AUGUST 1965

ANALYTICAL CHEMISTRY

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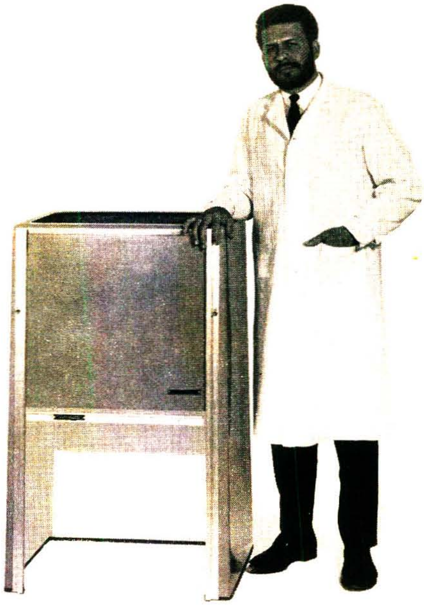

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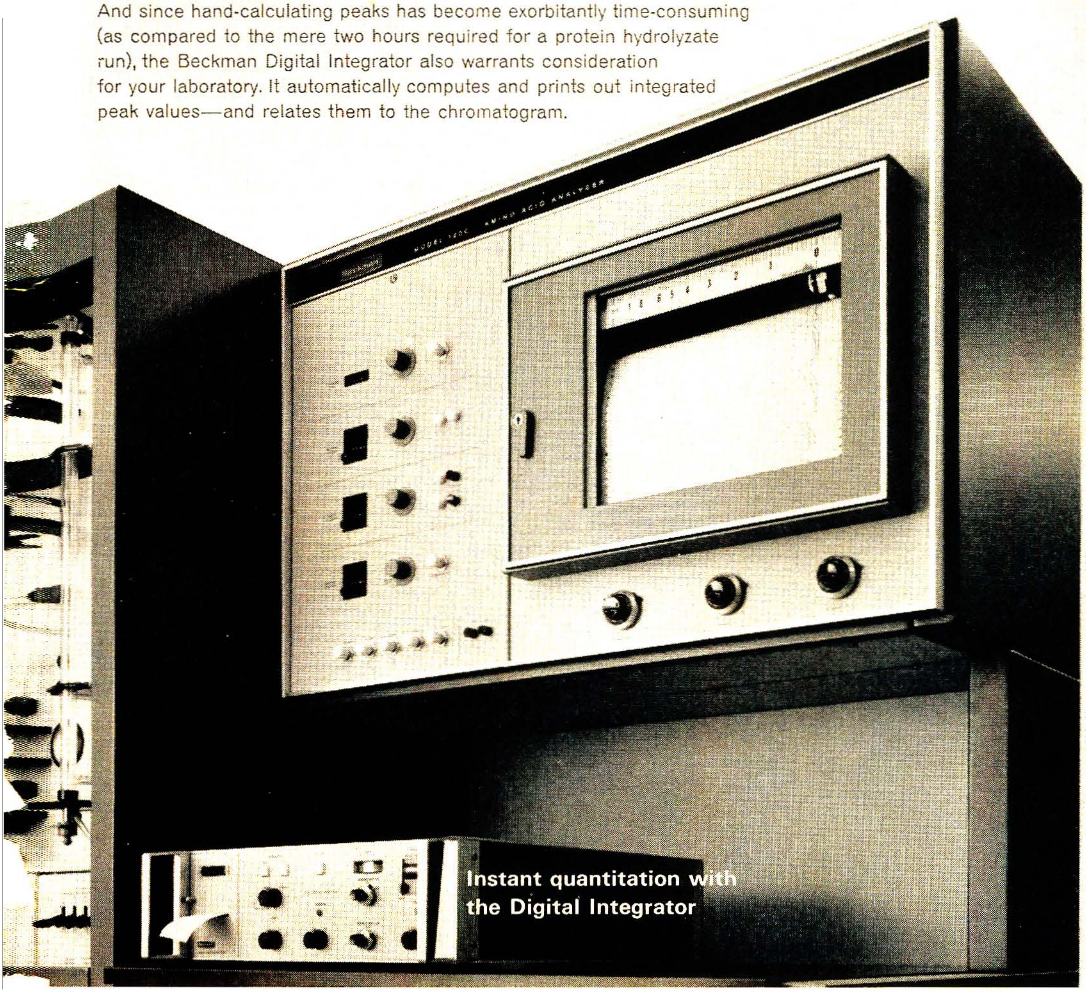

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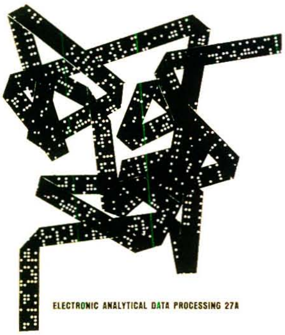
VOLUME 37, NO. 9 AUGUST 1965

ANALYTICAL CHEMISTRY



The cover design is related to the subject of this month's Report for Analytical Chemists: the application of electronic data processing principles to analytical data. See page 27 A.

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Issued July 22, 1965

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CONTENTS

REPORT FOR ANALYTICAL CHEMISTS

The rapid and accurate handling of large volumes of analytical data can be achieved by the application of electronic data processing principles to analytical data. An operable system is described in this month's Report for Analytical Chemists............ **27 A**

NEWS SECTION

The detailed technical programs of the Analytical Division, ACS Meeting, Sept. 12 to 17, and the Third International Gas Chromatography Symposium, Oct. 18 to 21, are given.......... **39 A**

EDITOR'S COLUMN

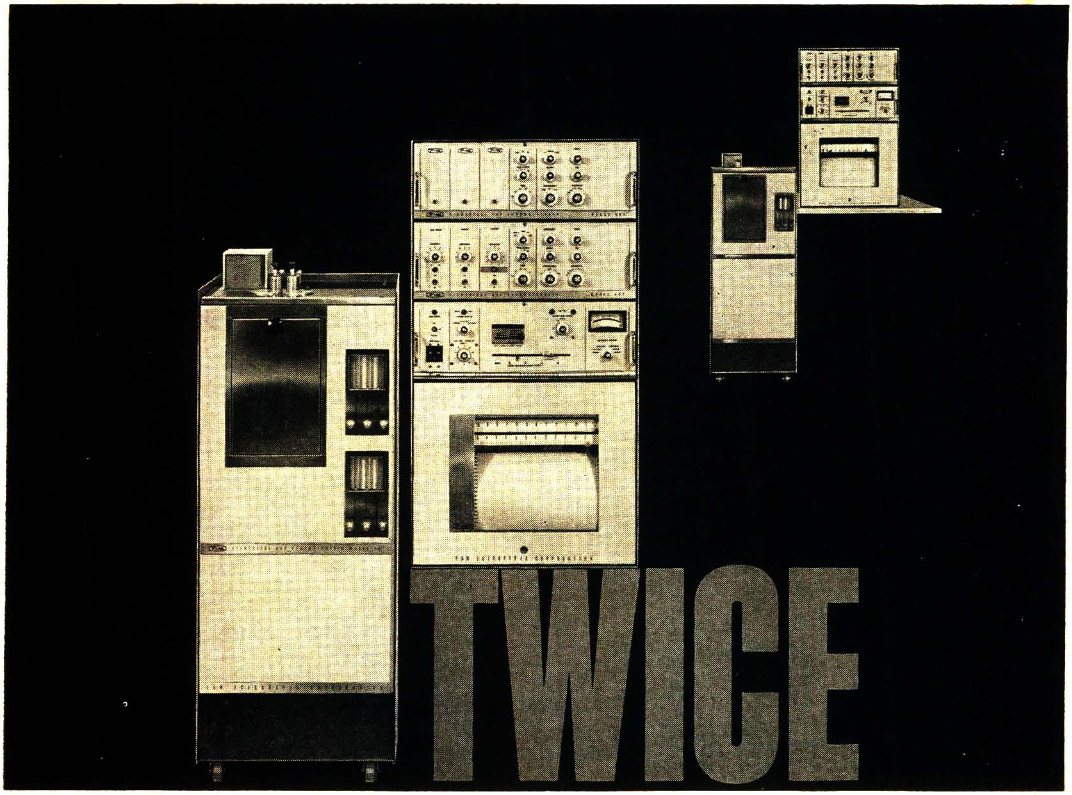
The importance of analytical chemistry in the establishment of tolerance levels for chemical pesticides is discussed......... **71 A**

LABORATORY OF THE MONTH

In an effort to bring readers up to date on equipment and instruments used in academic studies, a laboratory designed for research by undergraduate students is featured.................... **79 A**

INSTRUMENTATION

Dr. Müller is reminded by some recent publications of various fundamental principles of physics and work that was done years ago .... **87 A**



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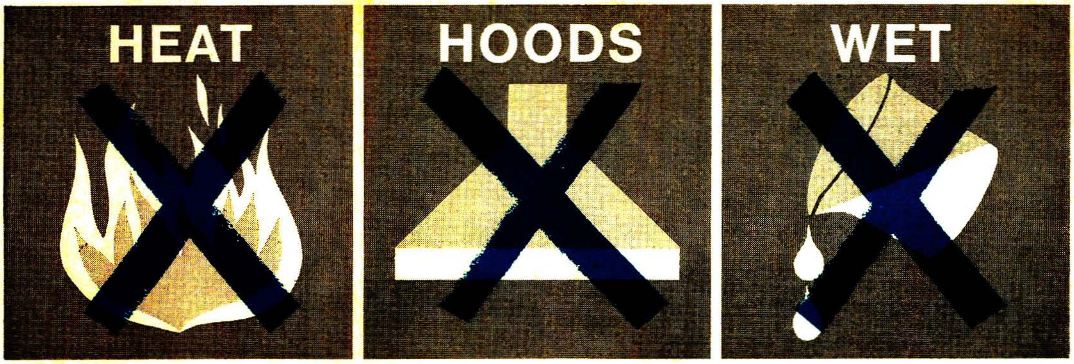

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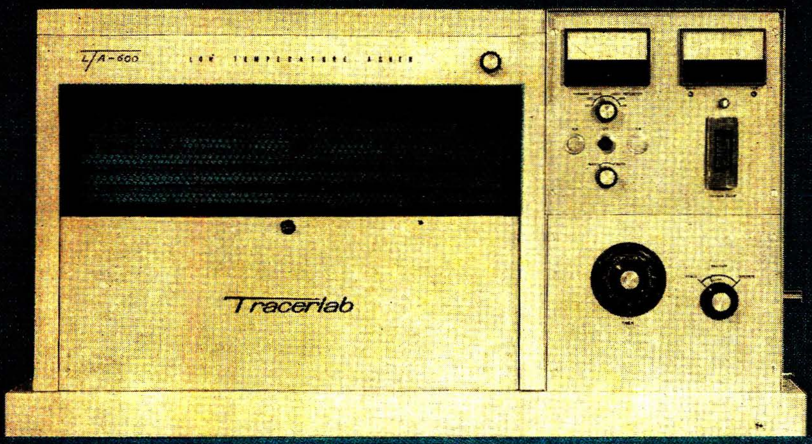

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AC BRIEFS

Highlights of the scientific and technical articles in this issue

A Stepwise Regression Program for Quantitative Interpretation of Mass Spectra

Basis of the program is a mathematical method of choosing from among a library of spectra a suitable small group of spectra such that the sum of the individual spectra after multiplying by the proper concentration factors gives the best least squares fit to the sample spectrum.

D. D. TUNNICLIFF and P. A. WADSWORTH, Shell Development Co., Emeryville, Calif.

Anal. Chem. 37, 1082 (1965)

Reactor Neutron Activation Analysis by the Single Comparator Method

The use of a single comparator (cobalt) instead of standards prepared from known weights of the elements to be determined was evaluated. Accuracy and precision were found to be similar to those of the relative method.

FRANCESCO GIRARDI, GIAMPAOLO GUZZI, and JULES PAULY, Servizio Chimica Nucleare, Centro Comune di Ricerche, Euratom, Ispra, Varese, Italy

Anal. Chem. 37, 1085 (1965)

Determination of Oxalate in Beer by Cerate Oxidimetry and the Application of Isotopically-Derived Correction Factor

Oxalic-C^{14} is used to establish the best conditions for the precipitation of calcium oxalate. A correction factor is obtained to calculate for the unprecipitated oxalate. With the described procedure, oxalate can be determined with an accuracy of ±0.5 mg. per liter.

GILBERT H. KOCH, Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wis., and F. M. STRONG Department of Biochemistry, University of Wisconsin, Madison, Wis.

Anal. Chem. 37, 1092 (1965)

Spectrophotometric Determination of Vanadium(V) with 6-Hydroxy-1,7-Phenanthroline

After development in aqueous solution containing 40% 1,2-propanediol, the colored complex is extracted into benzene for measurement at 480 $m\mu$. Interferences are reported.

J. A. DOUGHERTY and M. G. MELLON, Purdue University, Lafayette, Ind.

Anal. Chem. 37, 1096 (1965)

Mass Analysis of Subnanogram Quantities of Iodine

Negative iodine ions are generated in the source through bombardment of an iodine sample with an energetic positive gas-ion beam. Secondary negative ions are accelerated, mass analyzed, and detected. The lower limit of detection of an iodine isotope is shown to be 10^{-13} gram.

J. A. McHUGH and J. C. SHEFFIELD, General Electric Co., Schenectady, N. Y.

Anal. Chem. 37, 1099 (1965)

Pulse Polarographic Determination of Nickel and Vanadium

The procedure is applied to petroleum stocks containing 0.5 to 50 p.p.m. of either metal. Both metals are determined from one pulse polarogram reducing the time necessary for the analyses.

D. D. GILBERT, California Research Corp., Richmond, Calif.

Anal. Chem. 37, 1102 (1965)

Tracer Techniques in Sulfur Dioxide–Air Pollution Studies. Apparatus and Studies of Sulfur Dioxide Colorimetric and Conductometric Methods

Sulfur dioxide tagged with S^{35} was followed from its original pure state to its mixture at high dilution in purified air, to the sampling medium, and finally to the quantitation step, and was measured by proportional tube counting and scintillation solution counting techniques.

PAUL URONE, JAMES B. EVANS, and CLAUDIA M. NOYES, Department of Chemistry, University of Colorado, Boulder, Colo.

Anal. Chem. 37, 1104 (1965)

Accelerated Automatic Chromatographic Analysis of Amino Acids on a Spherical Resin

Acidic and neutral amino acids are analyzed on a 57- by 0.90-cm. resin column at a buffer volumetric input of 68 ml./hour (linear flow rate of 106 cm./hour). Basic amino acids are analyzed on a 5.0 by 0.90-cm. resin column at the same flow rate. Total analysis time is 4 hours, 5 minutes.

JAMES V. BENSON, JR., and JAMES A. PATTERSON, Beckman Instruments, Inc., Palo Alto, Calif.

Anal. Chem. 37, 1108 (1965)

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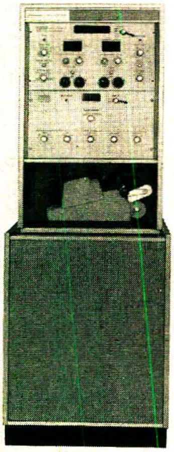
What are your requirements for liquid scintillation counting ?



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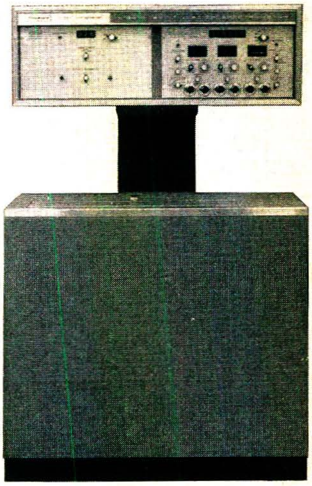

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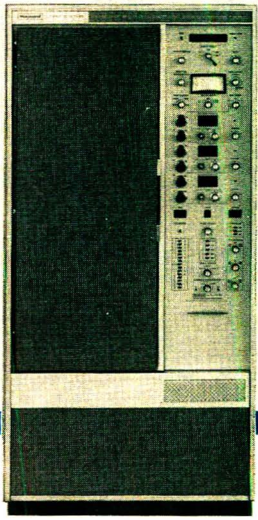

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Ion Exchange Separation of Americium and Cerium

Tracer amounts of americium are separated quantitatively from 30 mg. of cerium using Dowex 50W X12 ion-exchange resin and ammonium lactate as the eluant.

HAZEL D. PERDUE and HARRY G. HICKS, Lawrence Radiation Laboratory, University of California, Livermore, Calif.

Anal. Chem. 37, 1110 (1965)

Determination of Strontium in Environmental Media Using Neutron Activation

The method simplifies the comparator technique of activation analysis by mixing a monitor homogeneously with the sample. Prior to addition of the monitor (copper) and irradiation, the strontium is separated from the sample by oxalate and nitrate precipitations using the Ca in the sample as a carrier.

PAUL J. MAGNO and FORREST E. KNOWLES, JR., U. S. Department of Health, Education, and Welfare, Northeastern Radiological Health Laboratory, Winchester, Mass.

Anal. Chem. 37, 1112 (1965)

Determination of Mixtures of Hydrazine and Monomethylhydrazine by Reaction with Salicylaldehyde

The reaction takes place in the presence of an excess of perchloric acid. The perchloric acid neutralized by the sample is a direct measure of monomethylhydrazine. The hydrazine content is then determined by difference from a total base titration.

NICHOLAS M. SERENCHA, J. GORDON HANNA, and EDWARD J. KUCHAR, Olin Mathieson Chemical Corp., 275 Winchester Ave., New Haven 4, Conn.

Anal. Chem. 37, 1116 (1965)

Separation of Protium and Deuterium Forms of Carbohydrates by Gas Chromatography

Gas-liquid chromatographic columns with efficiencies of from 40,000 to 60,000 plates are used to completely separate glucose and glucose-d_7 and partially separate other carbohydrates.

RONALD BENTLEY, NRIPENDRA C. SAHA, and CHARLES C. SWEELEY, Department of Biochemistry and Nutrition, Graduate School of Public Health, University of Pittsburgh, Pittsburgh, Pa.

Anal. Chem. 37, 1118 (1965)

Use of Binomial Probability Distribution Tables for Calculation of Withdrawn Series of Countercurrent Distribution

The relationship between the Pascal and the binomial distribution and how the binomial probability distribution tables can be used for the calculation of the distribution of solute in a withdrawn series are discussed.

S. B. GHOSH, L. J. SCHAAD, and M. T. BUSH, Vanderbilt University, Nashville, Tenn.

Anal. Chem. 37, 1122 (1965)

Fluorometric Microdetermination of Heme Protein

As little as 0.01 μg. of heme protein in animal tissue is determined by conversion to the fluorescent porphyrin derivative by incubation with oxalic acid. The relative standard deviation is about 2%.

GEORGE R. MORRISON, Department of Preventive Medicine, Washington University School of Medicine, St. Louis, Mo.

Anal. Chem. 37, 1124 (1965)

Application of Lithium-Drifted Germanium Gamma-Ray Detectors to Neutron Activation Analysis. Nondestructive Analysis of Aluminum

Concentrations in p.p.m. of Mn, Sc, Hf, and Cr are determined in 99.9999% aluminum. The method is compared to other nondestructive analytical methods.

S. G. PRUSSIN, J. A. HARRIS, and J. M. HOLLANDER, Lawrence Radiation Laboratory, University of California, Berkeley, Calif.

Anal. Chem. 37, 1127 (1965)

Application of Anodic Dissolution Technique to Automated Analysis of Metals. Determination of Phosphorus in Copper

Rapid anodic dissolution is fully integrated with a color development procedure that has been time-optimized to be completed in 1 minute and 50 seconds. Total analysis time is 3 minutes.

SILVIO BARABAS and SYDNEY G. LEA, Noranda Research Centre, Pointe Claire, Quebec, Canada

Anal. Chem. 37, 1132 (1965)

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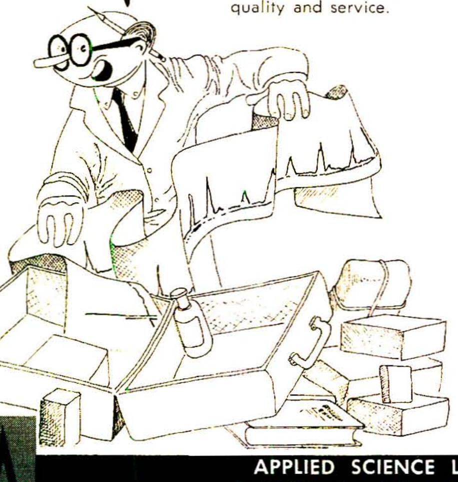

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Solvent Extraction of Metal Ions with Trifluoroacetylacetone

Cu, Fe, and Al can be effectively extracted from aqueous media (acetate-buffered) with chloroform which is 0.10*M* with respect to trifluoroacetylacetone. Graphs are given which show the pH range over which a metal or groups of metals will be quantitatively extracted from the system.

W. G. SCRIBNER, W. J. TREAT, and J. D. WEIS, Dayton Laboratory, Monsanto Research Corp., Dayton, Ohio 45407, and R. W. MOSHIER Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio

Anal. Chem. 37, 1136 (1965)

Variable Angle Reflection Attachment for the Ultraviolet, Visible, and Infrared

The attachment can be used to obtain attenuated total reflection spectra, to obtain indices of refraction by measurements of reflectivity at angles less than the critical angle or by the critical angle method itself.

WILFORD N. HANSEN, North American Aviation Science Center, Thousand Oaks, Calif. 91360

Anal. Chem. 37, 1142 (1965)

Radio Release Determination of Dichromate Ion in Natural Waters

The method is based on reacting the acidified sample with radioactive silver. Limit of sensitivity is 10 μg. of Cr(VI) per liter.

HAROLD G. RICHTER and ARTHUR S. GILLESPIE, JR., The Research Triangle Institute, Durham, N. C.

Anal. Chem. 37, 1146 (1965)

Solvent Extraction Studies with a Hydrochloric Acid–2-Ethylhexanol System

The distribution of 45 elements between 83% 2-ethylhexanol–17% petroleum ether and hydrochloric acid solutions are reported. A number of applications of the system are given.

K. A. ORLANDINI, M. A. WAHLGREN, and J. BARCLAY, Argonne National Laboratory, Argonne, Ill.

Anal. Chem. 37, 1148 (1965)

Gas Chromatographic Separation of Oxides of Nitrogen

Three columns, one of subambient temperature, are used to determine H_2, O_2, N_2, NO, CO, N_2O, CO_2, C_2H_6, C_2H_4, C_2H_2, and $NO_2(N_2O_4)$. A schematic of the instrument is presented.

J. M. TROWELL, Hercules Powder Co., P. O. Box 98, Magna, Utah

Anal. Chem. 37, 1152 (1965)

Spectrophotometric Determination of Gold with Azide

The method is based on measuring the absorbance of tetraazido-gold(III) at 325 mμ in water, for gold alone, or at 330 mμ in an *n*-butyl alcohol extract. Variables and foreign ions were studied.

RAY G. CLEM and E. H. HUFFMAN, Lawrence Radiation Laboratory, University of California, Berkeley, Calif.

Anal. Chem. 37, 1155 (1965)

Correspondence

Liquid-Liquid Extraction of Zirconium(IV) with Mesityl Oxide

S. M. KHOPKAR and S. C. DHARA, Department of Chemistry, Indian Institute of Technology, Bombay 76, India

Anal. Chem. 37, 1158 (1965)

Modification of Flask Method of Sulfur Determination. Determination of Sulfates with Sulfonazo III

BRETISLAV BUDESINSKY, Department of Analytical Chemistry, Nuclear Research Institute, Czechoslovak Academy of Sciences, Rzhezh near Prague, Czechoslovakia

Anal. Chem. 37, 1159 (1965)

Gas Chromatographic Analysis of Aromatic Hydrocarbons with Modified Bentonite Columns. Effect of Bentone 34 Concentration on Performance of Packed Columns

EDWARD W. CIEPLINSKI, Perkin-Elmer Corp., Norwalk, Conn.

Anal. Chem. 37, 1160 (1965)

Preparation of High Purity Acetonitrile

JERRY F. O'DONNELL, JAMES T. AYRES, and CHARLES K. MANN, Department of Chemistry, Florida State University, Tallahassee, Fla. 32306

Anal. Chem. 37, 1161 (1965)

Aqueous Sodium Borohydride Chemistry. The Coinage Metals, Copper, Silver, and Gold

L. F. HOHNSTEDT, B. O. MINIATAS, and SISTER M. CONCETTA WALLER, Department of Chemistry, Saint Louis University, Saint Louis 19, Mo.

Anal. Chem. 37, 1163 (1965)

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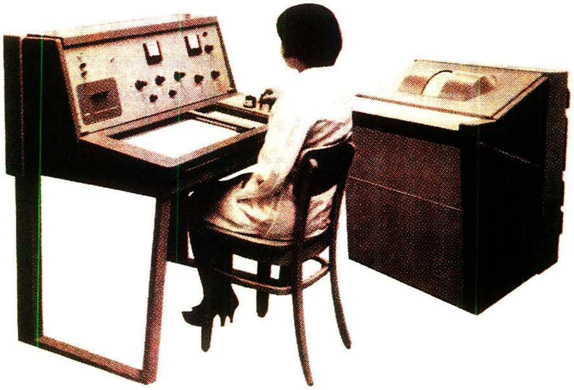

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Addendum. Simultaneous Use of Beta-Particle Transmission and Backscatter Gauges for Determining Hydrogen, Carbon, and Oxygen Percentages in Liquids

R. P. GARDNER, and J. W. DUNN III, Measurement and Controls Laboratory, Research Triangle Institute, Durham, N. C.

Anal. Chem. 37, 1164 (1965)

A Three-Column, Two-Detector Gas Chromatographic Method for the Simultaneous Analysis of a Mixture of Fixed Gases and Hydrocarbons

J. O. TERRY, and J. H. FUTRELL, Chemistry Research Laboratory, Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio

Anal. Chem. 37, 1165 (1965)

Purification of Hexamethylbenzene by Zone Refining and Determination of Its Melting Point

J. E. OVERBERGER and J. G. ASTON, Department of Chemistry, The Pennsylvania State University, University Park, Pa.

Anal. Chem. 37, 1167 (1965)

Factors Affecting the Selection of a Cobalt Analysis Line for Atomic Absorption Spectrometry

W. W. HARRISON, Department of Chemistry, University of Virginia, Charlottesville, Va.

Anal. Chem. 37, 1168 (1965)

Potentiometric Quantitative Determination of Sodium Aminoethylthiosulfates and Aminoethylthiosulfuric Acids

JOHN C. MACDONALD, Boston Laboratory, Monsanto Research Corp., Everett, Mass. 02149

Anal. Chem. 37, 1170 (1965)

Amperometric Titration of Primary Amides

WILLIAM R. POST, and CHARLES A. REYNOLDS, Department of Chemistry, University of Kansas, Lawrence, Kan.

Anal. Chem. 37, 1171 (1965)

Determination of Absorbed Ethylene and Propylene Oxides by Distillation and Titration

DON A. GUNTHER, Dept. of Research, American Sterilizer Co., Erie, Pa.

Anal. Chem. 37, 1172 (1965)

Aids For the Analytical Chemist

New Method for Determination of Hydrocarbon-in-Water Solubilities

EDWARD J. FARKAS, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

Anal. Chem. 37, 1173 (1965)

Preparation and Use of Lead-212 Tracer

CLAUDE W. SILL, and CONRAD P. WILLIS, Health and Safety Division, U. S. Atomic Energy Commission, Idaho Falls, Idaho 83401

Anal. Chem. 37, 1176 (1965)

Zone Refiner with Temperature Control

FRED ORDWAY National Bureau of Standards, Washington 25, D. C.

Anal. Chem. 37, 1178 (1965)

High Precision Conductivity Bridge

ROBERT L. WERSHAW and MARVIN C. GOLDBERG, U. S. Geological Survey, Denver, Colo. 80225

Anal. Chem. 37, 1180 (1965)

A Time Base Generator with Digital Readout of Nuclear Magnetic Resonance Line Positions

J. M. PURCELL and J. A. CONNELLY, Eastern Utilization Research and Development Division, U. S. Department of Agriculture, Philadelphia, Pa. 19118

Anal. Chem. 37, 1181 (1965)

Combining Gas Chromatography with Nuclear Magnetic Resonance Spectrometry

E. G. BRAME, JR., Manufacturing Division, Plastics Department, E. I. du Pont de Nemours & Co., Wilmington, Del. 19898

Anal. Chem. 37, 1183 (1965)

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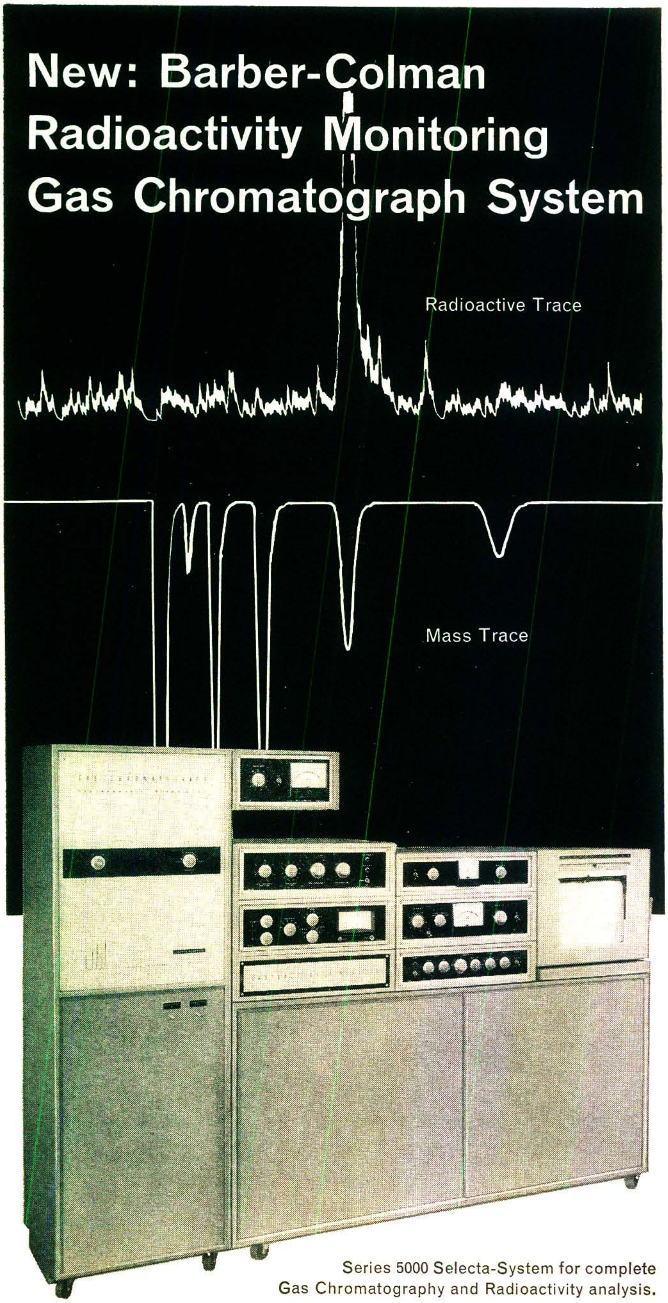

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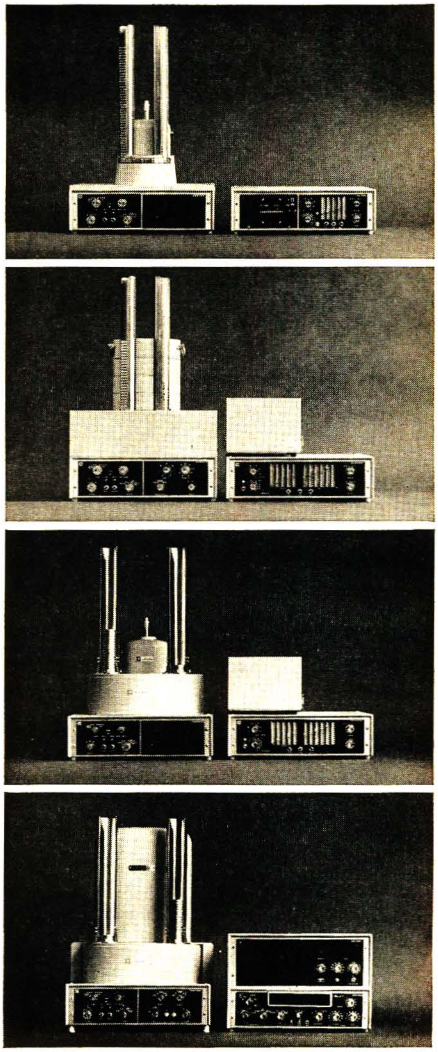

