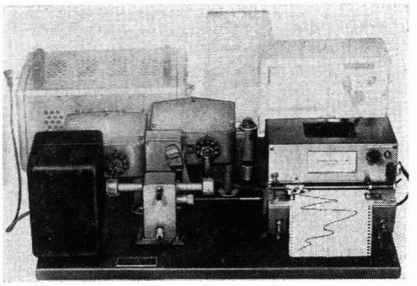
A complete line of thin layer chromatography materials and corresponding column materials can be supplied. Included are adsorbents, and ion exchangers such as silicic acid, alumina, and cellulose as well as custom adsorbents, all sized and purified for thin layer chromatography. A brochure, TLC-1 gives detailed technical descriptions, prices, an outline of the technique, and a bibliography containing over 200 literature references. Bio-Rad Laboratories, 32nd and Griffin Ave., Richmond, Calif. **415**



Liquid separator made of borosilicate glass is pressure-operated and designed for extracting substances rapidly and efficiently. The test tubes, suitable for centrifuging are available in three sizes: 60, 100, and 250 ml. Scientific Glass Apparatus Co., Inc., Bloomfield, N. J. **416**

Gas Chromatograph

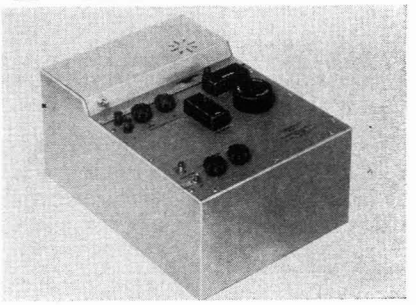
The "Anakro 1A" may be isothermally operated, manually programmed, or automatically programmed. The instrument features a four filament hot wire detector bridge, separate preheater, column, and cell compartments, and a twelve-step attenuation system. Housed in a cabinet measuring 24" × 12" × 8", the chromatograph is a compact, low-cost analytical instrument. Nester/Faust, 2401 Ogletown Rd., Newark, Del. **417**



SPECTROFLUOROMETER

Superior in versatility, sensitivity, and stability. For spectrofluorometric, transmittance, and absorption measurements. Volumes ranging from .2 cc to 10 cc may be investigated quantitatively and qualitatively. Modular construction lends itself to special applications. Available in manual and recording models.

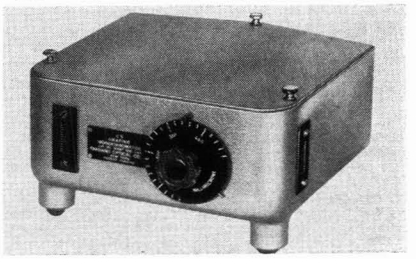
Farrand



FLUOROMETER

The most sensitive instrument of its kind. Provides precise, repeatable measurements. Direct ratios are read on a linear scale. Ideal for routine fluorometric investigation. Available with line-operated or battery power supply for photomultiplier.

Farrand



GRATING MONOCHROMATORS

Compact, rugged, precise. F/3.5 optical system featuring replicas from Farrand master gratings. Ranges from 220 millimicrons to 3 microns.

Catalog information available

Farrand
Optical Co. Inc.
BRONX BLVD. & 238th St. NEW YORK 70, N.Y.

Circle No. 48 on Readers' Service Card

safety that *moves* with the job!

HAWS

PORTABLE DRENCH SHOWER model 8878

Move it where it's needed, to deliver a flooding spray from 16-FULLJET nozzles and 4 foot sprays actuated by Push-Type ball valve. Platform is easily movable on rubber-tired casters: it's *instant* first aid for body contamination. Separate eye/face spray fountain rounds out the complete safety station. Functional parts are corrosion-resistant red brass. See *all* the specs: write to *Haws Drinking Faucet Company, 1443 Fourth Street, Berkeley 10, California.*

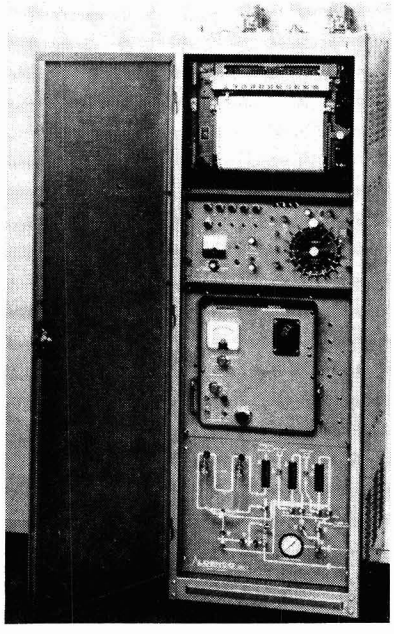
HAWS Since 1909

EMERGENCY EQUIPMENT

Circle No. 7 on Readers' Service Card

EPR Accessory

A new accessory is the V-4557 variable temperature accessory for use with the company's V-4502 electron paramagnetic resonance spectrometer systems. EPR sample temperatures can be controlled within ±2° C. over a range from −185° to 300° C. The accessory includes heat exchanger, dewar, dewar support, transfer tube, variable temperature dewar insert, and control console for rack mounting. Instrument Division, Varian Associates, Palo Alto, Calif. **418**



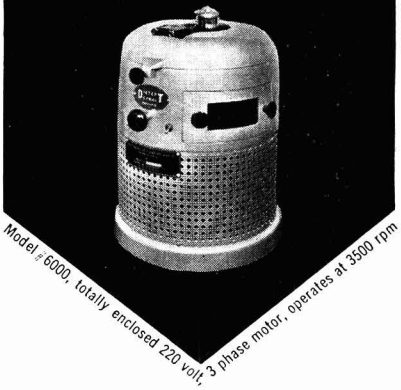
Multicomponent process chromatographic system, Model 15B-XP, consists of a two-stream sample system, programmer, analyzer, and recorder. The programmer has a master time disc, calibrated in seconds, so that it is possible to set accurately all function tabs after making an initial analysis of chromatogram readout. The systems are designed to give high sensitivity and high flexibility. LOENCO, Inc., 2092 North Lincoln Ave., Altadena, Calif. **419**

Flowmeter Kit

The Series 300 flowmeter kit, consists of 4 rotameters and 8 floats in a wood carrying case. The flowmeters have standard, ground tapered joints and are engraved with a 150-millimeter scale. Included are calibration curves for air and water. The Matheson Co., Inc., P. O. Box 85, East Rutherford, N. J. **420**

HOW INDUSTRY USES THE

DIETERT-DETROIT (BAHCO) MICRO-PARTICLE CLASSIFIER



Model 6000, totally enclosed 220 volt, 3 phase motor, operates at 3500 rpm

4 principal uses are:

1. **CLASSIFYING** laboratory quantities of fine materials for product or new material research.
2. **CONTROLLING** industrial processes using or producing fine materials.
3. **DETERMINING** the separating efficiency of air cleaners.
4. **PRE-TESTING** dust collector requirements.

DETERMINE PARTICLE SIZE DISTRIBUTION below 60 microns, in materials such as:

Beryllium Powder	Grinding Sand
Catalysts	Metal Oxides
Ceramic Powders	Penicillin
Chemicals	Polymers
Diatomaceous Earth	Powdered Metals
Drugs	Milk Solids
Dry Powders	Standard Dust Samples
Fly Ash	

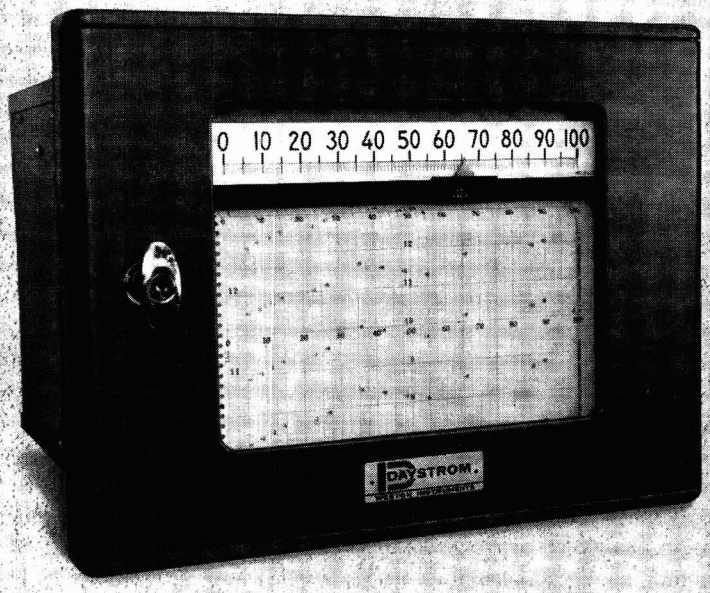
HARRY W. DIETERT CO.
CONTROL EQUIPMENT
9330 Roselawn • Detroit 4, Mich.

Send me details on Micro-Particle Classifier

Name_____
Address_____
Company_____
City_____ State_____

Circle No. 38 on Readers' Service Card

NOW
FROM WESTON



WESTON'S Multipoint Recorder offers the flexibility of programmed printing!

The Model 6704 Multipoint Recorder is now available with programmed printing . . . by pinboard selection, on a time basis or by computer. It can also be programmed while in operation. Its flexibility also makes Model 6704 ideal for laboratory and general purpose applications.

Features:

- Variable Selective Point Programming
- Points not printed are skipped at six times normal stepping rate

Significant options to illustrate flexibility of this outstanding instrument include:

- Programmed Multirange Switching
- Multispeed Chart Drive
- Programmed Selective Alarms
- Adjustable Zero—Adjustable Span

We'll be glad to discuss your particular requirements for the Model 6704 with programmed printing.

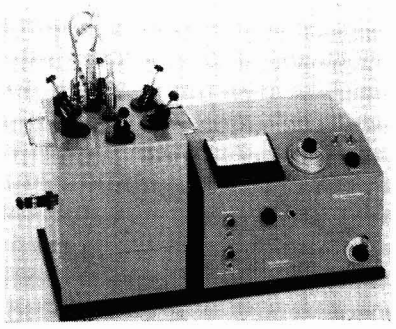
WESTON INSTRUMENTS & ELECTRONICS
Archbald, Pennsylvania Division of Daystrom, Incorporated

Circle No. 96 on Readers' Service Card

NEW PRODUCTS

Liquid Nitrogen Level Control

The Model 100GB-2, designed to maintain optimum level of liquid nitrogen in a cold trap, includes two dewar M-T alarm systems in the form of standard liquid nitrogen transfer tubes with integral sensing probes. The probe in the first dewar senses when the level of liquid nitrogen in the dewar has reached the lower end of the transfer tube and automatically switches over to the second dewar. When the dewar switching control is activated, a red light on the front panel alerts the operator to the fact that the first dewar is empty and must be replaced. Cryogenics, Inc., 5821 Seminary Rd., Alexandria, Va. **421**



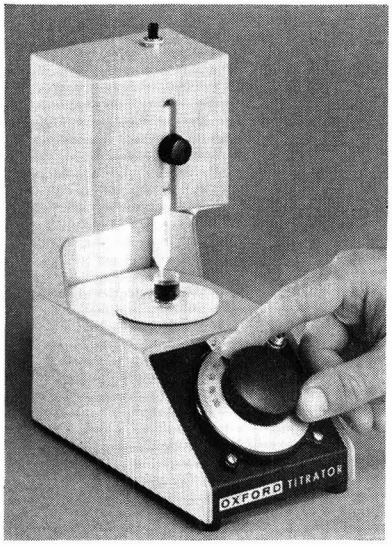
The Model 302 vapor pressure osmometer operates at temperatures up to 130° C. The instrument measures osmotic concentration of sample volumes down to 0.01 ml. by sensing the temperature difference between the sample and a reference drop of pure solvent in a thermally stable atmosphere saturated with the solvent vapor. Chamber temperature is controlled within ±0.001° C. Mechrolab, Inc., 1060 Linda Vista Ave., Mountain View, Calif. **422**

Reflex Klystrons

Six new millimeter reflex klystrons are available to operate in the 50 to 101 kilomegacycle frequency range. Designated as types QKK1148 through QKK1153, these tubes feature single mode operation for full band coverage and smooth single-vernier tuning. This new line is recommended for signal generator and local oscillator applications in fields such as high resolution radar, spectrum analysis spectroscopy, maser amplifier pumping, and harmonic generation of sub-millimeter waves. Raytheon Co., Microwave and Power Tube Division, Foundry Ave., Waltham 54, Mass. **423**

Digital Millivoltmeter

The Model 2660 DVM permits d.c. voltage measurements to be made at levels 100 times lower than is now possible with existing voltmeters without using accessory preamplification. Voltages from one microvolt to 1000 volts can be made in six overlapping ranges. Three microvolt accuracy with 100 megohm input impedance is possible with the lowest zero to 29.999 millivolt range. Houston Instrument Corp., 4950 Terminal Ave., Bellaire 101, Texas. **424**



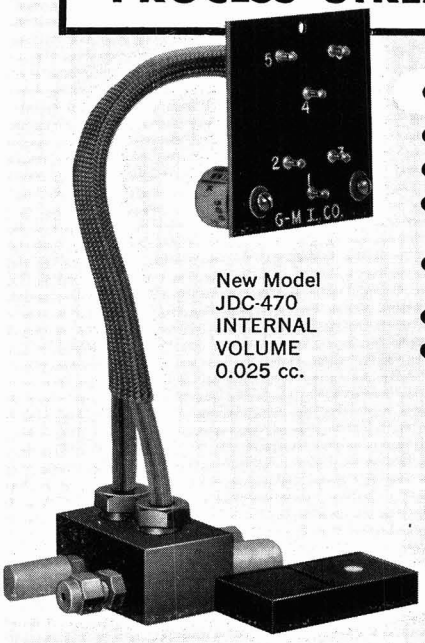
An integrated system of titrimetry includes the Model 301 titrator, packaged reagents, and disposable supplies. The system contains a built-in stirring mechanism, light source (white and ultraviolet), replaceable titrant reservoirs, and disposable pipets and titration cups. Oxford Laboratories, 273 North Bayshore Blvd., San Mateo, Calif. **425**

Optical Beam Splitters

A series of optical beam splitters are available for diverting measured portions of light beams. The Model 421, for example, centered at 6943 A., transmits 1% of the light in a forward direction and reflects 99% at 90°. The Model 422 transmits 96% of the light and reflects 4% at 90°. Other reflectivities and center frequencies can be supplied. Accessory devices are used to orient the beam splitter aperture and to adapt the splitter to the company's laser. Maser Optics, Inc., 89 Brighton Ave., Boston 34, Mass. **426**

GOW-MAC MICRO-VOLUME
THERMAL CONDUCTIVITY DETECTORS

—for Capillary Gas Chromatographs in
LABORATORY, PILOT PLANT, PROCESS STREAM ANALYSIS

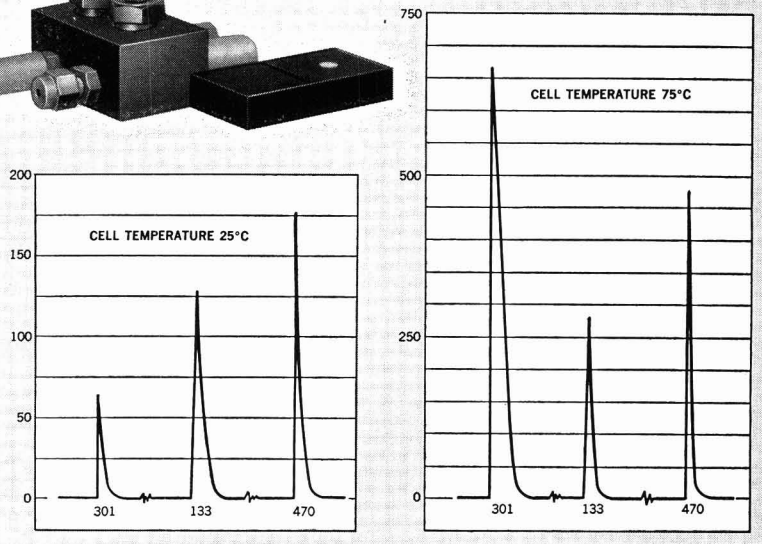


New Model JDC-470 INTERNAL VOLUME 0.025 cc.