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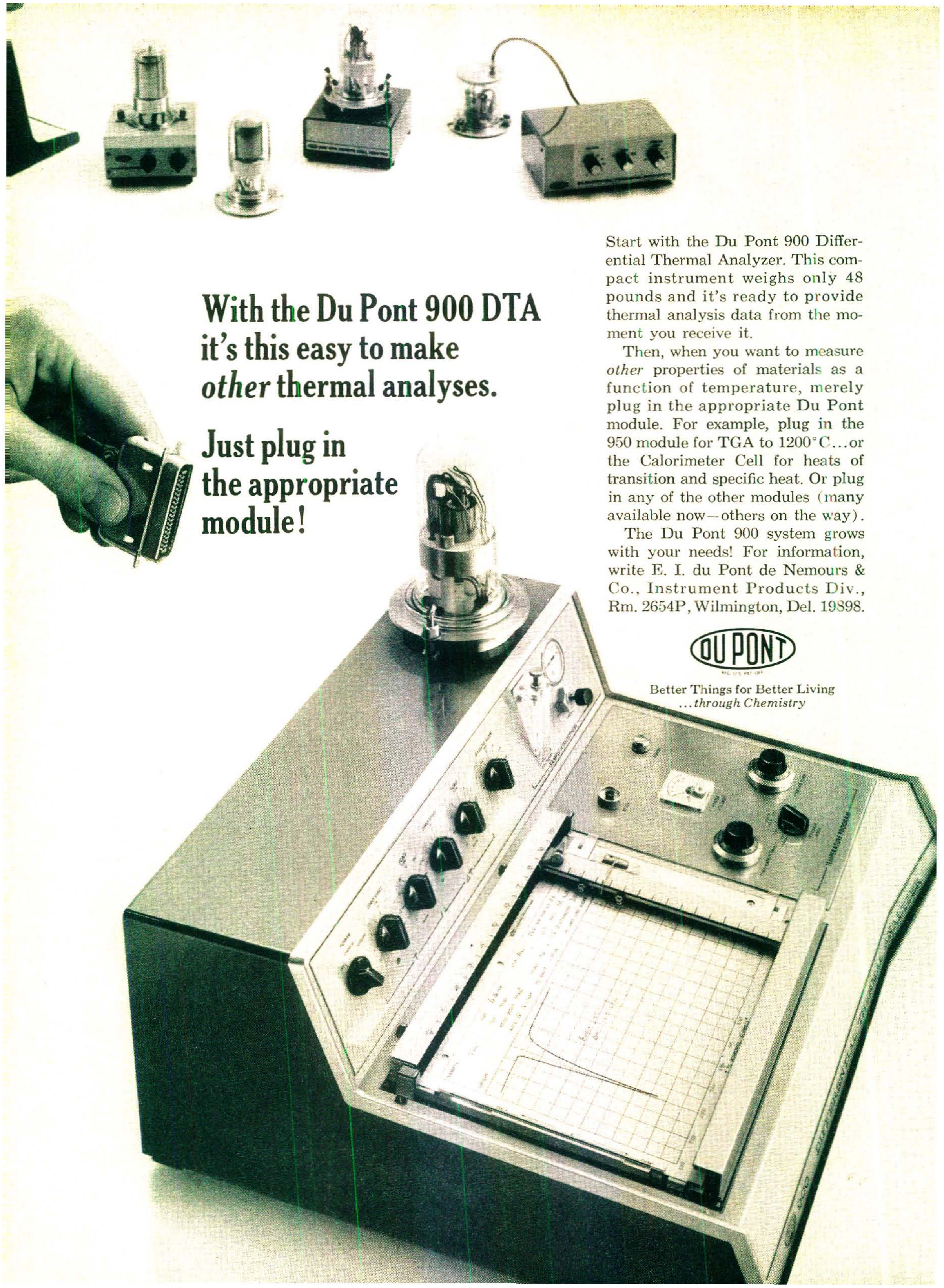

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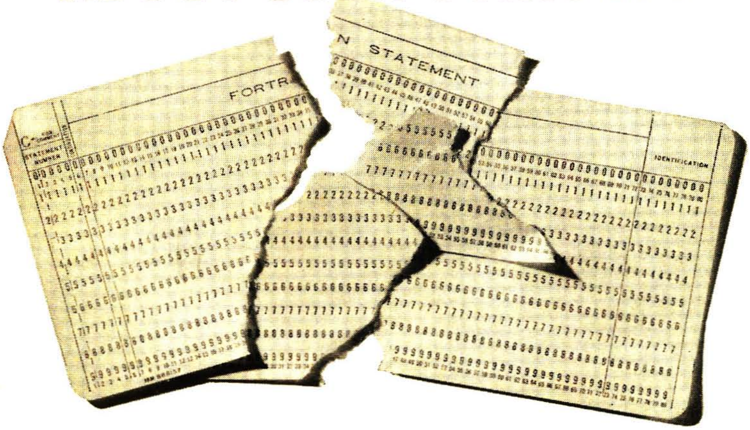

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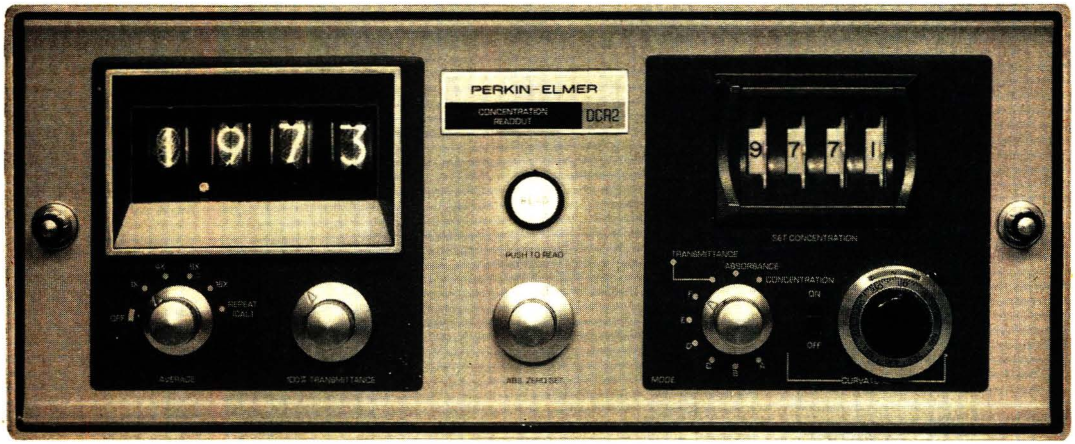

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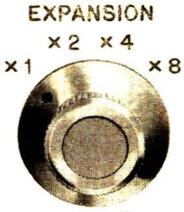

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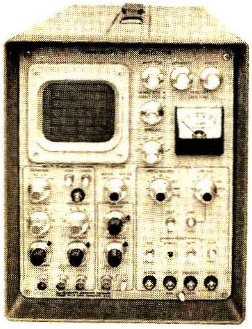

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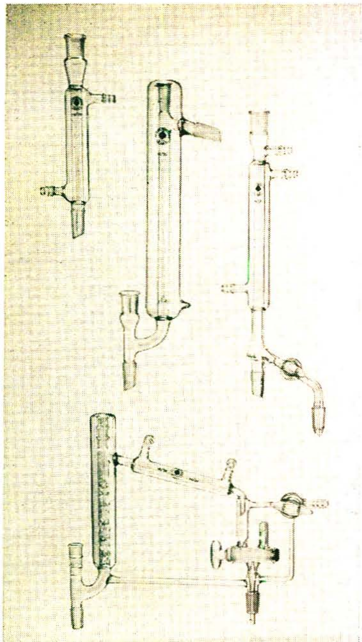

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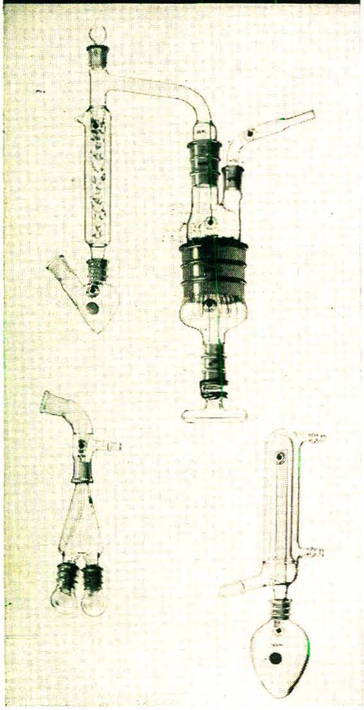

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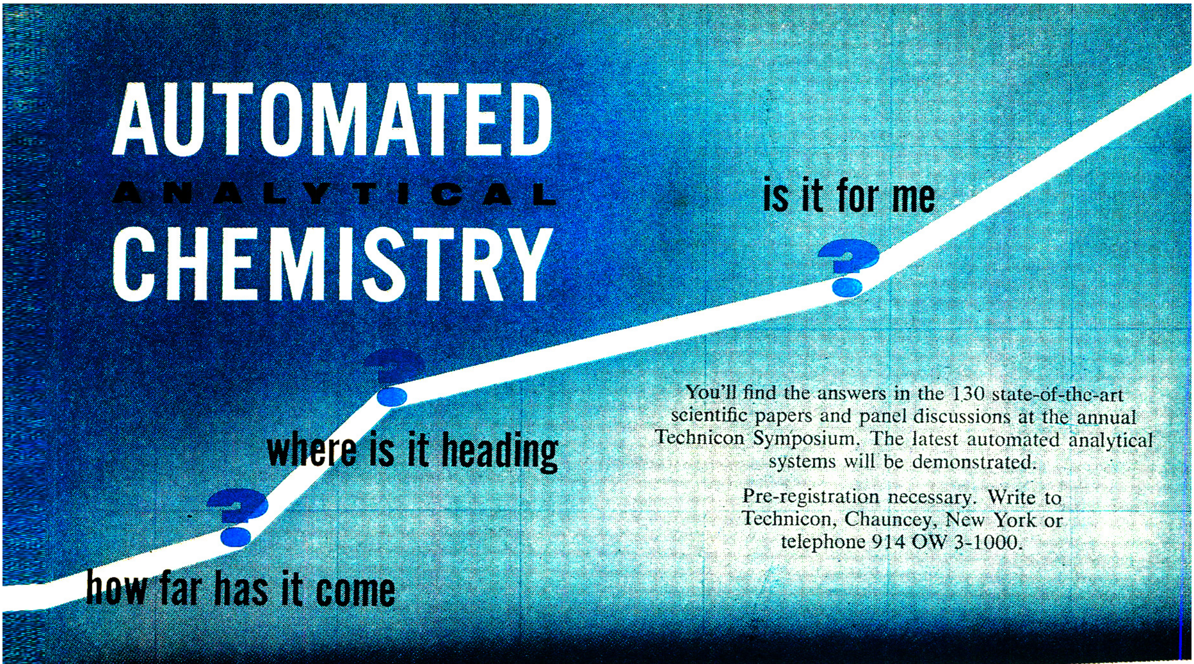

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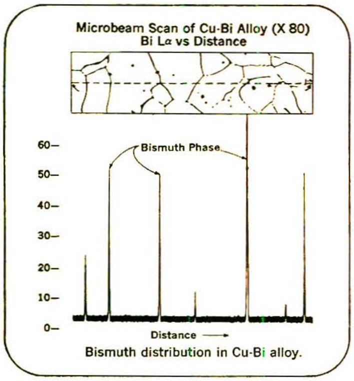

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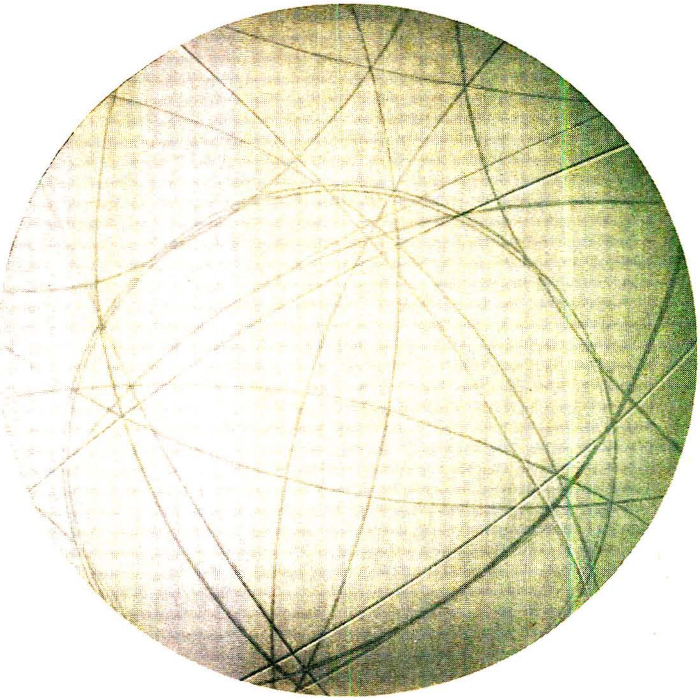

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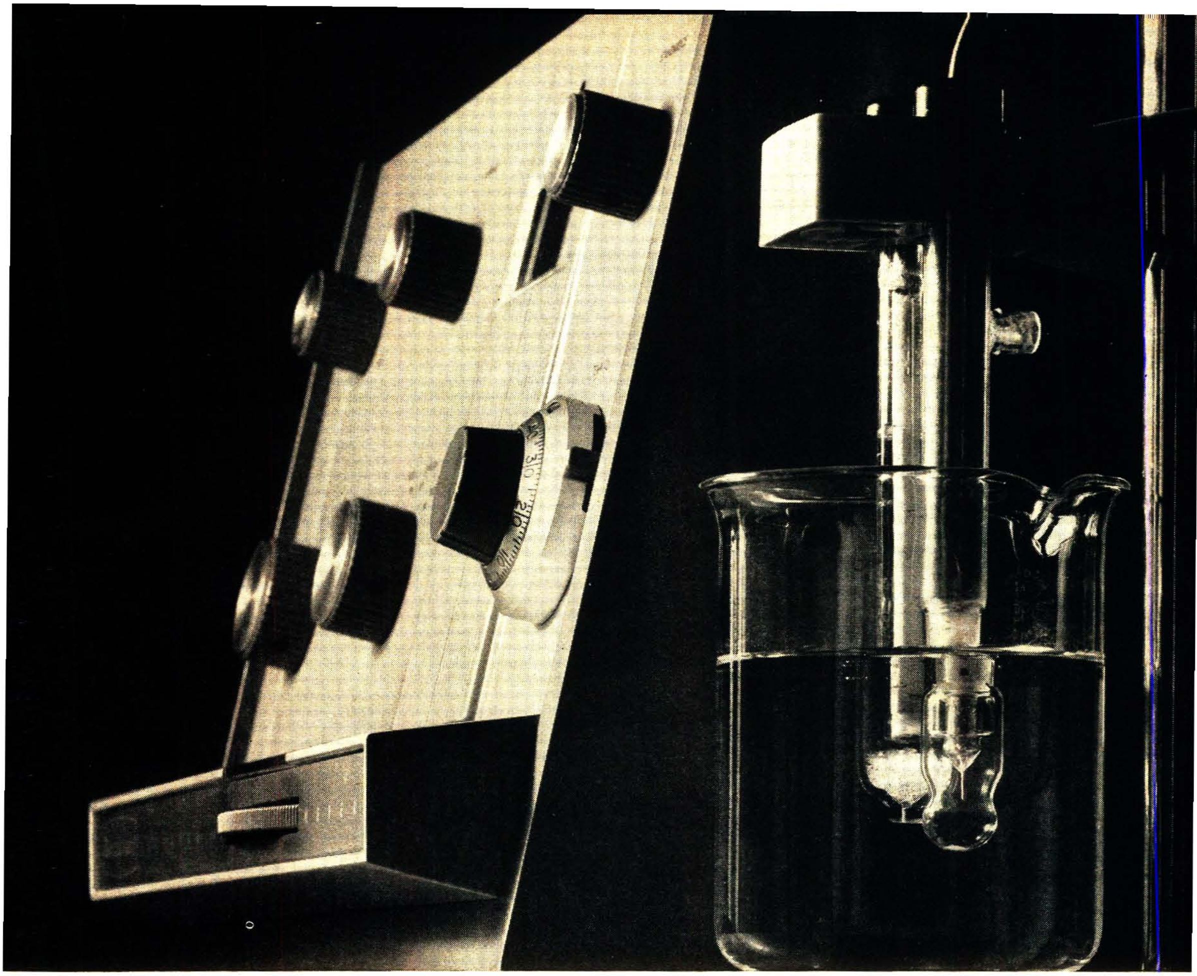

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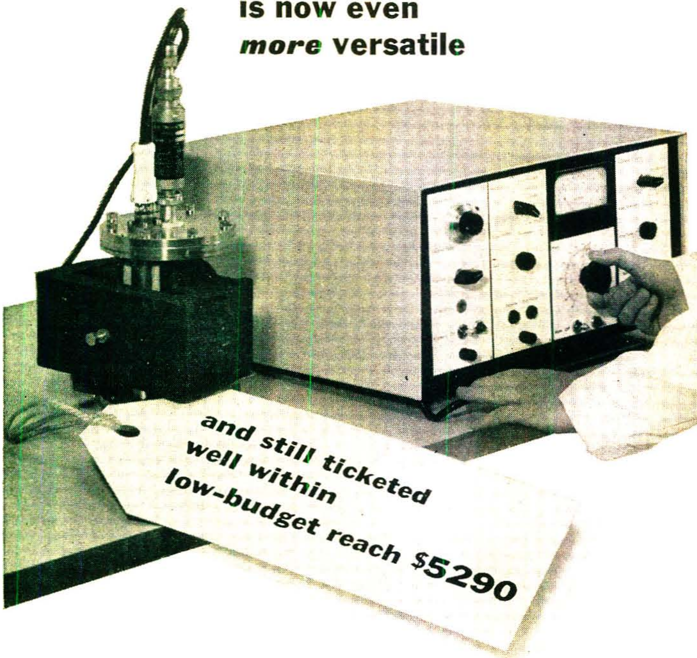

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Electronic Analytical Data Processing

by William A. A. Karau, Thomas B. Patterson, and Francis J. Balint

Gulf Research and Development Company, Harmarville, Pa.

Computer Techniques Make Possible the Handling of Large Volumes of Analytical Data and the Preparation of Management Control Reports

THE INTERACTION between man and machines has become increasingly commonplace in today's scientific and business community. Recent progress in this area was reported at the University of Pittsburgh's Knowledge Availability Systems Center, Electronic Information Handling Conference, held in October of 1964 (*4*). Speakers repeatedly emphasized the gigantic scope of the work to be done. Efforts to improve theory and applications have continued aggressively in organizations all over the country, from "sketch pad" research by Sutherland at M.I.T. (*6*) to computer-aided sociological research by Drs. Sydney and Beatrice Rome in California (*5*).

The use of computers in the laboratory has been reported for specific calculations such as chromatographic and spectrochemical analyses (*1*), and some of the problems of conversion of laboratory data to acceptable computer input have been discussed by Tompkins (*7*). The applications discussed here revolve about the reporting of data after results are known.

In a large laboratory, compilation and reporting are a burden. A task group at Gulf Research and Development Company has provided a reporting system to meet the following requirements:

- Speed—Continuous input and output, with a minimum of time in the system
- Accuracy—Minimization of transcription errors
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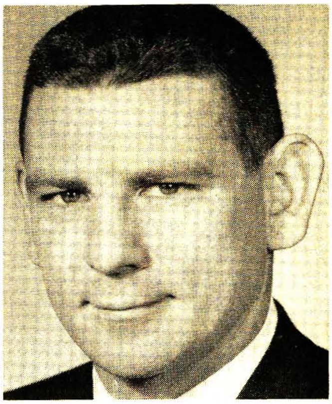
- Control—Provides backlog data, sample and test information pertaining to tests, analysis, and samples
- Economy—Reduces time spent on administrative functions and clerical details
- Versatility—The system is capable of expansion and modification to meet the needs of a growing organization and an increasing workload

All of these requirements are being handled in varying degrees, and efforts are continuing toward fulfilling all of the requirements.

Figure 1 shows samples in the



William A. A. Karau, above, is a chemical engineering graduate of the University of Delaware, and is engaged in digitizing output and computer applications with Gulf R&D

Thomas B. Patterson, above right, is a mathematics graduate of California State College in California, Pa. He is currently a liaison programmer in the Computational Analysis Section of Gulf R&D

Francis J. Balint, at right, holds a master's degree in mathematics from the University of Pittsburgh. He is currently employed by Gulf R&D as a senior projects engineer responsible for computer systems programming and operations

Figure 1

Figure 2

As samples for analysis are received they are tagged for identification and further processing, as shown in Figure 1 above

Figure 2, above right, shows keypunch operators punching sample information from the cover sheet onto cards

Master test cards, as shown in Figure 3 at right, are sent to the analyst along with the appropriate samples

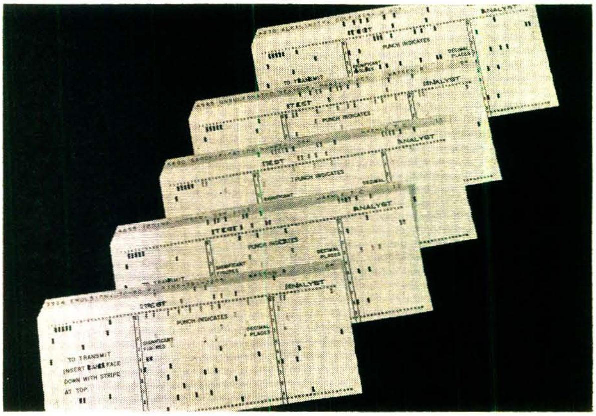


Figure 3

process of being received and numbered. A numbered two-part tag is attached to each sample, and the cover sheet is sent to the keypunch area. The sample and prepunched number cards are sent to the testing area in a concurrent flow. The prepunched cards are used by each analyst for transmissions and record keeping purposes. The prepunched sample number eliminates the human errors possible by "keying information at transmission time."

By disconnecting the testing and keypunching operations, each can flow at its own rate. In addition, computer runs may be made independently of the sequence of information from these operations.

The keypunch operators (see Figure 2) punch sample detail information from the cover sheet into cards, which are sent to the computer center via an IBM 066 transceiver circuit.

Meanwhile, an analyst has received the sample for testing. He has a master test card (Figure 3) for each test which contains a test number, an English text description, his name, his employee number, and a card-type code.

Using the IBM 1001 via a telephone circuit, the analyst transmits the test information (Master Card) as shown in Figure 4. Then, sample numbers and corresponding test answers are sent for each analysis that he has completed. This information for each sample is received in a single punched card at the electronic computer center.

At periodic intervals the data which are collected at the computer center are assembled and are used as computer input, as demonstrated in Figure 5. Every sample receiving new information is updated in a magnetic tape file, and this information can be produced automatically. For new samples, a receipt is printed; for new answers, a sponsor card is punched; for completed samples, a report is printed.

In Figure 6 each of these items is depicted: (1) The receipt shows the pertinent descriptive information and the list of tests to be performed. (2) Sponsor cards are issued for each answer, and contain sample and test identification in addition to the answer. The hold-

Figure 4

Figure 5

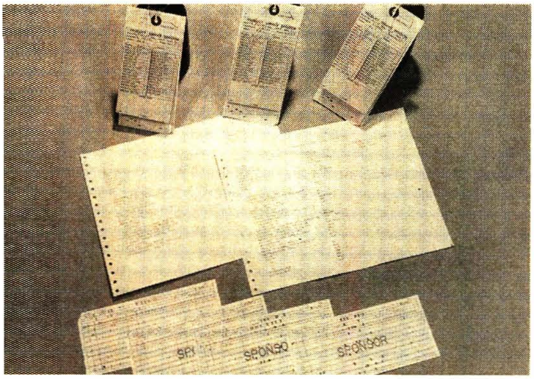


Figure 6

The analyst sends pertinent data via a telephone circuit, indicated in Figure 4 at above left

At periodic intervals the data collected at the computer center is assembled and used as computer input, as shown in the photo above (Figure 5)

The sample receipt, sponsor card, and finished report are shown in Figure 6 at left

ing up of data on partially finished reports is not permitted by this technique. The cards also serve as input to other computer programs. (3) The finished report contains all the data on the receipt plus the completed analysis of the sample.

CONTROL REPORTS

The system just described consists of sorting, collating, updating, and compiling operations. The development and cost of the computerized system were justified by the large volume involved. However, the real advantage of the system is the digestion of this volume of data into control reports. The control information is contained in backlogs, tests, and project, sample, and quality control summaries.

Backlogs

The keypunched heading information contains each sample's list of test requirements as well as identification data. A backlog scan for incomplete tests is made daily. There are three reports compiled showing the workload in chronological order: (1) An overall report shows the entire laboratory workload. (2) Section supervisor reports have each section workload listed separately. (3) Area reports list the workload of small areas independently.

These three reports are useful in several ways. The chronological ordering allows work-age restrictions to be enforced, and charts prepared from this statistic are used to detect bottlenecks. Section supervisors can use these reports to determine the nature of the workload and to rearrange personnel and test allocations.

These backlogs also act as an impersonal control system, exerting continuous restraint on the performance of analysts in the laboratory. Supervisors have increased responsibilities for helping their people, and pressure for greater output becomes a less important factor. This has the effect of improving relations between supervisors and workers (*2*).

Test Summary

The test summary monthly report summarizes the number and

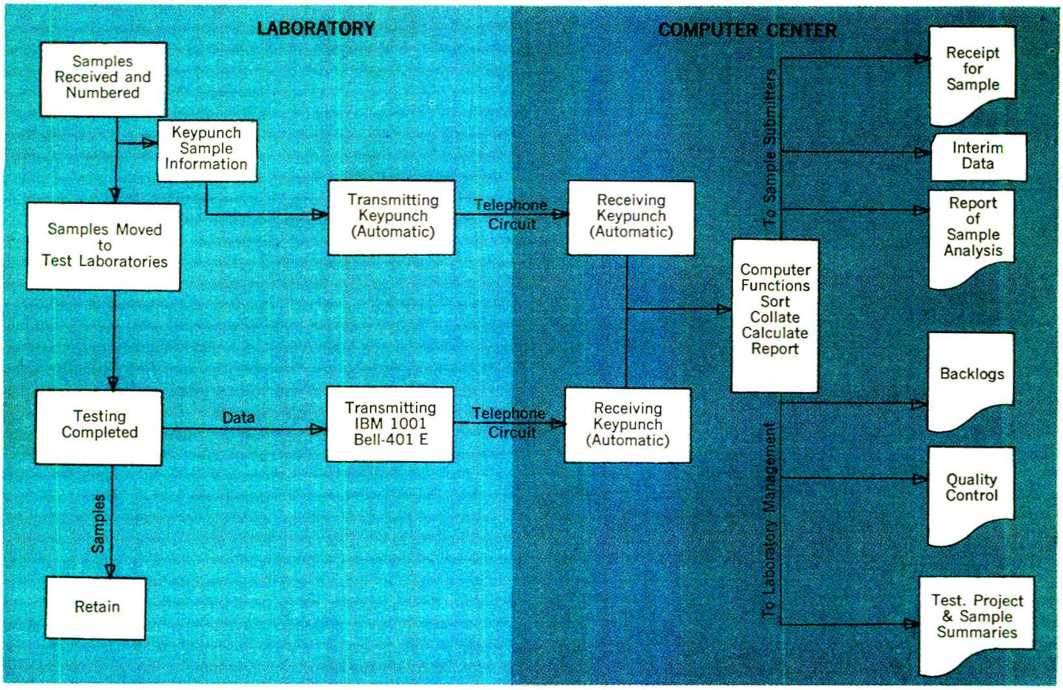


Figure 7. Flow diagram for handling analytical data by electronic computer methods

identity of the tests performed in a given laboratory area, and emphasizes changes in trends of test requirements. Elapsed time between requests for a test determines obsolescence. Again, reassignment of space, tests, and personnel can be made on a logical basis.

Sample and Project Summary

The monthly sample summary report tabulates the quantity and source of samples by the charge numbers of the submitting organization. A measure of the work performed can be made using a labor index, and each of 2000 tests is assigned a standard work index. A compilation of indices yields work measurements for each project.

The incoming sample tallies can be compared with the labor index to determine the activity of a project. Total charges against each project are additional bases for budget requirements. Charting the monthly charge figures provides a graphical picture of work movement and points up items requiring control action.

Analyst Summary and Check-Test Report

The production of the individual is measured by the analyst summary and check-test report. Using the labor index, the output of each analyst is measured in terms of these standard indicators. Because refinement of the system is a continuing effort, these theoretical labor indices are used rather than a "productive standard hour" advocated by Eilon (*3*). The summary provides a concise listing of each analyst's production in terms of stets and equivalent labor index.

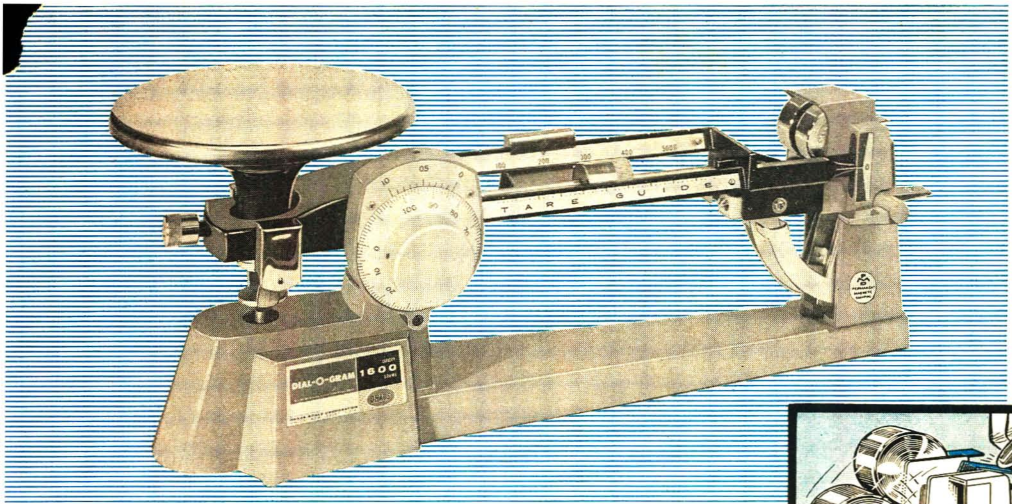
The two auxiliary reports provide condensations of check data, which are obtained for the following reasons: The sample originator requested duplicate determinations, a review of compiled data may indicate the need to verify certain values, or an analyst may discover technical reasons for rerunning an analysis. One summary of this information is in terms of the analyst, and one is in terms of the test, so the needs for refresher training and analytical problems are highlighted.

THE FUTURE

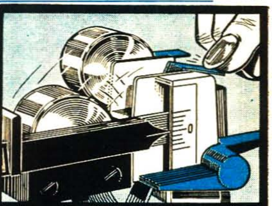
The chief aim of the task group is to take advantage of all computer capabilities, so current efforts are directed to more complex refinement. Routine calculations and comparisons of data with standards are done automatically. For instance, a crude oil report contains an analysis of the basic crude plus an analysis of each of several cuts distilled from the crude. Routine material balances can be used to verify the individual cut analysis. Other checking operations may include comparison with standard reports, product specifications, and test reliability.

Improvements in hardware will not be neglected. Installation of a remote input-output computer station is being studied. Since manufacturers are producing faster and more versatile machinery, every announcement holds promise of improved service.

The researchers take every opportunity to update the equipment and methods used in an effort to streamline the system.



Illustrated: Model 1650



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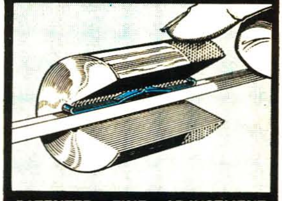

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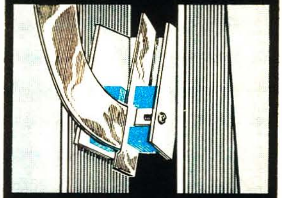

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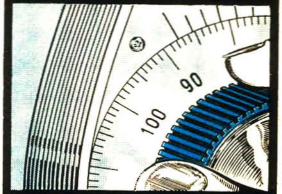

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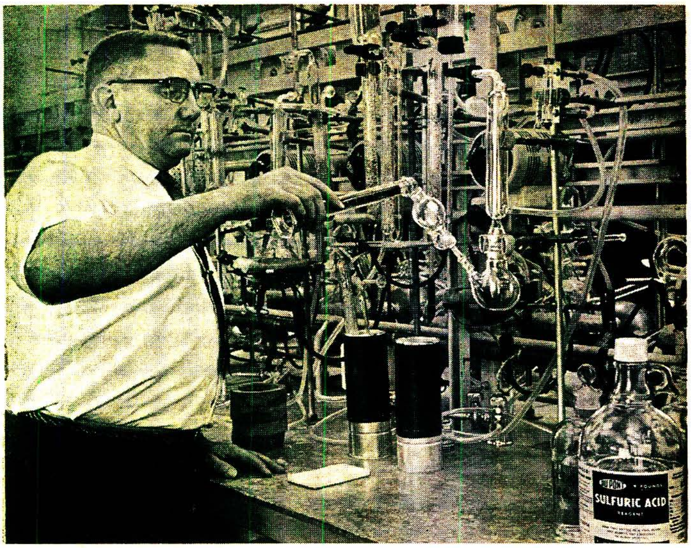

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Figure 7 shows the overall pla which has been developed. It should be noted that keypunching of sample information and transmission of test data are independent, both in terms of time and sequence of completion. This is a major contributing factor to the overall speed and efficiency of operation.

The system described accepts a large volume of varied data input on a continuous basis. It sorts, collates, checks, and reports the data without transcription errors. Computer output is used to control and analyze the day to day operation of the laboratory. In addition, quality and quantity of production are under constant and impartial scrutiny. The intrinsic character of the workload, the sources and quantities of samples, and the nature of analyses required become known.

Almost as valuable as these items are the cataloguing of tests and the subsequent published listing. The standard labor index assignments to individual tests reveal surprising cost patterns, and the assigning and updating of these standards are also enlightening. Estimates of costs of proposed programs are more reliable, and the return value in relation to cost for marginal test information can be easily evaluated.

The system is expandable in terms of volume of data processed and the tests performed. The comparison of routine report standards removes the detail-checking burden from the technical report writer, and more time to analyze the data and to draw conclusions will be available.

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(5) Rome, S., Rome, B., *Electronic Information Handling Conf.*, Pittsburgh, Pa., October 7–9, 1964.
(6) Sutherland, I. E., Technical Report 296, Lincoln Laboratory, M.I.T., January 30, 1963.
(7) Tompkins, H. E., *Am. J. Public Health* 53, 1953 (1963).

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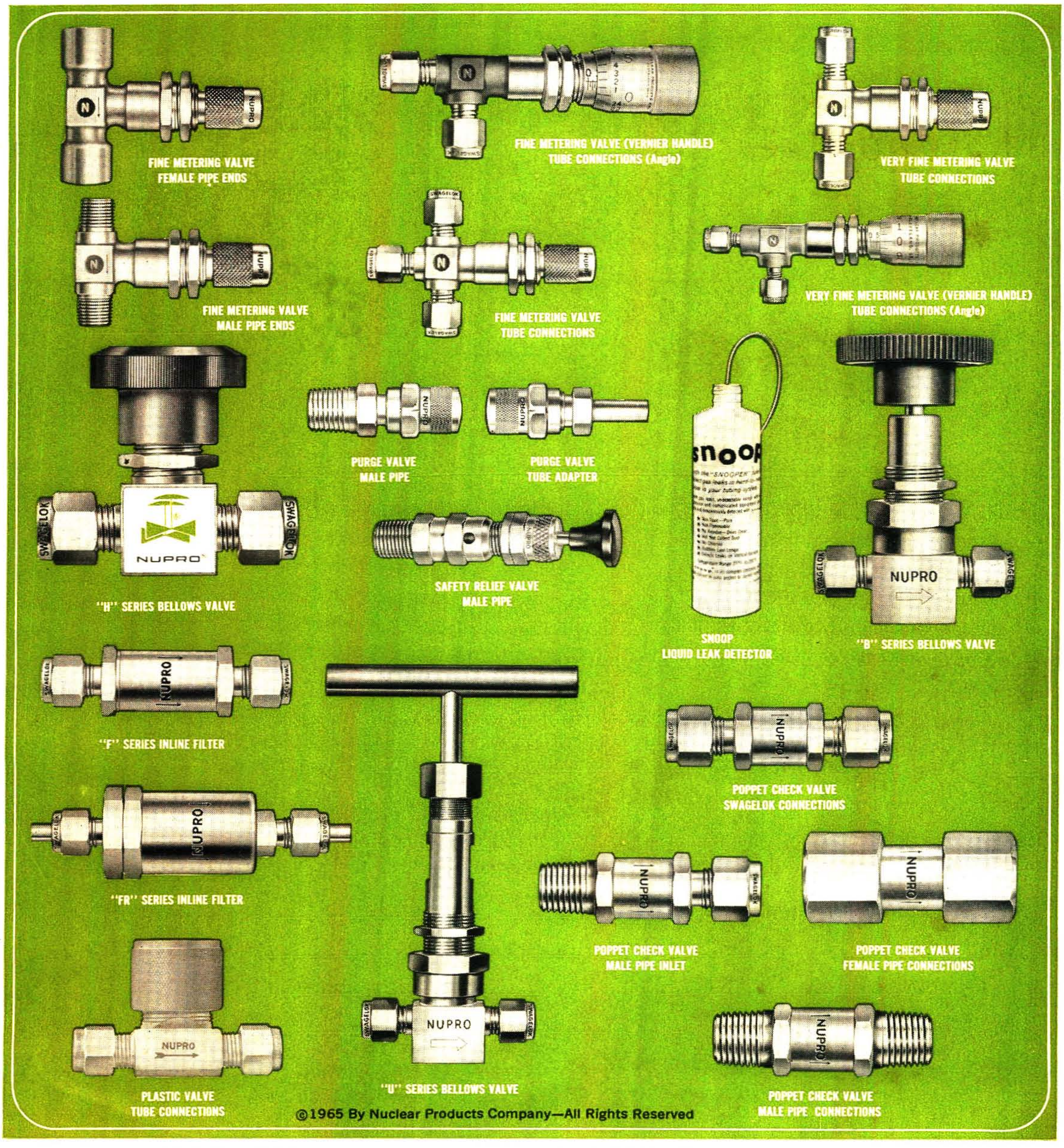

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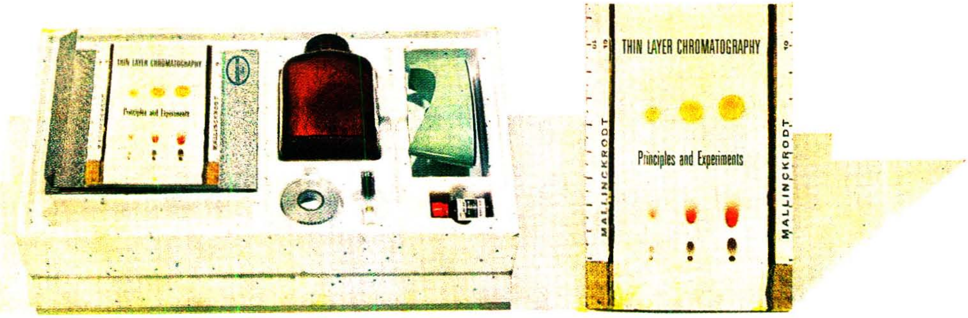

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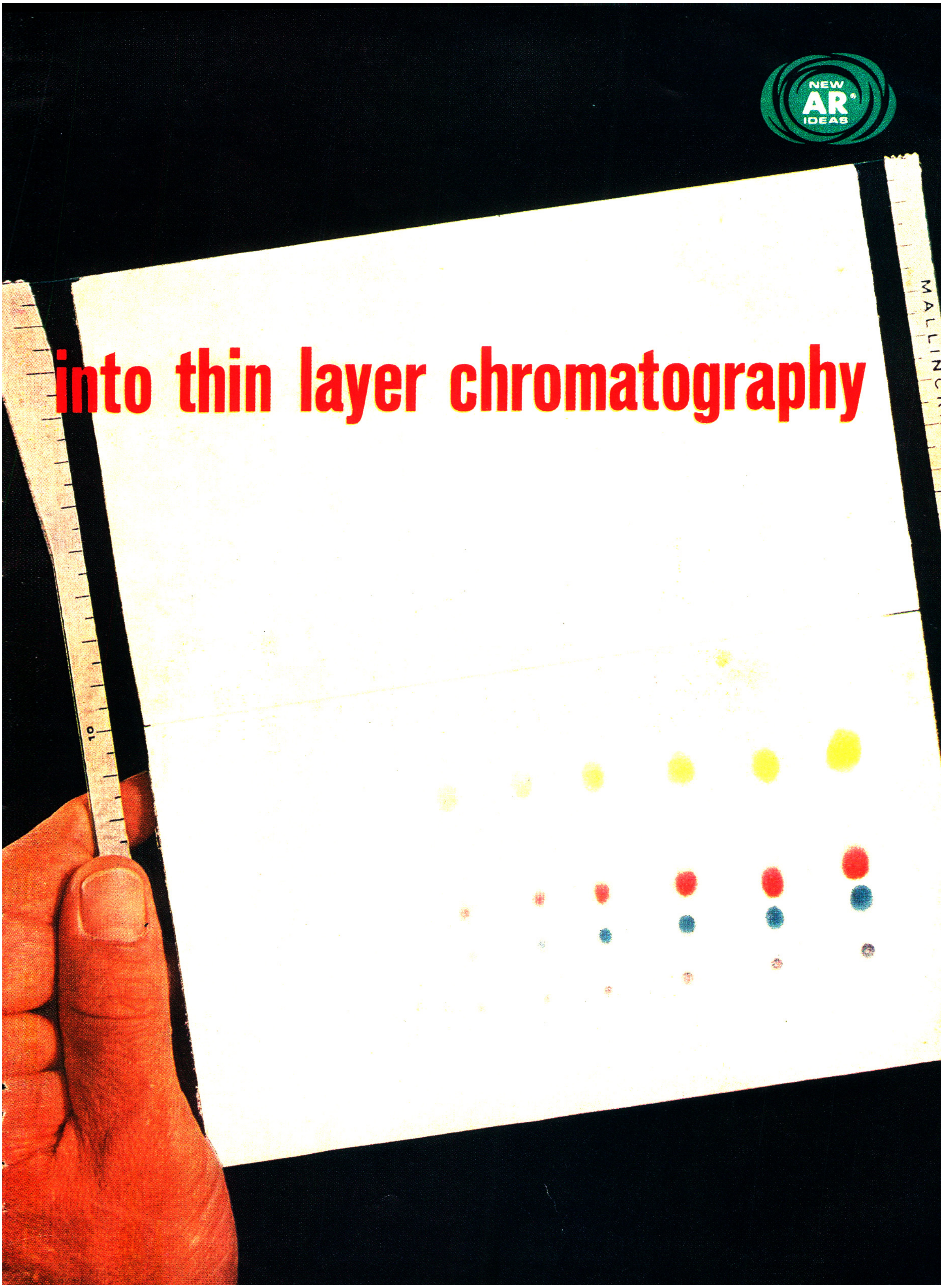

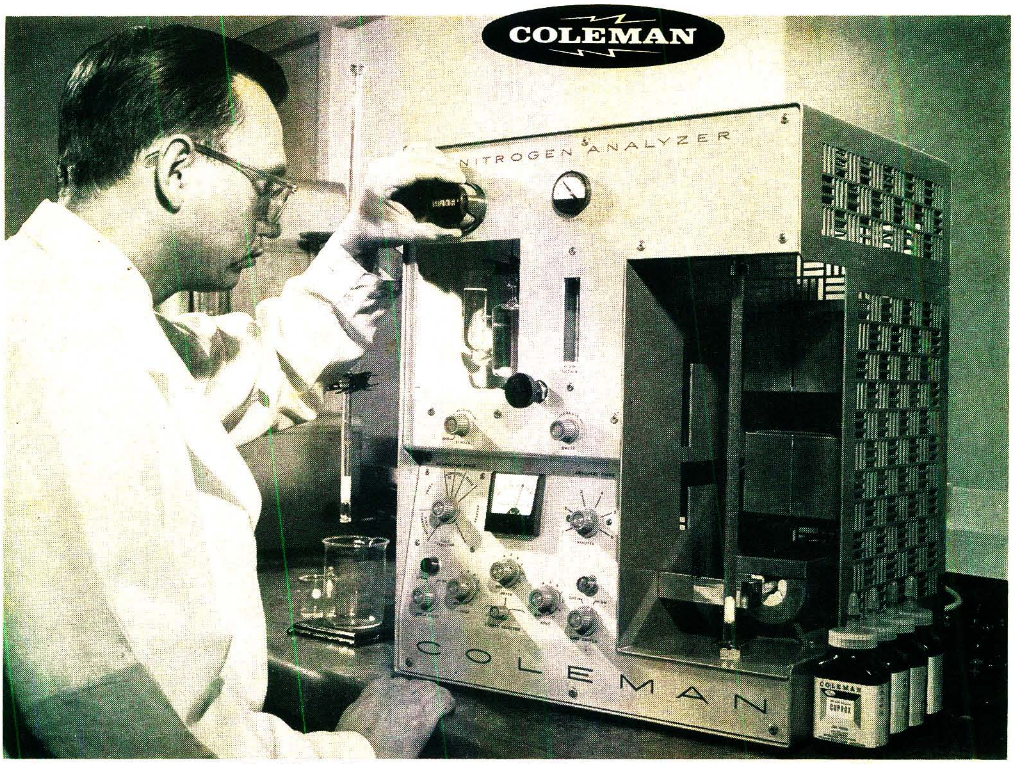

Scope of Coleman Nitrogen Analyzer extended to 20 ppm in trace studies by California Research Corporation*

* *California Research Corporation is the research arm of Standard Oil of California. Results of the work are reported in "Automatic Dumas Nitrogen Analysis of Lubricating Oils and Additives," by Farley, Guffy and Winkler, ANALYTICAL CHEMISTRY, Vol. 36, Page 1061, May 1964. Reprints and product literature are available from Coleman Instruments Corporation.*

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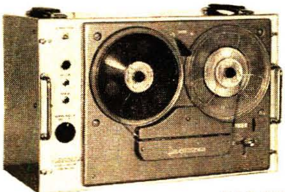

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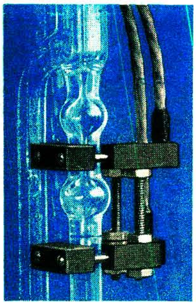

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ANALYTICAL CHEMISTRY

NEWS

150th ACS National Meeting Analytical Division

THE 150TH NATIONAL MEETING of the American Chemical Society will be held in Atlantic City, N. J., September 12 to 17. The complete program of the technical sessions appears in the August 9 issue of *Chemical and Engineering News*. All Analytical Division sessions will be held at the Deauville Hotel with the exception of the Friday meeting which will be held in the Convention Hall.

Topics of special symposia include: inorganic chromatographic separations, critical examination of optical methods of analysis, application of kinetics to analytical problems, and gas chromatography.

The Analytical Division dinner takes place Wednesday, Sept. 15 and will honor the Editor of ANALYTICAL CHEMISTRY, L. T. Hallett.

In addition to the technical program, a chemical exposition featuring chemicals, equipment, and services of 125 exhibitors will be held at the Convention Hall, Sept. 14 to 16.

More information on Analytical Division activities is available from John K. Taylor, National Bureau of Standards, Washington, D.C. 20234.

ANALYTICAL DIVISION PROGRAM

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Monday Morning, Sept. 13

SYMPOSIUM ON INORGANIC CHROMATOGRAPHIC SEPARATIONS

Donald H. Wilkins, Presiding

9:10 **Plate-Equilibrium Theory of Ion-Exchange Chromatography.** William Rieman III, Wright Laboratory, Rutgers, The State University, New Brunswick, N. J.

9:45 **Ion Exchange and Partition Chromatographic Separation of Metal Ions.** J. S. Fritz, Department of Chemistry, Iowa State University, Ames, Iowa.

10:30 **Separation of Inorganic Ions on Inorganic Compounds.** J. E. Rein, Phillips Petroleum Co., P. O. Box 2067, Idaho Falls, Idaho.

10:55 **Sequential Chromatographic Separation of Fission Product and Actinide Elements—A Review.** Leon Wish, U. S. Naval Radiological Defense Laboratory, San Francisco, Calif. 94135.

11:15 **Radiochromatographic Methods.** A. R. Landgrebe, National Bureau of Standards, Room 402, Chemistry Bldg., Washington, D. C. 20234.

11:35 **Separation of Uranium from Other Metals by Partition Chromatography.** J. S. Fritz, D. H. Schmitt, Department of Chemistry, Iowa State University, Ames, Iowa.

Monday Afternoon, Sept. 13

SYMPOSIUM ON INORGANIC CHROMATOGRAPHIC SEPARATIONS

James S. Fritz, Presiding

2:05 **Partition Paper Chromatography of the Rare Earths Using Methylenebis(di-n-hexylphosphine Oxide) and Di-(2-ethylhexyl)orthophosphoric Acid as the Stationary Phases.** J. W. O'Laughlin, J. W. Ferguson, G. J. Kamin, C. V. Banks, Iowa State University, Ames, Iowa 50012.

2:20 **Partition Column Chromatography Using Methylenebis(di-n-hexylphosphine Oxide) as the Stationary Phase.** J. W. O'Laughlin, Iowa State University, Ames, Iowa 50012.

2:40 **Reversed-Phase Chromatographic Separation of Zirconium and Hafnium.** J. S. Fritz, R. T. Frazee, Department of Chemistry, Iowa State University, Ames, Iowa.

2:55 **Monitoring an Anion-Exchange Separation of the Lower Condensed Phosphates with an Ion-Exchange-Membrane Cell.** H. L. Rothbart, Rutgers University, New Brunswick, N. J., A. D. Lindsay, Clarkson Institute of Technology, Potsdam, N. Y.

3:25 **Cation Exchange in Concentrated HBr Solutions.** Frederick Nelson, Donna Michelson, Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tenn. 37831.

3:45 **Anion Exchange Studies of Thorium, Rare Earths, and Scandium in Ammonium Thiocyanate–Organic Solvent–Water Mixtures.** Donald Pietrzyk, University of Iowa, Department of Chemistry, Iowa City, Iowa, Donald Kiser, Grain Processing, Muscatine, Iowa.

4:05 **Precipitation Ion Exchange.** G. H. Morrison, F. Tera, R. R. Ruch, Department of Chemistry, Cornell University, Ithaca, N. Y. 14850.

4:35 **Aspects of Inorganic Gel Chromatography.** Marvin S. Antelman, Antelman Research Assoc., Providence, R. I., Sister Denise Eby, St. Joseph College, Emmitsburg, Md.

Tuesday Morning, Sept. 14

SYMPOSIUM ON THE CRITICAL EXAMINATION OF OPTICAL METHODS OF ANALYSIS

V. A. Fassel, Presiding

9:05 **Ultraviolet and Light Absorption Spectrometry.** D. F. Boltz, Department of Chemistry, Wayne State University, Detroit, Mich.

9:45 **Infrared Spectrum—A Physical Constant?** M. K. Wilson, Chemistry Department, Tufts University, Medford, Mass.

10:40 **Raman Spectroscopy—A Critical Review.** R. N. Jones, Division of Pure Chemistry, National Research Council, Ottawa, Canada.

11:20 **Molecular Fluorescence and Phosphorescence Spectroscopy—A Critical Review.** D. M. Hercules, Department of Chemistry and Laboratory for Nuclear Science, M.I.T., Cambridge, Mass. 02139.

Tuesday Afternoon, Sept. 14

Section A

GENERAL PAPERS

A. F. Findeis, Presiding

2:05 **Determination of Microgram Quantities of Lead by Spectrophotometric Titration with Dithizone.** R. A. Jones, Ethyl Corp., Research Laboratories, Detroit, Mich., Anton Szutka, Department of Chemistry, University of Detroit, Detroit, Mich.

2:20 **Oxidation of Manganous with Sodium Perxenate: Application to the Determination of Manganese in Uranium.** R. W. Bane, Argonne National Laboratory, 9700 South Cass Ave., Argonne, Ill. 60440.

2:35 **The Use of Citrate–EDTA Masking for the Selective Determination of Iron with 1,10-Phenanthroline.** S. S.

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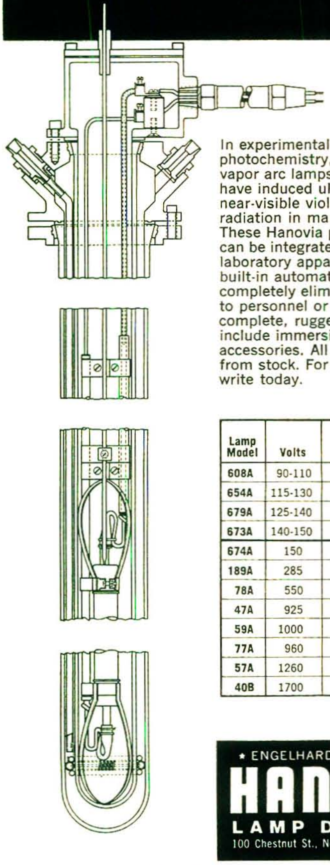

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674A	150	700	7.5	Pilot Plant and Commercial Scale
189A	285	1200	12.0	
78A	550	2000	21.0	
47A	925	3450	48.0	
59A	1000	4500	58.0	
77A	960	4500	42.0	
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Yamamura, J. H. Sikes, Phillips Petroleum Co., P. O. Box 2067, Idaho Falls, Idaho.

2:55 **Exchange Kinetics in the Calcium–EDTA System.** R. J. Kula, G. H. Reed, Department of Chemistry, University of Wisconsin, Madison, Wis.

3:30 **A Kinetic Study of the Cystine Catalysis of the Iodine–Azide Reaction.** W. E. Dahl, H. L. Pardue, Department of Chemistry, Purdue University, Lafayette, Ind.

3:50 **A Coordination Chain Reaction Involving Copper and Zinc Complexes.** D. W. Margerum, J. D. Carr, Department of Chemistry, Purdue University, Lafayette, Ind.

4:10 **A Spectrophotometric Study of Nickel Complexes with 2,3-Quinoxalinedithiol.** R. B. W. Earp, A. F. Findeis, School of Chemistry, University of Alabama, University, Ala.

4:30 **Sterically Hindered Organic Analytical Reagents 2-Methyl-8-Mercaptoquinoline.** Henry Freiser, Quintus Fernando, David Kealey, University of Arizona, Tucson, Ariz. 85721.

Tuesday Afternoon, Sept. 14

Section B

SYMPOSIUM ON THE CRITICAL EXAMINATION OF OPTICAL METHODS OF ANALYSIS

V. A. Fassel, Presiding

2:05 **A Critical Review of Atomic Absorption Spectroscopy.** Walter Slavin, Perkin-Elmer Corp., Norwalk, Conn. 06852.

2:45 **Flame Emission Spectroscopy—A Critical Review.** R. N. Kniseley, V. A. Fassel, Institute of Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa.

3:40 **Atomic Fluorescence Flame Spectrometry—A Critical Review.** James Winefordner, Department of Chemistry, University of Florida, Gainesville, Fla.

4:20 **Atomic Emission Spectroscopy Arc, Spark, and Plasma Jet.** B. F. Scribner, National Bureau of Standards, Washington, D. C. 20234.

Wednesday Morning, Sept. 15

Section A

GENERAL PAPERS

Daniel J. Macero, Presiding

9:05 **An Integral General Purpose Electrochemical Instrument.** J. W. Haagen-Smit, S. L. Pratt, Beckman Instruments, Inc., 2500 Harbor Blvd., Fullerton, Calif.

9:25 **New Approach to Residual Current Compensation in Polarography.** W. B. Schaap, Joseph DiSalvo, Department of Chemistry, Indiana University, Bloomington, Ind.

9:50 **Photo-Polarographic Behavior of Inorganic Depolarizers.** R. A. Durst, Department of Chemistry, Boston College, Chestnut Hill, Mass. 02167, J. K. Taylor, Analytical Chemistry Division, National Bureau of Standards, Washington, D. C. 20234.

10:10 **Polarographic Studies in Dimethylsulfone–Nitrate Complexes of Lead and Cadmium.** Clemens Auerbach, D. K. McGuire, Brookhaven National Laboratory, Upton, N. Y.

10:40 **Spot Electrolysis.** D. H. Evans, Department of Chemistry, Harvard University, Cambridge, Mass. 02138.

11:00 **Electrochemical Reduction of Carbon Dioxide in Nonaqueous Solvents.** D. T. Sawyer, L. V. Haynes, Department of Chemistry, University of California, Riverside, Calif.

11:30 **DIVISION BUSINESS MEETING**

Wednesday Morning, Sept. 15

Section B

SYMPOSIUM ON THE APPLICATION OF KINETICS TO ANALYTICAL PROBLEMS

Dale W. Margerum, Presiding

9:05 **Application of Differential Kinetics to Analytical Problems.** Sidney Siggia, J. G. Hanna, Olin Research Center, 275 Winchester Ave., New Haven, Conn. 06504.

9:30 **Discussion**

9:35 **A Critical Evaluation of Differential Reaction Rate Methods Employed for the Simultaneous Analysis of Closely Related Mixtures.** H. B. Mark, Jr., R. A. Greinke, Chemistry Department, University of Michigan, Ann Arbor, Mich. 48104, L. J. Papa, Jackson Laboratories, E. I. du Pont de Nemours Co., Deepwater, N. J.
10:10 **Discussion**
10:15 **Determination of Metals Using Coordination Kinetics.** D. W. Margerum, Department of Chemistry, Purdue University, Lafayette, Ind.
10:45 **Discussion**
10:50 **Analysis of Mixtures by NMR Taking Advantage of the Uncertainty Principle.** C. N. Reilley, R. J. Day, Department of Chemistry, University of North Carolina, Chapel Hill, N. C. 27515.
11:25 **Use of Solvent Extraction Techniques in Kinetic Studies and Its Analytical Implications.** Henry Freiser, Department of Arizona, Tucson, Ariz.

Wednesday Afternoon, Sept. 15

Section A

GENERAL PAPERS

Royce W. Murray, Presiding

2:05 **Asymmetric Effects of Adsorbed Optically Active Layers on Electrode Reactions of Optical Isomers.** R. W. Murray, Mutsuo Kodama, Department of Chemistry, University of North Carolina, Chapel Hill, N. C. 27515.
2:20 **Differential Controlled-Potential Coulometry Utilizing Radioisotopic Tracers.** P. A. Pella, National Bureau of Standards, Washington, D. C. 20234, A. R. Landgrebe, J. R. DeVoe, W. C. Purdy, University of Maryland, College Park, Md.
2:40 **Theory and Application of Cyclic Voltammetry for Measurement of Electrode Kinetics.** R. S. Nicholson, Chemistry Department, Michigan State University, East Lansing, Mich.
3:00 **Derivative Voltammetry with Irreversible Systems.** S. P. Perone, C. V. Evins, Department of Chemistry, Purdue University, Lafayette, Ind.
3:35 **Cyclic Chronopotentiometry–Electron Transfer Coupled with Homogeneous Chemical Reactions.** H. B. Herman, University of Georgia, Athens, Ga., A. J. Bard, University of Texas, Austin, Texas.
3:50 **Chronopotentiometry at an Inverted Mercury Drop Electrode.** R. J. Joyce, Beckman Instruments, 2500 Harbor Blvd., Fullerton, Calif.
4:10 **Detection of a Radical Intermediate during the Electrochemical Oxidation of 3-Aminophthalhydrazide.** W. G. Hodgson, D. L. Maricle, M. M. Rauhut, American Cyanamid Co., 1937 W. Main St., Stamford, Conn.
4:25 **Effect of Adsorbable Substances on Potentiostatic Current-Time Curves.** S. L. Phillips, IBM Corp., Dept. C27, Bldg. 702, Poughkeepsie, N. Y.
6:00 **DIVISION DINNER IN HONOR OF L. T. HALLETT**

Wednesday Afternoon, Sept. 15

Section B

SYMPOSIUM ON THE APPLICATIONS OF KINETICS TO ANALYTICAL PROBLEMS

Harry L. Pardue, Presiding

2:05 **Use of Enzymes in Analytical Chemistry.** G. G. Guilbault, Chemical Research and Development Laboratories, Edgewood Arsenal, Md.
2:45 **Discussion**
2:50 **Analytical Application of Immobilized Enzyme Systems.** G. P. Hicks, S. J. Updike, University of Wisconsin, 359 N. University Hospital, Madison, Wis. 53706.
3:20 **Discussion**
3:25 **Quantitative Analysis by Automatic Reaction-Rate Measurements.** H. L. Pardue, Chemistry Department, Purdue University, Lafayette, Ind.
4:00 **Discussion**
4:05 **Investigation of Some Rapid Analytical Reactions Using Specific-Ion Glass Electrodes.** G. A. Rechnitz, J. McClure, Department of Chemistry, University of Pennsylvania, Philadelphia, Pa. 19104.

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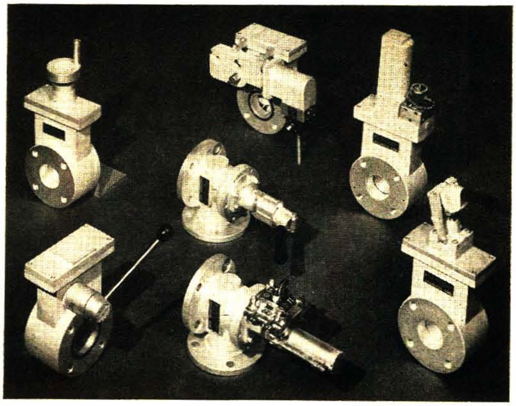

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4:25 Discussion
4:30 Adjusting Chemical Systems to Utilize Kinetic Methods. G. H. Schenk, T. W. Osolinski, Department of Chemistry, Wayne State University, Detroit, Mich. 48202.
4:50 Discussion

Thursday Morning, Sept. 16

SYMPOSIUM ON GAS CHROMATOGRAPHY

W. D. Cooke, Presiding

9:05 Gas Liquid Chromatographic Study of the Thermodynamics of Solution of Aromatic Compounds: A Tetrahalophthalate Liquid Phase. S. H. Langer, Chemical Engineering Department, University of Wisconsin, Madison, Wis. 53706, Howard Purnell, Department of Physical Chemistry, Lensfield, Cambridge, England.
9:35 Solute Adsorption at the Gas-Liquid Interface. D. E. Martire, Department of Chemistry, Georgetown University, Washington, D. C. 20007.
10:00 Mixed Carrier Gases: A Fundamental Approach to Quantitative Gas Chromatography Based on Kinetic Theory. Joseph Jordan, Barbara Kebbekus, Department of Chemistry, Pennsylvania State University, University Park, Pa.
10:50 Gas Liquid Chromatographic Studies on the Mechanism of Diastereomeric Ester Resolutions. H. C. Rose, R. L. Stern, B. L. Karger, Department of Chemistry, Northeastern University, Boston, Mass.
11:20 Quantitative Gas Chromatographic Analysis of Halogen Substituted Hydrocarbons Using Thermal Conductivity Cells. R. S. Fischer, D. M. Rosie, Chemistry Department, University of Rhode Island, Kingston, R. I.
11:40 The Gas Chromatographic Performance of Large Diameter Columns (Up to Four Inch). L. Mikkelsen, F. J. Debbrecht, A. J. Martin, F & M Scientific Corp., Avondale, Pa.

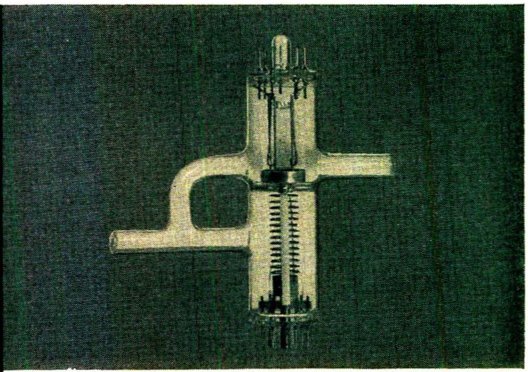
Thursday Afternoon, Sept. 16

Section A

GENERAL PAPERS

John K. Taylor, Presiding

2:05 Spectropolarimetric Titrimetry. The Determination of Both Optically Active and Inactive Weak Acids and Bases. K. H. Pearson, Stanley Kirschner, Department of Chemistry, Wayne State University, Detroit, Mich. 48202.
2:25 Analysis of Organometallic Fungicides and Related Compounds by Atomic Absorption Spectroscopy. B. J. Gudzinowicz, V. J. Luciano, Jarrell-Ash Co., 590 Lincoln St., Waltham, Mass.
2:40 Critical Factors in the Atomic Absorption Determination of the Alkaline Earth Elements in Glass. P. B. Adams, W. O. Passmore, Corning Glass Works, Corning, N. Y.
2:55 A Unified Treatment for the Interpretation of K-Edge X-Ray Absorption Spectra of Transition-Metal Compounds. R. M. Levy, J. R. Van Wazer, Monsanto Co., 800 N. Lindbergh Blvd., St. Louis, Mo. 63166.
3:30 Chelate–Water Adducts in Nitromethane Observed by Proton Nuclear Magnetic Resonance. C. E. Meloan, Kansas State University, Manhattan, Kan., D. R. Gere, Aerospace Research Laboratories, Wright-Patterson AFB, Ohio.
3:45 The Effect of Hydrogen Bonding on the NMR Spectra of Aliphatic Compounds. P. E. Peterson, Chemistry Department, St. Louis University, 1402 South Grand Blvd., St. Louis, Mo. 63104.
4:00 The Use of Mössbauer Effect to Study the Adsorption of Iron on Cationic Ion Exchange Resins. J. J. Spijkerman, A. R. Landgrebe, F. C. Ruegg, J. R. DeVoe, National Bureau of Standards, Washington, D. C. 20234.
4:15 Indicator Studies of Acid-Base Reactions in Benzene. Joseph Steigman, Department of Chemistry, Polytechnic



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Thursday Afternoon, Sept. 16

Section B

SYMPOSIUM ON GAS CHROMATOGRAPHY

Douglas M. Rosie, Presiding

2:05 **Boiling Points of C_{10}–C_{15} Straight Chain Alkylbenzene Isomers from Gas Chromatographic Retention Data.** F. Baumann, A. E. Straus, J. F. Johnson, California Research Corp., Richmond, Calif. 94802.

2:20 **Quantitative Gas Chromatography of Amino Acids. Chromatographic Separation of** n**-Butyl N-Trifluoroacetyl Esters.** F. Shahrokhi, C. W. Gehrke, University of Missouri, Room 4, Agriculture Bldg., Columbia, Mo.

2:40 **Inverse GLC—A New Approach for Studying Petroleum Asphalts.** T. C. Davis, J. C. Petersen, W. E. Haines, Laramie Petroleum Research Center, P. O. Box 3395, University Station, Laramie, Wyo.

3:00 **Studies of the Gas Density Cell.** D. M. Rosie, Department of Chemistry, University of Rhode Island, Kingston, R. I., J. T. Walsh, U. S. Army Natick Laboratories, Natick, Mass.

3:35 **Gas Chromatographic Determination of 2,3-Diketones at Nanogram Concentrations Using the Electron Affinity Detector.** B. J. Gudzinowicz, K. Johnson, Jarrell Ash Co., Waltham, Mass.

3:50 **The Detection of Drugs in the Blood of Race Horses Using Gas Chromatography.** W. A. Winsten, Hofstra University, Hempstead, N. Y., T. J. Manning, The Prerace Testing Research Laboratory, Roosevelt Raceway, Westbury, N. Y.

4:05 **Analog Computer Program for the Resolution of Overlapping Distribution Curves.** R. O. Butterfield, E. B. Lancaster, H. J. Dutton, Northern Utilization Research and Development Division, 1815 North University, Peoria, Ill. 61604.

Friday Morning, Sept. 17

GENERAL PAPERS

Eugene D. Olsen, Presiding

9:05 **Crosslinked Polyacrylamide Gel as a Dehydrating Agent.** A. E. Sherr, American Cyanamid Co., 1937 W. Main St., Stamford, Conn., A. M. Swift, American Cyanamid Co., Wayne, N. J.

9:15 **Rapid Removal of Alkali Metals from Quaternary Ammonium Bases by Ion Exchange.** E. D. Olsen, R. L. Poole, Jr., Department of Chemistry, University of South Florida, Tampa, Fla.

9:30 **The Detection of** in situ **Compound Instability of Two Dimensional Thin Layer Chromatography.** M. H. Penner, J. M. Talmage, M. Geller, Warner-Lambert Research Institute, Morris Plains, N. J.

9:50 **Ultrapurification by Counter-Current Crystallization: The Freezing Stair-Step Method.** C. P. Saylor, Analytical Chemistry Division, National Bureau of Standards, Washington, D.C. 20234.

10:05 **Determination of Rare Earths by Radiochromatography.** G. A. Welford, E. L. Chiotis, R. S. Morse, U. S. Atomic Energy Commission, 376 Hudson St., New York, N. Y. 10014.

10:20 **A New Method of Analysis Using Radioisotopic Tracers—A Concentration Dependent Method.** A. R. Landgrebe, L. T. McClendon, J. R. DeVoe, National Bureau of Standards, Washington, D.C. 20234.

10:40 **Determination of Dissolved Ammonia in Dilute Aqueous Solutions by Gas Chromatography.** R. W. Jenkins, Jr., C. H. Check, V. J. Linnenbom, U. S. Naval Research Laboratory, Washington, D. C. 20390.