- SENSITIVITY 10^{-10} gms/ml
- QUANTITATIVE ACCURACY
- NO EXPLOSION HAZARD
- FOLLOW PEAKS CLOSELY <0.5 sec.
- NON-DESTRUCTIVE TO SAMPLE
- INEXPENSIVE
- EASILY INSTALLED

Operating conditions—

HELIUM FLOW:	5 ml/min.
PAPER SPEED:	1"/min.
AIR SAMPLE:	0.05 ml



Models	133, 470 Thermistor	301 Hot Wire
Wiring diagram	9689	10358
DC Current 25°C	10 ma	365 ma
75°C	13 ma	365 ma

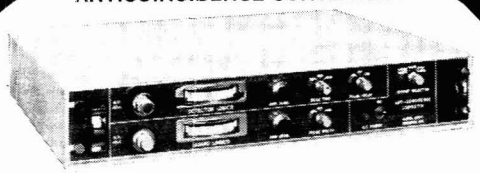
CALL OR WRITE FOR NEW BULLETIN MI-CE
GOW-MAC INSTRUMENT COMPANY
100 KINGS ROAD, MADISON, NEW JERSEY • Telephone: FRontier 7-3450
(AREA CODE 201)

GAS ANALYSIS INSTRUMENTS SINCE 1935

Circle No. 116 on Readers' Service Card

EXPAND TO LOW LEVEL COUNTING

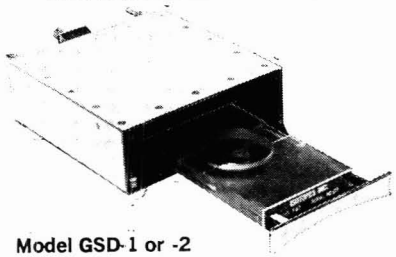
ANTICOINCIDENCE CONVERTER



Model ACC-1

- Solid state electronics
- High voltage variable control
- Detector and guard logics
- Output selector switch

LOW BACKGROUND DETECTOR



Model GSD-1 or -2

- Low background materials used in construction
- Replaceable thin window
- Choice of sizes: 1¼" or 2¼"
- Use Geiger or proportional

A New **ANTICOINCIDENCE SYSTEM** that you can add to high voltage supplies and scalers already in your laboratory.

The Anticoincidence Converter selects for counting after coincidence pulses, before coincidence pulses or detector pulses. Variable guard pulse width, detector delay time, and dead time provides optimum counting conditions for different activity levels. 100% efficient cosmic ray cancellation reduces background counts to the lowest possible level so that low level activity may be counted with precision and accuracy. Supplies negative or positive 10 volt output pulses at low impedance to match any scaler input.

SPECIFICATIONS	GEIGER	PROPORTIONAL
H. V. Input	variable 1500 v DC at 1 ma	variable 2500 v DC at 1 ma
Operating Voltage	1000-1100 v	1500-1600 v (α) 1875-1925 v (β) 1825-1900 v (soft X or γ)
Plateau Length	$>$ 300 v	250 v
Slope (per 100 v)	$<$ 1%	$<$ 2.5% (α) $<$ 3% (β) $<$ 2% (soft or γ)
Bkgd. 1¼" unshielded AC	6 cpm	6 cpm
Bkgd. 1¼" shielded AC	0.35 cpm	0.35 cpm

For further information write to:

ISOTOPES, INC.

123 Woodland Avenue, Westwood, New Jersey

Circle No. 143 on Readers' Service Card

Klett . . .

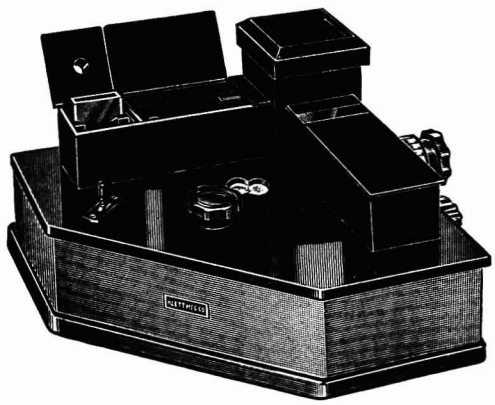
Photometers

Klett-Summerson

Photoelectric Glass Cell Colorimeter

No. 900-3

The Klett Fluorimeter



No. 2070

Designed for the rapid and accurate determination of thiamin, riboflavin, and other substances which fluoresce in solution. The sensitivity and stability are such that it has been found particularly useful in determining very small amounts of these substances.

KLETT SCIENTIFIC PRODUCTS

PHOTOELECTRIC COLORIMETERS • BIO-COLORIMETERS
GLASS ABSORPTION CELLS • COLORIMETER NEPHELOMETERS • GLASS STANDARDS • KLETT REAGENTS

Klett Manufacturing Co., Inc.

179 EAST 87TH STREET, NEW YORK, N. Y.

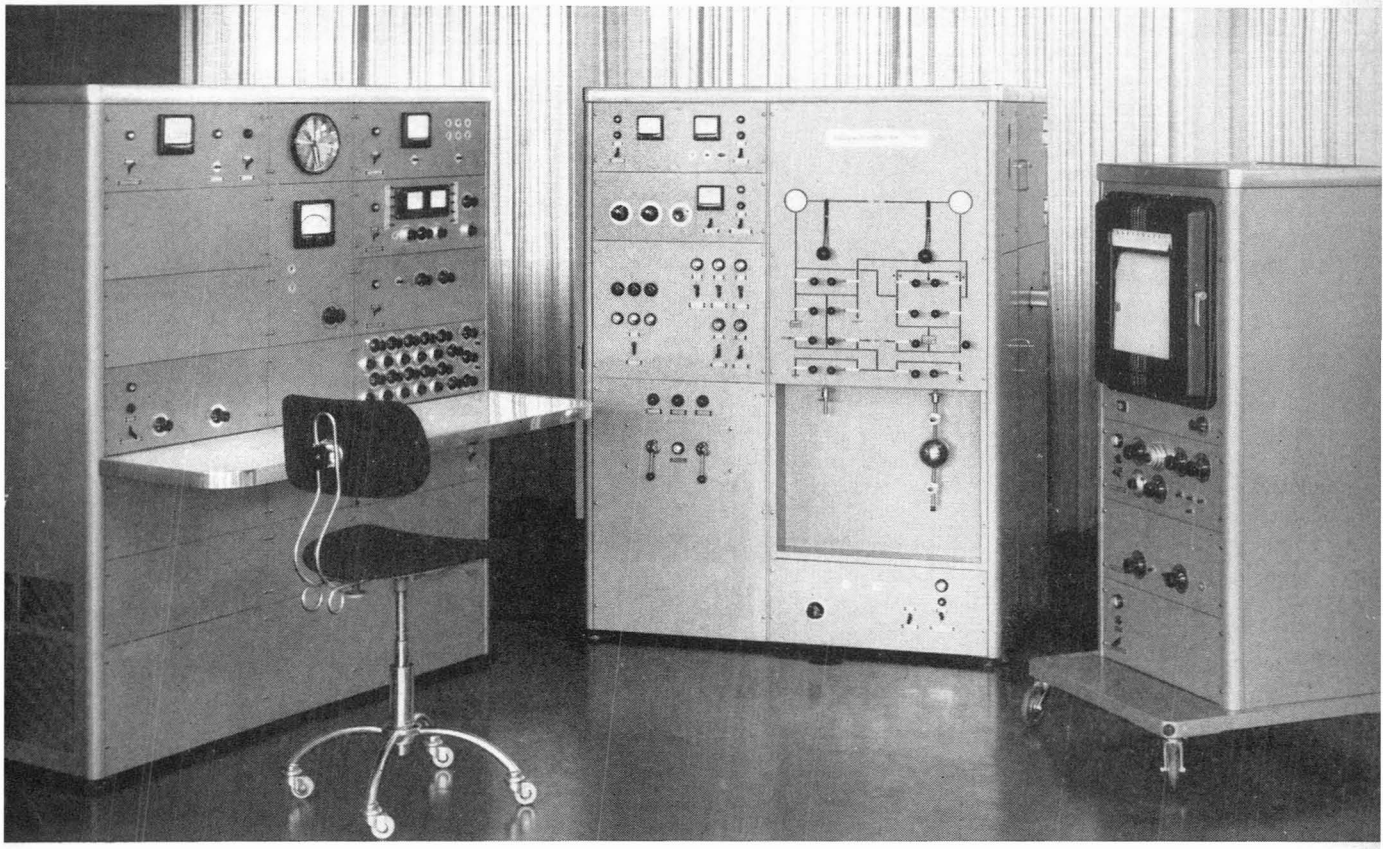
Circle No. 57 on Readers' Service Card

Circle No. 137 on Readers' Service Card →

Now available from Applied Physics Corporation

ATLAS **MAT** CH 4 MASS SPECTROMETER

for analysis and measurement of solids, liquids, gases



For data on the CH4 above, or other MAT instruments, send for Data File A306-73

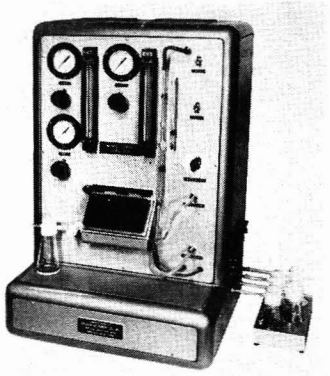
Marketed in the U.S. and Canada for the first time, MAT (Atlas **M**ess-und **A**nalysen**T**echnik GmbH Bremen) Mass Spectrometers and several other analytical instruments are now sold and serviced by Applied Physics Corporation. The CH 4 Mass Spectrometer offers versatility for quantitative and qualitative analyses with samples as small as 0.5 μMOL gas, 0.05 mm^3 liquid, 0.1 μgm solid. It is ideal for identifying gas chromatograph fractions, for isotope ratio and appearance potential measurements, and organic compound structure determinations. The CH4 has a variety of ion sources which may be changed easily, and special inlets for samples to 350°C, solid or chromatograph samples. Resolution is better than 1500, sensitivity less than 1 ppm. Output from electrometer amplifier or electron multiplier may be presented by standard 10-inch strip chart recorder, or by recording galvanometer or oscilloscope at fast scan speeds.

APPLIED PHYSICS CORPORATION
2724 SOUTH PECK ROAD · MONROVIA, CALIFORNIA

Cary INSTRUMENTS

Raman/UV/IR Recording Spectrophotometers • Spectropolarimeters • Vibrating Reed Electrometers & Amplifiers

TORCH ANALYZER



A new useful laboratory tool, developed by Socony Mobil Oil Company, to determine the hydrogen content of aliphatic and aromatic liquid hydrocarbons.

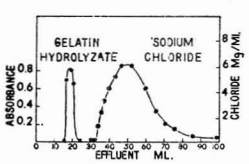
This new instrument functions rapidly, very precisely, and relatively inexpensively It is compact, requiring very little bench space, and was designed with the convenience of the operator in mind.

The apparatus can also be used for types of samples that do not burn completely in wick-type lamps, and would ordinarily have to be analyzed by other methods, at considerable expense.

For further information write to:

KOEHLER INSTRUMENT COMPANY, INC.
168-56 Douglas Ave.—Jamaica 33, N. Y.
Circle No. 58 on Readers' Service Card

Desalt Amino Acid Solutions Rapidly In One Step—Use BIO-RAD Ion Retardation Resins



Bio-Rad AG 11A8 (ion retardation resin) 1.14 cm² x 41 cm column, 1 ml/min. flow rate, loading 5 ml of 1% protein hydrolysate in 5% NaCl.

Demonstrated is the complete desalting of an amino acid solution in less than 30 minutes, using pure water as the eluting agent. The same method quantitatively removes HCl from peptide, protein and amino acid solutions.

Bio-Rad AG 11A8 is formed by polymerizing a cation exchanger inside an anion exchanger. The anion and cation exchange sites tend to neutralize each other but still attract mobile ions. The result—a resin which adsorbs selected anions and cations simultaneously in equivalent amounts.

For a reprint of the desalting method which appeared in Anal. Chem. *34*, 711 (1962), together with references on separations of amino acids and other biological compounds, check "Ion Exchange Resins" below. If you would like to try this method, check "50 g. sample AG 11A8."

BIO-RAD Laboratories
32ND & GRIFFIN AVE., RICHMOND 1, CALIF.
Gentlemen: I would appreciate further information on:

- ☐ Ion exchange resins
- ☐ Ion exchange celluloses
- ☐ 50 g sample AG 11A8
- ☐ Adsorbents for chromatography
- ☐ Labeled compounds (C^{13}, C^{14}, N^{15}, H^2)
- ☐ Stable isotopes
- ☐ "Chemtam" standard solutions

NAME_____ TITLE_____
ORGANIZATION_____
ADDRESS_____
CITY_____ STATE_____

Circle No. 2 on Readers' Service Card

WHEN A PROBLEM IS YOUR PROBLEM

Reach out and put your hand on CHEMICAL MATERIALS CATALOG. Process data problems start unraveling fast as soon as you enter the 5-way index to more than 500 pages of close-packed information—all the latest, detailed data on chemicals and raw materials.

CMC is ready to **come up with the facts** you need! Use it—let it help you, lead you to problem-solutions, widen your thinking.

No guess work, no groping. CMC takes you quickly to the answers.

CHEMICAL MATERIALS CATALOG
CMC
REINHOLD PUBLISHING CORPORATION
430 PARK AVENUE, NEW YORK 22, N. Y.
Circle No. 32 on Readers' Service Card

APPLICATION MANUALS WORTH WRITING FOR

Copies are available at no charge.