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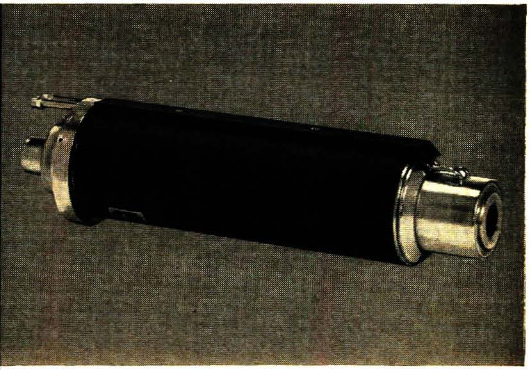

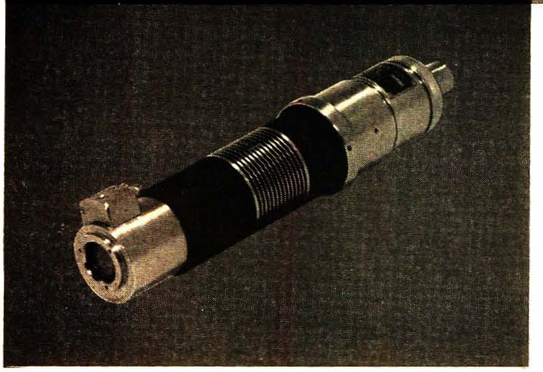

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Δ^4-Androstene-3, 17-dione-7α-T	500-1000
Cholesterol-T (G)	100-300
Cholesterol-7α-T	100-500
Cholesterol-7α-T	>2000
Cholesteryl-T (G) linoleate	50-350
Cholesteryl-7α-T linoleate	100-500
Cholesteryl-T (G) oleate	50-350
Cholesteryl-7α oleate	100-350
Cholesteryl oleate-(*nominally* 9, 10-T)	100-500
Cholesteryl-7α-T palmitate	500-1000
Cholesteryl palmitate-(*nominally* 9, 10-T)	100-300
Cholesteryl-T (G) stearate	50-350
Cholesteryl-7α-T stearate	100-500
Cholesteryl stearate-, (*nominally* 9, 10-T)	100-500
Corticosterone-1, 2-T	250-1000
Corticosterone-1, 2-T	>30,000
Cortisol-1, 2-T [Hydrocortisone-1, 2-T]	1000-2000
Cortisol-1, 2-T [Hydrocortisone-1, 2-T]	>30,000
Cortisone-T (G)	25-250
Dehydroe*pi*androsterone-7α-T	250-1000
Dehydroe*pi*androsterone-7α-T	>5000
Dehydroe*pi*androsterone-7α-T acetate	500-1800
Diethylstilboestrol-T (G)	100-500
Estradiol-T (G)	50-100
Estradiol-2, 4-T	500-1000
Estradiol-6, 7-T	100-500
Estradiol-6, 7-T 17β-acetate	500-1000
Estradiol-6, 7-T 17β-acetate	>3000
Estrone-T (G)	100-200
Estrone-6, 7-T	100-500
Hexestrol-T [*meso*-3, 4-*bis-p*-Hydroxyphenyl-*n*-hexane-(*nominally* 2, 3, 4, 5-T)]	100-1000
Δ^5-Pregnenolone-16-T	1000-1500
Δ^5-Pregnenolone-7α-T	100-500
Progesterone-T (G)	100-500
Progesterone-7α-T	100-500
Testosterone-1, 2-T	500-1000
Testosterone-1, 2-T	>15,000
Testosterone-7α-T	500-1000

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Third International Symposium on Advances in Gas Chromatography

The University of Houston is sponsoring the Third International Symposium on Advances in Gas Chromatography to be held at the Sheraton-Lincoln Hotel in Houston, Texas, on October 18–21, 1965. The meeting consists of papers by outstanding scientists from the U. S. and abroad. Topics include recent advances in theory, ancillary chromatographic devices, new column techniques, and the analysis of flavors. A special session on new detectors for liquid chromatographic systems for compounds of biological interest has also been included. Informal discussion groups are being planned for preparative scale chromatography, flavors, column design, and biochemical chromatography. An exhibition of the latest chromatographic instrumentation and accessories as well as a book exhibit will be held during the symposium. Attendance at the symposium is limited and applications will be accepted in order of receipt of the registration forms. Details of the meeting and registration forms are available from Prof. A. Zlatkis, Chemistry Department, University of Houston, Houston, Texas.

PROGRAM

Monday Morning, Oct. 18

A. I. M. Keulemans, Presiding

9:00 **Introductory Remarks.** A. Zlatkis, Symposium Chairman. J. O. Allred, Vice-President, University of Houston.

9:10 **Life Detection by Gas Chromatography.** J. E. Lovelock, University of Houston, Houston, Texas.

9:40 **Resolution of Optical Isomers by Gas Chromatography.** E. Gil-Av, Weizmann Institute of Science, Rehovoth, Israel.

10:10 **Gas Chromatography of Volatile Metal Complexes.** R. E. Sievers, Wright-Patterson Air Force Base, Dayton, Ohio.

11:00 **An Electrical Discharge Pyrolyzer for Gas Chromatography.** J. C. Sternberg, Beckman Instruments, Inc., Fullerton, Calif.

11:30 **Gas Chromatography of Isotopic Molecules by Open Tubular Columns.** A. Liberti, Istituto Chimica Analitica-Universita-Napoli, Italy.

Monday, Afternoon, Oct. 18

S. Dal Nogare, Presiding

2:00 **A Simple Approach to the Rate Theory of Gas Chromatography.** I. Halasz, Institut fur physikalische Chemie der Universitat Frankfurt am Main, Germany.

2:30 **Electrostatic Interactions in Gas Solid Chromatography.** J. King, Jr., Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif.

3:00 **Evidence for Turbulence and "Coupling" in Chromatographic Columns.** J. H. Knox, University of Edinburgh, Edinburgh, Scotland.

4:00 **Correlation of Retention Data and Structural Parameters of Carboxyl Compounds.** J. F. Haken, University of New South Wales, Kensington, N.S.W., Australia.

4:20 **Support Effects on Retention Volumes in Gas Chromatography: Practical and Theoretical Aspects.** P. Urone, University of Colorado, Boulder, Colo.

Tuesday Morning, Oct. 19

S. R. Lipsky, Presiding

9:00 **Ultrasonic Velocity Instrumentation for Liquid and Gas Chromatography Effluent Detection.** K. Abel, National Heart Institute, Bethesda, Md.

9:30 **Design and Operation of Gas Phase Ionization Detectors for Liquid Chromatography.** E. Haahti, University of Turku, Turku, Finland.

10:00 **A Liquid Chromatographic System for the Analysis of Macromolecules.** J. Stouffer, Baylor University College of Medicine, Houston, Texas.

11:00 **A Flame Ionization Detector for Liquid-Liquid Chromatography.** A. Karmen, The Johns Hopkins University, Baltimore, Md.

11:30 **Separation of Derivatives of Biogenic Amines.** E. C. Horning, Baylor University College of Medicine, Houston, Texas.

Tuesday Afternoon, Oct. 19

L. S. Ettre, Presiding

2:00 **Investigation of Formamide as a Useful Gas Chromatography Stationary Phase of Extreme Selectivity and Without Flame Ionization Signal.** J. Janak, Czechoslovak Academy of Sciences, Brno, Czechoslovakia.

2:30 **Determination of the Polarity of Stationary Phases Used in Gas Chromatography.** P. Chovin, Laboratoire Municipal, Prefecture de Police, Paris, France.

3:00 **Clean Gases for Chromatography.** B. Osborne Prescott, Shell Development Company, Houston, Texas.

3:30 **Preparative Scale Separation of Multicomponent Mixtures by Continuous Gas Chromatography.** P. E. Barker, University of Birmingham, Birmingham, England.

Wednesday Morning, Oct. 20

J. L. Monkman, Presiding

9:00 **Contemporary Gas-Solid Chromatography.** C. G. Scott, Lobitos Oilfields Ltd., Cheshire, England.

9:30 **Micro-Packed Columns for High Speed Gas Chromatography.** I. Halasz, Institut fur physikalische Chemie der Universitat Frankfurt am Main, Germany.

10:30 **High Resolution Capillary Adsorption Columns for Gas Chromatography.** R. D. Schwartz, Shell Development Company, Houston, Texas.

11:00 **Application of High Pressure Gas Chromatography to Micro Packed**

Columns. J. C. Giddings, University of Utah, Salt Lake City, Utah.
11:30 **High Speed Chromatography.** V. Pretorius, University of Pretoria, Pretoria, South Africa.

Wednesday Afternoon Oct. 20

H. R. Felton, Presiding

2:00 **Quality and Flavors of Wine, Rum, and Brandy by Gas Chromatography.** E. Bayer, Chemisches Institut der Universitat, Tubingen, Germany.
2:30 **Gas Chromatographic Analysis of Steam Volatile Aroma Constituents: Application to Coffee, Tea, and Cocoa Aromas.** D. Reymond, Research Laboratories for Nestle's Products, Vevey, Switzerland.
3:00 **Gas Chromatography of Sesquiterpenoids.** R. Teranishi, Western Regional Research Laboratory, Albany, Calif.
3:30 **Behavior of Stationary Phases at Cryogenic Temperatures.** C. Merritt, Jr., U. S. Army Natick Laboratories, Natick, Mass.

Thursday Morning, Oct. 21

C. G. Scott, Presiding

9:00 **The Efficiency of Molecule Separators in Gas Chromatography-Mass Spectrometry Instruments.** R. Ryhage, Karolinska Institutet, Stockholm, Sweden.
9:30 **Micro Gas Chromatography.** W. F. Wilhite, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif.
10:00 **A Specific Detector for Phosphorous and for Sulfur Compounds—Sensitive to Subnanogram Quantities.** S. S. Brody, Melpar, Inc., Falls Church, Va.
11:00 **New Column Systems for Gas Chromatography.** R. P. W. Scott, Unilever Research Laboratories, Sharnbrook, England.
11:45 **Summary.** J. H. Knox, University of Edinburgh, Edinburgh, Scotland.

Conference on Analytical Chemistry in Nuclear Technology

The ninth conference on analytical chemistry in nuclear technology will be held in Gatlinburg, Tenn., October 12 to 14. This meeting is sponsored by the Analytical Chemistry Division of the Oak Ridge National Laboratory. The conferences will be held in the Huff House of the Mountain View Hotel. Six sessions will cover the following subjects: analytical chemistry of the transuranium elements; symposium on the role of analytical chemistry in pure materials research; selected papers on bioanalytical techniques; and miscellaneous subjects.

Participation in the conference is on the basis of invited contributions; however, a limited number of other papers will be accepted if the subject matter is

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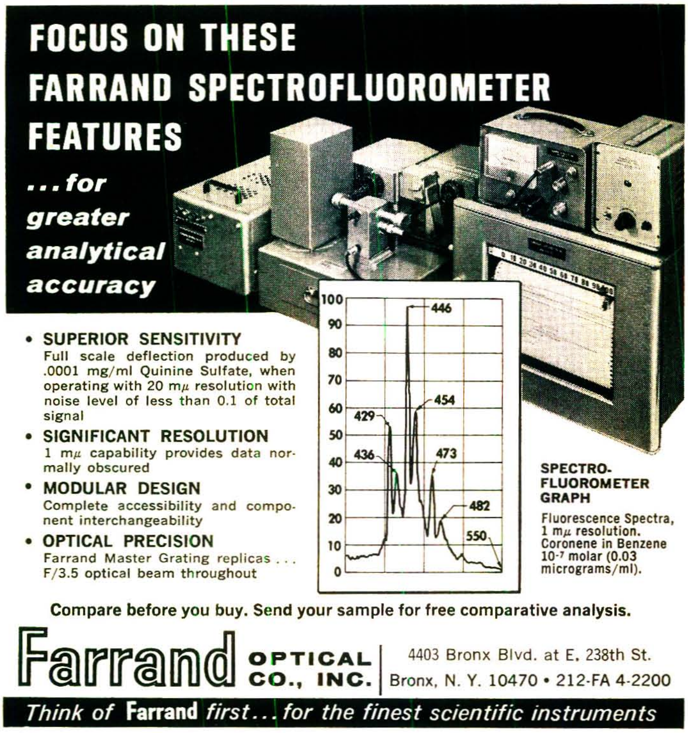
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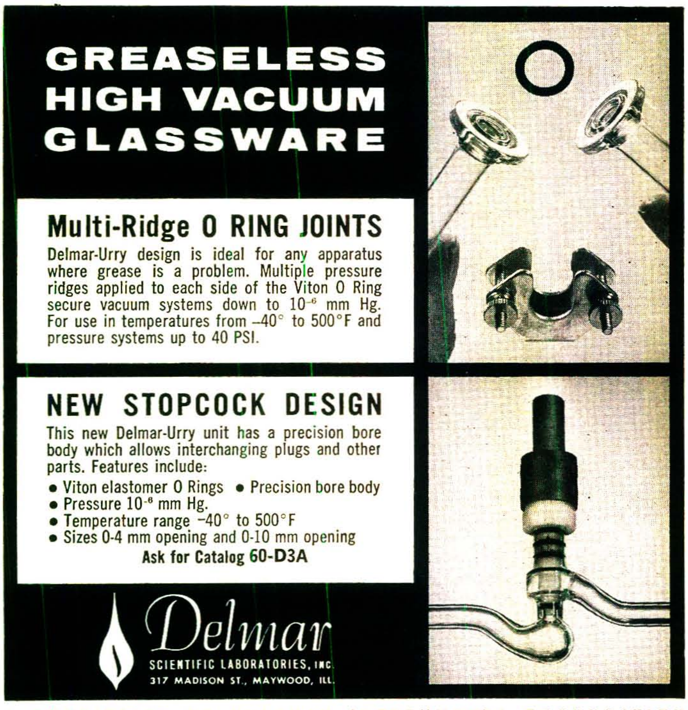
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relevant to the purposes of the conference and meets with the approval of the program committee. Inquiries concerning the conference should be directed to Mr. C. D. Susano, Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tenn. 37831.

Symposium on Automation in Analytical Chemistry

A symposium, sponsored by Technicon Controls, Inc., on automation in analytical chemistry will be held at the Statler-Hilton Hotel, N. Y., September 8 to 10. Reports will cover significant developments in a variety of industries, including power and water, food and beverage, pharmaceutical, agricultural, pulp and paper, and metallurgy, as well as automated analysis of air, water, and waste pollution, and automated control techniques applicable to many industries. Other sessions will cover advances in the automation of diagnostic and clinical procedures and the use of automation in medical research. More than 130 papers will be presented along with panel discussions and colloquia. Admission is free but requires preregistration. Further information is available by writing Technicon, Chauncey, N. Y.

Gas Chromatography Workshop

The School of Pharmacy of the University of Southern California will hold a workshop on biomedical applications of gas chromatography, September 13 to 16. This workshop is held in cooperation with F & M Scientific Corp. For applications and further information, write Dr. Walter Wolf, School of Pharmacy, University of Southern California, Los Angeles, Calif. 90007.

International Symposium on Nuclear Magnetic Resonance

An international symposium on novel applications of nuclear magnetic resonance will be held at the Akasaka Prince Hotel, Tokyo, Japan, September 1 to 3. A presymposium meeting on NMR in analytical chemistry will be held at the University of Tokyo, August 30 or 31, and a postsymposium meeting on applications on NMR will be held at Kyoto, September 5 or 6. The meetings are sponsored by the Chemical, Physical, and Pharmaceutical Societies of Japan and the Japan Societies for Analytical Chemistry and Applied Physics. Cosponsors are the American Chemical

Society Division of Physical Chemistry and the International Union of Pure and Applied Chemistry. About 50 Japanese and 30 foreign speakers are scheduled. The language of the symposium is English. For further information write Dr. Shizuo Fujiwara, Department of Chemistry, University of Tokyo, Tokyo, Japan.

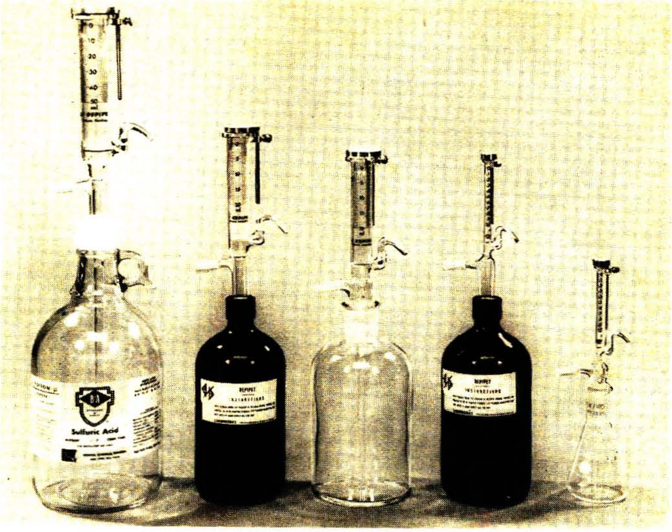
Pittsburgh Diffraction Conference

The twenty-third annual Pittsburgh Diffraction Conference will be held Nov. 3 to 5 at the Mellon Institute, Pittsburgh, Pa. Papers are invited on any aspect of diffraction, crystallography, or crystal physics. Special sessions will be held on metals; ceramics; structures; crystal physics, lattice dynamics, crystalline imperfections; instrumentation and techniques. A symposium will be held on texture and preferred orientation in polymers. Guest speaker Thursday evening will be Elizabeth Wood of Bell Telephone Laboratories. Inquiries for presenting papers and abstracts, not to exceed 400 words, should be sent to Dr. B. R. Banerjee, Crucible Steel Co., 234 Atwood, Pittsburgh, Pa. 15213. Abstracts are due before September 17. Information for the exhibition of equipment is available from Dr. Gordon Sargent, Mellon Institute, 440 Fifth Ave., Pittsburgh, Pa. 15213. General information is available from Paul A. Flinn, Carnegie Institute of Technology, Pittsburgh, Pa. 15213.

AOAC Annual Meeting

The 79th annual meeting of the Association of Official Agricultural Chemists will be held Oct. 11 to 14 at the Marriott Motor Hotel, Twin Bridges, Washington, D. C. Noted scientists will give addresses on topics such as statistics, modern instrumentation, laser beam applications, and organoleptic techniques. Over 200 other scientific papers on analytical methods will be presented on a variety of topics, including antibiotics, cosmetics, drugs, feeds, foods, food additives, fertilizers, sanitation analysis, microbiological assays, flavors, and others.

The banquet Monday evening, Oct. 11, will feature Dr. Harold A. Wooster, Office of Scientific Research, United States Air Force, who will speak on a topic of general interest. The American Light Company will entertain. Another important event will be the presentation of the Harvey W. Wiley Award to a scientist who has made outstanding contributions to analytical methodology. About 35 exhibitors will show



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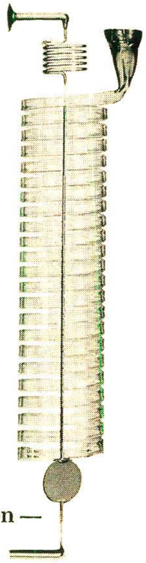

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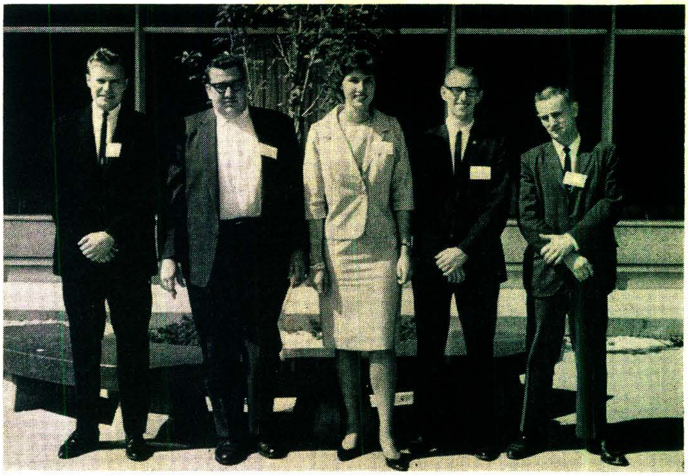

Participants of the Undergraduate Chemical Research Symposium were (l. to r.): Conrad Schmakel, University of Illinois; Ken Kosanke, Wisconsin State University; Collene Delaney, Purdue University; Ralph Allen, Cornell College; Jerry King, Butler University; and William Kator (not shown), Indiana University. This symposium was part of the Analytical Chemistry Summer Program held June 8 to 11 at the University of Wisconsin, Madison, Wis. Prize winning student papers were those given by Ralph Allen, 1st prize, and Collene Delaney, 2nd prize

the latest equipment and supplies in appropriate analytical areas of interest to the Association. Additional information for those who wish to present papers, to exhibit, or to obtain the program may be obtained from Luther G. Ensminger, Association of Official Agricultural Chemists, Box 540, Benjamin Franklin Station, Washington, D. C. 20044.

Gel Permeation Chromatography

A seminar for users of gel permeation chromatography will be held September 16 and 17 at the Sheraton-Boston Hotel, Prudential Center, Boston, Mass. The program will include a number of papers by users of gel permeation. Both formal and informal discussions on various topics relating to the technique will take place. Information on this meeting is available by writing Waters Assoc., Inc., 61 Fountain St., Framingham, Mass. 07102.

SAS Affiliates with American Institute of Physics

The American Institute of Physics has named the Society for Applied Spectroscopy an affiliate member. The Institute will provide publishing and printing services for *Applied Spectroscopy,* official journal of the Society.

The Society for Applied Spectroscopy with 2600 members includes 24 local sections devoted to the dissemination of knowledge and information about spectroscopy and allied sciences. The President of the SAS is John R. Ferraro, Argonne National Laboratory.

Internal Reflection Spectroscopy Workshops

Wilks Scientific Corp. will sponsor six two-day workshops on internal reflection spectroscopy at its headquarters in South Norwalk, Conn. Dates for the courses are: Sept. 21, 22; Oct. 5, 6; Oct. 19, 20; Nov. 9, 10; Nov. 30, Dec. 1; Dec. 14, 15. There is no charge for attendance but enrollment is limited to 14 per session. For more information write to Mr. Gregory Propster, Wilks Scientific Corp., Box 441, South Norwalk, Conn.

Industry Items

LKB Instruments, Inc., manufacturers and suppliers of laboratory equipment, has moved to larger quarters at Parklawn Drive, Rockville, Md. 20852.

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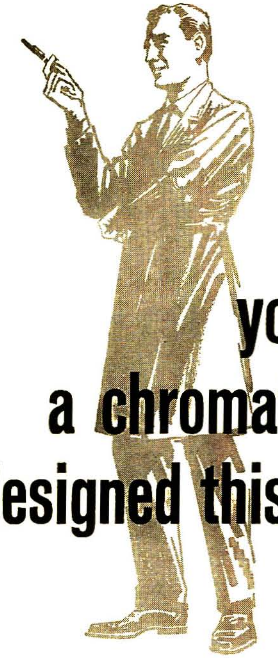

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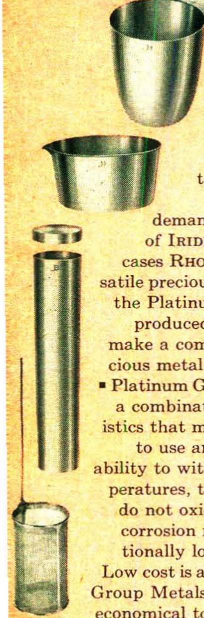

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CALENDAR OF EVENTS

Aug. 1 to 8	**IX Latin America Chemical Congress.** San Juan, Puerto Rico. Includes analytical chemistry sessions. *Contact:* Rafael M. Méndez, Box 2647, Río Piedras, Puerto Rico.
Aug. 2 to 6	**2nd Instrument Society of America Research Conference on Instrumentation Science.** William Smith College, Geneva, N. Y. *Contact:* Karl B. Schnelle, Jr., 530 William Penn Place, Pittsburgh, Pa. 15219.
Aug. 2 to 6	**Gordon Research Conference on Ion Exchange.** New London, N. H. *Contact:* Dr. W. George Parks, Gordon Research Conferences, University of Rhode Island, Kingston, R. I.
Aug. 9 to 13	**Gordon Research Conference on Analytical Chemistry.** New Hampton School, New Hampton, N. H. *Contact:* Dr. W. George Parks, Gordon Research Conferences, University of Rhode Island, Kingston, R. I. Page 49 A, May.
Aug. 11 to 13	**Twentieth Calorimetry Conference.** Ames, Iowa. Sponsor: Institute of Atomic Research, Iowa State University. *Contact:* Ralph Hultgren, University of California, Berkeley, Calif. Page 90 A, Feb.
Aug. 14 to 20	**8th European Spectroscopy Conference.** Copenhagen, Denmark. *Contact:* Borge Bak, University of Copenhagen, Department of Chemical Physics, IHIC Orsted Institutet, 5 Universitetsparen, Copenhagen, Denmark.
Aug. 22 to 27	**International Symposium on Microchemical Techniques.** University Park, Pa. Sponsors: American Microchemical Society, IUPAC. *Contact:* Mr. Howard Francis, Jr., Pennsalt Chemicals Corp., 900 First Ave., King of Prussia, Pa. Page 75 A, July.
Aug. 23 to 27	**Gordon Research Conference on Separation and Purification.** New London, N. H. *Contact:* Dr. W. George Parks, Gordon Research Conferences, University of Rhode Island, Kingston, R. I.
Aug. 25 to 27	**Annual Denver Research Institute X-Ray Conference.** Denver, Colo. *Contact:* Denver Research Institute, University of Denver, Colo. 80210. Page 53 A, Mar.
Aug. 25 to 28	**23rd Annual Meeting Electron Microscopy Society of America.** Statler-Hilton Hotel, New York City. *Contact:* Dr. Leonard Ross, Department of Anatomy, Cornell University Medical College, 1300 York Ave., New York City. Page 46 A, Apr.
Aug. 29 to Sept. 2	**17th Annual Meeting of the American Association of Clinical Chemists.** Sheraton-Park Hotel, Chicago, Ill. *Contact:* Mr. Alvin Dubin, Cook County Hospital, Chicago, Ill. 60612.
Aug. 30 to Sept. 3	**Fourth National Meeting of Society for Applied Spectroscopy.** Denver-Hilton Hotel, Denver, Colo. *Contact:* Merlyn L. Salmon, Fluo-X-Spec Laboratory, 718 Sherman St., Denver, Colo. Page 49 A, Mar.
Aug. 30 to Sept. 4	**International Symposium on Macromolecular Chemistry.** Prague, Czechoslovakia. Includes section on methods used in research of chemical or steric structure and properties of macromolecular compounds and systems. *Contact:* Organizing Committee, International Symposium on Macromolecular Chemistry, 1888 Petriny, Prague 6, Czechoslovakia.

Coming Events

Sept. 1 to 3—**International Symposium on Nuclear Magnetic Resonance.** Akasaka Prince Hotel, Tokyo, Japan. *Contact:* Dr. Shizuo Fujiwar, Department of Chemistry, University of Tokyo, Tokyo, Japan. Page 46 A, Aug.

Sept. 6 to 9—**First International Conference on Thermal Analysis.** Aberdeen, Scotland. Theme: Thermal Techniques and Their Applicability. *Contact:* Dr. C. B. Murphy, Bldg. 5, Rm. 159, General Electric Co., Schenectady 5, N. Y. Page 89 A, Feb.

Sept. 8 to 10—**1965 Technicon International Symposium on Automation in Analytical Chemistry.** Statler-Hilton Hotel, New York City. Sponsor: Technicon Instruments Corp. *Contact:* Edwin C. Whitehead, Technicon, Chauncey, N. Y. Page 46 A, Aug.

Sept. 9 to 12—**EUCHEM Conference on Mass Spectrometry.** Sarlat, France. *Contact:* Prof. M. Fetizon, École Polytechnique, 17 Rue Descartes, Paris 5, France. Page 53 A, Mar.

Sept. 12 to 17—**150th National ACS Meeting.** Atlantic City, N. J. Includes Analytical Division Sessions. *Contact:* Dr. John K. Taylor, National Bureau of Standards, Washington, D. C. 20234. Page 39 A, Aug.

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Sept. 13—Second Symposium on Biological Applications of Gas Chromatography. Ecole Polytechnique, Paris, France. *Contact:* G. Guiochon, Ecole Polytechnique, 17, rue Descartes, Paris 5, France.

Sept. 13 to 18—National Meeting of the German Chemical Society and Kekulé Centennial. Includes Analytical Chemistry Section Meeting on Electroanalysis of Organic Substances. *Contact:* KDCh-Geschäfsstelle, Frankfurt (Main), Postfach 9075, Germany.

Sept. 15—Symposium on Thermometric Titrimetry. Birmingham University. *Contact:* M. L. Richardson, John & E. Sturge Ltd., Lifford Chemical Works, Lifford Lane, Kings Norton, Birmingham, 30, England. Page 51 A, Mar.

Sept. 21 to 24—Sixteenth Testing Conference, TAPPI. Netherland-Hilton Hotel, Cincinnati, Ohio. *Contact:* A. Edward Dembitz, Technical Association of the Pulp and Paper Industry, 360 Lexington Ave., New York 17, N. Y.

Sept. 22 to 24—Fourth Annual Meeting on the Practice of Gas Chromatography. Sheraton-Jefferson Hotel, St. Louis, Mo. Sponsor: Committee E-19 on Gas Chromatography of ASTM. *Contact:* Nathaniel Brenner, Perkin-Elmer Corp., Main Ave., Norwalk, Conn.

Sept. 22 to 24—Fourth Annual Pacific Conference on Spectroscopy, Instrumentation, and Chemistry. Huntington-Sheraton Hotel, Pasadena, Calif. *Contact:* W. T. Barnes, General Dynamics Corp., Pomona, Calif. Page 44 A, Apr.

Sept. 25—3rd International Meeting, Journées Internationales de la Séparation Immédiate et de la Chromatographie. Athens, Greece. *Contact:* Dr. G. Patissakis, Professor of the Technical University of Athens, G. A. M. S., 1 rue Gaston Boissier, Paris 15e, France. Page 54 A, Mar.

Sept. 27 to 28—Informal Conference on Vacuum Microbalance Techniques. Nassau Inn, Palmer Square, Princeton, N. J. *Contact:* Dr. Klaus H. Behrndt, Bell Telephone Laboratories, Murray Hill, N. J. Page 54 A, June.

Oct. 4 to 6—Meeting on Industrial Organic Analysis. Drawbridge Inn, Sarnia, Ontario. Sponsor: Analytical Chemistry Division of the Chemical Institute of Canada. *Contact:* R. M. Small, Research Department, Polymer Corp., Ltd., Sarnia, Ont., Canada. Page 50 A, Mar.

Oct. 4 to 7—20th Annual Instrument Society of America Conference on Instrumentation and Exhibit. Sports Arena, Los Angeles, Calif. *Contact:* ISA, Penn-Sheraton Hotel, 530 William Penn Place, Pittsburgh, Pa. 15219.

Oct. 4 to 7—Annual Research Equipment Exhibit and Instrument Symposium. National Institutes of Health, Bethesda, Md. *Contact:* James B. Davis, National Institutes of Health, Bethesda, Md. 20014. Page 55 A, June.

Oct. 10 to 14—Fifth Annual Conference on Pharmaceutical Analysis. King's Gateway-Land O'Lakes, Wis. *Contact:* The University of Wisconsin, School of Pharmacy, Madison, Wis.

Oct. 11 to 14—Association of Official Agricultural Chemists 79th Annual Meeting. Marriott Twin Bridges Motor Hotel, Washington, D. C. *Contact:* Luther G. Ensminger, Association of Official Agricultural Chemists, Box 540, Benjamin Franklin Station, Washington, D. C. 20044. Page 47 A, Aug.

Oct. 12 to 14—Ninth Conference on Analytical Chemistry in Nuclear Technology. Mountain View Hotel, Gatlinburg, Tenn. *Contact:* Mr. C. D. Susano, Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tenn. 37831. Page 45 A, Aug.

Oct. 13 to 19—INTERKAMA, International Congress and Exhibition for Instrumentation and Automation. Düsseldorf, Germany. *Contact:* Nordwestdeutsche Ausstellungs- und Messe-Gesellschaft mbH, 4 Düsseldorf 10, Postfach 10 203, Germany/Allemagne.

Oct. 18 to 20—Twelfth Ottawa Symposium on Applied Spectroscopy. Ottawa, Canada. *Contact:* R. V. Baker, Aluminum Co. of Canada, Ltd., Arvida, Quebec, Canada. Page 45 A, Apr.

Oct. 18 to 21—Third International Symposium on Advances in Gas Chromatography. Sheraton-Lincoln Hotel, Houston, Texas. *Contact:* Prof. A. Zlatkis, Department of Chemistry, University of Houston, Houston, Texas. Page 44 A, Aug.

Oct. 18 to 22—25th National Convention of the Society for Nondestructive Testing. Embassy Hotel, Detroit, Mich. *Contact:* Society for Nondestructive Testing, Inc., 914 Chicago Ave., Evanston, Ill.

Oct. 19 to 21—13th Anachem Conference. Wayne State University, Detroit, Mich. *Contact:* Dr. George Schenk, Department of Chemistry, Wayne State University, Detroit, Mich. 48202. Page 45 A, Apr.

Oct. 31 to Nov. 5—ASTM Fifth Pacific Area National Meeting and 4th West Coast Materials Testing Exhibit. Olympic Hotel, Seattle, Wash. *Contact:* American Society for Testing and Materials, 1916 Race St., Philadelphia 3, Pa.

Nov. 3 to 5—Twenty-Third Pittsburgh Diffraction Conference. Mellon Institute, Pittsburgh, Pa. *Contact:* Paul A. Flinn, Carnegie Institute of Technology, Pittsburgh 13, Pa. Page 47 A, Aug.

Nov. 5 to 15—First Midwest Regional ACS Meeting. University of Missouri, Kansas City, Mo. Includes topics of interest to analytical chemists. *Contact:* John A. Landgrebe, Department of Chemistry, University of Kansas, Lawrence, Kan.

Nov. 11 to 13—Third Conference on X-Ray Analysis, Japan. Osaka, Japan. *Contact:* Kozo Momoki, Yokohoma National University, Ooka-machi, Minami-ku, Yokohamashi, Japan. Page 55 A, June.

Nov. 16 to 18—AtomFair '65. Sheraton-Park Hotel, Washington, D. C. Held in conjunction with the annual conference of the Atomic Industrial Forum and the 1965 winter meeting of the American Nuclear Society. *Contact:* AtomFair, 850 Third Ave., New York, N. Y. 10022.

Nov. 17 to 19—Seventh Eastern Analytical Symposium. Statler Hilton Hotel, New York City. *Contact:* Bourdon F. Scribner, Spectrochemistry Division, National Bureau of Standards, Washington, D. C. 20234. Page 44 A, Apr.

Nov. 18 to 19—Conference on Computational Methods in Crystallography. Institution of Electrical Engineers, London, England. *Contact:* The Institute of Physics and The Physical Society, 47 Belgrave Square, London, S. W. 1, England. Page 54 A, June.

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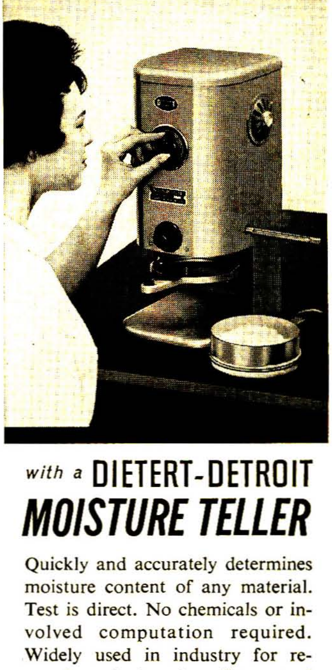

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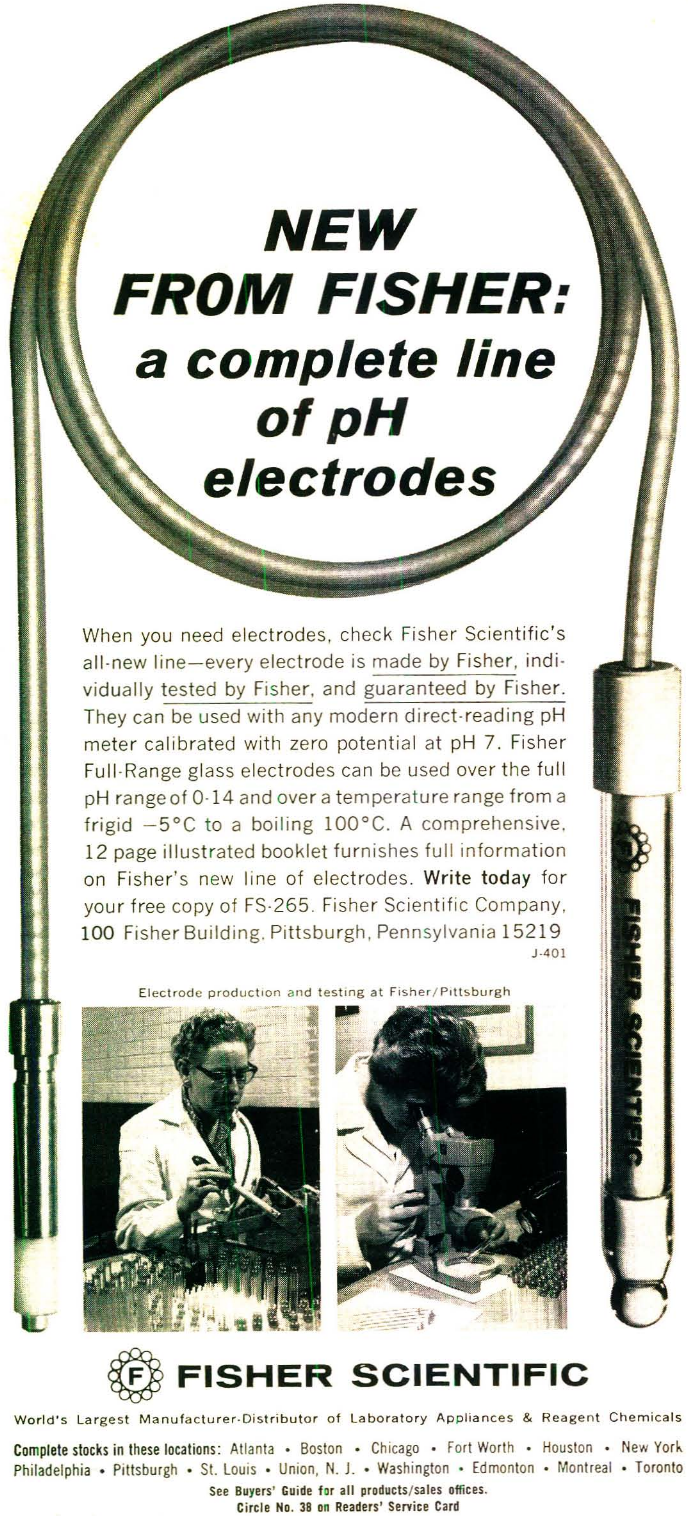

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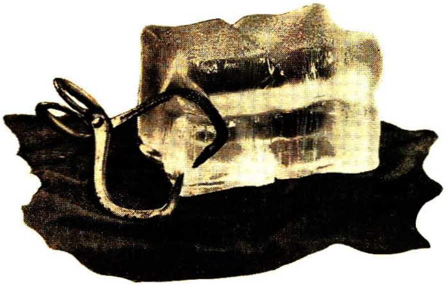

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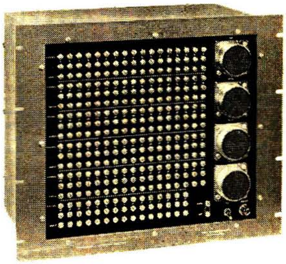

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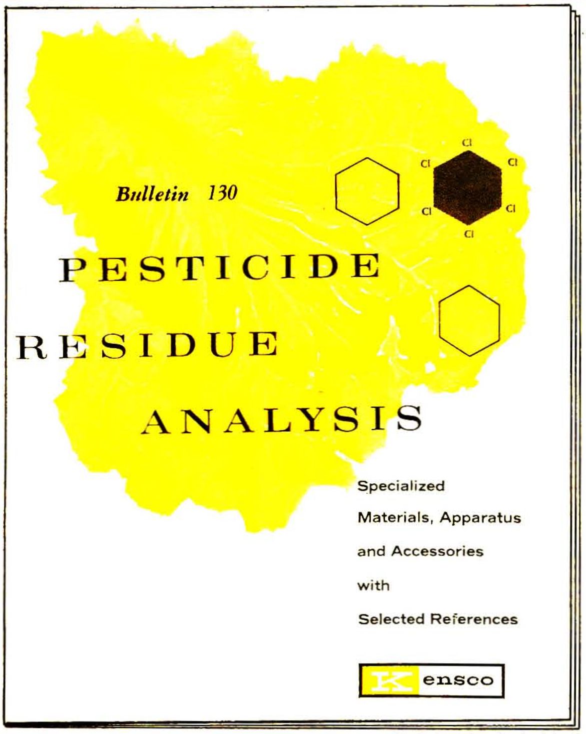

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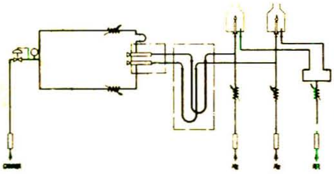

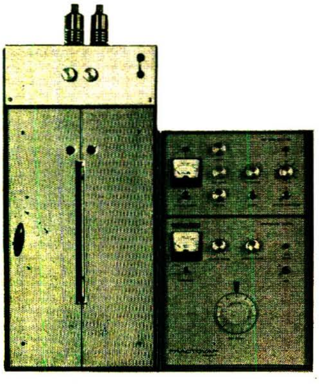

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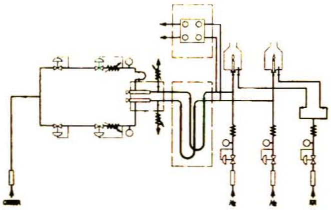

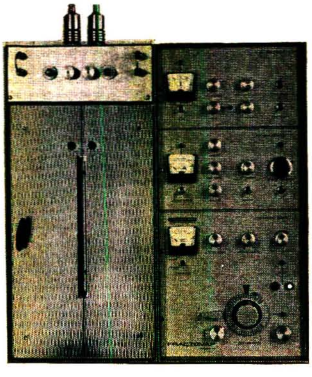

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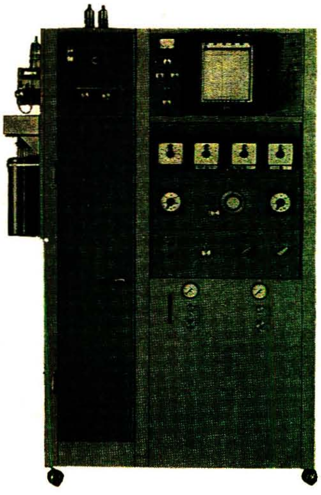

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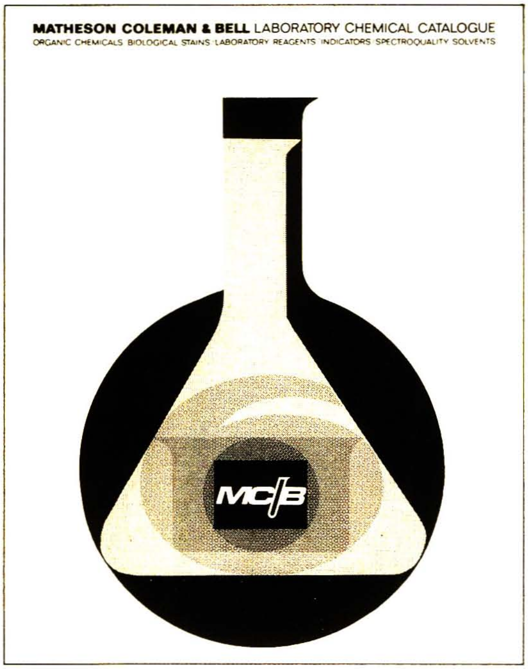

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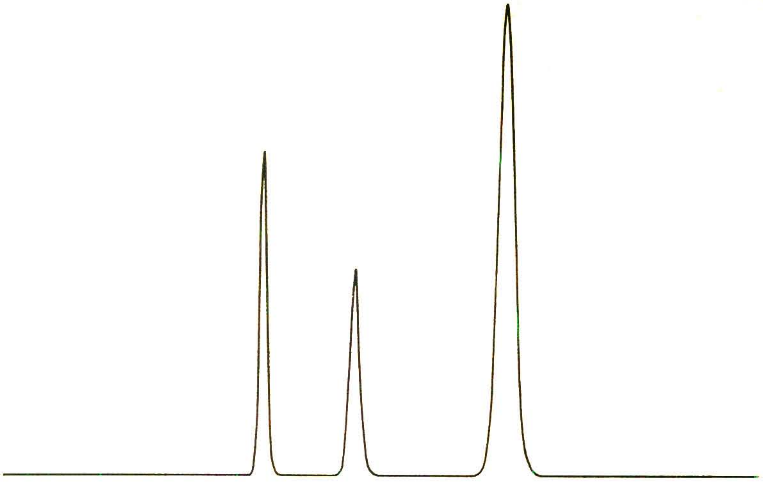

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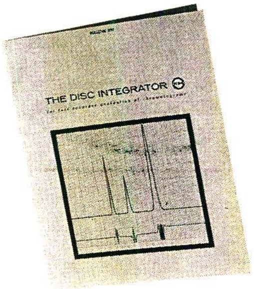

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ANALYTICAL CHEMISTRY NEW BOOKS

Acid-Base Equilibria. *Edward J. King. xi + 341 pages. The Macmillan Co., 60 Fifth Ave., New York, N. Y. 1965. $17.50.*

Reviewed by Roger G. Bates, National Bureau of Standards, Washington, D. C.

In his preface to this volume, which is part of a series designated collectively "The International Encyclopedia of Physical Chemistry and Chemical Physics," the author states that his aim has been "to write a survey that is comprehensive and up to date but not exhaustive." He adds "Topics such as neutral salt effects and the pressure coefficient of acidity constants, which are slighted in briefer treatments, have been covered." A casual perusal of this excellent book is sufficient to convince one that the author has fulfilled his aim in admirable fashion. Indeed, in my opinion he has produced the most authoritative and readable exposition that has appeared on this subject.

Professor King's style is clear and straightforward; his development of the subject is logical, and the treatment strikes a nice balance between the theoretical and the phenomenological. Tables of useful data, many derived or recalculated by the author, are a valuable feature of the book. Coverage of the literature is necessarily selective rather than exhaustive but reflects a wide familiarity with the key developments. A subject index and an author index, too often omitted these days, add to the usefulness of the book as a reference. A section on notation appears at the beginning of the volume. It follows IUPAC recommendations where they exist and may well serve as a guide to future authors in the field of electrolyte solutions.

The book consists of 12 chapters, one half of which discuss specifically the methods most useful for determining acidity constants. Conductance, e.m.f., pH measurements, and optical methods are all dealt with soundly and with a breadth of view that transcends their application to acid-base measurements alone. Sample calculations are given; they should prove invaluable to anyone determining a pK value for the first time. The author has carefully assigned units to all quantities. One wonders, however, if the growing tendency to give units to equilibrium constants (e.g., mol kg^{-1}) should not be discouraged when the scale of concentration has already been made clear.

Most of the novelty and excitement comes in the last six chapters. Chapter 7 is a noteworthy survey of 46 pages on the relation between acidity constants and molecular structure. An attempt is made to separate internal and environmental effects in a useful way, while solvation, induction and resonance, and electrostatic treatments (including the Kirkwood-Westheimer theory) are explored. The proton affinity is introduced as a useful concept. However, the reader, noting that the present values for the proton affinity of ethanol are considerably greater than those for water and nearly as large as those for ammonia, is unlikely to have great confidence in the methods for measuring this quantity.

Temperature and pressure effects on pK are capably discussed in chapter 8. It is hoped that the excellent discussion, illustrated with actual data, will serve as a warning to those who persist in placing too much reliance on thermodynamic data derived from pK values at too few temperatures. Chapter 9 on polyprotic acids is a successful treatment of a difficult subject. The relationships among the experimentally determined "macroscopic" acidity constants and the "microscopic" constants for the individual acidic groups are set forth, and electrostatic interactions in the dissociation of polyelectrolytes and in the titration of proteins are described.

The last three chapters treat medium effects, acid-base equilibria in nonaqueous solvents, and acidity functions clearly and systematically. There is a good discussion of the relative basicities of solvents and of electrostatic effects, and the reader is left with the heartening thought that the failure of the 1/D relationship to account successfully for solvent effects on pK is not, after all, a convincing denunciation of the Born equation. It is surprising, perhaps, that King devotes so little attention in these chapters to solvent effects on the pK of cation acids, where the isoelectric character of the dissociation process reduces considerably the errors in estimating electrostatic terms. Medium effects for the hydrogen ion, in particular the work of Grunwald and his associates, might appropriately have been considered here as well.

A careful reading of this book revealed only a handful of typographical errors and even fewer additional errors of any importance. They are inconsequential defects in a volume that should be received enthusiastically by all who deal with the pervasive but often obscure domain of acid-base behavior.

Practical Chromatographic Techniques. *A. H. Gordon, J. E. Eastoe. viii + 200 pages. D. van Nostrand Co., Inc. 120 Alexander St., Princeton, N. J. 1964. $7.95.*

Reviewed by H. K. Mangold, University of Minnesota, The Hormel Institute, Austin, Minn.

According to the authors, this book "is directed towards the interests of the beginner" who wishes to acquaint himself with established chromatographic techniques. It is written in a fluent and lucid style which is a pleasure to read.

The principles of chromatography are skillfully described in sufficient detail for easy comprehension.

Approximately one third of the treatise is devoted to ion exchange chromatography in columns and on paper, and another large segment to partition chromatography on paper. Fractionations of amino acids and peptides are dealt with rather intensively; examples of such separations are presented, and working conditions are described in some detail. This emphasis on water-soluble natural products reflects the major research interest of the authors. In their opinion, chromatography based on adsorption is less often employed than either partition or ion exchange chromatography. As a consequence, only the principles of adsorption chromatography are explained, and very well, whereas examples and experimental conditions applicable to the various forms of adsorption chromatography are omitted. Similarly, reversed phase partition chromatography, on paper, is mentioned only in passing (p. 94).

Both thin layer chromatography and vapor phase chromatography were well established when this book appeared, and these techniques still are being practiced very widely and most successfully. Nevertheless, thin layer chromatography is treated only briefly, at the end of the volume, more or less as an appendix, and vapor phase chromatography is merely mentioned. The latter technique is said to be dealt with "in another volume in this (?) series" (p. 10).

Under the heading "The Literature of Chromatography" (p. 41), the authors refer to a few scientific journals "which should permit the reader to trace any information required." The second edition (1957) of the textbook "Chromatography" by Lederer and Lederer, also is mentioned but more recent and more extensive treatises, are not listed. In

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the reviewer's opinion, the following books should have been included: Lederer's two volumes "Chromatographie en chimie organique et biologique" of 1959–60, the standard text "Chromatography" by Heftmann (1961), and the comprehensive work "Paper Chromatography" by Hais and Macek (three volumes, 1963–64).

In general, reference to original publications is limited to papers that appeared five years ago, or even earlier. While acknowledging the difficulty in choosing the most significant contributions from the flood of recent literature, it is felt that references to fairly new publications should be made in a book dealing with a rapidly developing field such as chromatography.

A monograph that emphasizes the "practical points" should inform the reader about sources of commercially available supplies and equipment. The authors have made an attempt to provide this information. But, can the majority of readers be expected to know that "L.K.B." refers to LKB-Produkter AB, Stockholm-Bromma 1, Sweden—e.g., pp. 51, 52, or where "H J. Elliott, Ltd." is located?

A list of commercial fraction collectors (pp. 62–63) mentions manufacturers but does not provide their addresses. Similarly, a table (p. 69) specifying the characteristics of Whatman papers and their applicability in chromatography may be useful, but the reader probably will wish to know the address of the manufacturer or distributors.

In the reviewer's opinion, the favorable aspects of this book are greatly diminished by the authors' failure to accomplish their primary objective—to help "the reader to build up *a working knowledge* of chromatography."

Treatise on Analytical Chemistry. Part II. Analytical Chemistry of the Elements, Volume 6. *I. M. Kolthoff and P. J. Elving, editors with the assistance of E. B. Sandell. xxii + 627 pages. Interscience Publishers, Inc., 605 Third Ave., New York 16, N. Y. 1964. $23.*

Reviewed by Donald T. Sawyer, Department of Chemistry, University of California, Riverside, Calif.

This is the eighth volume to be published of part II, Analytical Chemistry of the Elements, and brings this part of the Treatise to within two or possibly three volumes of completion. Several previous reviews of other volumes from both Part I and Part II have appeared in ANALYTICAL CHEMISTRY and have discussed the scope and philosophy of the entire Treatise. The goal for Part II, as stated by the editors, is a critical review of the analytical chemistry, inorganic and organic, of all the elements.

Volume 6 contains five chapters by seven different authors: Beryllium (B.R.F. Kjellgren, C. W. Schwengfeier, Jr., and E. Stanley Melick); Lead (T. W. Gilbert, Jr.); Niobium and Tantalum (Silve Kallmann); Technetium (James W. Cobble); and Actinium, Astatine, Francium, Polonium, and Protactinium (Jacob Sedlet).

For some time there has been a need for a concise and modern review of the analytical methods available for beryllium, lead, niobium, and tantalum. The three chapters devoted to these elements meet this need and provide an almost exhaustive summary of their analytical chemistry; this is particularly true for niobium and tantalum. A well chosen balance between classical and instrumental methods has been selected to give readers a sound background of the available methods and their relative merits. The selectivity and specificity of the methods are presented in a clear and useful manner which should ensure that these three chapters will maintain their usefulness for many years.

As in the past, each chapter begins with a fairly complete summary of the history, occurrence, industrial uses, production, toxicology, physical and chemical properties, and sampling problems for each element and its compounds. This is followed by an overall review of the available methods of detection and analysis, both physical and chemical. Next, the most important methods and procedures are discussed critically and in detail. Finally, several specific procedures are recommended together with detailed instructions. Each chapter is concluded with an extensive set of references.

The last two chapters are devoted to the chemistry and methods of analysis for a group of radioactive elements, all of which are either synthetic or members of a decay series. The chapter on technetium provides an up-to-date summary of the chemistry for this 20th century element as well as a review of the known chemical methods of analysis. A complete discussion of useful separation procedures and radiochemical methods also is given. The final chapter discusses five relatively unimportant elements; the material probably is of interest only to those concerned with radiochemistry and its analytical problems. This is not to imply that the chapter is poor or incomplete, but that these elements occur in extremely specialized situations.

In summary, analytical chemists will find a major portion of this volume an almost essential addition to their reference library. Hopefully the editors will be able to complete Part II of the Treatise in the near future and thereby provide a readily available comprehensive summary of the analytical chemistry of the elements and their compounds.

The Solvent Extraction of Metal Chelates. *Jiri' Stary. xiv + 240 pages. Macmillan Co., 60 Fifth Ave., New York 11, N. Y. 1964. $8.50.*

Reviewed by George H. Morrison, Department of Chemistry, Cornell University, Ithaca, N. Y.

Although remarkable advances have been made in the direct determination of elements by modern instrumental methods, chemical separations continue to play an important role in the analysis of complex materials. This book treats in detail one aspect of the broad field of solvent extraction separations, namely the interaction of cations with suitable organic chelating agents.

The treatment of the subject is well organized and starts out with a chapter on the composition and stability of metal chelates in which the chemistry of chelate complexation is clearly presented. This is followed by a chapter on the theory of solvent extraction of metal chelates in which the partition equilibria are expressed by a number of relatively simple equations that relate extractability to the various pertinent experimental parameters.

It is in the treatment of the analytical applications of metal chelate extractions that the author has done a great service by collecting the great wealth of material that has accumulated in the literature in the past decade, including a fair number of papers not readily accessible to the Western world. These extractions are organized in this book according to systems employing the following reagents and their derivatives: β-diketones, tropolone, 8-hydroxyquinoline, oximes, nitrosophenols, nitrosoarylhydroxylamines, hydroxamic acids, 1-(2-pyridylazo)-2-naphthol, 8-mercaptoquinoline, diphenylthiocarbazone, dithiocarbamates, xanthates, dialkyl- and diaryl-dithiophosphoric acids, dithiols, and miscellaneous reagents. This section is particularly useful in that the author has included extraction curves—e.g., % E *vs.* pH of aqueous phase—for many elements in a number of the more popular chelate systems. Also included are detailed tables with optimum conditions for extraction.

Finally, one selective procedure for the isolation of each of forty-eight metals in the form of a chelate complex is presented.

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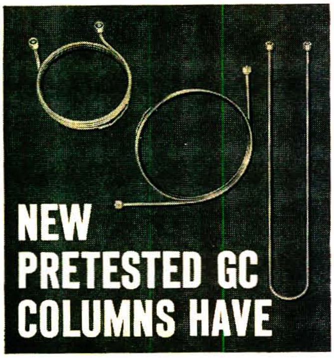

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the compilations of stability constants of metal ion complexes with a number of masking agents, extraction constants, and pH$_{1/2}$ values for a sizeable number of metal ion chelates, and dissociation constants and solubility data of organic reagents.

Of special interest is the description of the technique of substoichiometric determinations developed by Ruzicka and Stary. This method, which permits the determination of a metal without its quantitative isolation from the analysis sample, is particularly useful when used with activation analysis or isotope dilution analysis. In the former case the selectivity of separation is increased, and in the latter the sensitivity of the method is substantially increased.

While it does not introduce any new concepts, this small book provides a recent comprehensive treatment of the subject of metal chelate extractions which should serve as a good additional reference book to chemists concerned with separations problems.

Coincidence Tables for Atomic Spectroscopy. *Josef Kuba, Ludvík Kučera, František Plzák, Miloslav Dvořák, Jan Mráz. xxxi + 1136 pages. Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 10017. 1965. $23.50.*

These tables contain the principal lines for emission spectral analysis together with coincidences within the wavelength range from 2000 to 9250 A.

Formula Index to NMR Literature Data. Volume 1: References Prior to 1961. *M. Gertrude Howell, Andrew S. Kende, John S. Webb, editors. xi + 206 pages. Plenum Press, 2227 West 17th St., New York, N. Y. 10011. 1965. $17.50.*

This volume is designed to provide a literature guide to those organic compounds having proton magnetic spectra described in whole or in part in the literature up to 1961. Over 2500 compounds are identified by empirical and structural formulas or by trivial name.

Translators and Translations: Services and Sources in Science and Technology. *Frances E. Kaiser, editor. Second edition. 224 pages. Special Libraries Association, 31 East 10th St., New York, N. Y. 10003. 1965. $14.50.*

This volume contains information on 470 free-lance translators and 87 commercial translating firms located in the United States, Canada, and Europe. Included are names, addresses, telephone numbers, education, professional experience, volume of translating performed annually, and subject and language proficiencies. Sources of translation information and a large bibliography are presented. There are five detailed computer-produced indexes: language, subject, geographical, publications, and international and national information centers, depositories, and affiliated societies.

Uranium Carbides, Nitrides and Silicides. *International Atomic Energy Agency, 174 pages. National Agency for International Publications, Inc., 317 East 34th St., New York, N. Y. 10016. 1965. $4.*

This bibliography contains 790 references to the literature published during the period 1961-1963. The references are presented alphabetically by author. Author and subject indexes are included.

Chemical Guide to Europe 1965. *137 pages. Noyes Development Corp., 16-18 Railroad Ave., P. O. Drawer 900, Pearl River, N. Y. 10965. 1965. $15.*

This publication describes the 1000 leading European chemical manufacturers in 18 countries with the following information: name and address, ownership, plant locations and products, local subsidiaries and affiliates, foreign subsidiaries and affiliates, principal executives, annual sales, and number of employees.

Dictionary of Nuclear Physics and Nuclear Chemistry. *Hans Rau, editor. Second edition, revised. 351 pages. Reinhold Publishing Corp., 430 Park Ave., New York, N. Y. 10022. 1965. $8.75.*

This volume contains approximately eight thousand English/German and German/English technical and scientific terms pertaining to uranium mining, reactor design and construction, nuclear fission, nuclear chemistry, and isotope research. Particular consideration has been devoted to nuclear-physical and nuclear-chemical symbols and abbreviations.

Nuclear Techniques in Analytical Chemistry. *Alfred J. Moses. vii + 142 pages. MacMillan Co., 60 Fifth Ave., New York, N. Y. 1965. $6.50.*

This monograph contains ten chapters and six appendices which discuss the use of radio techniques in analytical chemistry. A brief review of the fundamental concepts and definitions of radiochemistry as well as a summary of radiation characteristics are presented. The principles, procedures, and applications of activation analysis are discussed in three chapters (40 pages).

Equipment designed for the safe handling of isotopes as well as instrumentation for the preparation and detection of labeled tracers is described. Specific procedures are given for the determination of uranium and thorium.

A chart of the nuclides, activation data, counting standards, monographs on the radiochemistry of the elements, and abbreviations constitute the contents of the appendices.

In summary, a wide range of topics is covered in this well documented monograph.

The following can be obtained from the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

Part 30, 1965 Book of ASTM Standards on General Testing Methods; Fatigue; Statistical Methods; Appearance Tests; Temperature Measurement; Effect of Temperature on the Properties of Metals. *866 pages. Hard cover. $14.; to ASTM members, $9.80.*

This volume contains 98 standards of which 32% are new, revised, or changed in status since the 1964 edition. Tests for ductility, compression, conditioning and weathering, density, elastic properties, hardness, impact, linear thermal expansion, microscopy, rhealogical properties, shear and torsion, subsieve, tension, and thickness are presented.

Apparatus for testing and other chapters are included.

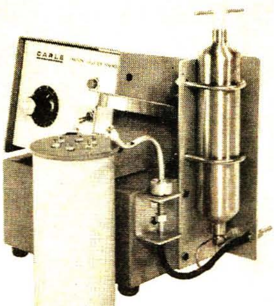
Part 31, 1965 Book of ASTM Standards on Metallography; Nondestructive Testing; Radioisotopes and Radiation Effects; Industrial Chemicals; Emission, Absorption, and Mass Spectroscopy. *740 pages. Hard cover. $13.; to ASTM members, $9.10.*

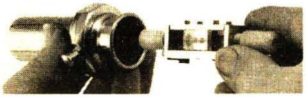
This volume contains 67 standards of which 25% are new, revised, or changed in status since publication of the 1964 edition.

ASTM 1964 Gillett Memorial Lecture "Materials Trends and Significant Testing" *by Nathan E. Promisel. 40 pages. $1.50; to ASTM members, $1.05.*

This lecture presents trends in materials research and development, using specific metallic and nonmetallic areas and probable applications as examples,

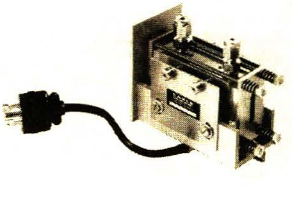
GC-IR SOLUTION FRACTION COLLECTOR





The new Carle Solution Fraction Collector meters carbon tetrachloride or other infrared solvents into the chromatograph's effluent stream, mixing the solvent and separated fractions prior to their condensation in small refrigerated glass traps. Solutions of fractions are transferred directly from the traps to the small (one microliter) centrifuge cell by spinning in a standard 50cc centrifuge cup. The centrifuge cell's one microliter volume fits entirely within the infrared beam, insuring maximum economy of trace fractions. Fractions in solution are much simpler to handle because of greater bulk and the method is equally applicable to volatile or high-boiling compounds. The new apparatus and associated technique eliminate fogging and aerosol formation while efficiently collecting and identifying fractions in amounts as low as a few micrograms.

HEATED MICRO GAS CELL FOR GC-IR



The Carle Heated Micro Gas Cell is a small-volume (2.5 cc) long-path flow cell that can be used in several ways. Used in series with a conventional detector it is well-suited to scanning slow peaks or fast monitoring pre-selected wave lengths for functional group detection. It also functions well with minimum sample in static studies. Self-contained heater adjusts to 250°C while cell maintains thermal isolation from any IR spectrophotometer. For complete details contact:

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problems of testing for assessing behavior characteristics and for quality control, and some related tests, domestic and international test programs, results and interpretations.

U. S. Government Publications

The following publications are available from the Clearinghouse for Federal Scientific and Technical Information, U. S. Department of Commerce, Springfield, Va. 22151.

A Report Guide to Gamma Radiographic Literature, *AD 612 042N, $4.* **A Report Guide to Thermal Testing Literature,** *AD 612 043N, $2.* **A Report Guide to Liquid Penetrant Literature,** *AD 612 044N, $3.* **A Report Guide to Literature in the Fields of Fluoroscopy and Remote Viewing Techniques.** *AD 612 045N, $2.* **A Report Guide to Autoradiographic and Microradio-Literature,** *AD 612 047N, $2. Army Materials Technology Division, Watertown, Mass. Aug. 1964.*

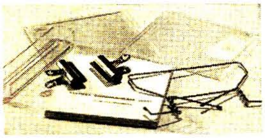
The main objective of these compilations is to provide simple and fast access to information on testing and to provide sufficient information in the form of abstracts and word descriptors to make the listings useful.

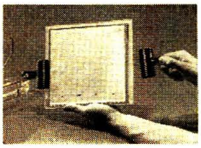
Analytical Chemistry Division Annual Progress Report for Period Ending November 15, 1964. *135 pages. Union Carbide for the AEC. Order ORNL-3750N. $5.*

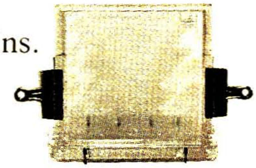
The details of the design and construction of a prototype controlled-potential d.c. polarograph-voltammeter are presented. The device was built for use with short droptime Smoler vertical-orifice dropping-mercury electrodes and solid working electrodes. Also covered in the report are the construction of high sensitivity coulometric titrators, a safety circuit for the multiplier phototube of the Model VII flame spectrophotometer. Analytical studies of molten salt systems, the effects of radiation on analytical methods, and the chemical analysis of advanced reactor fuels are included.

Indexes to the Oak Ridge National Laboratory Master Analytical Manual. Revision 2. *Helen P. Raaen and Ann S. Klein, editors. v + 155 pages. United States Atomic Energy Commission, Division of Technical Information, Oak Ridge National Laboratory. Oak Ridge, Tenn. 1965. $1.75.*

The EASTMAN CHROMAGRAM System for thin-layer chromatography consists of EASTMAN CHROMAGRAM Sheet and EASTMAN CHROMAGRAM Developing Apparatus. It makes TLC – once messy and cumbersome – fast, neat, and uncomplicated. Gone are the bulk and expense of coating equipment and the problems of breakage and siliceous dust. You take EASTMAN CHROMAGRAM Sheet out of a box, spot it, place it in the EASTMAN CHROMAGRAM Developing Apparatus, and separation begins.







EASTMAN CHROMAGRAM Sheet comes in two types: Type K301R with fluorescent indicator and Type K301R2 without fluorescent indicator. Both types are inert poly(ethylene terephthalate) with an adsorbent layer of polyvinyl-alcohol-bound silica gel 100 microns thick; over-all thickness is 0.3mm. The 20cm x 20cm sheets are packed 20 to the box. They are easily cut to desired sizes and shapes—you need stock only the one size.

EASTMAN CHROMAGRAM Developing Apparatus comprises two identical 23cm-square plates made with bosses, ridges, and flats that work together; a solvent trough, an easel, and a pair of spring clips. The apparatus involves no presaturation or lining with solvent-soaked filter paper. It takes little bench space, and that only when in actual use.

You can obtain EASTMAN CHROMAGRAM Sheet and Apparatus from your regular supplier of EASTMAN Organic Chemicals. Also available directly from *Distillation Products Industries*, Rochester, N.Y. 14603, at $35.50 for the apparatus and $23.20 per box of sheet (prices are subject to change without notice and do not include transportation).

"CHROMAGRAM" is a trademark.
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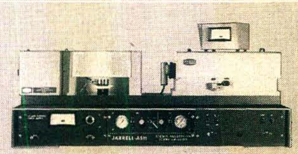
The first direct reading polychromator in the atomic absorption field. A precision analytical instrument for high speed quantitative analysis of very low concentrations of metallic elements in agricultural, biomedical or industrial samples.

- **performs up to 600 analyses per hour**
- **combines both atomic absorption and flame emission spectrometry**
- **sound-muffled HETCO* Burner**
- **choice of readout systems**
- **all solid state electronics**
- **determines up to 12 elements simultaneously**

Model 82-600



FOR MAXIMUM VERSATILITY

Designed to handle difficult trace metal analysis problems, this Jarrell-Ash unit is the most versatile atomic absorption spectrometer available today. Based on the famous Model 82-000 Ebert Spectrometer, the system contains a unique multi-pass optical system and provides facilities for altering system components and adding new developments. Easy spectrum scanning with electrical wavelength drive!

- **performs up to 120 analyses per hour**
- **combines both atomic absorption and flame emission spectrometry**
- **sound-muffled HETCO* Burner (pre-mix burner also available)**
- **standard meter readout or optional direct plug-in recorder readout**
- **lowest possible detection limits**
- **choice of interchangeable burners, gratings, photomultiplier and hollow cathode tubes**
- **six-lamp Hollow Cathode Turret**

82-500 Series

FOR ROUTINE ANALYSIS

This Atomic Absorption/Flame Spectrometer has been designed specifically for routine analysis where dependability, simplicity of operation, compactness and price are of prime importance. Many desirable features of the more costly instrument have been incorporated into this budget price atomic absorption spectrometer.