ADM-30 Detection and Analysis of Contamination. Outlines the measurement of particulate contamination in fluids with Millipore filters as applied to fine chemicals, aerospace hydraulic fluids, air, nuclear energy, fuels, lubricants, electroplating, crystal growth. 36 pages

ADM-60 Ultracleaning of Fluids and Systems. Illustrates the design of both open-end and recirculating systems for cleaning hydraulic fluids with Millipore filters in test stands, fill-flush and bleed stands and in airborne vehicles. Also covers ultrasonic and solvent-type cleaning systems. 36 pages

ADM-70 Microchemical and Instrumental Analysis. Describes techniques for using Millipore filters in optical microscopy, morphology, electron microscopy, microchemistry, ring oven analysis, infrared and ultra-violet absorption spectroscopy, flame photometry, radioactivity analysis and other analytical methods. 48 pages

OTHER TECHNICAL LITERATURE AVAILABLE

TB-961 Millipore General Brochure. Describes all Millipore filters, apparatus and accessories together with an outline of principal applications. Complete specifications and prices are included. 40 pages

BIBLIOGRAPHY A reference listing of published information concerning applications of Millipore filters. 24 pages

Millipore® FILTER CORPORATION
115 ASHBY ROAD, BEDFORD, MASS.

Millipore filters are cellulose plastic porous membranes made in twelve different pore-size grades from 8 microns down to 10 millimicrons. All particles larger than pore size are retained on the filter surface.

Circle No. 68 on Readers' Service Card

NEW CHEMICALS

CHEMICALS
REAGENTS
MATERIALS

Single Crystals

Single crystals of alpha titanium, magnesium fluoride, and manganese zinc ferrite are now available from general production, rather than on a research effort basis. Data on alpha titanium are meager, but single crystal magnesium fluoride has been shown to be a preferred window material from the infrared to the ultraviolet, scanning a range from 11 microns down to 0.2 micron with 98 to 99% transparency over the whole region. Single crystal manganese zinc ferrite shows evidence of usefulness in the microwave region and its availability should stimulate research in this application. Semi-Elements, Inc., Saxonburg Blvd., Saxonburg, Pa. **501**

TLC Adsorbent

A new cellulose ion exchange material produced by Serva of Heidelberg, Germany, has been specifically prepared for the separation of nucleotides by thin layer chromatography. This product is polyethyleneimine cellulose, PEI-Cellulose. Gallard-Schlesinger Chemical Mfg. Corp., 1001 Franklin Ave., Garden City, L. I., N. Y. **502**

Radiochemical Catalog

A 32-page catalog and price list of certified tagged radiochemicals, including over 700 carbon-14 and tritium labeled compounds is available. The illustrated catalog also contains information on deuterium compounds, counting standards, instrument calibration sources, and many license-free calibrated and uncalibrated sources. Atomic Accessories, Inc., 811 West Merrick Rd., Valley Stream, N. Y. **503**

Dinitrophenyl Amino Acids

Dinitrophenyl (DNP) amino acids which have been completely tested for their conformance to theoretical, physical, and chemical properties including UV absorption are available as single materials, or as kits containing groups. In addition, two PTH amino acid kits are offered. The two PTH amino acid kits contain 35 PTH amino acids. In addition to previously offered DNP amino acid kits, kits can be purchased with the purchaser's choice of 12 or 24 DNP amino acids.

Detailed literature on these materials and references to their use in the scientific literature are available on request. Mann Research Laboratories, Inc., 136 Liberty St., New York 6. N. Y. **504**

Radiochemicals

Atropine-α-C^{14} with a specific activity of 1.07 mc./mM is available for general pharmacological and anticholinesterase studies. Also available is crystalline *dl*-tropic acid-α-C^{14} having a specific activity of 1.06 mc./mM. Tracerlab, 1601 Trapelo Rd., Waltham 54, Mass. **505**

High Purity Solvents

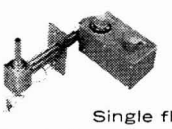
A line of solvents, redistilled at high reflux ratio in all-glass equipment is useful for zero-tolerance residue analysis, counter-current distribution analysis, and spectrophotometric work. Some 18 solvents (others on request) are available in one-gallon bottles, packaged in cases for four. Among the solvents are acetone, acetonitrile, benzene, butanol-1, butanol-2, cyclohexane, ethyl acetate, methanol, methyl ethyl ketone, methyl isobutyl ketone, propanol-2, and toluene. Burdick & Jackson Laboratories, 1953 S. Harvey St., Muskegon, Mich. **506**

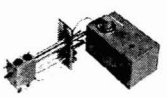
NBS Metal Standards

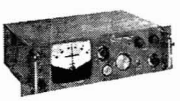
Four groups of metal standard samples have been issued by the National Bureau of Standards. Included in the new standards are four high temperature alloys, ten copper-base alloys, two Zircaloy-2 standards, and a leaded steel standard. In addition, a revised certificate of analysis has been issued for one Zircaloy-2 and two zirconium metal standards which were made available earlier.

Standard samples issued by the Bureau are described in Standard Materials, NBS Miscellaneous Publication 241, available for 30 cents from the Superintendent of Documents, U. S. Gov't Printing Office, Washington 25, D. C.

SINGLE AND DUAL
HYDROGEN FLAME
IONIZATION DETECTORS


Single flame


Dual flame


Model 21B Electrometer

INCREASE THE SENSITIVITY OF YOUR GAS CHROMATOGRAPH

The LOENCO Single or Dual Hydrogen Flame Ionization Detectors, in conjunction with the Model 21B Electrometer, make a gas chromatographic quantitative analysis of organic compounds in parts per billion possible. This represents a sensitivity range several orders of magnitude beyond that of a thermal conductivity detector.
Either of these detectors can be installed in the oven of your gas chromatograph or are available with the LOENCO Model 70 Dual Column Programmed Gas Chromatograph or the LOENCO Model 15B Series Gas Chromatograph.
For complete information write for Data Sheet LOE-10.

LOENCO inc.
ANALYTICAL CONTROL INSTRUMENTATION
2092 N. LINCOLN AVE. / ALTADENA, CALIF. / SY 4-2588 (AC 213)

Circle No. 123 on Readers' Service Card

Circle No. 149 on Readers' Service Card

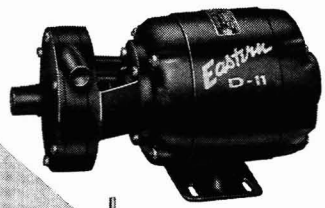
Eastern "job-sized" pumps and stirrers save

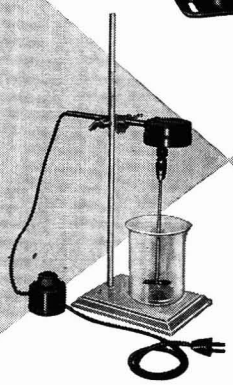
weight • space • power • costs

Eastern has **just** the right pumps or mixer for your laboratory or pilot plant application. The wide range of Eastern products lets you choose standard units so closely geared to the job that they might have been created just for it.

A complete engineering service to help you, and a big selection of more compact, versatile, high performance pumps and stirrers — this is the formula for your quick and easy choice.

Send for laboratory equipment bulletin No. 1540





A wide range . . .
in midget pumps: centrifugal and positive pressure models—motors from 1/30 to 1/3 hp, capacities to 20 gph, pressures to 60 psi.

in variable speed stirrers: From 1/100 to 1/15 hp non-sparking motor with clamp or ring stand just right for **your** lab use.

LFE

EASTERN INDUSTRIES

A DIVISION OF LABORATORY FOR ELECTRONICS, INC.
100 SKIFF STREET • HAMDEN 14, CONNECTICUT

Circle No. 114 on Readers' Service Card

MANUFACTURERS' LITERATURE

X-Ray Analysis. A single sheet describes and illustrates the spectrodiffractometer. The instrument can be used for x-ray fluorescence or x-ray diffraction analysis without elaborate conversion times or realignments. Bulletin No. 1077. Picker X-Ray Corp., White Plains, N. Y. **601**

Power Supplies. High voltage power supplies including specifications and illustrations are covered in a 4-page bulletin. The instruments feature solid state circuitry and modular design. Radiation Instrument Development Laboratory, 4501 West North Ave., Melrose Park, Ill. **602**

Electronic Test Equipment. A 16-page short-form catalog gives descriptions of the company's complete line of laboratory test equipment. This includes recorders, a.c. and d.c. voltmeters, d.c. amplifiers, a.c./d.c. converters, log frequency/d.c. converters, and test calibration units. Houston Instrument Corp., 4950 Terminal Ave., Bellaire 101, Texas. **603**

Electronic Instruments. A 44-page catalog describes the company's full line of electronic instruments. Sections cover measurement of d.c. and a.c. voltage, d.c. current, low and high resistance, d.c. and a.c. amplification, d.c. high voltage supplies, nuclear instrumentation, and space instrumentation. Keithley Instruments, Inc., 12415 Euclid Ave., Cleveland 6, Ohio. **604**

Analytical Instruments. A 4-page catalog describes the following: Model 810 dual column flame ionization GC, Model 720 dual column programmed high temperature GC, Model 700 dual column isothermal GC, Model 770 automatic preparative GC, Model 180 carbon hydrogen nitrogen analyzer, Model 400 biomedical analyzer, Model 450 blood gas analyzer, and a line of accessories. F&M Scientific Corp., Avondale, Pa. **605**

Polarographic Analyzer. Bulletin GB1a describes the Mervyn Mark IV square wave polarographic analyzer. This is said to be the most sensitive polarographic analyzer available. Gulton Industries, Inc., 212 Durham Ave., Metuchen, N. J. **606**

Scientific Equipment. An 8-page condensed catalog illustrates and gives brief descriptions of the EM-20 electron microscope, electron optical systems,

automatic valving vacuum evaporators, other vacuum equipment, and the company's line of 0 to 90 kv. high voltage generators. Catalog C 100. Mikros, Inc., 7634 W. W. Capitol Highway, Portland 19, Ore. **607**

Gas Chromatograph. Bulletin F-11583 describes the Model 61C gas chromatograph and its use for the analysis of pesticides. The chromatograph features an electron attachment detector, and coiled glass-packed columns. Barber-Colman Co., Rockford, Ill. **608**

Ultraviolet in the Lab. A 4-page brochure illustrates the value of short-wave and long-wave ultraviolet in the laboratory for paper chromatography, photochemistry, fluorochemistry, and other applications. Bulletin No. 134. Ultra-Violet Products, Inc., San Gabriel, Calif. **609**

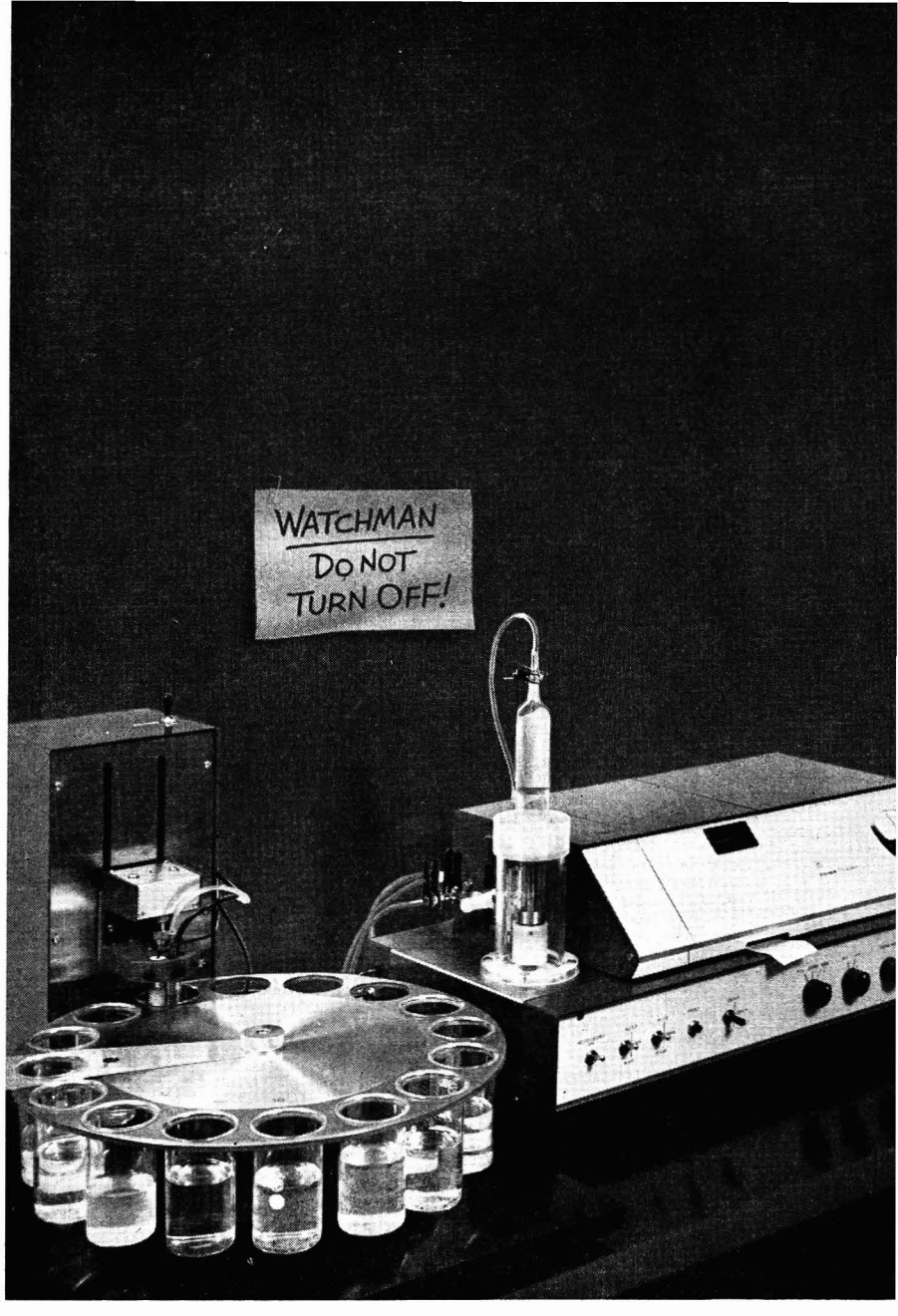
Direct Writing Recorders. A 4-page bulletin describes direct writing recorders. The systems record up to 8 channels of complex signals or more economical systems record up to 8 medium level signals. Single, two, and three channel recorders are illustrated and described. American Optical Co., Instrument Division Industrial Electronics, Buffalo 15, N. Y. **610**

Dual Column GC. A 4-page bulletin describes the Model 60-31, a gas chromatograph with dual system throughout—columns, injectors, detectors, and outlet collection ports. Specifications and illustrations of the instrument are included. Bulletin 3231 A. Research Specialties Co., 200 South Garrard Blvd., Richmond, Calif. **611**

Compact GC. Bulletin 3262, 4 pages, illustrates and describes the Model 62 gas chromatograph. The basic instrument has a hydrogen flame ionization detector, but a variety of accessories permits modifications. Research Specialties Co., 200 South Garrard Blvd., Richmond, Calif. **612**

Atomic Absorption Spectrometer. A 2-page bulletin describes the company's dual purpose spectrometer for flame and atomic absorption analysis. Bulletin 82-350. Jarrell-Ash Co., 26 Farwell St., Newtonville 60, Mass. **613**

Ion Beam Generator. A 4-page bulletin describes an ion beam generator for the production of steady, controllable beams of metal ions. Included are specifications, a schematic diagram, circuit diagram, and tables of typical operating conditions. Bulletin IGB-1. CBS Laboratories, High Ridge Rd., Stamford, Conn. **614**



STILL ON THE JOB even after the chemist has gone home. The new Fisher Titralyzer* will run up to 16 titrations and print out the results for him to pick up in the morning. The tape shows titrant volumes to the nearest 0.01 ml — higher precision than he can get manually with any but micro equipment. Any kind of repetitive potentiometric titration is handled with ease. Price: $2,750. Available under Fisher Financing Plan. **More details on Titralyzer** in Bulletin FS-245. Write Fisher Scientific Company, 100 Fisher Building, Pittsburgh 19, Pennsylvania.