- **performs up to 120 analyses per hour**
- **combines both atomic absorption and flame emission spectrometry**
- **sound-muffled HETCO* Burner**
- **standard meter readout or optional plug-in recorder readout**
- **pre-aligned optics**
- **reliable all solid state electronics**
- **requires less than 3 sq. feet of bench space**
- **simple to operate — minimum number of controls**

Model 82-700

Need more convincing? Write for complete technical information about the instrument that interests you. Copies of new 16mm color sound movie "Atomic Absorption Spectrometry" now available. Write: Jarrell-Ash, Film Library.

*HETCO is the name of a new High Efficiency Total Consumption Burner by Jarrell-Ash

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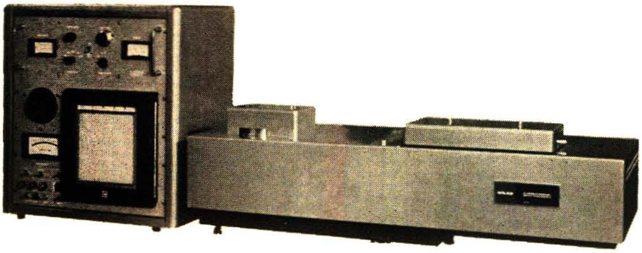
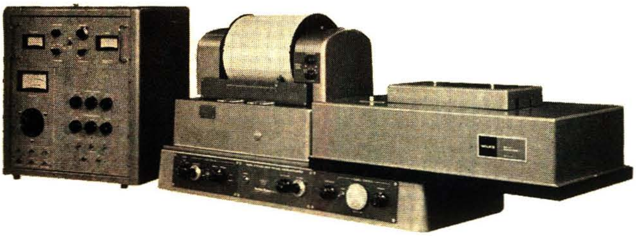
GC SEPARATES, INFRARED IDENTIFIES TOGETHER THEY MAKE A POWERFUL TEAM



Model 11 Rapid Scan Chromatograph-Spectrograph



Model 16 GC-IR Analyzer Modification Kit

The Gas Chromatograph efficiently breaks down a mixture into its components but does not easily identify them — a job best done by the infrared spectrophotometer. When used together, the two techniques make an analytical combination of great all around usefulness.

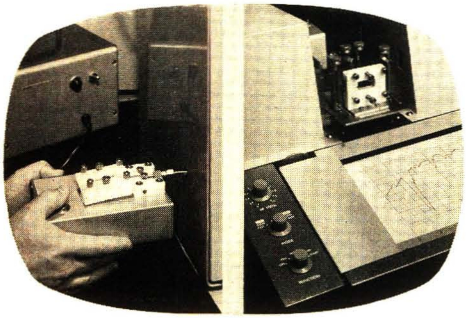
Combining GC and IR — by no means an easy task — is a specialty of Wilks Scientific. Out of two years intensive research have come three different instrumental approaches, each of considerable versatility and each designed to meet the circumstances of a particular laboratory.

The Model 11 Rapid Scan Chromatograph-Spectrograph is a specially built infrared spectrometer utilizing reflecting tube optics and capable of high speed spectral recording of GC fractions as they appear in the carrier gas as well as normal speed spectral recording of isolated fractions. Many modes of operation are possible, giving the instrument great flexibility. Sensitivity is in the neighborhood of 0.05 microliter.

The Model 16 GC-IR Analyzer is a modification kit that will fit on several different infrared spectrophotometers which also makes use of the reflecting tube optical system. On high performance instruments equipped with scale expansion as little as 0.01 microliter is sufficient for identification.

The MIR-15 Remote GC-IR Analyzer combines thermo-electric cooling and internal reflection spectroscopy to trap a GC fraction in a form that permits direct infrared analysis. This device is an attachment that fits most standard infrared spectrophotometers without modification and does not require that the chromatograph and spectrometer be close together. About 0.5 microliter is sufficient to provide a qualitative infrared spectrum.

We will be pleased to help you determine which of these instrumental approaches will be best suited to your laboratory. Write for details.



collect — analyze

MIR-15 Remote GC-IR Analyzer Attachment

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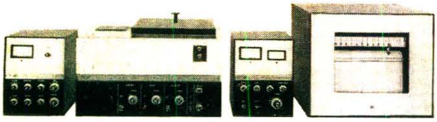
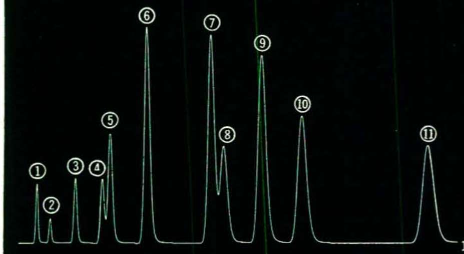


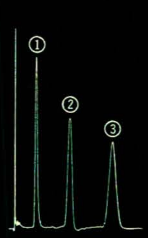
LOW-COST GAS CHROMATOGRAPH···

1—GASES



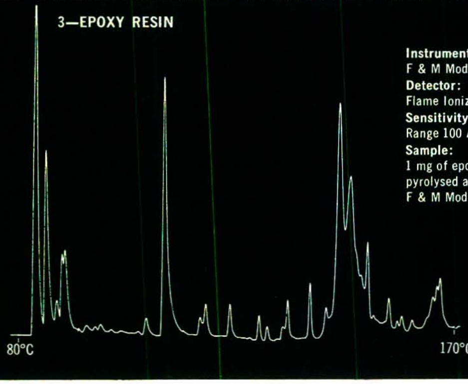
Instrument:
F & M Model 700
Detector:
Thermal Conductivity
Sensitivity:
Atten. 16X
Sample:
1 | Nitrogen & Methane;
2 | Ethane;
3 | Propane;
4 | Propylene;
5 | Isobutane;
6 | Butane;
7 | Isobutene & 1-Butene;
8 | 2-Methyl Butane;
9 | Trans-Butene-2;
10 | Cis-Butene;
11 | 1-3 Butadiene

2—PESTICIDES



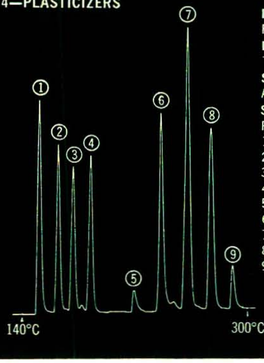
Instrument:
F & M Model 700
Detector:
Electron Capture
Sensitivity:
Range 100 Atten. 5
Sample:
1 | Lindane;
2 | Telodrin;
3 | Dieldrin
(all at 1 ppm)

3—EPOXY RESIN



Instrument:
F & M Model 700
Detector:
Flame Ionization
Sensitivity:
Range 100 Atten. 2
Sample:
1 mg of epoxy resin, pyrolysed at 900°C in F & M Model 80

4—PLASTICIZERS



Instrument:
F & M Model 700
Detector:
Thermal Conductivity
Sensitivity:
Atten. 4X
Sample:
Phthalate diesters:
1 | diallyl;
2 | diisobutyl;
3 | di-n-butyl;
4 | di-n-amyl;
5 | diphenyl;
6 | dioctyl;
7 | octyl-decyl;
8 | octyl-decyl (adipate);
9 | didecyl.

···TAMES TOUGH SAMPLES

There's one big difference between F & M's Series 700 Laboratory Gas Chromatograph and other low-cost instruments: performance. No matter how tough the sample, the 700 easily handles it with results that often surpass those obtained with some of the high-priced chromatographs. ▪ These four chromatograms give you an idea of how the Series 700 tames a wide range of tough samples. ▪ *Sample 1:* A relatively complex, hard-to-separate mixture of gases was handled with ease by the 700, with excellent qualitative and quantitative results. ▪ *Sample 2:* With its electron capture detector operating at only 1/500 of full sensitivity, the F & M 700 easily detected 1 ppm of these pesticides, with almost perfect peak shapes. ▪ *Sample 3:* This detailed "fingerprint" identification of a complex epoxy resin was produced by the 700 in conjunction with a Model 80 Pyrolysis Unit operating at 900°C, with excellent baseline stability. ▪ *Sample 4:* Viscous, tough-to-handle plasticizers were easily separated by the 700, with rapid column temperature programming between 140 and 300°C; note the near-perfection of peak shapes. ▪ Why does the F & M 700 perform so much better than other low-cost gas chromatographs? Because its designers never compromised performance standards in order to keep the price down; instead, automatic features for analytical convenience were left out but this was done in such a way that even these can later be added to the basic instrument as the need arises and the budget permits. ▪ Write for Bulletin 7000 . . . or call your F & M representative. F & M Scientific Corporation, Route 41 and Starr Road, Avondale, Pennsylvania; phone (215) 268-2281. In Europe: F & M Scientific Europa N.V., Basisweg (Sloterdijk) Amsterdam, The Netherlands.

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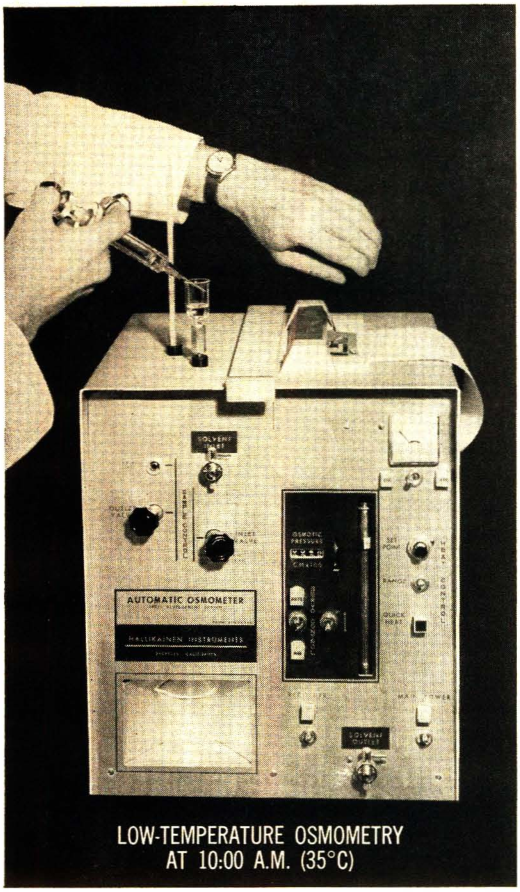
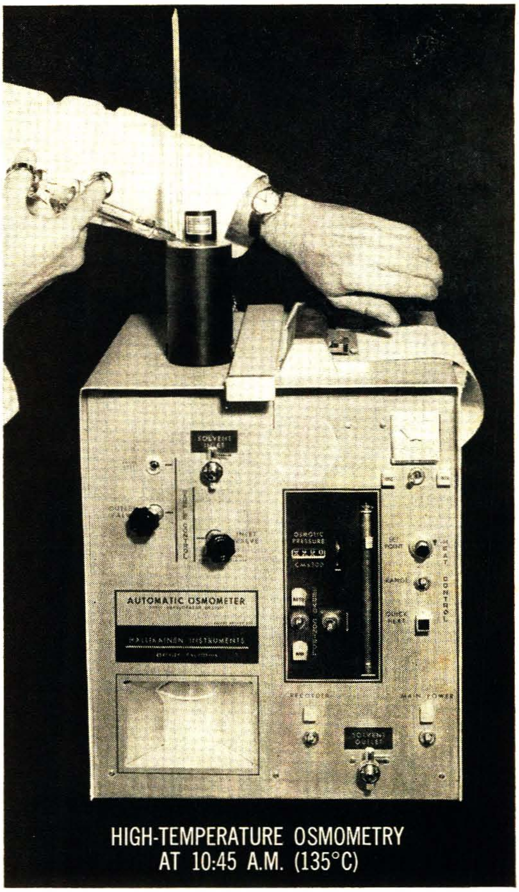
In the final analysis, it's **F&M**


LOW-TEMPERATURE OSMOMETRY
AT 10:00 A.M. (35°C)


HIGH-TEMPERATURE OSMOMETRY
AT 10:45 A.M. (135°C)

Quick-Change Osmometry

Same osmometer — plus! Now, *within the same hour,* you can use it for measurements at both 35°C and 135°C. Far cry from the 24-hour shut-down that once attended standard temperature conversion!

The key to quicker temperature switching lies in Hallikainen's Model 1361 Automatic Osmometer, now redesigned to add new capability to an established top performer.

The new standard Model 1361 incorporates cartridge heaters and insulation required for high-temperature osmometry. To convert from low temperature to high temperature work, all you need do is install an accessory thermostatted sample funnel and a spare cell, with membrane and solvent in place. Quick equilibration comes from precooking the spare cell in a Hallikainen Tube Heater, or equivalent.

The new Model 1361 retains all the impressive performance features of its predecessor, including: Direct-reading digital readouts of osmotic pressure within 5 to 10 minutes of sample injection; measurement accuracy on the order of 0.01 cm over a 10 cm range (for a full range of 5,000 to 500,000 MW); a trim, bench-hugging 12″ x 15″ x 13″ cabinet, with built-in chart recorder.

We're not suggesting that you quick-change osmometers. But we feel Model 1361 warrants comparison with anything you now own or are thinking about buying. Why not send for the product brochure today?

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Instruments
750 National Ct., Richmond, Calif. 94804

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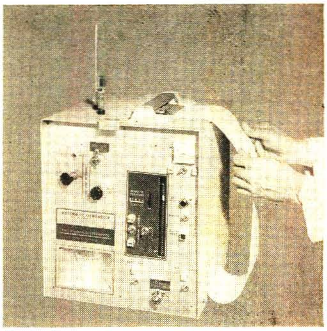

Respondents living outside North America, South America, and Japan are invited to address their inquiries to: Hallikainen Instruments Ltd., Blackwall Lane, Greenwich, London SE10, England.

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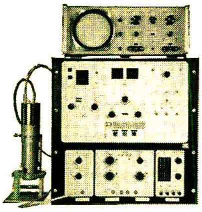

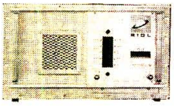

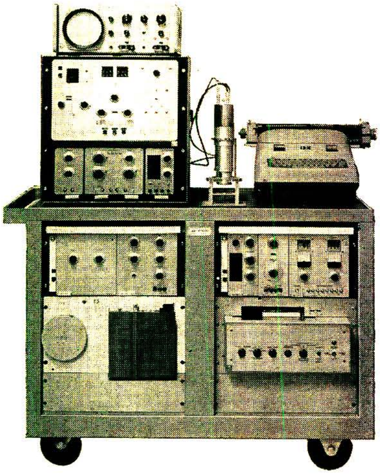

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Now make separations that approach the purity of gas chromatography with much higher through-puts. Nester/Faust's new spinning band still employs a *Teflon* band in an annular configuration for high plate efficiency, low hold-up and low pressure drop to produce previously unattainable rectification. This spiral band design gives high vapor liquid contact. As an example: a 5mm x 24″ annular still separated heptane from methylcyclohexane with a product purity of 99.52%. Similar results have been attained when distilling a mixture of cis and trans decalin.

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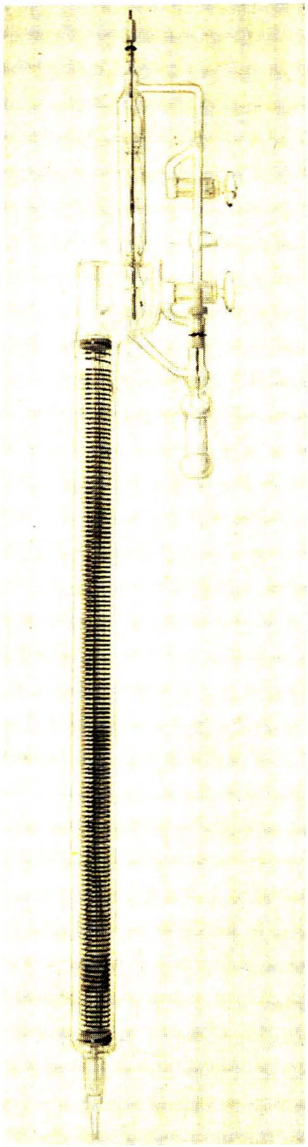

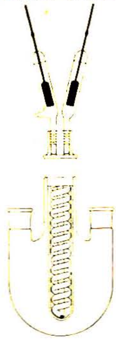

Ultra Violet Light Source

An inexpensive, quartz U.V. source for photochemical reactions. It is a low pressure, immersion type which operates at 50 watts input with 60% spectral output efficiency.

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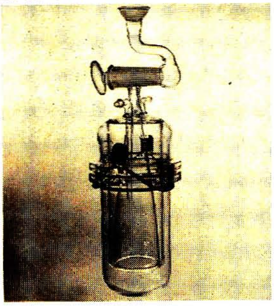

McCarter Sublimer

Our unique vacuum sublimer combines rapid sublimation with easy sublimate removal and protection of the delicate crystals prior to removal.

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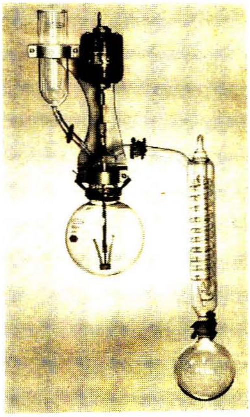

Rotary Spray Evaporator

Speed evaporation of solvents and aqueous solutions with this high speed evaporator. Water evaporation at rates up to 32cc per minute.

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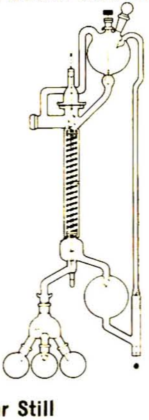

Molecular Still

The Nester/Faust molecular still allows you to separate materials that are unstable at their boiling point. It is designed to prevent polymerization or thermal degradation, and recycle undistilled material without interruption or breaking vacuum.

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For complete specification and description of each instrument, write for literature today: *Glass Products Division*, Nester/Faust Manufacturing Corporation, 2401 Ogletown Road, Newark, Delaware.

NESTER/FAUST

See This Equipment at ACS Booths 614–616

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*Patents pending

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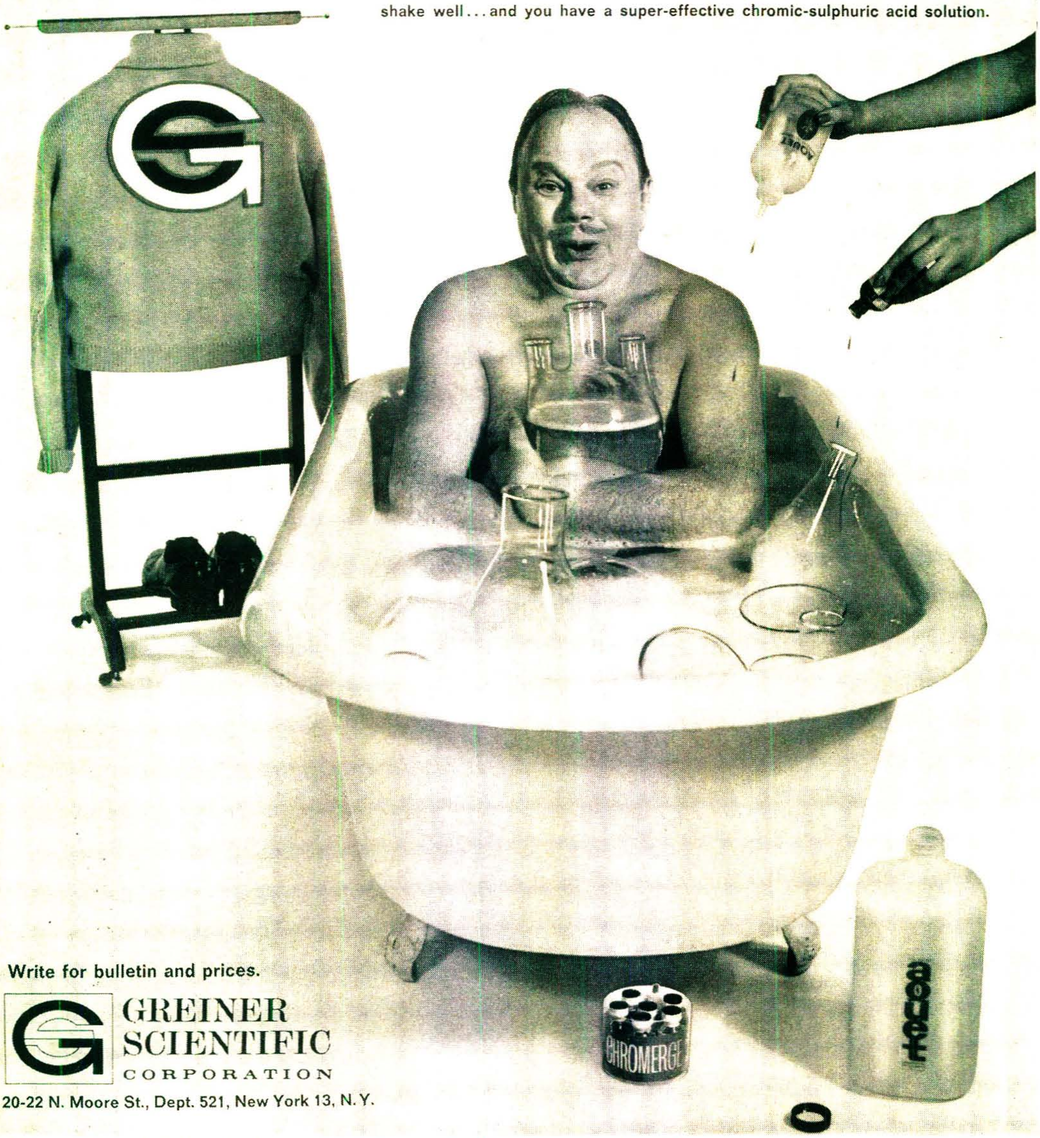

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the EDITOR'S column

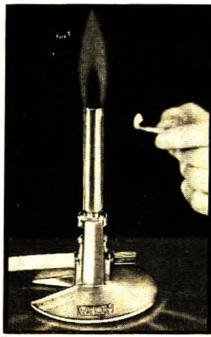
L. T. Hallett, Editor

A RECENT REPORT by the surveys and investigations staff, Subcommittee on the Department of Agriculture, Committee on Appropriations of the House of Representatives, reveals that there are still controversies concerning the tolerance levels for pesticide residues established by the Food and Drug Administration.

In the period 1955 to 1962, the FDA established tolerances ranging from 0.1 p.p.m. to 100 p.p.m. for various pesticides in and on different crops. For some of the pesticides the analytical methods used at the time could not measure or even detect (with legal confidence) residues below 0.1 p.p.m. In establishing a tolerance, if a residue was not above the 0.1 p.p.m. level, a tolerance of zero was fixed instead of 0.1 p.p.m. This, in effect, defined the range from 0 to 0.1 p.p.m. as being regarded as zero. Many scientists thought that this was a mistake, and that a definite figure should be established for a tolerance.

In the past three years there has been a considerable advancement in the sensitivity and sophistication of instruments used for measuring pesticide residues. These advancements make possible the detection of residues as low as 0.001 p.p.m. in some areas. As a result the FDA decided in 1963 that whereas previously the range of 0 to 0.1 p.p.m. had been regarded as zero, the range of 0 to 0.01 p.p.m. would now be regarded as zero. Therefore, pesticide residues in the range of 0.01 to 0.1 p.p.m. which were previously legal suddenly became illegal.

This action has resulted in many problems, according to the Report, since presumably at the time a petition was previously approved by the FDA, pesticide residues in the



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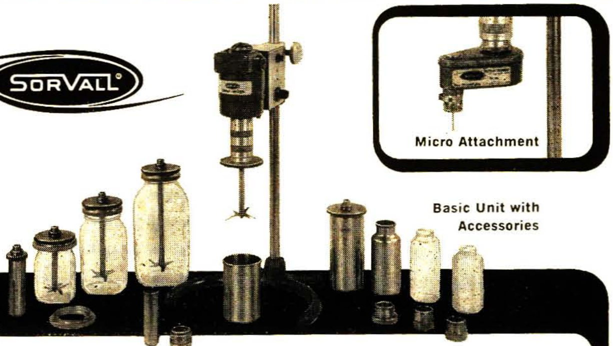

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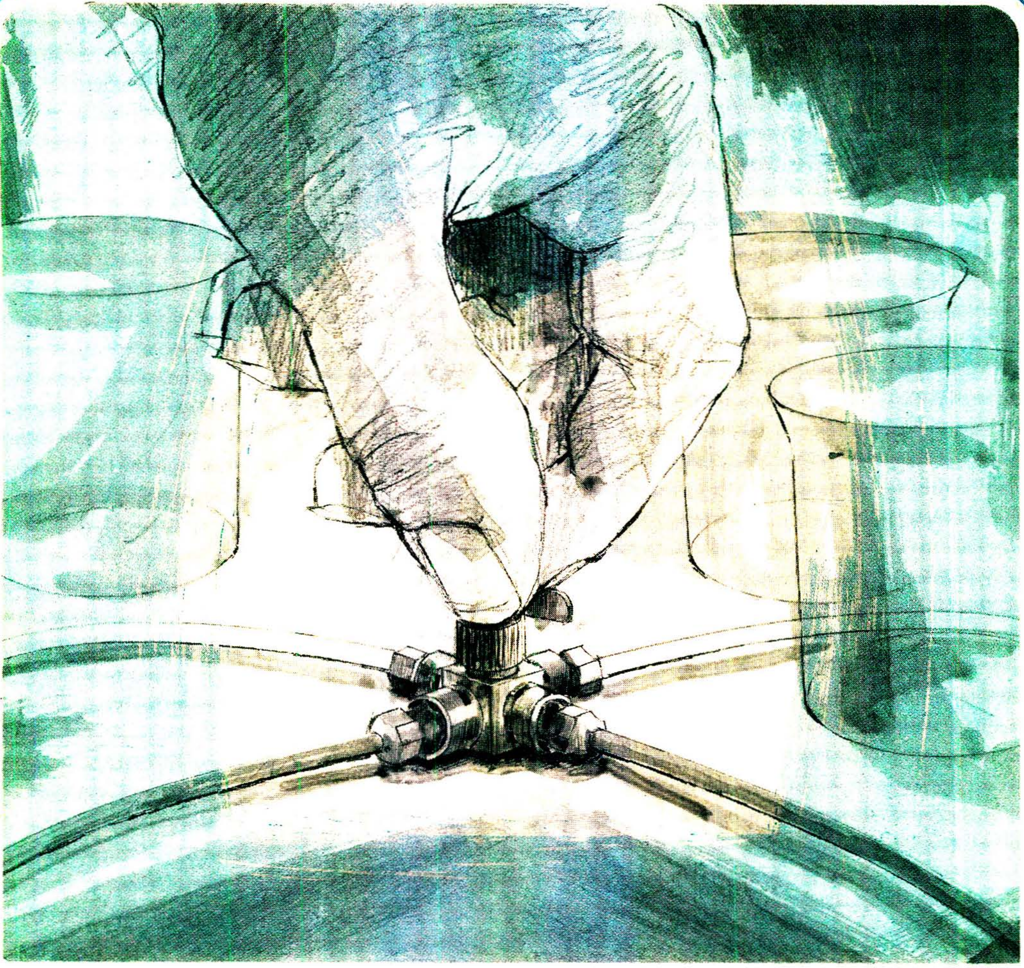

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range of 0 to 0.1 p.p.m. posed no hazard to man. It is not that residues are more toxic than before, but that new developments in analytical instrumentation have made possible detection of residues that were considered insignificant previously. For example, the amount of DDT in milk was detectable at the 0.1 p.p.m. level in 1955, but by 1963 it was detectable at the 0.001 p.p.m. level.

The continued interest of chemists in the problems of pesticides *vis-a-vis* human tolerance levels is evidenced by the large number of papers presented before the Pesticide Subdivision of the Division of Agricultural and Food Chemistry at the 149th ACS National Meeting. The PESTICIDE RESIDUES review [ANAL. CHEM. 37, 131R (April 1965] points up an important fact: ". . . There is an urgent need for general procedures that can identify and measure a large number of chemicals at one time. They must be highly sensitive and accurate, since it is essential that all monitoring of our environment be at a level considerably below any "tolerance" or otherwise critical level, so that trends can be more readily recognized and assessed for significance."

A great concern for the standardization of analytical methods for pesticide residues has been expressed on a worldwide level. At the meeting of the Pesticides Section of the International Union of Pure and Applied Chemistry held in Rome in October of 1964, it was stated that methods for pesticide residues are required that are not only specific for the pesticide, its metabolites, or degradation products, but also specific for application in the food concerned.

The 6th Pesticides Congress sponsored by the IUPAC will be held in Vienna in 1967, and will include a broad program that involves the chemistry of insecticides.

All of the preceding reveals the exceedingly important role that analytical chemistry plays and will continue to play in the establishment of health and safety standards.

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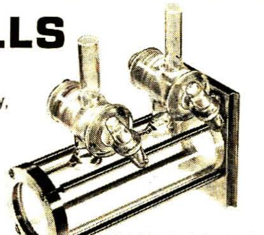

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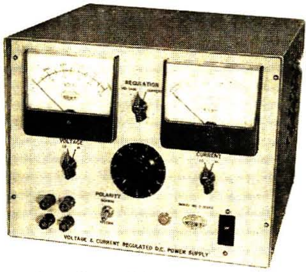

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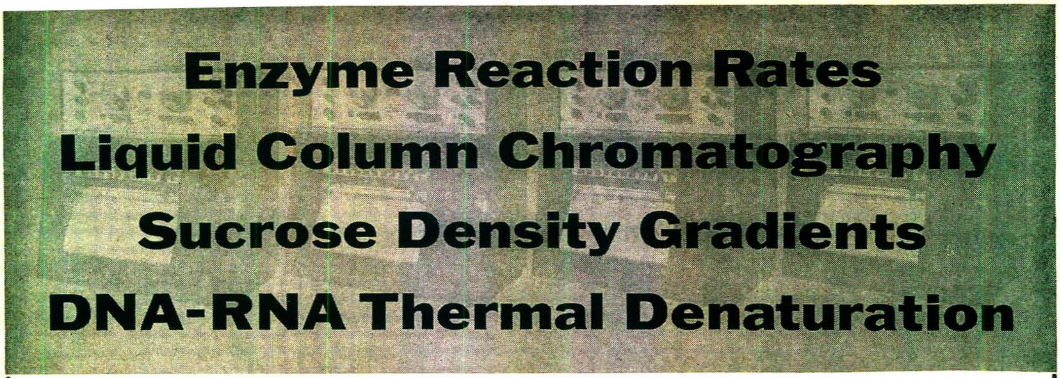

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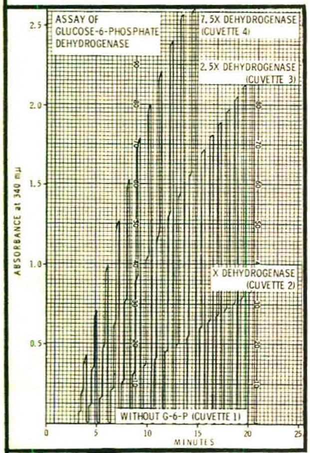

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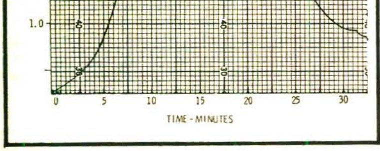

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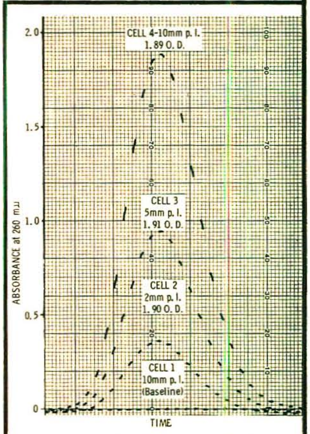

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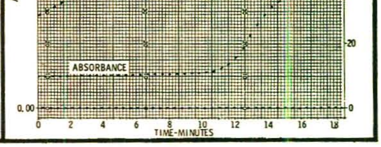

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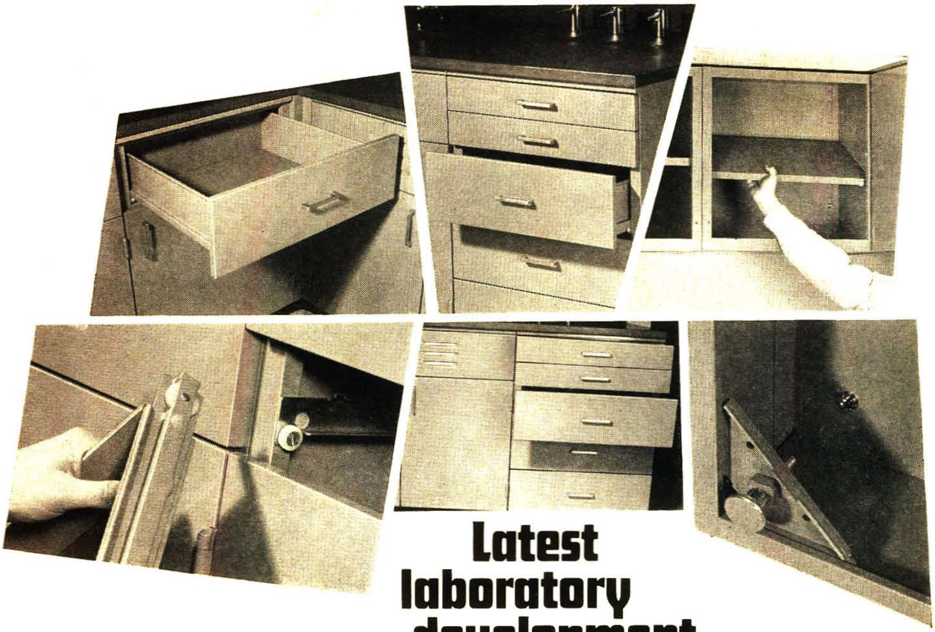