* Fisher Scientific Company Trademark J-330

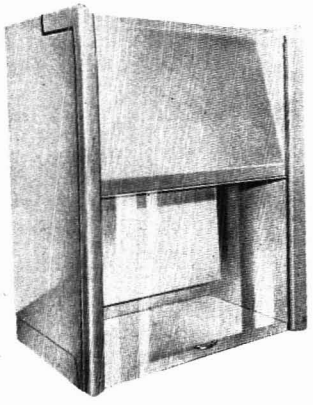
FISHER SCIENTIFIC

World's Largest Manufacturer-Distributor of Laboratory Appliances & Reagent Chemicals

Atlanta • Boston • Chicago • Fort Worth • Houston • New York • Philadelphia
Pittsburgh • St. Louis • Union, N. J. • Washington • Edmonton • Montreal • Toronto

Circle No. 45 on Readers' Service Card

New! Fiberglass "47" FUME HOOD



LAB CON CO Fiberglass "47" FUME HOOD in white, green or laboratory gray. Complete with motor, blower, sash, interior light..... **$495**

P-17 Fiberglass VENT ADAPTOR Converts rectangular blower outlet to round opening which will accept stack of 7" C.D..... **$9.75**

RUGGED! Special heat-resistant polyester and fiberglass with smooth, porcelain-like exterior. Resistant to chemical attack. Will not support combustion

HANDSOME! Smooth line design and special finish adds to the general appearance of your laboratory. Thin-wall design adds interior working space.

LIGHT! Superstructure is 47" × 29" × 60" high! Weight with blower only 175 pounds, making it a semiportable unit. Can be mounted on any conventional 47" base cabinet or table, wood or steel.

NON-CLOUDING SASH! Special, clear, resistant coating of ¼" Plexiglass sash prevents clouding. Operates smoothly on fine counterweight system.

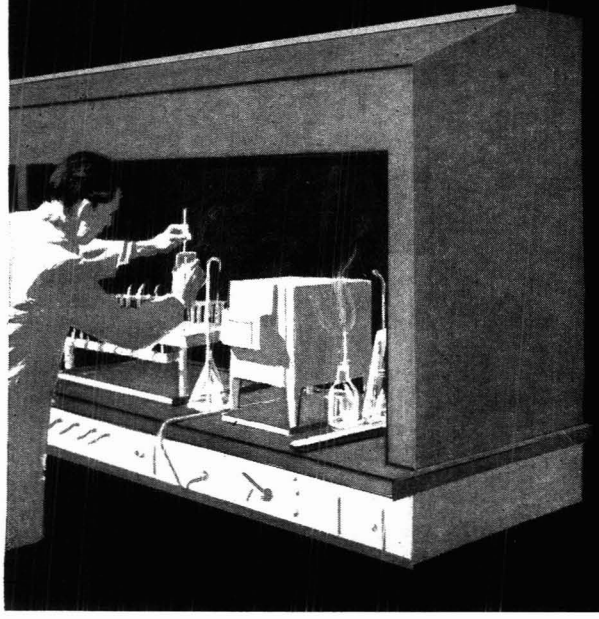
QUIET, HIDDEN BLOWER! Powered by ¼ h.p., 115-volt motor, delivers 515 c.f.m. at ¼" s.p. mounted in boxlike rear recess. All wiring to vapor-tight light and to blower molded into hood body and to panel switches.

READY TO USE! Single 6-foot cord and plug connects all electrical equipment to any convenience outlet. No electrician necessary. Normally your lab handyman can install it.

STANDARD SCIENTIFIC Supply Corp. 808 BROADWAY NEW YORK 3, N.Y.
LABORATORY APPARATUS REAGENTS AND CHEMICALS
75th Anniversary Year

Circle No. 86 on Readers' Service Card

Durable Alberene Stone fume hoods



for perchloric acid and other severe uses

ALBERENE STONE for 75 years the only permanently satisfactory material for chemical laboratory table tops, shelving, sinks, splash backs, drain boards and fume hoods. Prompt delivery. ALBERENE STONE – A DIVISION OF THE GEORGIA MARBLE COMPANY. For FREE literature and technical assistance address: THE ALBERMAR COMPANY, 386 PARK AVE. SOUTH, NEW YORK 16, N. Y., DEPT. C.

Circle No. 9 on Readers' Service Card

MANUFACTURERS' LITERATURE

The Hall Effect. A 23-page, small booklet titled "The Hall Effect and Its Applications" contains sections on history and theory, practical Hall Effect devices, and instructions for putting the Hall Effect to work. F. W. Bell, Inc., 1356 Norton Ave., Columbus 12, Ohio. **615**

Laboratory Equipment. A 44-page catalog includes illustrations, specifications, and application information on laboratory sinks and sink assemblies, service fixtures, fittings and accessories, table tops, reagent shelves, and pegboards. Metalab Equipment Co., 270 Duffy Ave., Hicksville, L. I., N. Y. **616**

Flame Ionization Detector. Bulletin F-11580, 2 pages, describes a high temperature flame detector for gas chromatographs. Barber-Colman, Rockford, Ill. **617**

Automatic Titrator. An 8-page bulletin describes the Titralyzer Automatic Titrator which can handle up to 16 samples per cycle and prints results to ±0.01 ml. Bulletin FS-230T. Fisher Scientific Co., 711 Forbes Ave., Pittsburgh 19, Pa. **618**

Flow Control. A 5-page bulletin describes a line of adjustable and fixed area cavitating venturis. These devices can be used as flow meters, flow regulators, or throttling valves. They are particularly suited for use with corrosive and difficult to handle liquids. Fox Valve Development Co., Inc., 84 Johnson Ave., Hackensack, N. J. **619**

8-Hydroxyquinolate Bibliography. A bibliography covering the precipitation of metal 8-hydroxyquinolates by precipitation from homogeneous solutions using the reagent 8-acetoxyquinoline is available. Burdick & Jackson Laboratories, 1953 S. Harvey St., Muskegon, Mich. **620**

Analytical Instrumentation. A 16-page brochure covers instrumentation and analytical testing services available from the company. Included are spectrograph power sources, spectrographs, spec scanners, sample holders, microphotometers, photographic processors, calculators, monitors, and the plasma arc. Also covered are the analytical services provided by the company. National Spectrographic Laboratories, Inc., 6300 Euclid Ave., Cleveland 3, Ohio. **621**

UV Microcells. A single sheet describes the UV-O cells, short path length UV microcells. The path length of these cells can be varied between 0 and 2 mm. Limit Research Corp., P. O. Box 852, Darien, Conn. **622**

GC Columns and Accessories. A 12-page catalog contains complete information and prices on the company's columns and accessories for gas chromatography. Over 180 different liquid phases, adsorbents, and column supports and 9 standard column packings are included. F & M Scientific Corp., Avondale, Pa. **623**

Plastic Labware. A 6-page brochure presents the latest in plastic laboratory ware. Brochure M-563. The Nalge Co., Inc., Rochester, N. Y. **624**

X-Y Recorders. An 8-page brochure gives specifications, pictures, and typical performance curves for the Model HR-95 and HR-97 X-Y recorders. Also included are descriptions of the converters and accessories for these recorders. Houston Instrument Corp., 4950 Terminal Ave., Bellaire 101, Texas. **625**

X-Y Recorder. A 4-page bulletin gives the specifications of the Model F-80 X-Y recorder. This is an all-transistorized instrument which has a range-to-range accuracy of 0.3% when switching attenuator and a reproducibility of 0.1%. Varian Associates, 611 Hansen Way, Palo Alto, Calif. **626**

Strip Chart Recorders. A detailed 6-page bulletin describes 12 JY Series of 5″ and 10″ potentiometric strip chart recorders. Applications, theory of operation, and comparisons with competitive models are discussed along with complete specifications. Bulletin JY100. Datapulse, Inc., 509 Hindry Ave., Inglewood 1, Calif. **627**

Analog and Event Recorders. A data sheet illustrates and explains Ana-Vent recorders. These instruments combine both analog data and event data on a single chart. Techni-Rite Electronics, Inc., 65 Centerville Rd., Warwick, R. I. **628**

Pulse Generator. A 4-page brochure describes the Model 106. This instrument offers linear, variable rise and fall times from less than 10 nanoseconds. The bulletin suggests applications and illustrates the unit's waveform capabilities with oscilloscope photos. Bulletin 106. Datapulse, Inc., 509 Hindry Ave., Inglewood 1, Calif. **629**

Electrophoresis Technique. A 20-page small-form manual, illustrated with photographs, charts, and diagrams, gives suggestions for electrophoresis of serum protein at room temperature, for staining, clearing, and scanning membranes, and for planimetric analysis of electrophoregrams. Manual 51199. Gelman Instrument Co., Chelsea, Mich. **630**

Company Periodicals

Requests for copies of the following publications, catalogs, etc., should be sent directly to the address shown. Business or professional letterheads are requested.

Scientific Apparatus and Methods. Vol. 12, No. 1. This 16-page issue features articles on the dual recording titrator as a pH-stat, the Leeds and Northrup pH meter, and the 1600 series of Micro-Tek gas chromatographs. Also included is a chart of equilibrium constants of inorganic compounds. E. H. Sargent & Co., 4647 West Foster Ave., Chicago 30, Ill.

Atomlight. No. 28. The May issue, 12 pages, contains an article on "Isotopic Methods for Steroids in Human Blood" and one on "Paired Labeling with I^{125} and I^{131}." This issue also announces price reductions on C^{14} and tritium labeled compounds. New England Nuclear Corp., 575 Albany St., Boston 18, Mass.

The INFOrmer. No. 1. This is the first issue of a new quarterly. The 4-page bulletin describes the company's CRS-20 chromatograph data processing system, the low-cost CRS-10 printing electronic digital integrator, and other analytical instruments. Infotronics Corp., 1401 South Post Oak Rd., Houston 27, Texas.

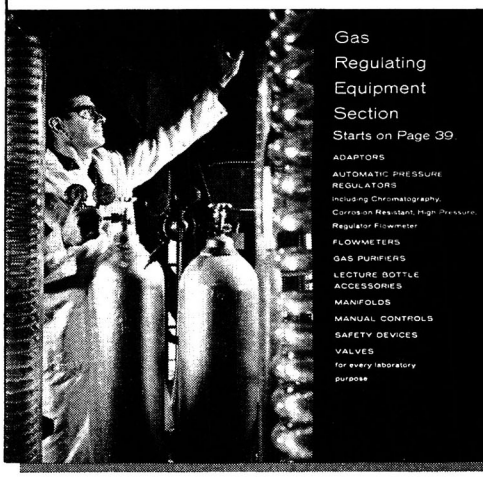
CIC Newsletter. No. 20. This 4-page issue describes the use of multiple reflection in attenuated total reflectance infrared analysis. Also, a new micro gas cell for Beckman IR-4, 7, and 9 spectrophotometers is illustrated and described. Connecticut Instrument Co., Wilton, Conn.

The Programmer. No. 1. This is the first issue of a publication devoted to gas chromatography instrumentation and procedures. The company's new instruments are described in this issue. F & M Scientific Corp., Avondale, Pa.

The Analyzer. The April issue, 18 pages, includes articles on computer control in an oil refinery, quality control using infrared, and gas chromatographic determination of blood gases. Scientific and Process Instruments Division, Beckman Instruments, Inc., Fullerton, Calif.

Gas-Chrom Newsletter. The June issue features a description of chromatograph modifications for improved steroid analysis, including provisions for sample injection directly into a glass column. Applied Science Laboratories, Inc., State College, Pa.

1963 / Matheson
Compressed Gases and Fluid Controls
The Matheson Company, Inc. / P.O. Box 85 / East Rutherford, N.J.
Area Code 201 933-2400 (In New York, Enterprise 6869) TWX-RFD 840
Joliet, Illinois / La Porte, Texas / Newark, California / Whitby, Ontario



It's the most complete catalog of compressed gases and accessories ever published . . . and we want to make sure a copy is available to everyone who might use compressed gases. If we've neglected to send your free copy, won't you please let us know, today? Thanks.

Now published in 4 regional editions, with prices and data on 95 Gases and Gas Mixtures and Regulating Equipment. Shipments from plants in East Rutherford, N. J.; Joliet, Ill.; La Porte, Texas; Newark, Calif.; Whitby, Ont.

The Matheson Company, Inc.
East Rutherford, N. J.
Please send your 1963 Compressed Gas Catalog

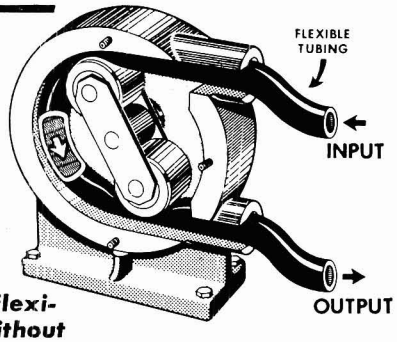
Name_____

Firm_____

Address_____

City_____

The Pump That *Never* Gets Wet



Fluids flow through a flexible tube without contacting the pump.

CAPACITIES UP TO 185 G.P.H.

RANDOLPH PUMP

For Literature and prices, write the
RANDOLPH CO.
1018 Rosine Street,
Houston 19, Texas
JAckson 6-2091

Circle No. 142 on Readers' Service Card

ANALYTICAL CHEMIST

An Important Appointment To Be Made At The Aerospace Research Center

Your interest is enlisted in a recently established scientific community entirely concerned with scientific and technical investigations; totally divorced from administrative or development duties.

Studies here are related as closely as possible to urgent needs of government agencies, determined through personal consultation with their representatives. Particular (but not exclusive) emphasis is placed on problems bearing on navigation, guidance and control of upper atmosphere and space vehicles. . .areas where General Precision has long held a leadership position in the development of systems and components.

One principal staff scientist now sought is an Analytical Chemist who will direct and coordinate the research activities of a modern instrumentation laboratory, organizing research programs in materials analysis and evaluation. Within this laboratory facility are analytical tools such as optical and emission spectrometers, mass spectrograph, grating spectrograph, x-ray diffraction and fluorescence equipment. Excellent opportunities to publish. PhD required.

We invite you to communicate directly with Dr. D. Grafstein, Principal Staff Scientist, Aerospace Research Center, 1150 McBride Avenue, Dept. 26-G, Little Falls, New Jersey.

GENERAL PRECISION AEROSPACE
GENERAL PRECISION, INC.