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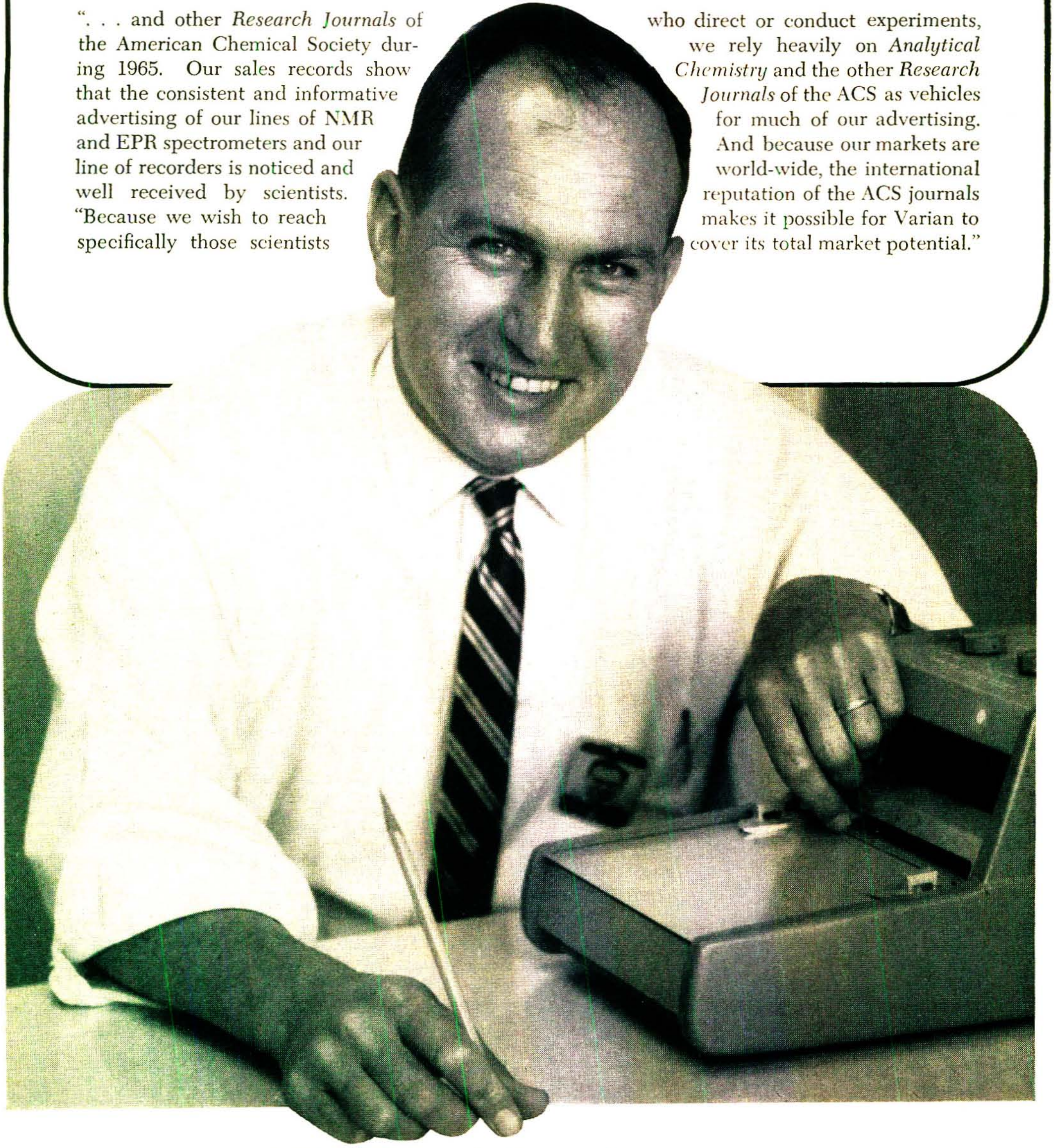

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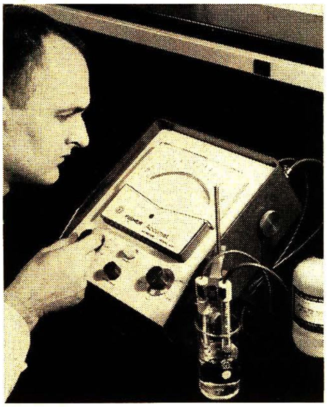

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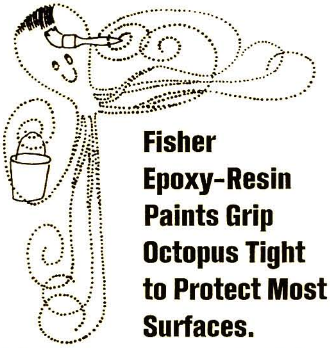

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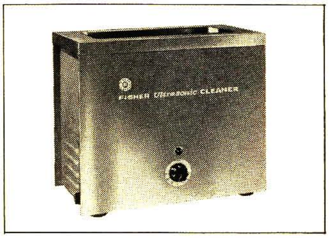

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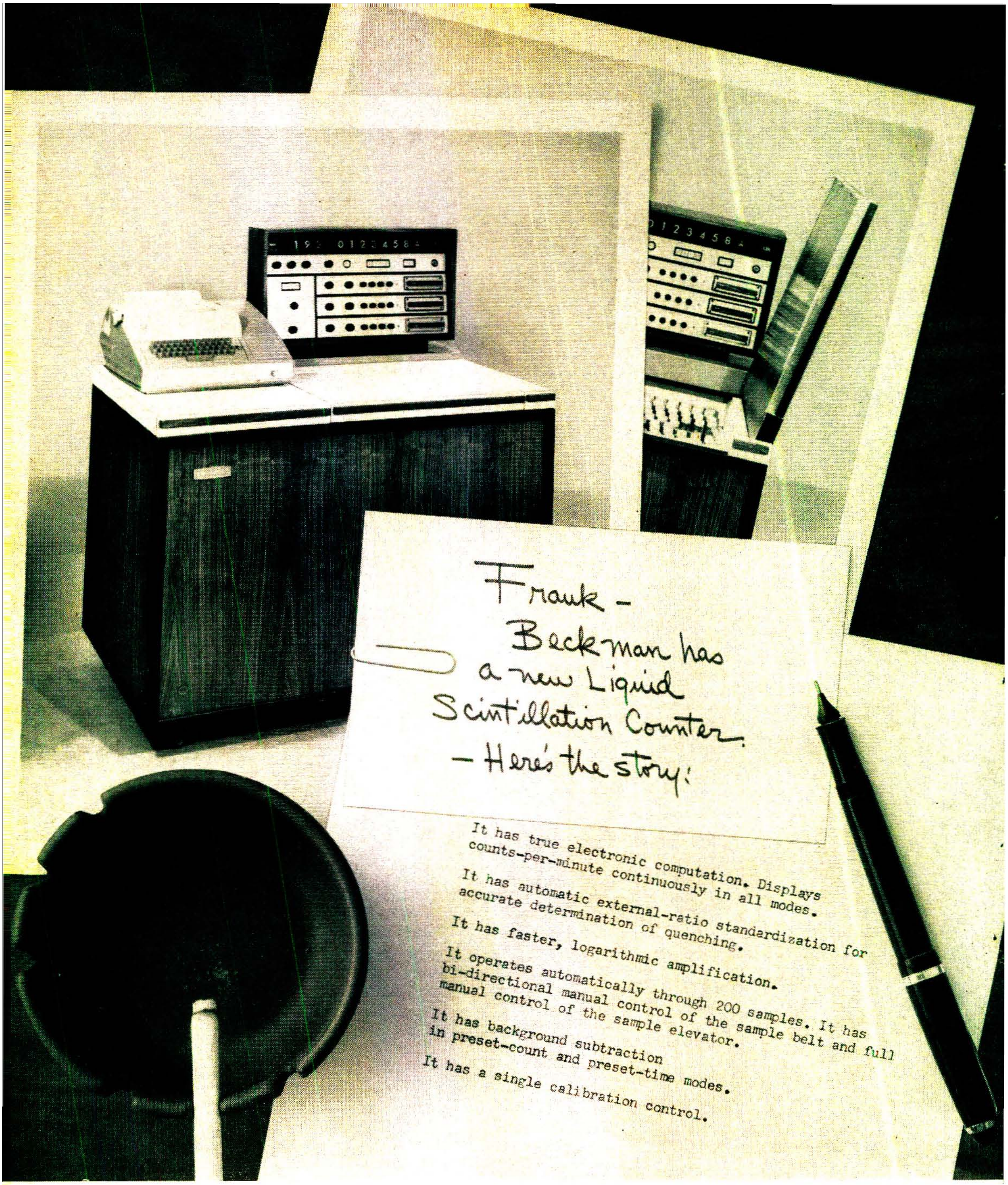

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Pomona College Has Advanced Undergraduate Teaching Facilities

The editors feel that recent trends in the design of academic laboratories should be of interest to analytical chemists. In a recent feature [Anal. Chem. 37 (7), 93A (1965)] a new laboratory designed primarily for graduate research was presented. This month the outstanding facilities of a college which is engaged exclusively in undergraduate teaching and research are depicted.

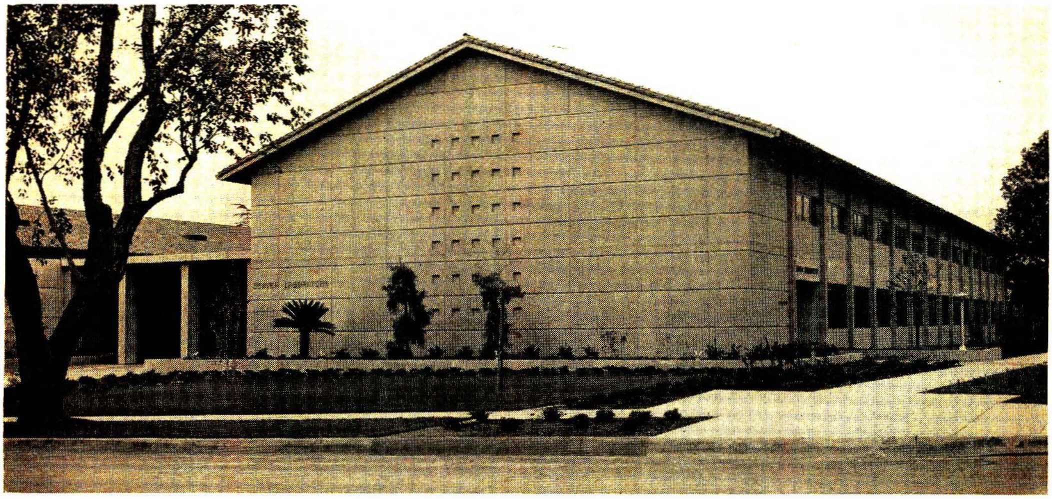
IN FEBRUARY OF THIS YEAR the Chemistry Department at Pomona College moved into the third and newest wing of the Seaver Science Center, named for the late Dr. Frank R. Seaver, president of Hydril Company and a trustee and alumnus of Pomona College. Pomona College was founded in 1887—it is a private coeducational undergraduate college of arts and sciences located near Los Angeles. It has a fulltime faculty of 105 and a student body of 1100.

One of the measures of quality of the new Seaver Chemistry Lab is the unusually high level of instrumentation in use at all stages of an instructional program which places heavy emphasis on the research aspects of teaching. Even in the freshman year, where all of the elementary instruction in quantitative analysis is given, the students use spectrophotometers, pH meters, and automatic balances.

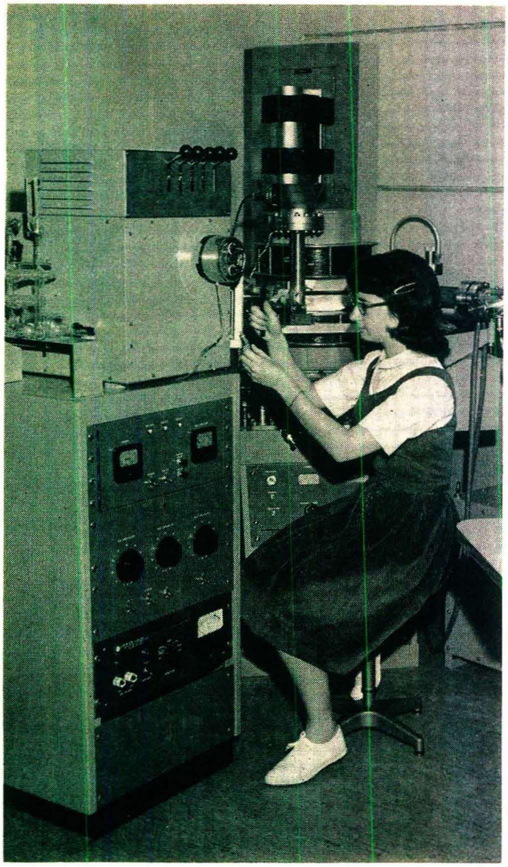
Sophomores routinely use a recording infrared spectrophotometer in their organic course along with gas chromatographs and a polarimeter, in a lab that provides each student with as much stainless steel hood space as regular bench space. The desks themselves are stocked with individual magnetic stirring hot plates as well as sets of regular and micro standard taper glassware. Melting point units are conveniently located throughout the lab. In the advanced organic laboratory each student has at his disposal stainless steel hoods that are 9 ft. high and 12 ft. long. These hoods enclose stainless steel racks for mounting equipment, electrical outlets with independently variable voltage, piped nitrogen, vacuum, and other conventional utilities; they have both high- and low-speed ventilation and large sliding panels of tempered safety glass. An additional safety glass shield separates the front half of the hood from the back half. The advanced student also uses an osmometer and any of the larger pieces of research equipment.

The students in biochemistry courses use a preparative ultracentrifuge, and analytical ultracentrifuge, an amino acid analyzer, a ratio recording spectrophotometer, a high voltage electrophoresis apparatus, and a refrigerated scintillation counter.

In addition to the usual instructional equipment and vacuum racks, the students in physical and advanced analytical chemistry take advantage of recording infrared and ultraviolet spectrophotometers, an NMR instrument, a mass spectrometer, and a neutron generator with pneumatic dual transfer system and associated scintillation counter and 400 channel analyzer. With the exception of the neutron generator, the group of last-named instruments is housed in a complex of 10 rooms, one instrument to a room (each of which is provided with special "smog-filtered" air with close humidity control). A research grade electron microscope is another of the instruments housed in one of these



Seaver Chemistry Laboratory at Pomona College is one of three wings of the Seaver Science Center which cost over $6,500,000; the chemistry wing has 56,400 square feet of usable floor space



Mass Spectrometer is routinely used by students in research and advanced analytical course work

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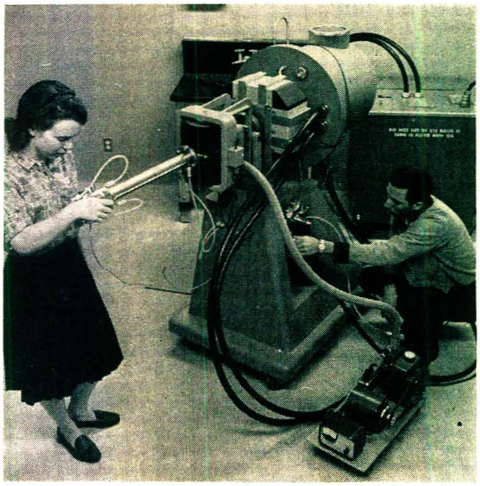
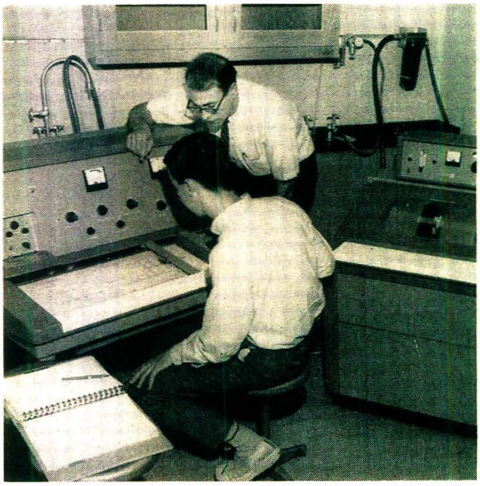
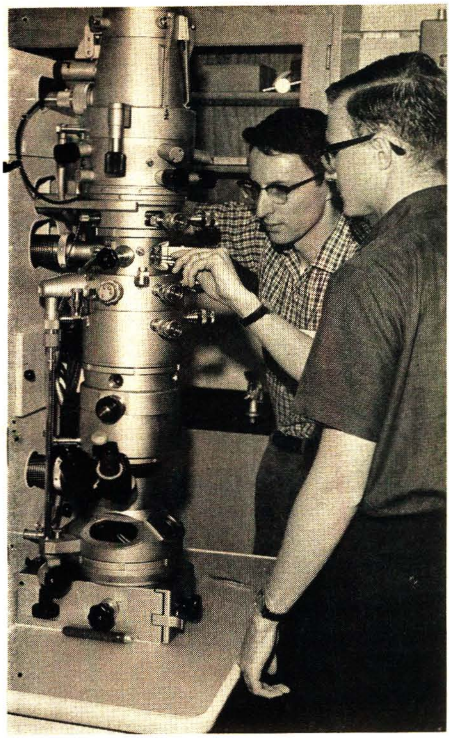


LABORATORY OF THE MONTH



NMR equipment is used in both course work and research by students of physical and advanced analytical chemistry

Physical and analytical laboratory, showing a central island with associated custom-made stainless steel constant temperature water baths



Research electron microscope is available to undergraduate students for various teaching and research projects

special rooms. The walls and roof of the neutron generator room are of reinforced concrete, 5 ft. thick; the room is located in association with two low-level radiation labs and a counting room.

Of course these instruments are not simply teaching instruments, for they are also involved in the research programs carried on jointly by the faculty, the students, and post-doctoral fellows. There are no graduate students or graduate courses.

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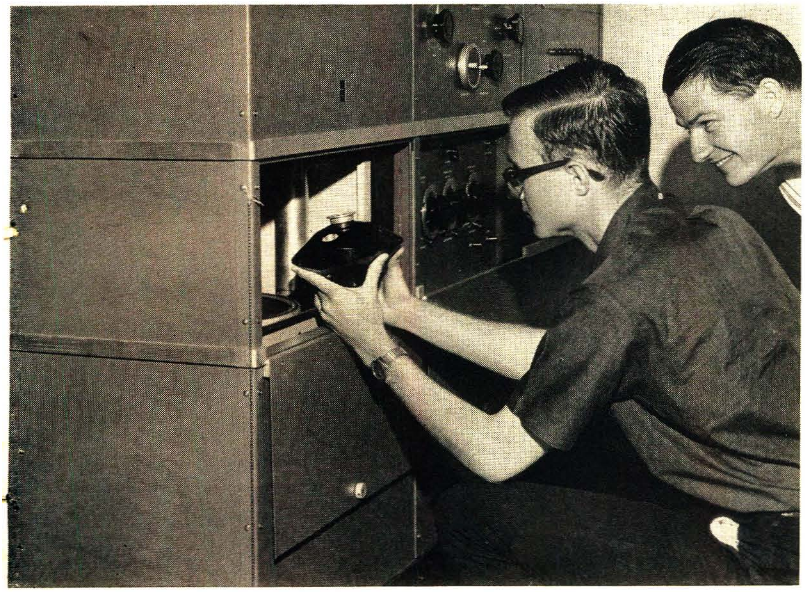

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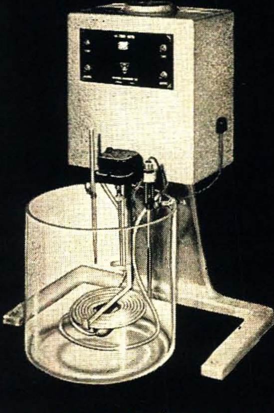

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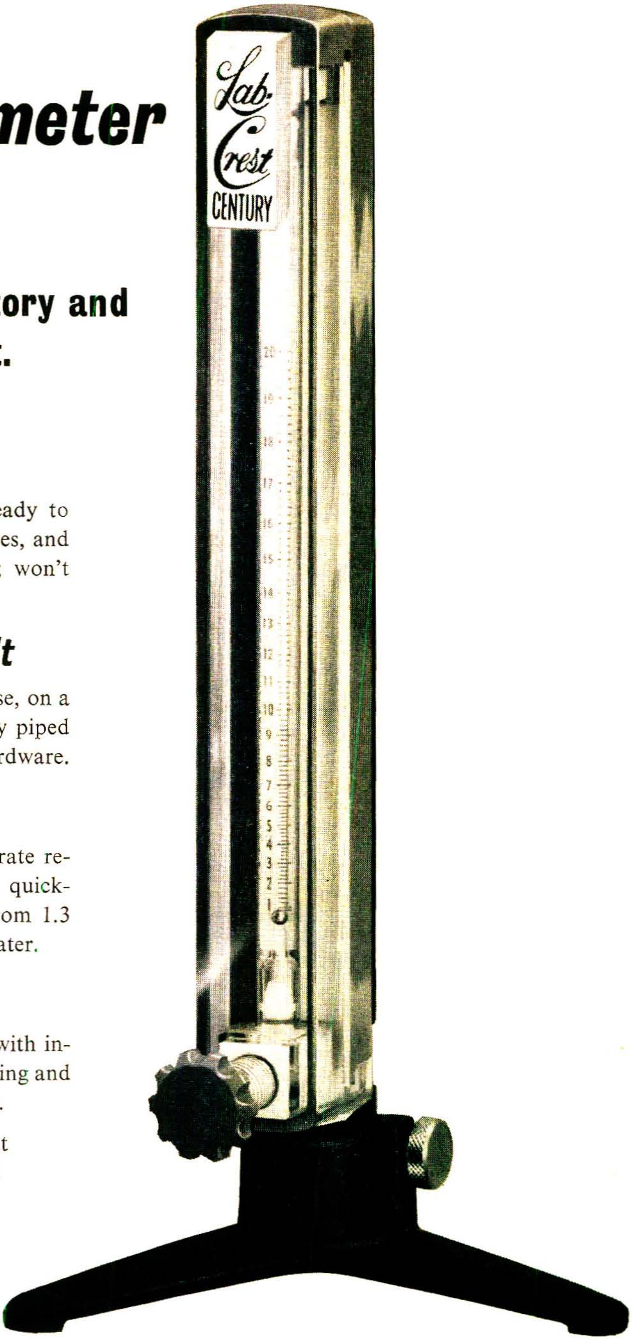

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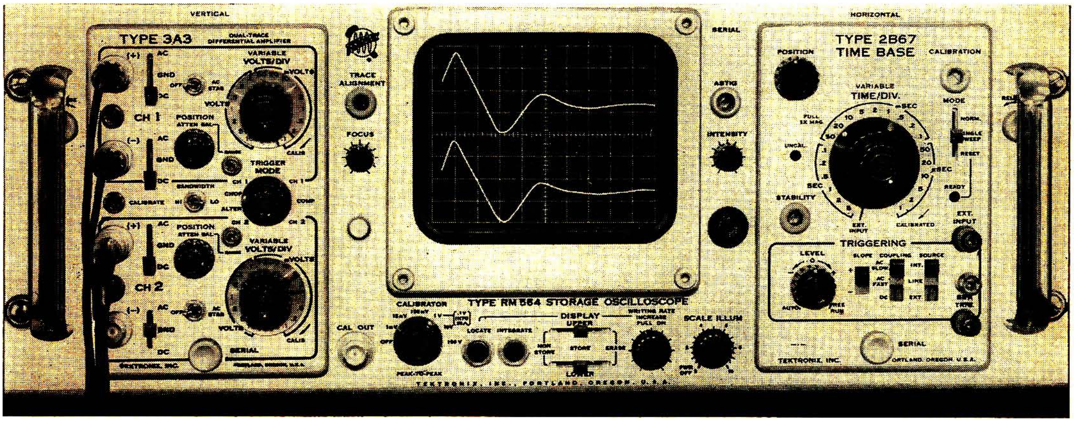

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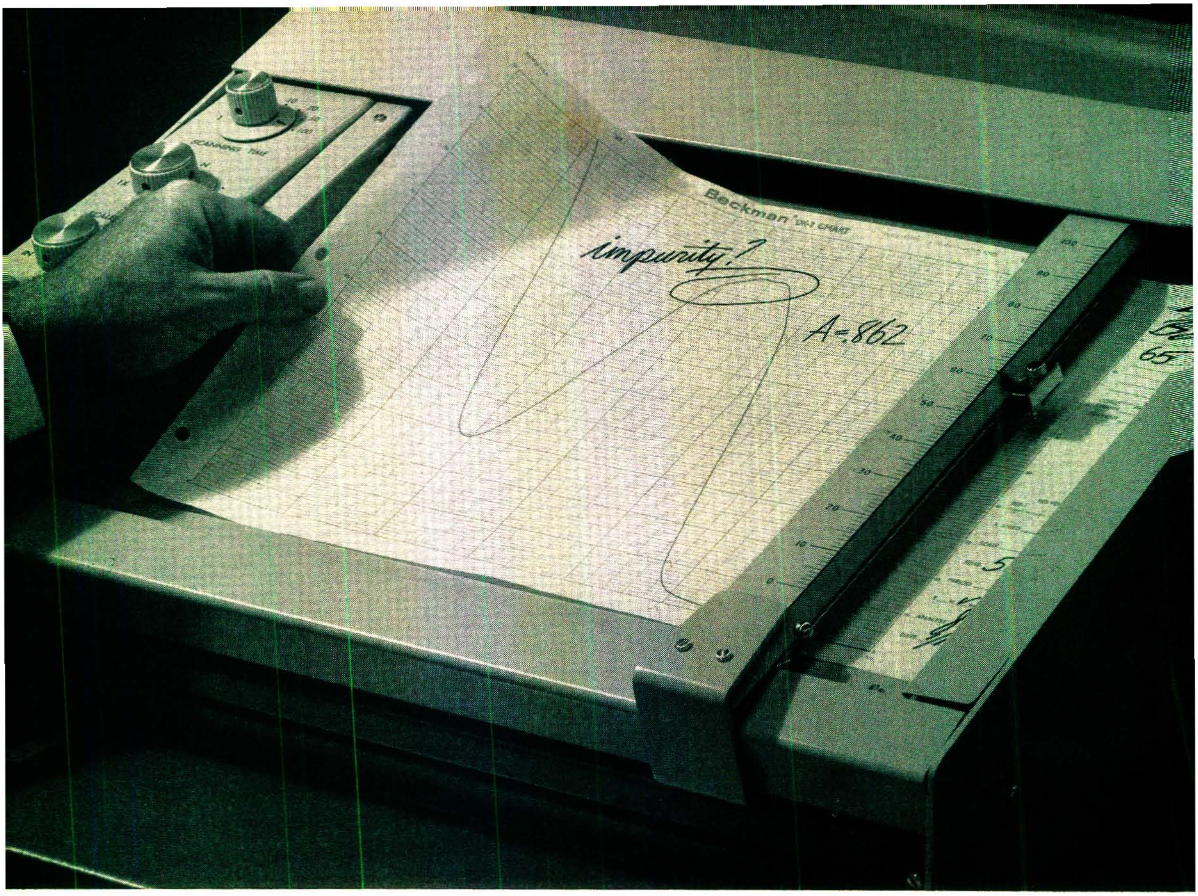

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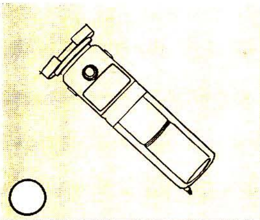
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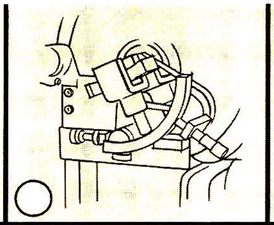
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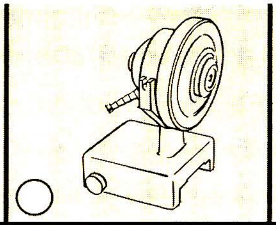
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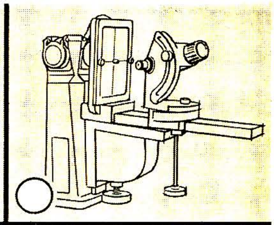
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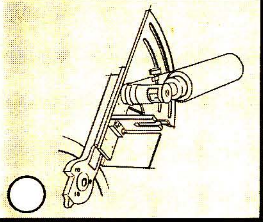
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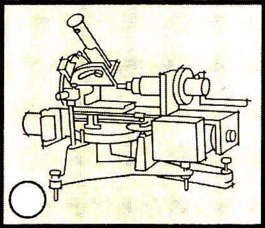
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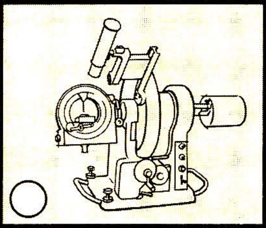
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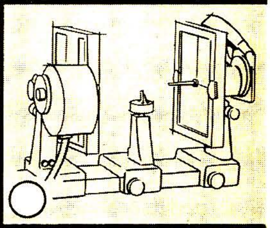
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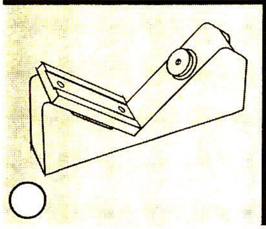
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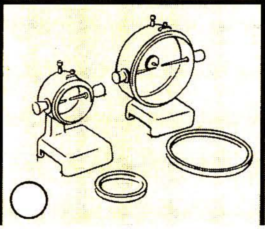
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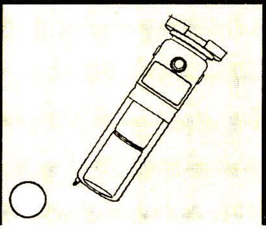
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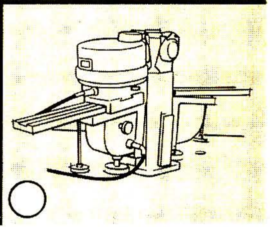
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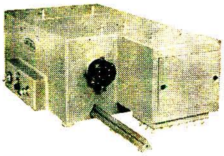

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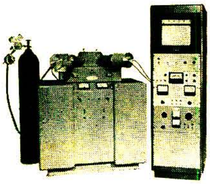

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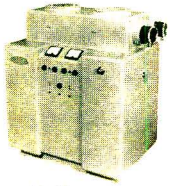

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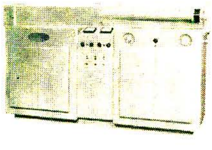

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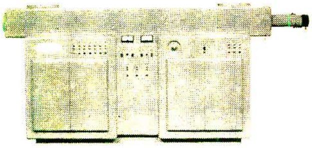

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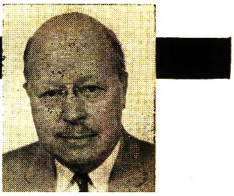

Where Did I Hear That Before?

by Ralph H. Müller

We have little hope for exoneration if we once more plead for mercy in attempting to keep abreast of advances in instrumentation. We take some relief in noting that, with the rush of publications, there is a lot of duplication and, more often than one would wish, one encounters a development which at once prompts the remark—"where did I hear that before?" The topics which we discuss in this column, have cost us considerable homework. Rather than merely cite author, journal, volume, and page, we have racked our brain to see what was new, what was going on, and what one might do if the situation were analyzed a little more thoroughly.

For example, R. F. Howarth [*Rev. Sci. Instr.* 36, No. 5, 667 (1965)] in discussing the "Incandescent Lamp as a Control System Element" finds that there is a 5% region in the light flux *vs.* lamp voltage which is nearly linear. As a matter of fact, the relationship is exponential over the whole range. Some 25 years ago, we required our graduate students to scan an incandescent lamp with a phototube and vacuum tube voltmeter and to plot the log of the photocurrent against the log of the lamp voltage. The relationship is strictly linear, indicating that the luminous flux may be related to the lamp voltage by $I = aV^n$. Typical data ("Experimental Electronics," Müller, Garman, and Droz, Prentice Hall, 1942, p. 71) indicate a value of $n = 4.05$. It is not surprising that incandescent lamp manufacturers, as early as 1914, made very careful studies of lamp characteristics as a function of operating voltage. In most electrical engineering handbooks, one can find the information, usually expressed as ratios—i.e., $\frac{x_1}{x_2} = \left(\frac{V_1}{V_2}\right)^k$. Values of the exponent k for properties x such as lumens *vs.* volts, watts *vs.* volts, lumens per watt *vs.* volts, and lamp life *vs.* volts are given as an approximate guide. Actually, the exact value of k must be determined for every individual lamp. The average value of k (lumens *vs.* volts) for gas filled tungsten lamps is 3.6. For untreated carbon filaments, the value of k can be as high as 6.9.

Howarth has described an elaborate arrangement for maintaining constant flux from a lamp. A photomultiplier controls a magnetic amplifier to feed back current to the lamp. The arrangement attains 0.25% constancy all day at room temperature for line voltage variations of 2.5% or less. In contrast, a comparatively simple arrangement ("Experimental Electronics," p. 112) produced residual variations of voltage across a 100-watt lamp of 0.01% for line voltage variations of 4%.

In this method, a pentode detected voltage variations in comparison with a voltage reference (voltage regulator tube). The output of the pentode controlled two power tubes in shunt with a ballast resistor in series with the lamp. For long periods of operation, this scheme ignores a second order effect. As Howarth has pointed out, lamp bulbs blacken with age. The effect is accompanied by a reduction in filament diameter, which, in turn, increases its brilliance. Unfortunately, these two effects do not cancel each other.

In our opinion, the design of an inexpensive light source of very high constancy has not been attained. With present day resources, it should be possible to maintain constant lamp voltage to within 1 part in 50,000 or better. Second order corrections should be done photoelectrically or possibly by optical means. There is still a need for light sources of high constancy even though most optical instruments avoid the problem by dual beam or rapid intercomparison techniques.