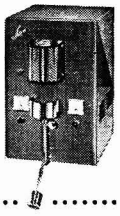
KEARFOTT DIVISION
GPL DIVISION
SYSTEMS DIVISION
RESEARCH CENTER

An Equal Opportunity Employer

Laboratory Furnaces

INDUCTION FURNACES

Temperatures above 3000°F. Ready for instant use at all times. Low operating cost. One and two tube models.



BOX FURNACES

Unique new features provide for operator safety and long element life. Temperatures up to 3000°F. Only $1595 with automatic temperature control.

COMBUSTION FURNACES

Longer element life. Easy maintenance. Many years of trouble-free operation. Temperatures up to 3000°F.

Other models of two and four tube combustion furnaces also available as standard items from the manufacturer of the most complete line of quality laboratory combustion furnaces in the world.

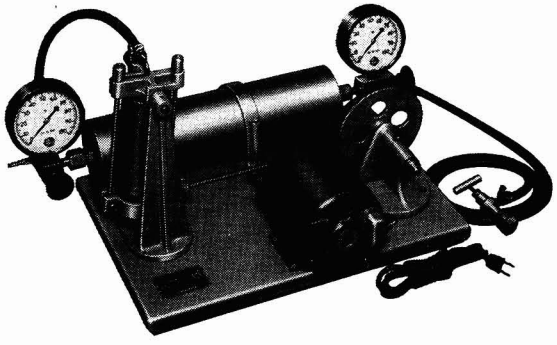
Write for Technical Bulletin

LABORATORY EQUIPMENT CORP.
3067 Hilltop Road St. Joseph, Michigan

Circle No. 62 on Readers' Service Card

Hydrogenation Apparatus

PARR Series 3910



For catalytic reduction, condensation and other reactions with hydrogen

Either 250 or 500 ml. glass bottles can be used in this sturdy shaker apparatus for reactions at pressures up to 5 atm. (60 psig.) New needle valves with replaceable plastic seats, separate gages to show tank and bottle pressures, and improved bearings in the shaker mechanism are provided. A larger unit with interchangeable 1 and 2 liter bottles is also available.

Ask for New Specification 3900

PARR INSTRUMENT COMPANY
211 Fifty-Third St. **Moline, Illinois**

Circle No. 74 on Readers' Service Card

For your convenience—short "refreshers" on last month's ads. Obtain free information on any of the products or services described by circling the corresponding key number in the "Product Capsules" portion of the reply card preceding this section.

Acids. Info on nitric, sulfuric, hydrochloric, and glacial acetic acids. **48**

Analyzers. Data on six-instrument materials evaluation system. **193**

Analyzers. Catalog on microprobe unit for sample areas from 1 to 200 microns. **204**

Analyzers. Details on 400 channel pulse height unit. **168**

Analyzers. Bulletin offered on carbon, hydrogen, nitrogen unit. **129**

Analyzers. IR moisture unit with built-in electronic calculator. **133**

Analyzers. Unit classifies 1000 particles in under 15 minutes. **124**

Analyzers. Bulletin on 400, 1024, and 4096 channel analyzers. **101**

Analyzers. Data sheet on light weight, portable moisture unit. **90**

Analyzers. Info on unit for high resolution microanalysis of amino acids. **176**

Analyzers. 512 channel pulse-height unit has built-in spectrum resolver. **200**

Analyzers. 18-page brochure on electron microbeam analyzer offered. **145**

Analyzers. Details on differential thermal unit. **56**

Analyzers. Info on 400 channel transistorized unit and accessories. **21**

Balances. Manual on deci-micro torsion unit with quartz flexure bearings. **126**

Balances. Analytical recording unit has built-in vacuum system. **34**

Balances. Info on unit with built-in calibrated ring weights. **92**

Balances. Catalog on complete line offered. **100**

Balances. Single pan unit has eye-level readout. **33**

Balances. Bulletin on compact units in all metal case. **32**

Balances. Single-pan unit has 1000 mg. optical range. **29**

Blenders. Unit pre-blends, disperses, granulates. **103**

Blenders. Unit has 15 amp, 3 speed motor. **5**

Blow Torches. Flameless unit for fast heat up to 1000° F. **8**

Bombs. Specs on line of oxygen bombs offered. **102**

Calorimeters. Info on differential scanning unit offered. **192**

Carts. 32-page brochure on new fiberglass cart offered. **84**

Catalyst Carriers. Test kit and brochure on inert crystalline materials. **52**

Cells. Info on line of glass absorption cells offered. **80**

Cells. Bulletin on UV microcells for highly absorbent samples. **156**

Centrifuges. Bulletin on automatic, reverse rotation unit. **25**

Centrifuges. Catalog on line of centrifuges and laboratory instruments. **167**

Centrifuges. 20-page product guide details complete line. **174**

Chemicals. Info on 500 page chemical materials catalog offered. **2**

Chemicals. Data on 5 organic research chemicals. **57**

Chloroform. Catalog details chloroform, acetone, and alcohol reagents. **109**

Chromatographs. 30-page "Comprehensive Bibliography of Thin Layer Chromatography" offered. **143**

Chromatographs. Info on easily assembled G.C. kit. **67**

Chromatographs. Data on line of G.C. instruments, accessories. **179**

Chromatographs. Dual column gas unit with temp. programmer accessory. **111**

Chromatographs. Bulletin on 50 different G.C. systems. **40**

Chromatography Accessories. Catalog on columns, adsorbents, etc. **136**

Conductivity Units. Info on conductivity bridges and cells offered. **74**

Controllers. Silicon controller rectifier has steel cabinet. **73**

Controllers. Bulletin on direct dial indicating temp. unit. **55**

Controllers. Info on temp. unit with pneumatic amplification. **128**

Counters. Two meter vacuum atom-counter analyzes iron and steel. **187**

Crystals. Data on optical crystal blanks and optical maser crystals. **9**

Densitometer. Details on new, recording unit for TLC. **106**

Detectors. 36-page booklet "Synthetic Optical Crystals," offered. **71**

Detectors. Bulletin on unit with d.c. or pulse power supply. **163**

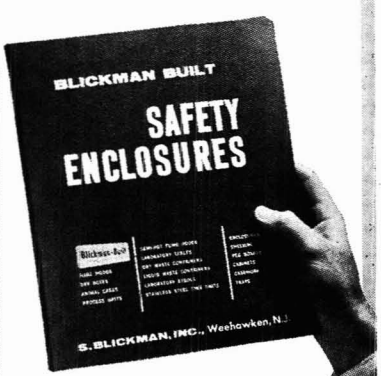
Detergents. Info on detergent for laboratory apparatus. **91**

Detergents. Test package offered on detergent for glassware and metal. **95**

Dichrographs. Unit has a variety of scan speeds and automatic slit control. **131**

(*Continued on page 120 A*)

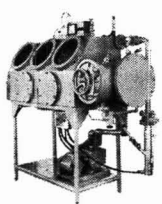
Valuable Reference



for Researchers Working with

- TOXIC CHEMICALS
- RADIOACTIVE MATERIALS
- CONTAMINANTS
- MIRACLE METALS

This new book is a comprehensive reference on safety enclosures for handling a wide variety of hazardous substances. Profusely illustrated, it contains detailed descriptions of regular and vacuum dry boxes, biological safety cabinets, fume hoods, pressurized enclosures, controlled-atmosphere boxes, waste containers, laboratory furniture and sinks, process units and unitized dry box systems. You'll find an enclosure to meet almost any contamination or safety problem. Send for your copy now.



VACUUM DRY BOX
For controlled-atmosphere work. Stainless steel. One of many safety enclosures described.

S. BLICKMAN, INC.
9607 Gregory Ave. • Weehawken, N. J.

☐ Please send book on safety enclosures
☐ Also send catalog on laboratory furniture

NAME_____
TITLE_____
COMPANY_____
ADDRESS_____
CITY_____ STATE_____

Blickman-Built *for Years of Reliable Service*

Circle No. 29 on Readers' Service Card

Product Capsules

Dilutors. Info on automatic, direct-reading unit for repeat dilutions. **113**

Dispensers. All plastic unit is resistant to corrosives. **162**

Distillation Columns. Info on spinning band units for high vacuum. **14**

Dryers. Data on new, mechanically refrigerated mobile freeze dryer. **119**

Dryers. New unit for air and gases has pressures to 90 p.s.i.g. **70**

Electrodes. Bulletin on complete line of pH electrodes. **140**

Electrodes. 6 inch long electrodes for direct reader spark analysis. **97**

Electrophoresis Units. Separates and elutes 20 protein fractions from serum in one column. **51**

Evaporators. Info on multiple vapor source vacuum coating units. **59**

Evaporators. Brochure on all glass and teflon rotary unit. **139**

Filter Paper. Catalog and samples of prefolded filter paper. **31**

Filter Paper. Info and samples of complete line offered. **172**

Filter Paper. Data on line of qualitative and quantitative filters. **190**

Filters. Application manuals on line of filters offered. **93**

Filters. Details on line of stainless steel filters offered. **99**

Fluorometers. Unit takes 16 readings in two minutes. **43**

Furnaces. Bulletin on unit with temp. range to 2800° F. **138**

Furnaces. Details on x-ray diffractometer unit. **175**

Furnaces. New casebook describes 60 furnace applications. **85**

Furnaces. New, 1600° C. unit heated by carbon or tungsten resistance. **127**

Furniture. Catalog on complete line offered. **27**

Gases. Details on certified calibration gases. **38**

G.C. Supports. Catalog on diatomaceous earth supports offered. **63**

Gels. Brochure on new gels for macromolecule separation. **105**

Glove Boxes. Plexiglas unit has 12-inch diameter side openings. **68**

Heating Units. Catalog of high frequency induction heating units. **87**

Heating Units. Single unit heating jacket has built-in controls. **201**

Hoods. 32-page brochure on two new fiberglass fume hoods. **83**

Hot Plates. 6 inch square unit heats to 700° F. **118**

Instruments. Bulletin on electrical measuring and calibrating units. **47**

Instruments. Data on line of x-ray and IR units. **198**

Integraters. Unit integrates a variable that has already been recorded. **112**

Interferometers. Catalog on high resolving power apparatus. **60**

Joints. Details on teflon joints for non-vacuum applications. **30**

Labels. Info on temp. resistant tapes and labels. **108**

Microscopes. Data on electron unit with 30,000x magnification. **61**

Microscopes. Electron unit with 600x to 200,000x magnification. **64**

Microscopes. Electron unit has new specimen chamber. **116**

Mixers. Data on unit for prolonged or rapid controlled mixing. **54**

Molecular Weight Apparatus. Bulletin details isothermal unit. **121**

Monitors. Info on refractive index monitor offered. **98**

Monitors. Portable moisture unit continuously measures gases. **24**

Monitors. Info on moisture unit for solids, liquids, gases. **23**

Mortars. Data on boron carbide mortar and pestle sets. **11**

Pellets. Info on P_2O_5 and other pellets available. **114**

pH Meters. Details on unit with no zero drift. **22**

pH Meters. Data on line of 6 meters and electrodes. **72**

Photometers. File on single light source unit for liquid streams analysis. **88**

Photometers. Bulletin on new flame unit offered. **150**

Photometers. Info on colorimeters and fluorimeters. **79**

Photometers. Brochure offered on new flame unit. **37**

Product Capsules

Pipets. Safety pipet filler holds liquids indefinitely. **153**

Polarographs. Low cost recording unit has 10" chart. **170**

Power Supplies. Unit has automatic safety control. **173**

Presses. Bulletin on 12 ton unit and guage. **53**

Presses. Bulletin on hydraulic unit with 20 ton capacity. **89**

Pumps. Data file offered on solution metering unit. **181**

Pumps. Folder on midget pumps and stirrers offered. **147**

Pumps. Info on ion and Ti sublimation unit. **18**

Pumps. Catalog offered on three stage mercury diffusion unit. **58**

Pycnometers. Data file on unit for surface active materials. **182**

Racks. Info on portable lab racks and carts. **202**

Radiochemicals. Bulletin details eight new carbon-14 compounds. **180**

Recorders. Details on 29 lb. unit with all-transistor circuitry. **184**

Recorders. Bulletin on unit with 250 mm. chart. **171**

Recorders. Brochure on multiple sample absorbance indicator-recorder. **66**

Recorders. Unit has adjustable zero and range. **19**

Recorders. Bulletin on unit which uses standard graph paper. **152**

Recorders. Unit has programmed printing and multispeed chart drive. **185**

Recorders. Data on unit with 12" chart. **12**

Recorders. Info on potentiometers for millivolt measurement. **94**

Refractometers. Direct reading unit requires minute samples. **36**

Refractometers. Catalog on complete line offered. **41**

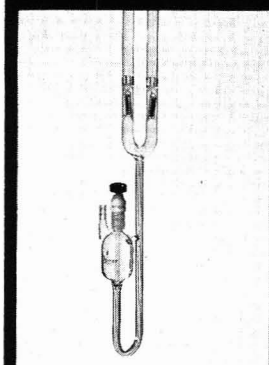
Resins. Reference chart on ion exchange resins offered. **65**

Rotameter Kits. Bulletin describes full line of laboratory kits. **50**

Scales. Catalog on complete line offered. **3**

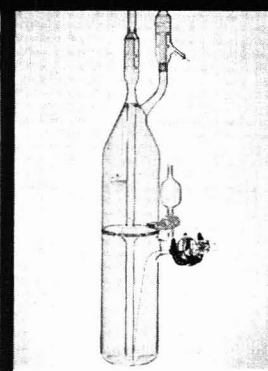
(Continued on page 122 A)

Delmar High Vacuum Equipment



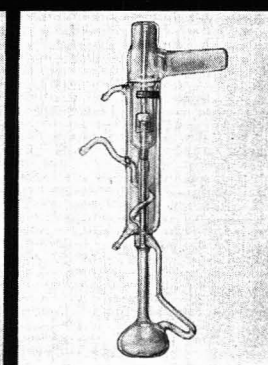
GREASELESS, MERCURY FLOAT VALVES

Utilizes a mercury sealed needle valve and dependable float plungers to prevent valve failure and leakage. 12 and 15 mm sizes.



TOEPLER PUMPS

New design offers advantages in cycling speed, positive closure, space saving and economy. 250, 500 and 1000 cc sizes. Relay control box available as accessory.



VAN HESPEN MERCURY DIFFUSION PUMPS

Attains pressures of 10^{-6} mm in a few minutes in systems up to 5 liters volume. Compact and economical. Available with inverted boiler tube and heater.

Delmar SCIENTIFIC LABORATORIES
317 MADISON ST., MAYWOOD, ILL.

WRITE FOR CATALOG 60D2A

A SUBSIDIARY OF COLEMAN INSTRUMENTS, INC.

Circle No. 113 on Readers' Service Card

GAS-CHROM NEWSLETTER

Vol. 4, No. 3 APPLIED SCIENCE LABORATORIES, INC. June 1963

Headlines From June 1963 Issue
New Products of Research at Applied Science

CYCLODEXTRIN STATIONARY PHASES
(According to Schlenk, et al;
Anal. Chem. Vol. 34, Pg. 1529 (1962)

COMPARISON OF ESTERIFICATION PROCEDURES
(BCl_3-Methanol vs. BF_3-Methanol)

NEW FATTY ACID STANDARDS
(C_{20} Saturates and Unsaturates)

CHROMATOGRAPH MODIFICATION FOR STEROID ANALYSIS

COLUMNS FOR ETHYLBENZINE-XYLENE ANALYSIS

Catalog Available — *"GAS CHROMATOGRAPHY SUPPLIES and FATTY ACID STANDARDS"*

Write for Your FREE Copy of The Complete Newsletter

APPLIED SCIENCE LABORATORIES, INC.
P. O. Box 140, State College, Pa.
Phone Area 814 ADams 8-2406

Circle No. 102 on Readers' Service Card

Product Capsules

Services. Info on radiochemical measurement service. **7**

Shakers. Bulletin details all-purpose, variable-speed unit. **137**

Solvent Bottles. New amber bottles available in 5 and 8 pint sizes. **39**

Spatulas. Info on line of micro and semi-micro spatulas. **196**

Spectro Accessories. Data on new micro-ATR accessory. **142**

Spectro Supplies. Catalog details metallic salts, electrodes, etc. **154**

Spectrofluorometers. Unit has two quartz monochromators. **125**

Spectrometers. Details on automatic liquid scintillation unit. **122**

Spectrometers. Info on time-of-flight mass unit. **46**

Spectrometers. Bulletin details multichannel flame unit. **155**

Spectrometers. Unit for nuclear magnetic resonance. **183**

Spectrophotometers. Specs on new atomic absorption unit. **104**

SARGENT
THERMONITOR® CONTROLLED
CONSTANT TEMPERATURE BATH

ALL-ELECTRONIC, NO CONTACT BREAKING • REGULATING ACCURACY, ±0.01 TO 0.001° C • SPACE UNIFORMITY, ±0.01° C • INSTANT CORRECTION OF AMBIENT CHANGES • FAST RECOVERY AFTER LOADING • TEMPERATURE REPRODUCIBLE BY DIAL SETTING TO 0.02° C • FULL VISIBILITY

Designed and Manufactured by E. H. Sargent & Co.

For complete information, write for Bulletin WB-1

SARGENT® SCIENTIFIC LABORATORY INSTRUMENTS • APPARATUS • SUPPLIES • CHEMICALS

E. H. SARGENT & CO., 4647 WEST FOSTER AVE., CHICAGO 30, ILLINOIS
DETROIT 4, MICH. • DALLAS 35, TEXAS • BIRMINGHAM 4, ALA. • SPRINGFIELD, N. J. • ANAHEIM, CALIF.

Circle No. 50 on Readers' Service Card

Spectrophotometers. Data file on continuous flow unit. **45**

Spectrophotometers. Bulletin on flame photometry unit. **161**

Spectrophotometers. Data file on UV unit. **44**

Spectrophotometers. Bulletin on direct reading, UV-VIS unit. **141**

Spectrophotometers. Info on double-beam unit. **132**

Spectrophotometers. Data file offered on unit and accessories. **134**

Spectrophotometers. Data file and sample spectra offered. **135**

Spectrophotometers. Details on new automated system. **197**

Spectrophotometers. Brochure and sample spectra on UV-VIS unit. **191**

Spectroscopic Instruments. Spectrophotofluorometer, monochromator. **194**

Standards. Info on line of primary standards offered. **189**

Stirrers. Data on line of light and heavy duty units. **165**

Stirrers. Bulletin on multiple-spindle magnetic unit. **4**

Stirrers. Catalog on line of 38 units offered. **1**

Stirrers. Info on immersible magnetic stirrers. **123**

Supplies. Catalog on line of laboratory supplies offered. **120**

Syringes. Info on syringe repair service. **69**

Thermometers. Unit has rotary setting magnet. **115**

Timers. "Guide to the correct selection of a timer or chromograph," offered. **10**

Trays. Catalog on polyethylene fabricated unbreakable trays. **26**

Tubes. Info on line of industrial tubes. **203**

Tube Fittings. Available in $^1/_{16}$" to 1" o.d. **15**

Ultrasonic Units. Details on high intensity sonic processor. **35**

Vacuum Units. Info on pumps, gauges, and valves. **78**

Viscometers. Brochure on line of nine units. **49**

(Continued on page 123 A)

Product Capsules

Voltmeters. Catalog on unit which measures .002 microvolts. **199**

Ware, Glass. Info on complete line offered. **157**

Ware, Glass. Catalog on greaseless, hi-vacuum glassware. **144**

Ware, Glass. Specs on line of fritted ware. **28**

Ware, Plastic. Info on polyethylene aspirator bottles. **96**

Ware, Quartz. 30-page catalog on line of fused quartz ware. **13**

Ware, Stone. Info on line of stone surface material. **17**

Washers. Data on washer-rinser unit for glassware. **81**

X-Ray Units. Details on x-ray diffraction units. **107**

X-Ray Units. Catalog on x-ray fluorescence and diffraction. **166**

Product Capsules

an AC service for subscribers

Presenting short "refreshers" on last month's ads in order to help you obtain free information of value to both you and your company. Simply circle corresponding key numbers in the "Product Capsules" portion of the reply card on page 98 B.

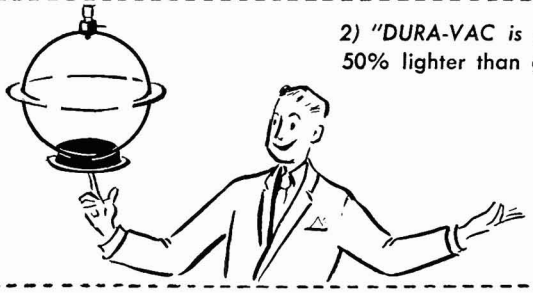
DURA-VAC®

PLASTIC DESICCATOR

COMBINES THE LIGHT WEIGHT, THE IMPACT AND SHATTER RESISTANCE OF PLASTIC WITH THE TRANSPARENCY OF GLASS.

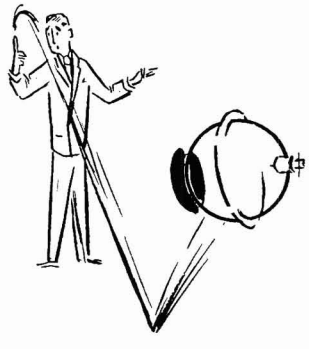
1) "DURA-VAC is transparent."
92% light transmission.

2) "DURA-VAC is featherweight."
50% lighter than glass.



3) "DURA-VAC is strong and safe."
Yes, DURA-VAC is strong and safe. It is extremely implosion resistant. You can even drop it and 99 times out of a 100, DURA-VAC will remain intact.

4, 5, 6) "DURA-VAC has other advantages":
The patented self-releasing lid does not stick, does not freeze to bottom during evacuation. DURA-VAC has a large working area: holds 2 lbs. of Drierite or similar material. DURA-VAC has a unique stopcock with upward vents that prevent returning air from disturbing contents.



® T.M. Ace Glass Incorporated

Find out all about DURA-VAC. Write Dept. A for Bulletins #5810 and #5815.

ACE GLASS INCORPORATED

Louisville, Ky., Vineland N. J. Springfield, Mass.

LABORATORY SUPPLY CENTER

INSTRUMENTS FOR LEASING

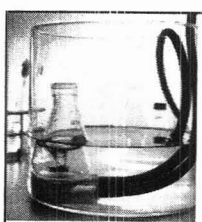
ANALYTICAL INSTRUMENTS YOU CAN LEASE

- Gas Chromatographs
- Spectrophotometers
- Special Instruments
- Instrument Accessories
- Instrument Building Blocks

Exactly the right instrument for your application . . . on the lease or lease/purchase plan that will best fit your budget or financial accounting requirements. For details, write to Instrument Division, Perkin-Elmer Corporation, 751 Main Ave., Norwalk, Conn.

PERKIN-ELMER

EQUIPMENT



BRONWILL MAG-JET...

The First Immersible Magnetic Stirrer

MAG-JET is a low cost magnetic stirrer that can be immersed with complete safety, in your own bath. Requires no electricity . . . operates on water pressure, air pressure or equivalent vacuum. **MAG-JET** is a compact, enclosed turbine, made of sturdy cast aluminum with an impeller that rides in jewelled bearings.

BRONWILL MAG-JET with stirring bar, Cat. No. 26-1 . . . . . $16.95 each (less 10% for 12 or more)

BRONWILL SCIENTIFIC
A DIVISION OF WILL SCIENTIFIC, INC.
2043 N. Goodman St., Rochester 1, N.Y.

MATERIALS

EASTERN—"A Source For All Seasons"

Acids: 4-Aminohippuric, Citraconic, 3,3-Dimethylglutaric, Mandelic & others.
Salts: Sodium Butyrate, Caprylate, Cinnamate, Dihydroxytartrate, Hippurate, β-Glycerophosphate, α-Naphthyl-phosphate, Rhodizonate, Thioglycolate.
Esters: Ethyl Crotonate, Furoate, Glycolate, α-Hydroxy-isobutyrate, Pyruvate.
Reagents: Tetraphenylarsonium Chloride, Toluene-3,4-dithiol, Phenol Red, Diphenylurea, Phenylthiourea, Phenylurea, Phenylurethan, N-Methylurea, C-Phenylglycine, N-Phenylglycine, 8-Chlorotheophylline, Reinecke Salt, Allylurea, Benzoic Anhydride, Bromocresol Purple, 1,4-Cyclohexanediol, Dimethylglyoxime, s-Diphenylcarbazone, 4-Hydroxybenzophenone.

Write for list K-63 of other organic chemicals
Tel: Code (201) 696-1700

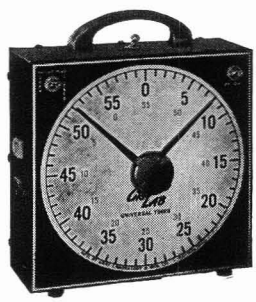
EASTERN CHEMICAL CORPORATION BOX K PEQUANNOCK, N. J.

1919—1963
LaMotte Chemical
Chestertown, Maryland U.S.A.
Specialists in
Colorimetric Techniques
Reagents—Standards—Comparators
Send for illustrated Controls Catalog
Dept. AC

YOUR ANNOUNCEMENT of Equipment or Chemicals for Sale and/or Wanted, and Professional Services, can carry YOUR MESSAGE to the readers of the leading work-magazine for instrumentation, control and analysis. *Rates on Request.*

ANALYTICAL CHEMISTRY
Advertising Office
430 Park Avenue New York 22, N. Y.

EQUIPMENT



ELECTRIC
LAB TIMER
Giant 8" Dial

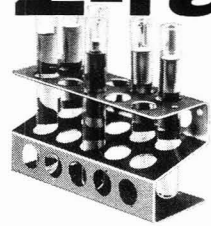
GRA-LAB INTERVAL TIMERS Automatic signalling and switching Various models, each with 3600 possible settings.

GRA-LAB MICRO TIMERS 1/10 sec. or 1/1000 min. stop clocks. Remote start stop control. Write for catalog.

DIMCO-GRAY COMPANY
210 E. SIXTH ST., DAYTON 2, OHIO

REFRACTOMETERS & RELATED PRODUCTS
Sales—Service—Repair
Send for our descriptive literature
VALENTINE INSTRUMENT COMPANY
2184 Primrose Ave., Vista, California
Tel: Area Code 714-727-0839

Z-rack!

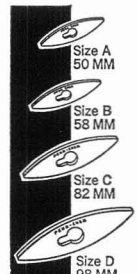


The ideal test tube rack

- one-piece stainless
- 11 Sizes — from micro tubes to 250 ml. bottles
- space-saving stacking

Available from your local dealer

MACALASTER
SCIENTIFIC CORPORATION
243 BROADWAY • CAMBRIDGE 39, MASSACHUSETTS



TEFLON®
STIRRING BLADES PAT PEND
STANDARD SIZES A, B, C, D.
This unique design removes the "flip-over" objection to other blades when stirring in round bottom flasks. Unbreakable, non-scratching. Can be used with any standard "button tip" stirring rod. A great time saver!
*DUPONT TRADEMARK

SIZE A	$1.65 each	12 for $17.80
SIZE B	$1.85 each	12 for $19.90
SIZE C	$2.10 each	12 for $22.60
SIZE D	$2.25 each	12 for $24.30

ASSORTMENT $20.75
3 of A, 4 of B, 3 of C and 2 of D

F.O.B. Lancaster, Pa., No C.O.D. Satisfaction guaranteed. Free Catalog.

Penn-Chem Corporation
BOX 58, LANCASTER, PA.

EQUIPMENT

SERVALL

THE WORLD'S FINEST
LABORATORY CENTRIFUGES
Refrigerated • Angle • Horizontal
Continuous Flow • Special Application
Low to Superspeed • Automatic • Manual
Small to Large Capacities

INSTRUMENTS
Ultra-Microtomes • Homogenizers
Cell Fractionators • Pipettes

FREE: 20 page Product Guide - write

Ivan Sorvall, Inc.
Pearl St., Norwalk, Conn.

MEL-TEMP® MEASURES CAPILLARY MELTING POINTS

- room temperature to 400°C
- 500°C with special thermometer
- rapid heating and cooling
- one to three samples

MEL-TEMP is an integrated capillary melting point apparatus whose heater is controlled by a variable transformer. Excellent viewing is provided by a built in light and a 6-power lens. The attractive gray hammertone base occupies 4" x 5".

only **$97.50** Includes vial m.p. capillaries and 0-400°C thermometer.
f.o.b. Cambridge

SPECIAL THERMOMETER
100-500°C in 1 C°, fits MEL-TEMP, borosilicate glass, Helium filled, 76 mm imm. $7.50 each

Pat'd. in U.S.A. and Canada

Write for Bulletin 60

LABORATORY DEVICES
P.O. BOX 68, CAMBRIDGE 39, MASS.

SPECIAL
LIGHT SOURCES
by GATES Sodium Lab. Arc

- Mercury Point Sources
- Sodium Vapor
- Mercury Vapor
- Raymaster Blacklight (long and short wave ultraviolet)
- Zirconium Concentrated Arc Lamps
- Imported Special Lamps
- Photochemical or High Intensity "Uviarcs"
- Auxiliary Operating Equipment for Above

Write for FREE Catalog or Contact your Laboratory Supply Dealer

GEORGE W. GATES & CO.
Box 216, Franklin Square, L. I., N. Y.

Your Professional Card can carry Your message to the readers of the leading work-magazine for instrumentation, control, and analysis. *Rates on Request.*

ANALYTICAL CHEMISTRY
Advertising Office:
430 Park Avenue New York 22, N. Y.

SERVICES

OXYGEN ANALYSIS

WITH GENERAL ATOMIC'S ACTIVATION ANALYSIS SERVICE

Analysis for oxygen is one of the many elemental analyses available at General Atomic on a routine basis. Neutron activation analysis is rapid, sensitive and economical. Typical price, about $20 per sample. For free 8-page brochure and information, contact Activation Analysis Service, AA18 General Atomic, P.O. Box 608, San Diego 12, Calif.

GENERAL DYNAMICS
GENERAL ATOMIC DIVISION

CLARK
MICROANALYTICAL LABORATORY
CH, N, S, Halogen, Fluorine, Oxygen, Alkoxyl, Alkimide, Acetyl, Terminal, Methyl, etc. by specialists in organic microchemical analysis.
Howard S. Clark, *Director*
P. O. Box 17, Urbana, Ill.—Telephone AREA 217 367-8406

AMINO ACID ANALYSIS
...of proteins, peptides, tissue extracts, foods, and physiological fluids by the Spackman, Moore, Stein ion-exchange method, using the latest Beckman-Spinco Analyzer.
Inquiries for rates and other details are invited

Oxford Laboratories®
Analytical Division
273 N. Bayshore Blvd.
San Mateo 4, Calif.

MASS SPECTROMETER SERVICE
PETROLEUM ANALYTICAL RESEARCH CORP.
P. O. Box 12334 Houston 17, Texas
Tel. Mission 9-2753

NMR ANALYTICAL SERVICE
- Qualitative Analysis
- Quantitative Analysis
- Process & Quality Control

NMR Specialties INC.
NMR-145 Greensburg Road, New Kensington, Pa.

Jarrell Ash
ANALYTICAL LABORATORY SERVICES
NEW LASER MICROPROBE NOW IN DAILY ANALYTICAL SERVICE FOR RAPID MICRO-ANALYSIS
JARRELL-ASH
26 Farwell St., Newtonville 60, Mass., DEcatur 2-2130

No. 21 in the ADVANCES IN CHEMISTRY SERIES

OZONE CHEMISTRY AND TECHNOLOGY

These 60 papers were presented at the International Ozone Conference in Chicago in 1956. This event marked the first occasion for an international exchange of information concerning ozone in both science and technology. It brought together men from leading companies, research institutes, and the National Science Foundation, differing widely in their reasons for interest in ozone but in a position to gain from a comparison of experience.

Major areas covered in their discussions were ozone chemistry . . . high concentration ozone . . . ozone technology . . . ozone analysis . . . organic chemistry . . . atmospheric ozone . . . ozone formation in electric discharge . . . ozone toxicity and sterilization . . . reaction kinetics . . . water purification.

Once primarily an important reagent of the organic chemist, ozone now claims the interest of meterologists, photochemists, organic and analytical chemists, and plant physiologists. This volume provides a focal point for varied approaches to its use and development.

465 pages. Cloth bound. Price: $7.00

Order from:
Special Issues Sales
American Chemical Society
1155 Sixteenth Street, N. W.
Washington 6, D. C.

ALPHABETICAL LIST OF ADVERTISERS

Ace Glass, Inc. 123
Heller Creative Advertising

Air Products and Chemicals, Inc. 56
Robert Conahay Inc.

The Alberene Co. 116
G. M. Basford Co.

Alconox, Inc. 88
Firestone Advertising Agency, Inc.

Allied Chemical Corporation, General Chemical Div. ..... OBC
Kastor, Hilton, Chesley, Clifford & Atherton, Inc.

Aloe Scientific Div. of Brunswick Corp. 22
Frank Block Associates

American Optical Co. 31
Gelia and Wells, Inc.

Analytical Chemistry 54-55

H. Reeve Angel & Co., Inc. .....
Eckstein-Stone, Inc.

Applied Physics Corp. 95:111
Charles Bowes Advertising, Inc.

Applied Science Laboratories, Inc. 121
Horace S. Hand Advertising, Inc.

Assembly Products, Inc. 58
Thomas R. Sundheim, Inc.

Baird-Atomic, Inc. 32
F. P. Walther Jr. and Associates, Inc.

J. T. Baker Chemical Co. 13C
Widrick & Miller, Inc.

Barber-Colman Co., Wheelco Instruments Div. 18
E. R. Hollingsworth & Associates, Inc.

Baush & Lomb, Inc. 70:103
Wolff Associates, Inc.

Beckman Instruments, Inc.
Scientific-Process Div. 97
Spinco Div. 77
Erwin Wasey, Ruthrauff & Ryan, Inc.

Bellco Glass Co. 68
John B. Ferguson Jr.

James G. Biddle Co. 58
The Roland G.E. Ullman Organization Inc.

Bio-Rad Laboratories 112
Cappel, Pera & Reid, Inc.

J. Bishop & Co. 74
Richardson, Thomas & Bushman, Inc.

S. Blickman, Inc. 120
J. M. Kesslinger & Associates

Brinkmann Instruments, Inc. 66:89
The Shaller-Rubin Co., Inc.

Bronwill Scientific, A Div. of Will Scientific 78
Wolff Associates, Inc.

Buchler Instruments, Inc. 38
Firestone Advertising Agency, Inc.

California Laboratory Equipment Co. . 44
Reynolds & Associates

Canal Industrial Corp. 12
G. Bruce West Advertising Agency, Inc.

Chemical Materials Catalog, Reinhold Publishing Corporation 112
Persons Advertising, Inc.

Clay-Adams 94
Cortez F. Enloe, Inc.

Coleman Instruments, Inc. 62:63:98B
Hollander Advertising Agency

Connecticut Instrument Corp. 84
Albert A. Kohler Co., Inc.

Consolidated Electrodynamics Corp. 52:53
Hixson & Jorgensen, Inc.

Coors Porcelain Co. 102
Tallant Yates Adv., Inc.

Delmar Scientific Laboratories 121
Hollander Advertising Agency

Harry W. Dietert Co. 107
Watkins-Rogers, Inc.

Disc Instruments, Inc. 5
Jay Chiat and Associates

Eastern Industries, Inc. 114
Herrick, Gibney, Hill, Inc.

Erb & Gray Scientific, Inc. 44
Hershberger Advertising

F & M Scientific Corp. 6
Richardson, Thomas & Bushman, Inc.

Farrand Optical Co., Inc. 106
Robert McAndrew

Fisher Scientific Corp. 67:115
Fuller & Smith & Ross, Inc.

General Electric Co., (X-Ray Dept.) .. 86
Klau-Van Pietersom-Dunlap, Inc.

General Precision Aerospace 118
Deutsch & Shea, Inc.

Gow-Mac Instrument Co. 109
George Homer Martin Associates

Hamilton Co., Inc. 61
Swain/Mealer, Inc.

W. A. Hammond Drierite Co. 74

Haws Drinking Faucet Co. 107
Pacific Advertising Staff

Gerald K. Heller Co. 92
R & L Advertising Agency, Inc.

Hofman Labs. 65

Houston Instrument Co. 88
Cooley & Pate, Inc.

Illinois Water Treatment Co. 80
Cummings, Brand, McPherson Associates, Inc.

Instrumentation Associates, Inc. 92
A. D. Norbeck Co., Inc.

Isomet Corp. 98C
Larry Alpaugh

Isotopes, Inc. 58:110
A. D. Norbeck Co., Inc.

Jarrell-Ash Co. 72
Andrews Associates

Kane Engineering Laboratories 38
G. Coakley & Co.

Kensington Scientific Corp. 64
Reynolds & Associates

Kewaunee Technical Furniture Co. 114
Phillipps Associates, Inc.

Klett Mfg. Co., Inc. 68:110

Koehler Instrument Co., Inc. 112

Kontes Glass Co. 37
Garceau, Hargrave & McCullough, Inc.

Lab Industries 92
Aardvark Advertising

Lab-Line Instruments, Inc., (Dynatronics Instr. Corp.) 98B
Caffe, Ltd.

Laboratory Construction Co. 76
Valentine-Radford, Inc.

Laboratory Equipment Corp. 118
Jones & Taylor, Inc.

Leeds & Northrup Co. 47
John B. Ferguson Jr.

Limit Research Corp. 86
Arthur B. W. Toft
William Hill Field Advertising

Lindberg Engineering Co., Div. of Basic Products Corp. 36
Klau-Van Pietersom-Dunlap, Inc.

Linde Co., Div. of Union Carbide Corp. 28
J. M. Mathes, Inc.

Loenco, Inc. 113
Writing & Advertising, Inc.

Manostat Corporation 1
Fairfax, Inc.

The Matheson Co., Inc. 43:117
Leonard M. Sive & Associates

Matheson, Coleman & Bell, Div. of the Matheson Co., Inc. 85
Leonard M. Sive & Associates

The Mettler Instrument Corp. 8
Harold Cressingham

Microchemical Specialties Co. 96
General Advertising Agency

Millipore Filter Corp. 112
Culver Advertising, Inc.

Mine and Smelter Supply Co. 70
Walter L. Schump Advertising

Mixing Equipment Co. 84
The Rumrill Co., Inc.

The Nalge Co., Inc. 29
Wolff Associates, Inc.

National Instrument Laboratories 64
Leni Ellinger Agency

Nester & Faust 127
Evans, Dill, and Company

Nikon, Inc. 60
Gilbert and Felix, Inc.

Nuclear-Chicago Corp. Texas Nuclear Corporation, Subsidiary 72
Sidney Clayton & Associates

Ohaus Scale Corp. 100
Robert M. Baldwin Co.

Owens-Illinois Consumer and Technical Products Div. (Formerly Kimble Glass Co.) 33
Meldrum and Fewsmith, Inc.

Packard Instrument Co., Inc. IBC:10
Ross Llewellyn, Inc.

Parr Instrument Co. 118
F. Willard Hills Adv. Service

Pennsylvania Fluorocarbon Co., Inc. .. 96
John B. Ferguson, Jr.

Perkin-Elmer Corp. 57:59
Gaynor & Ducas, Inc.

Philadelphia Laboratories 102
Lavenson Bureau of Advertising, Inc.

Philips Electronics, Inc. 17:69

Phoenix Precision Instrument, Inc. 36
Braun and Miller Advertising Agency

Photovolt Corp. 93
The M. B. Pearlman Co.

Picker X-Ray Corp. 7
Gotham-Vladimir Advertising, Inc.

Pilot Chemicals, Inc. 76
Larcom Randall Advertising, Inc.

Radiation Counter Laboratories, Inc. .. 40:71
James & Thomas

Radiation Instrument Development Laboratory, Inc. 46
Albert Jay Rosenthal & Co.

Randolph Company 118
Barlow/Gregg/George & Associates

Research Specialties Co. 14:34:79
Hoefer, Dieterich & Brown, Inc.

Rochester Scientific Co., Inc. 106

Sadtler Research Laboratories 20
The Roland G.E. Ullman Organization, Inc.

E. H. Sargent Co. 99:122
Fulton, Morrissey Co.

Scientific Glass Apparatus Co., Inc. .. 39

Scientific Industries, Inc. 58
Dan Jaffe Advertising, Inc.

Scientific Products, Div. of American Hospital Supply Corp. 75
Alex T. Franz, Inc.

Sigmamotor, Inc. 96
Gelia and Wells, Inc.

Ivan Sorvall, Inc. 45
Arthur B. W. Toft
William Hill Field Advertising

Spex Industries, Inc. 94
Seymour Nussenbaum

ALPHABETICAL LIST OF ADVERTISERS

Springer-Verlag 48
Standard Scientific Supply Corp. 116
Firestone Advertising Agency, Inc.
C. H. Stoelting Co. 92
Mandabach and Simms, Inc.

W. A. Taylor & Co. 94
Emery Advertising Corp.
Technical Measurement Corp. 90
Culver Advertising Agency, Inc.
Technicon Controls, Inc. 23
Mediad, Inc.
Texas Instruments, Inc. 35
Robinson-Gerrard-McGary, Inc.
Texas Nuclear Corporation Subsidiary of Nuclear Chicago Corp. 72
Sidney Clayton & Associates
Thermolyne Corp. 78
Howard H. Monk & Associates, Inc.
Thermovac Industries Corp. 56
M. B. Brucker Co., Inc.
Arthur H. Thomas Co. 98:98C
Torsion Balance Co. 19
Michel-Cather, Inc.

Ultra Carbon Corp. 24
Church and Guisewite Advertising, Inc.
U. S. Stoneware Co. 30
Ralph Gross, Inc.

Varian Associates 16:50:51:80:105
Hoefer, Dieterich & Brown, Inc.
The Victoreen Instrument Co. 87
Palm & Patterson, Inc.

The Welch Scientific Co. 104
Armstrong Advertising Agency, Inc.
The Welch Scientific Co. 65
H. A. Hooker Advertising Agency, Inc.
Weston Instruments 108
G. M. Basford Co.
Whitey Research Tool Co. 21
Falls Advertising Co.
Wild-Heerbrugg Instruments, Inc. 47
Duncan-Brooks, Inc.
Wilkens-Anderson Co. 83
Mandabach & Simms, Inc.

Carl Zeiss, Inc. 73
G. M. Basford Co.

Laboratory Supply Center 124-125

Bronwill Scientific, Div. of Will Scientific, Inc.
Clark Microanalytical Laboratory
Dimco-Gray Co.
Eastern Chemical Corp.
George W. Gates Co.
General Atomic Div. of General Dynamics Corp.
Jarrell-Ash Co.
Laboratory Devices
LaMotte Chemical Products Co.
Macalaster Scientific Corp.
NMR Specialties, Inc.
Oxford Laboratories
Penn-Chem Corp.
Perkin-Elmer Corp.
Petroleum Analytical Research Co.
Ivan Sorvall, Inc.
Valentine Instrument Co.

REINHOLD PUBLISHING CORPORATION

Advertising Management for the American Chemical Society Publications

430 Park Ave., New York 22, N. Y.

Cable Address: REINPUB NYK

SALES REPRESENTATIVES

Thomas N. J. Koerwer, Advertising Sales Manager

New York 22 . . . Sam W. Percy, J. Barry Stanford, Clay S. Holden, Reinhold Publishing Corp., 430 Park Ave., 212-688-8600

Chicago 2 . . . Eugene P. Eldridge, Reinhold Publishing Corp., 111 W. Washington St., 312-726-8497

Cleveland 14 . . . Rodney D. Long (Cleveland Manager, Reinhold Publishing Corp.), East-Ohio Bldg., 1717 East 9th St., 216-771-4011

San Francisco 5 . . . Morton McDonald, McDonald-Thompson, Inc., 625 Market St., 415-297-5377

Los Angeles 5 . . . George E. Halleman, Jr., McDonald-Thompson, Inc., 3727 W. 6th St., 213-387-5391

Seattle 4 . . . T. H. Abney, McDonald-Thompson, Inc., 1008 Western Ave., 206-623-3766

Portland 1 . . . Francis M. Eaton, McDonald-Thompson, Inc., 2035 S.W. 58th Avenue, 503-222-1546

Denver 3 . . . Robert H. Heidersbach, Mel G. Carlson, McDonald-Thompson, Inc., 840 Lincoln St., 303-825-3325

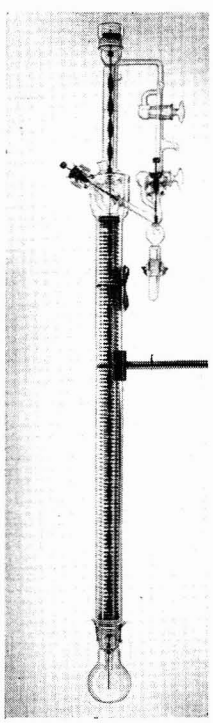
Houston 6 . . . Frank I. Vickrey, McDonald-Thompson, Inc., 3217 Montrose Blvd., 713-529-6711

Dallas 19 . . . C. Parker Harris, McDonald-Thompson, Inc., 2727 Oak Lawn Ave., 214-521-1266

Tulsa 14 . . . Max C. Nelson, McDonald-Thompson, Inc., 2570 South Harvard, 918-742-9961

Great Britain and Western Europe . . . Brayton Nichols, The American Magazine Group, 44 Conduit Street, London W. 1, England

Japan . . . Genzo Uchida, Bancho Koheki Co., Ltd., 5-5 Hayabusa-cho, Chiyoda-ku, Tokyo, Japan



NESTER SPINNING BAND DISTILLATION COLUMNS

An improved type for use under high vacuum . . . developed to meet the need for a laboratory still superior to conventional types in the fractionation of heat-sensitive or high-boiling, high viscosity liquids.

The columns contain spiral screen bands having 300 teeth per inch contacting the walls of the still. This construction provides violent agitation of the reflux liquid and gives intimate contact of descending and ascending vapors. The reflux ratio of the still is controlled by means of an adjustable needle valve eliminating the possibility of leakage.

• high fractionating efficiency • designed to operate at low pressures down to 10^{-5} mm Hg • free from leaks, contamination of stopcock lubricants, mechanical difficulties • extremely low tendency to flood • available in a variety of sizes of minimum cost.

for purchase or more information, call or write

nester / faust

2401 OGLETOWN RD.
NEWARK, DELAWARE

Circle No. 127 on Readers' Service Card

Future Articles

Listed below are papers to appear in forthcoming issues of Analytical Chemistry

---

A Simple Method for the Microdetermination of Boron, Alone or Simultaneously with Nitrogen and/or Phosphorus, in Organoboranes

R. C. Rittner and Robert Culmo

Determination of Submicrogram Quantities of Manganese, Sodium, and Copper in Natural Diamonds by Neutron Activation Analysis

E. C. Lightowlers

An Infrared Spectroscopic Study of the Integrated Area of the Methylene Rocking Band of Aliphatic Molecules

H. F. Smith and A. S. Rosenberg

Spectrophotometric Determination of Nitrate with 2,6-Xylenol Reagent

A. M. Hartley and R. I. Asai

Indirect Determination of Thorium with (Ethylene dinitrilo)tetraacetic Acid

D. R. Rogers and W. B. Brown

Gravimetric Determination of Germanium in Silicon-Germanium Alloys

K. L. Cheng and B. L. Goydish

Cyclic Chronopotentiometry, Diffusion Controlled Electrode Reaction of a Single Component System

H. B. Herman and A. J. Bard

Continuous Elemental Analysis of Gas Chromatographic Effluents: Application to the Analysis of Labeled Compounds

F. Cacace, Romano Cipollini, and Giorgio Perez

Rearrangement Technique for Analysis of Alkylbenzenes by Mass Spectrometry

E. W. Boyer, M. C. Hamming, and H. T. Ford

Coulostatic Anodic Stripping with a Mercury Electrode

Akiko Aramata and Paul Delahay

Identification of Triisobutylene and Tetraisobutylene Isomers by a Combination of Gas Chromatography and Nuclear Magnetic Resonance Techniques

S. A. Francis and E. D. Archer

Process Gas Chromatograph with Ultraviolet Detector

J. Merritt, F. Comendant, S. T. Abrams, and V. N. Smith

Spectrofluorometric Study of the Complexation of Indium Ion with 2-Methyl-8-quinolinol in Absolute Ethyl Alcohol

W. E. Ohnesorge

High Speed Controlled Potential Coulometry

A. J. Bard

New Microfluorometric Method for the Simultaneous Determination of Digitoxin and Digoxin

I. M. Jakovljevic

Estimation and Correction of Post-Column Dead Volume Effect in Chromatography

F. A. Vandenheuvel

Modifications in Mercury Porosimetry

L. K. Frevel and L. J. Kressley

O,O'-Dihydroxyazo Compounds as Fluorometric Reagents for Magnesium

Rodney Olsen and Harvey Diehl

Fluorometric and Spectrophotometric Determination of Magnesium with O,O'-Dihydroxyazobenzene

Harvey Diehl, Rodney Olsen, G. I. Spelholtz, and Richard Jensen

Determination of Alkoxy Groups in Alkoxysilanes by Acid-Catalyzed Acetylation

J. A. Magnuson

Effect of Adsorption and Electrode Oxidation on the Oxidation of Oxalic Acid at Platinum Electrodes

F. C. Anson and F. A. Schultz

Porous Glass as an Adsorption Medium for Gas Chromatography

H. L. MacDonell, J. M. Noonan, and J. P. Williams

Automatic Amperometric Measurement of Reaction Rates: Enzymatic Determination of Glucose in Serum, Plasma, and Whole Blood

H. L. Pardue

Controlled Pressure, Controlled Atmosphere Thermogravimetry with a Conventional Null-Type Recording Balance

B. G. Hurd

The Brown Front in Paper Chromatography

R. A. Schwane and G. N. Kowkabany

Separation of Titanium by Cation Exchange and Its Spectrophotometric Determination with Disodium-1,2-dihydroxybenzene-3,5-disulfonate

B. T. Kenna and F. J. Conrad

Dicesium Plutonium Hexachloride, a Proposed Primary Standard for Plutonium

F. J. Miner, R. P. DeGrazio, and J. T. Byrne

Microactivation Analysis for Oxygen in the Actinide Metals

A. C. Demildt

Quantitative Analysis of Submicrogram Amounts of High Boiling Compounds by Flame Ionization Gas Liquid Chromatography

F. A. Vandenheuvel

Acid-Base Equilibria in Tertiary Butyl Alcohol

Leland Marple and J. S. Fritz

A Separation of Titanium from Rare Earths, Beryllium, Niobium, Iron, Aluminum, Thorium, Magnesium, Manganese, and Other Elements by Cation Exchange Chromatography

F. W. E. Strelow

Volumetric Determination of Concentrations of Sulfuryl Fluoride in Air

S. G. Heuser

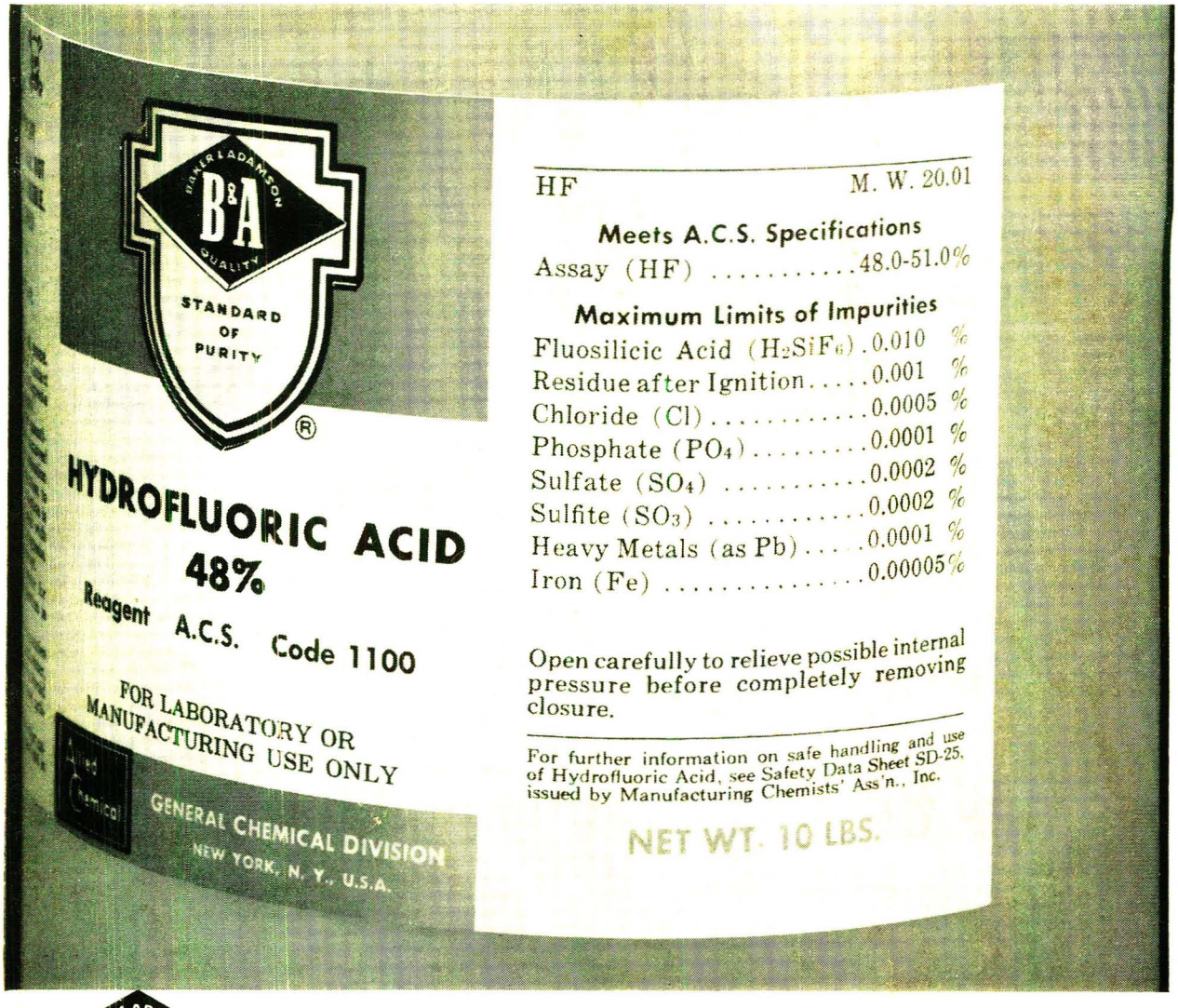
Flame Spectrophotometric Determination of Cesium and Rubidium in Oilfield Waters

A. G. Collins

Use of Phosgene in the Determination of Hydroxyl Groups in Polymers

D. G. Bush, L. J. Kunzelsauer, and S. H. Merrill

Circle No. 73 on Readers' Service Card ⟶



BAKER & ADAMSON B&A QUALITY ®

REAGENTS AND "C.P." ACIDS *are the purest you can buy*

The label is your guarantee

When you buy B&A® Reagents and Acids, you're getting the highest purity available. Purity that meets or exceeds A.C.S. requirements. Purity that meets tight, *predetermined* specifications batch after batch.

Can you get what you need from B&A? Most likely. We offer you more than 1000 products. In quantities ranging from quarter-pound bottles to carload lots.

Can you get fast delivery? Absolutely! There are 20 B&A stock points in the U.S. and Canada. B&A products are also distributed by leading laboratory supply houses. You can usually figure on delivery within 24 hours.

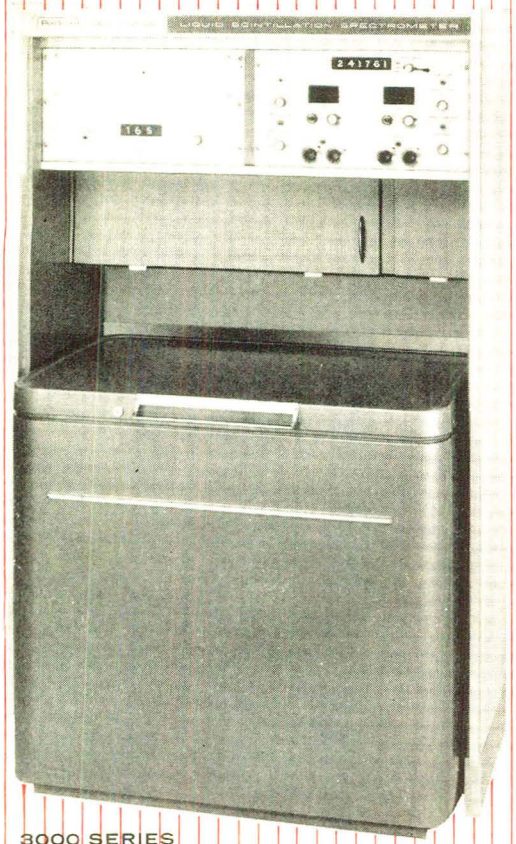
Want information on quantities, packaging and prices? Call or write your nearest Baker & Adamson sales office.

BAKER & ADAMSON®
Setting the Pace in Chemical Purity Since 1882

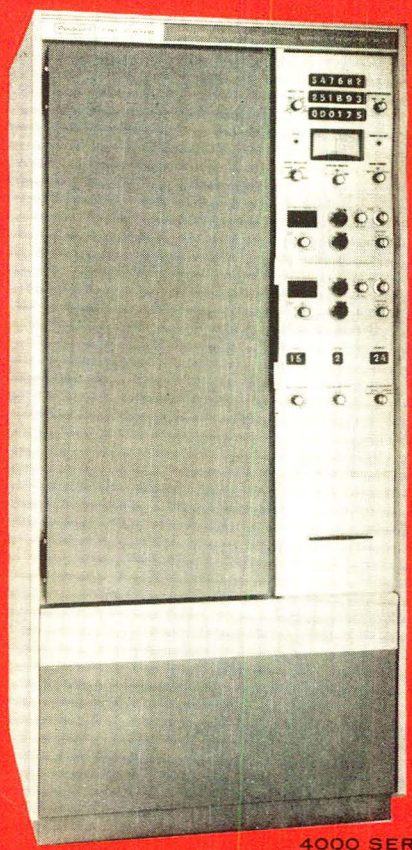
Allied Chemical

GENERAL CHEMICAL DIVISION
P.O. Box 353, Morristown, N.J.

Circle No. 23 on Readers' Service Card



3000 SERIES



4000 SERIES

THIS IS THE SHAPE OF MODERN TRI-CARB® LIQUID SCINTILLATION SPECTROMETERS

Here—in two entirely new series of instruments—are the most advanced liquid scintillation counting systems ever made. Series 3000 and 4000 TRI-CARB Spectrometers incorporate greatly improved optical, electronic, and mechanical components to provide research workers counting alpha, beta, and gamma-emitting isotopes with the ultimate in quality, reliability, and user convenience.

Significant improvements in both series include: a new concept in detector and shielding design; matched 13-stage photomultiplier tubes; built-in automatic background subtraction; completely new, high speed solid-state circuitry designed for maximum linearity and stability; fast, serial entry printout compatible with modern data processing systems.

SPECIFIC FEATURES OF EACH SERIES:

3000 SERIES Manual, semi-automatic, or automatic (200 sample capacity) operation; 1, 2, or 3 channels; mobile room temperature or temperature controlled console; optional data printer or printing calculator.

4000 SERIES Completely automatic; 2 or 3 channels; revolutionary sample changer handles complete trays of samples instead of individual vials. As many as 15 trays, each holding 24 samples can be loaded into changer for automatic counting. Program may be interrupted at any time for special tray counts. Optional data printer or printing calculator.

For complete details, call your Packard Sales Engineer, or write for Bulletins.

Packard

PACKARD INSTRUMENT COMPANY, INC.

BOX 428 • LA GRANGE, ILLINOIS • AREA CODE 312 • 485-6330

Circle No. 73 on Readers' Service Card