The British, God bless 'em, are still intrigued with the use of D'Arsonval movements as torque measuring elements. Many years ago, one of them showed that a force applied to the pointer of a milliammeter can be compensated and determined by applying a measured current to the meter. What Lee Cahn has done with this principle in his series of indicating and recording electrobalances has been a delight to behold. The method has countless applications but most of us are too busy doing more and more thermogravimetric analyses to get around to the problem. From the University of Cambridge, M. R. Head and N. B. Surrey [*J. Sci. Instr.* 42, 349 (1965)] comes a description of a Low Speed Anemometer. It was designed to measure air velocities in an apparatus used to determine the rate of climb of very small flying insects. The pointer of a milliammeter is fitted with a small vane (0.001-inch Melinex polyester film). The impinging air deflects the pointer from its equilibrium position to which it can be restored by sending a measured current through the meter. The authors point out that the arrangement can be made self-balancing. They also suggest that the relationship between restoring current I and the air velocity V could be made more linear by using a vane consisting of small fibers about which flow is substantially viscous. We know nothing about aerodynamics but their statement about making the curve more *linear* puzzled us because it was delightfully curvaceous throughout. Inasmuch as we have complained recently about curves in the literature which have no recognizable mathematical ancestry and in admiration of their fine work, we tried to find out "what goes on." After tracing their curve, enlarging it, and picking off points, we found that a log–log plot of V *vs.* I is linear, indicating that the air velocity is proportional to the 0.575 power of the restoring current. This looked near enough to the 0.5 power or the square root of I. Indeed, a plot of V^2 *vs.* I predicts their data to within 2% in the form $V^2 = 1.84\ I$ where V is in feet per second and I in milliamperes. It then occurred to us that their ingenious instrument was behaving in the best traditions of elementary physics because a gas of given mass (density) moving with a velocity V has kinetic energy of $\frac{1}{2}mV^2$. It is interesting to note that the scheme could be used to analyze gas mixtures because, if impelled at a known and constant velocity, the torque produced would be proportional to the mean density. There will be no need for any of us to rush into production on this. It was done commercially about 40 years ago. The A.E.G. Ranarex gas analyzer used two small turbine blades rotating in opposite directions. One was driven by a constant speed motor or reference gas, the other by the gas mixture to be analyzed. The fans did not rotate freely, but were coupled with a delicate linkage carrying a pointer. The latter indicated on a scale the differential torque and was calibrated in per cent constituent—i.e., CO_2 in air, NH_3 in air or moisture in air. An extended description is to be found in the "Chemie-Ingenieur, 4 teil Physikalisch-Chemische Analyse im Betriebe," Akademische Verlagsgesellschaft, M.B.H., Leipzig, 1933.

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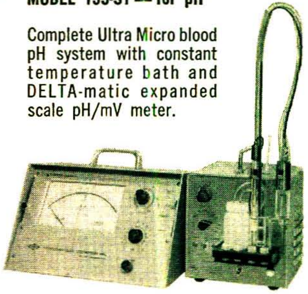

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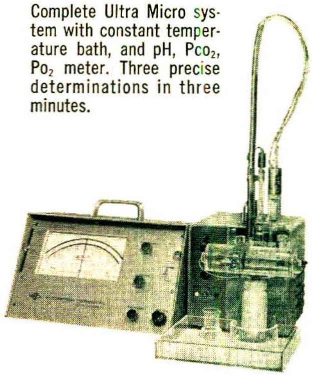

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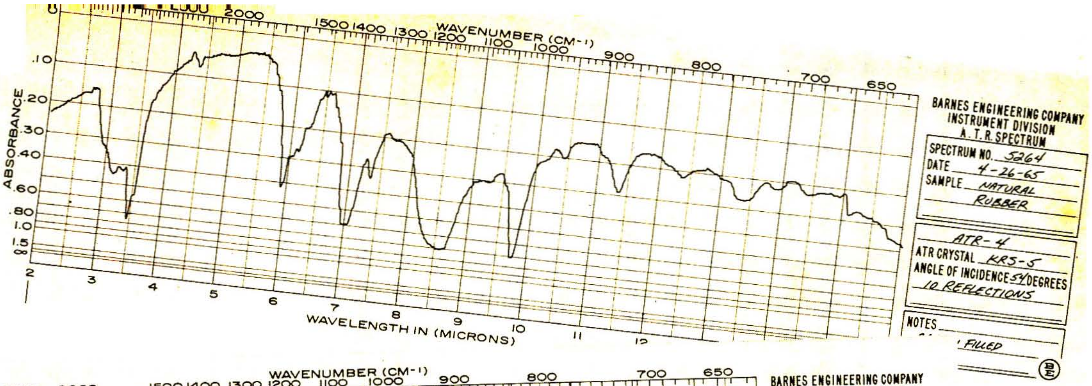

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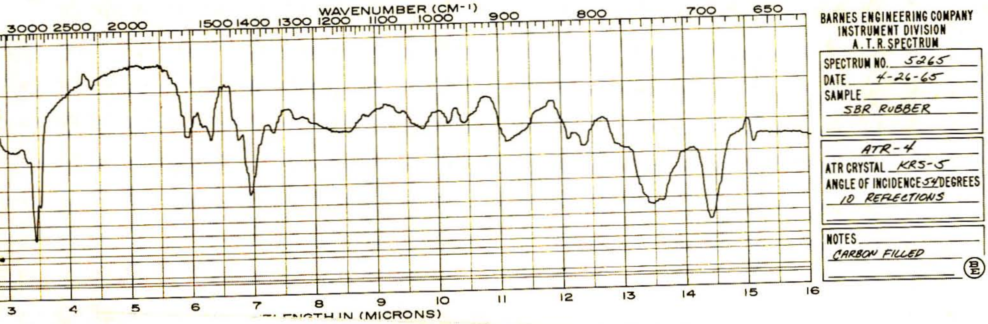

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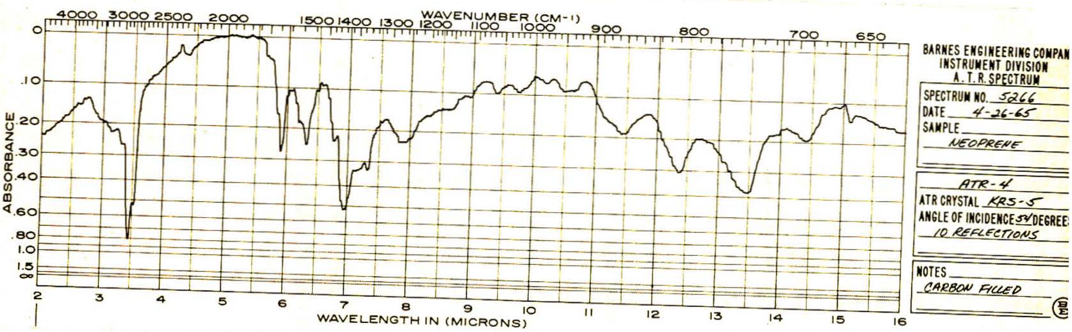

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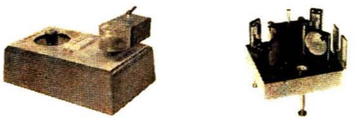

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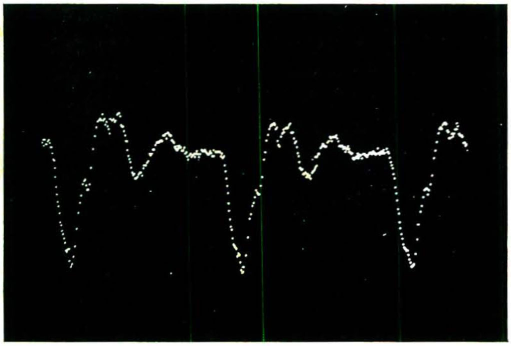

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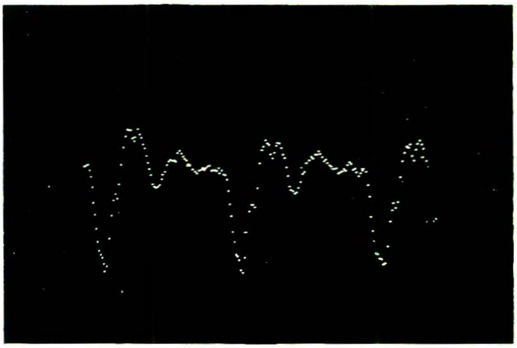

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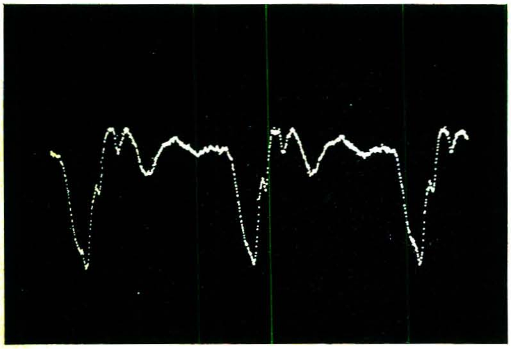

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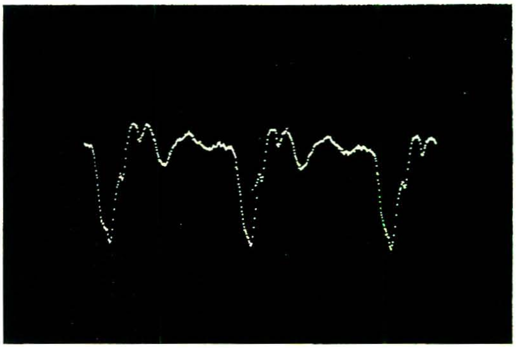

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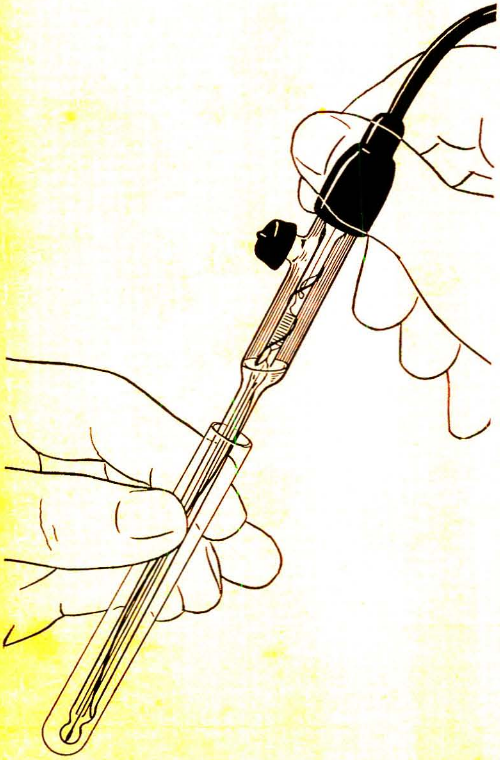
- **For samples from 0.2 ml to a tankful**
- **Stem 1/4-inch diameter**
- **Ideal for titrations*—fast response—compact size**



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The single ¼-inch stem can be used with samples of small volume as well as with larger quantities, and is more convenient for transfer by hand from sample to sample than bringing the sample to electrodes in a fixed position.

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*See H. V. Malmstadt and E. H. Piepmeier, *Analytical Chemistry, Vol. 37, No. 1 (January, 1965), p. 34*

Detailed descriptive bulletin, consisting of pp 464-468 of our 1965 catalog, sent upon request

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(for Branch Offices, see page 127 A)

Education and Management

OVER the past fifty years, education, particularly scientific, has become an important factor in managerial success. Previously, wealth and good connections weighed heavily on the side of the young man who rose to the top.

A recent survey sponsored by *Scientific American* and conducted by Market Statistics, Inc., has explored the educational backgrounds of 1000 top officers—presidents, chairmen, or executive vice presidents—of the 600 largest nonfinancial corporations. Some of these mature men in evaluating their training expressed their regret that their education did not give wider exposure to the arts and humanities. Conversely, men who were educated in the arts expressed a desire for more understanding of technical matters.

As we reach the levels of management, success depends increasingly on understanding and human relationships. Corporations today must make money, but they must also be part of the community. Scientific competence does not necessarily lead to an understanding of the aspirations of human beings. It is unfortunate that we have had to produce a generation of lopsided managerial scientists who, by their own evaluation, feel hampered in the performance of their jobs by their lack of appreciation of humanities. Many of these men will remedy their own deficiencies because they have the ability to correct their weaknesses as they rise to the top. It would seem that at top managerial levels the well-rounded individual can contribute most effectively to his profession, company, and community.

Science and things of the spirit should complement each other. Our large schools are recognizing this and our young scientists are accepting the humanities as worthy of study.

L. T. Hallett

A Stepwise Regression Program for Quantitative Interpretation of Mass Spectra

D. D. TUNNICLIFF and P. A. WADSWORTH
Shell Development Co., Emeryville, Calif.

▶ A computer program that gives both qualitative and quantitative results for the sample without requiring prior detailed knowledge as to the composition has been developed for mass spectrometric analyses. The program is based on a mathematical method of choosing from among a large library of spectra a suitable small group of spectra such that the sum of the individual spectra after multiplying by the proper concentration factors gives the best least-squares fit to the sample spectrum. The library may contain as many as 150 reference spectra with data for 110 masses for each spectrum.

SIMULTANEOUS DETERMINATION of several components by mass spectrometry is usually based on selecting the most significant peak(s) for each compound expected in the sample and then solving the set of simultaneous equations that defines the relations between peak intensities and concentrations. This method is simple and gives good results when the qualitative composition of the sample is known. However, if the sample contains one or more unexpected components, the results for some components may be considerably in error. Such errors may be detected by a difference between the observed and predicted intensity at a peak not used in the simultaneous equations or by a difference between the sum of the computed partial pressures and the observed sample pressure. A large negative value for the concentration of one or more components is also evidence of an error. If there is any evidence of such errors, the calculations can be repeated using a different set of components.

Efficient use of the above approach requires considerable previous knowledge about the qualitative composition of the sample. Samples containing unexpected components, at the worst, may give undetected erroneous results or, at the best, may require additional calculation with a corresponding delay in obtaining the results. In addition, the use of this method of calculation requires considerable skill and judgment in choosing the best set of masses for the analysis of a particular sample, in evaluating the results of the calculation, and in deciding what procedure to take if there is evidence of an error.

A new computer program that avoids most of these difficulties has been developed. This program makes use of a large library of reference spectra of individual pure compounds. Up to 150 spectra may be included in the library. If the spectra of all components in the sample are present in the spectral library, the program automatically determines both the qualitative and quantitative composition of the sample without requiring any advance information as to the sample composition. Since the calculations are based on a least-squares fit to the observed intensities for as many as 110 masses, no preselection of the most significant mass for each component is required. In fact, the inclusion of the additional data both improves the discrimination between compounds with similar spectra and aids in detecting errors in the data.

This new program is based on a modification of a stepwise regression program written by Efroymson (*1*). The regression procedure is a mathematical method of choosing from the library of reference spectra a small group of spectra which, when each is multiplied by a suitable concentration factor, will give the best fit to the sample spectrum as determined by a least-squares criterion. During the regression the calculations proceed in a stepwise fashion. At each step, an additional spectrum is selected to give the greatest improvement in the variance of the fit of the predicted spectrum to the sample spectrum. The concentration factors for all spectra previously chosen are recomputed at each step. A spectrum chosen previously may be rejected at a later step if the change in variance caused by removing this spectrum is less than a preset value. This stepwise procedure continues until either the ratio of the concentration to the standard error for the next spectrum to be chosen is less than a preset value; the ratio of the computed to expected standard error between the observed and computed spectra is less than a preset value; or the change for two consecutive steps of the ratio of the computed to expected standard error is less than a preset value.

General Description of the Program. The library of reference spectra is loaded ahead of time on magnetic tape using a separate program. The data are ordered in such a manner as to facilitate exclusion from the calculations of those compounds that could not be present because of the lack of any significant intensity at the higher mass range. Also included on the magnetic tape are a list of the masses to be used and instructions for reporting the results.

Occasionally, the spectrum of two or more compounds of interest will be so similar that it is preferable to report only the sum of the concentrations. Two alternate procedures are provided for such compounds. If the spectra are very much alike, the best approach is to prepare a composite spectrum based on the usual relative concentrations of each component. This composite spectrum is then included in the library of reference spectra. However, if the spectra are sufficiently different to permit even an approximate calculation of the individual components, it is preferable to include the spectrum of each individual compound in the library of reference spectra and to add the computed concentrations before reporting. When applicable, the second method will give more accurate results if the relative concentrations of the compounds being grouped together varies widely.

The computer input consists of the program deck, a small set of instruction cards, and the spectral data for each sample. Usually these data are first recorded on punched-paper tape using a MASCOT and later converted to punched cards using an IBM 47 tape-to-card punch. Alternatively, these punched cards containing the data are prepared using a Contact Telereader.

The calculations proceed sample-by-sample, the results being reported for one sample before calculations are started on the next sample. The first phase consists of reading and editing the sample spectral data, picking out the intensity data corresponding to the selected list of masses, applying the appropriate galvanometer sensitivity factors, and correcting for background. The maximum mass with a significant intensity is found, and the list of com-

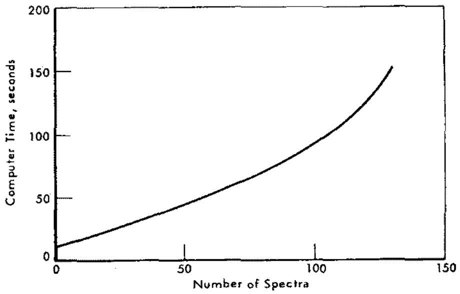

Figure 1. Relation between number of spectra and computer time required

pounds to be considered for the regression is reduced accordingly. A weighting factor is applied to both the calibration data and the observed intensity for each mass. Except for low intensities this weighting factor is proportional to the reciprocal of the observed intensity. This assumes that the probable error in each intensity measurement is a constant percentage of the intensity.

The next phase consists of forming the regression matrix and proceeding through the regression. After finishing the regression, any components with negative concentrations are removed since they do not represent a real solution. The regression is entered again and finally any new compounds with negative concentrations are removed.

The last phase of the program consists of preparing the output. The first part of the output is a table of the observed and predicted (calculated from the computed concentrations) intensities for each mass. Another section is a table of the computed concentrations and standard errors for each component before normalizing and editing but after taking the sums for those compounds which are to be reported together.

Compounds with concentrations less than a preset value are eliminated, the results normalized to total 100 per cent and a final report is prepared in duplicate. The reported results are all rounded off according to the following equation

$$\mathrm{NSF} = \mathrm{A}_0 + \mathrm{LOG}_{10}\left(\frac{\mathrm{CON}}{\mathrm{ERROR}}\right) - \frac{\mathrm{C}}{9.0} - \mathrm{A}_1(\mathrm{R} - 1)^{\mathrm{A}_2}$$

where

NSF = number of significant figures in the reported concentration (after truncation)
CON = computed concentration
ERROR = computed standard error
C = computed concentration with decimal point adjusted so that there is only one digit to the left of the decimal point
R = ratio of computed standard error in the fit between the observed and predicted spectra to the expected error assuming 1% error in all intensities
A_0, A_1, A_2 = adjustable constants (current values are 1.6, 0.2, and 1.5, respectively).

The first three terms take into account the effect on the number of significant figures of the ratio of the computed concentration to the standard error and the size of the first non-zero digit. The last term reduces the number of significant figures if a poor fit to the sample data is obtained. This may be due either to an error in the input data or to the presence of a compound in the sample whose spectrum was not included in the library of reference spectra. The values for A_0 and A_1 listed above give an accuracy of approximately 1–5 units in the last reported figure as based on the computed standard error.

Options and Special Features. Considerable flexibility in the calculations is available through the use of several options. Some of these are described below.

Since the amount of computer time required is dependent upon the number of compounds to be considered, there is an economic benefit in making use of any prior knowledge as to the qualitative composition of the sample. This can be done by defining subgroups of spectra which are used for the calculations. However, if the ratio of the standard error to the expected error in the fit exceeds a preset value, then the calculations are automatically repeated using a second group option (usually the entire set of spectra). Since these subgroups are defined by merely listing the serial number of the desired spectra, they are readily redefined as required.

As many different magnetic tapes with different sets of reference spectra may be prepared as desired and then any two of these may be mounted on the computer at the same time. Either tape may be specified for the calculations for a given sample. One tape may contain spectral data for a large set of commonly encountered compounds, the other tape may contain data for a set of compounds of only temporary interest.

Any selected list of compounds can be omitted from the final report and the results for the balance normalized to 100%. This permits reporting results on a water-free or air-free basis, if desired.

Computer Costs. As mentioned previously, the computing time is dependent upon the number of reference spectra considered in the regression. Figure 1 shows the computer time required on an IBM 7040 as a function of the number of spectra which may enter the regression. An IBM 7094 has been found to be about 4.8 times faster for these calculations.

Discussion. This program, with minor modifications, has been used successfully for about 2 years for the daily calculation of routine mass spectrometric analyses. Also, it has been tested using data for several hypothetical samples. The data for these samples were computed using the calibration data and the desired concentration of each component, and then random errors were added to each computed intensity such that the standard deviation between the true and modified intensities is 1% of the value. Tables I to III show the results obtained for the analysis of hypothetical samples *A*, *B*, and *C*. The different computed values represent results calculated for a different distribution of random errors in the sample data. All of these results were obtained using a library of 129 reference spectra with no subgroup designation.

The errors in the qualitative composition observed in Table III for some of the calculations are a result of marked similarity between combinations of one set of spectra and combinations of other spectra. Similarity between just two spectra is easily detected by examining the coefficients in the correlation matrix. These coefficients may range from 0.0 to 1.0 depending on the degree of similarity of the two spectra. If very nearly 1.0, then one of the two spectra should be eliminated. If the set of reference spectra should contain two identical spectra, then the first one of the two considered will be the one chosen. However, if two spectra differ only slightly, then the one chosen will be the spectrum which gives the smallest variance even though the difference may be very small. In this case, very small differences in the experimental data can influence the choice.

The possibility that the composite spectrum of one group of spectra is very similar to the composite spectrum of another group of different spectra is very difficult to detect. The effect of this condition on the calculations was investigated through the use of a separate program which predicted that the composite spectrum of sample *D* and sample *E* as given in Table IV would be very similar. The computed intensities of these two mixtures agreed to about 5% at all the major peaks with a few slightly larger differences in peaks of lower intensity. Four different distributions of random errors were added to the computed spectrum of each sample and then these data were used as input to the regression program which used the entire library of 129 spectra for the calculations. The computed results for sample *D* were excellent. The largest error consisted of finding 0.8% 1-pentene which was not actually present.

The results for sample *E* were not so good. Most of the errors could be attributed to finding several of the compounds listed for sample *D* and these errors in the qualitative composition led to errors in the quantitative composition. Some of these errors were as large as 5%. The small differences between the four different sets of data for sample *E* had a considerable effect on both the qualitative and quantitative results. However, considering the fact that these particular mixtures were the worst possible combinations and that manual calculations would be virtually impossible, the results were surprisingly good.

Although the program endeavors to find the set of spectra which gives the best fit to the observed spectrum, there can be several nearly equivalent solutions in such cases. Since no purely mathematical solution can find the correct answer to such a problem, the true results can be obtained only by supplying additional information to the computer. This may be done by using the subgroup option to restrict the list

Table I. Results for Hypothetical Sample *A*

Compound	Actual, %	Found, %				
n-Butane	40.0	40.1	39.7	40.5	40.2	40.2
Isobutane	15.0	14.8	15.5	14.6	14.9	15.1
Nitrogen	15.0	15.1	15.0	14.6	14.9	15.0
Carbon monoxide	20.0	20.1	19.6	20.2	20.0	19.8
Acetone	10.0	9.8	10.1	10.1	10.0	9.9
Acetaldehyde Ethylene oxide	...	..	0.2	...	...	...

Table II. Results for Hypothetical Sample *B*

Compound	Actual, %	Found, %				
n-Pentane	5.0	5.0	5.0	4.9	5.0	4.9
Isopentane	15.0	15.1	15.1	15.2	15.3	15.2
n-Butane	5.0	5.2	5.1	5.1	5.0	4.9
Isobutane	13.0	12.9	12.9	12.7	12.6	13.3
Butenes	22.0	21.7	22.4	22.2	21.9	21.9
Isobutene, 12.0%						
trans-2-Butene, 5.0%						
cis-2-Butene, 5.0%						
Propane	20.0	19.8	20.0	20.0	20.0	20.1
Nitrogen	8.0	8.5	7.7	7.9	8.2	7.7
Carbon monoxide	12.0	11.8	11.8	12.0	12.0	12.2

Table III. Results for Hypothetical Sample C

Compound	Actual, %	Found, %				
Ethene	10.0	10.0	10.7	9.2	10.0	10.1
Ethane	5.0	5.1	5.0	5.1	4.9	5.1
Propene	3.0	2.9	1.8	2.4	2.3	2.5
Propane	2.0	1.9	2.0	1.9	2.1	2.0
Butenes	5.0	5.2	5.4	5.5	4.7	4.5
1-Butene, 2.0%						
trans-2-Butene, 3.0%						
n-Butane	15.0	15.0	15.0	15.4	14.5	15.0
Isobutane	10.0	9.8	8.9	9.2	11.2	10.4
Pentenes	5.0	4.9	4.6	5.0	3.3	5.1
3-Methyl-1-butene						
n-Pentane	5.0	4.9	4.7	5.5	...	4.6
Isopentane	20.0	20.3	20.5	19.7	20.8	20.6
n-Hexane	5.0	5.0	5.0	5.1	5.0	4.9
Cyclohexane	3.0	2.9	2.3	3.1	1.8	3.1
Methylcyclopentane	2.0	2.1	...	1.6	...	2.0
Methylcyclohexane	10.0	10.0	10.0	10.0	10.0	10.0
Propadiene + methylacetylene	...					0.2
1-Pentene + ethylcyclopropane	...				1.3	
1-Hexene	...		3.1		5.2	
Hexenes (branched)	...		0.9		0.5	
Furan	...		0.1		0.1	
Methyl ethyl ketone	...				1.8	
Carbon tetrafluoride	...			0.2		
Acrolein	...			1.1		
Carbon monoxide					0.5	

Table IV. Composition of Hypothetical Samples *D* and *E*

	Sample *D*
27.05%	*n*-Pentane
0.96	3-Methyl-1-butene
10.75	Isobutane
4.19	Isobutene
8.20	Ethane
0.09	Nitrogen
2.06	Isopropyl alcohol
0.63	Isobutyl alcohol
4.50	Diethyl ether
6.75	Acetone
10.48	Diethyl ketone
2.82	Acetaldehyde
3.27	Propylene oxide
2.41	Methyl formate
0.62	2-Methylpentane
14.55	3-Methylpentane
0.09	1-Hexene
0.50	Cyclopentane
0.11	Methylamine
	Sample *E*
20.37%	Isopentane
9.70	*n*-Butane
2.54	1-Butene
5.29	Propane
4.38	Ethene
0.03	Ethyl alcohol
1.60	Allyl alcohol
1.84	*n*-Propyl alcohol
0.76	*tert*-Butyl alcohol
4.39	*n*-Butyl alcohol
2.15	*Sec*-Butyl alcohol
8.05	Methyl ethyl ketone
5.77	Propionaldehyde
6.51	Methyl acetate
19.40	*n*-Hexane
2.10	1-Pentene
0.07	3-Methyl-1-pentene
1.73	Acetic acid
1.68	Nitric oxide
1.64	2,2-Dimethylpropane

of spectra considered and thus eliminate impossible components. Another approach is to use a provision which forces any selected group of spectra—preferably the major components—to enter the regression at the beginning of the calculations and then allow the regression to find the remaining components.

Table V shows the stepwise operation of the regression procedure for the first sample from Table I. The variance starts at a high value and the computed results are considerably in error. However, as additional spectra are chosen for the regression, the variance becomes smaller and the computed concentrations approach the true value.

Table V. Steps in Regression

Compound	Actual, %	Found, %				
		Step 1	Step 2	Step 3	Step 4	Step 5
n-Butane	40.0	64.5	62.8	53.5	40.2	40.1
Isobutane	15.0				14.1	14.8
Nitrogen	15.0					15.1
Carbon monoxide	20.0		23.6	22.0	23.0	20.1
Acetone	10.0			13.0	12.2	9.8
Variance, %		33.9	24.6	17.6	11.2	1.0

Another possible approach for the calculation of mass spectrometric data would be a direct least-squares solution of the set of equations formed by including all possible compounds. However, in practice this method is not as satisfactory as the stepwise regression method. In the least-squares method, the inclusion of compounds which are not present will decrease the value of the determinant and thus increase the probable error in the computed results for compounds actually present. However, with the regression procedure the probable error is based on the value of the determinant for only the compounds found and not for the compounds considered. Another disadvantage of the least-squares method is that the number of compounds considered cannot exceed the number of masses for which intensity data are available. In the regression procedure, it is only the number of compounds found which cannot exceed the number of masses. The only limitation on the number of compounds considered is the amount of storage space available in the computer and the amount of computer time available. The provision in this program for 150 reference spectra on each magnetic tape is believed to be quite adequate.

The program described in this report is written mostly in Fortran IV for operation under the IBSYS System. A few subroutines written in machine-language are also required. The authors can supply on request a more extensive report which describes the operation of the program with complete listings of the source decks.

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Reactor Neutron Activation Analysis by the Single Comparator Method

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▶ A method of activation analysis, based on the irradiation and counting of a single comparator (cobalt) instead of standards prepared from known weights of the elements to be determined, has been critically evaluated. The influence of the variation of experimental parameters such as reactor neutron spectrum, neutron flux, and yield of γ-ray spectrometers, has been studied. In a series of trial runs the accuracy and precision were found similar to those of the relative method. The method can find most useful applications in automated analysis, or when a large number of elements are determined in one sample.

Neutron activation analysis by the relative method, until now used nearly exclusively, requires preparation and counting of a comparator for each element to be determined. These operations are time-consuming and can introduce sources of error, particularly when automated systems of activation analysis are used.

Recently the possibility of eliminating the comparators by using a direct or absolute method was considered (*10*). The results obtained using γ-ray spectrometry to measure induced radioactivity show that this procedure cannot yet compete in accuracy with the relative method. This has been attributed to the uncertainties which still exist in the knowledge of nuclear constants required for the calculations, especially cross sections and γ-ray abundances of radionuclides.

Although the accuracy was poor, the precision of results was generally similar to that of the relative method. This suggests that results of the same quality as those given by the relative method are possible, if the factor depending on nuclear constants is not derived by calculation, but determined experimentally by irradiating known weights of the element under study with a neutron flux monitor. Then the unknown sample would be irradiated with a similar flux monitor, which would be used as a single comparator for different elements.

The two major difficulties of the absolute method—the necessity of measuring "total" photopeak surfaces and evaluating the effective activation rates of the elements as a function of the neutron energy spectrum available—would also be avoided, as the experimental parameters of activation and counting are not important, if they are kept constant. The accuracy of the method is strictly dependent on the validity of this assumption.

The single comparator method is often applied in activation analysis, when the activating flux (neutrons or gamma or charged particles) is produced by particle accelerators, as the small volume available and the high flux gradient pose severe limitations on the choice of comparators.

In reactor neutron activation it was used only occasionally, when many elements were determined simultaneously (*9*) or when samples and standards could not be irradiated together (*1*). A somewhat similar method utilizes elements present in known quantities in the matrix itself as internal standard (*15*, *18*) with the advantage of correcting flux perturbations within the matrix. Continuous flux monitoring by means of suitable radiation detectors placed near the irradiation positions has also been used in an automated system (*19*). Computer coupling assured the automatic correction of the flux variations during the irradiation.

In none of this work has the method been critically evaluated. The important advantages that could be gained by the use of a single comparator method for routine determination of a high number of elements have induced us to study its accuracy, precision, and limits of applicability as a first step to an automated computer-coupled activation analysis system. In this work all the activity measurements were made by γ-ray spectrometry and the treatment was limited to applications of this technique.

EXPERIMENTAL

Principle of Method. The weight, W, of an irradiated element is related to the photopeak counting rate, A_p, of the radioisotope measured by the relation:

$$W = \frac{A_p}{\Phi SD} \frac{M}{\hat{\sigma}\delta NEa} \qquad (1)$$

where

M = atomic weight of the irradiated element
δ = isotopic abundance of the target nuclide
$\hat{\sigma}$ = effective activation cross section for the neutron energy spectrum used
N = Avogadro number
E = efficiency of the detector for the γ-ray measured
a = γ-ray abundance in decay scheme
Φ = neutron flux
S = saturation factor,
$S = 1 - e^{-\lambda T}$, depending on irradiation time T and decay constant λ
D = decay factor, $D = e^{-\lambda t}$, where t is decay time

When the neutron flux is measured by irradiating a known weight of an element (neutron flux monitor) and measuring the induced radioactivity by γ-ray spectrometry, the same relation holds:

$$\Phi = \frac{A_p{}^*}{S^*D^*W^*} \frac{M^*}{\hat{\sigma}^*\delta^*NE^*a^*} \qquad (2)$$

where the asterisks refer to the neutron flux monitor.

By substituting Φ taken from Equation 2 in Equation 1, we have:

$$W = k \frac{A_p}{A_p{}^*} \frac{S^*D^*}{SD} W^* \qquad (3)$$

where

$$k = \frac{\dfrac{\hat{\sigma}^*\delta^*NE^*a^*}{M^*}}{\dfrac{\hat{\sigma}\delta NEa}{M}} \qquad (4)$$

If k is calculated by means of Equation 4 after evaluating the individual nuclear constants appearing in Equation 4 on the basis of literature data, the analysis is done by an absolute method identical to that described previously (*10*). k can also be obtained experimentally from Equation 3 by irradiating a known amount of element and of the single comparator chosen and measuring their photopeak counting rates and saturation and decay factors.

Once the k value has been determined, the unknown sample can be irradiated with a known weight of the single comparator and Equation 3 used, if it is assumed that k is constant—that is, that no variations occurred in the quantities appearing in Equation 4 between the moment of the determination of k and the actual analysis.

The accuracy of the results depends on the accuracy of the determination of the quantities appearing in Equation 3, and the constancy of the k values.

The determination of A_p, $A_p{}^*$, and W^* is also necessary for analysis by the relative method and, if the half life of the radioisotope measured is short, ratio D^*/D must also be determined. The single comparator method introduces as additional sources of errors only those related to the measurement of SD, S^*D^*, and k. The first two factors depend only on irradiation and decay times and are generally easily determined with good precision. The other sources of error are related to the measurement of k and its constancy with time.

Procedure. Sample Preparation. For the assessment of k values, known quantities of spectroscopically pure reagents, generally from Johnson, Matthey and Co., Ltd., were sealed in silica vials. Solid samples, aqueous solutions, and homogenized solid mixtures with magnesium oxide were used, depending on the neutron absorption behavior of the element studied.

The samples for the analysis were sealed in similar silica vials.

The single comparator is a wire of a cobalt alloy (1% Co, 9% Mg, and 90% Al). The homogeneity of the wire was tested by neutron activation and the concentration of cobalt measured by both neutron activation and a colorimetric procedure. The wire is cut in constant lengths containing 0.211 ± 0.002 mg. of cobalt. Silica vials and comparator are packed together in aluminum foil and irradiated.

Irradiation. The irradiations were performed in the Ispra I reactor. The neutron flux and the fractional epithermal contribution of the irradiation positions are reported in Figure 1. The irradiated samples are received from the reactor together with the exact irradiation timing. The integrated reactor power is also reported for long irradiations.

The reactor operates at a constant power of 5 Mw. for 12-day cycles. The power level is varied only on agreement of all the reactor users.

Radioactivity Measurements. After the irradiation the silica vials are opened and counting sources prepared from the irradiated specimens. The elements irradiated for the assessment of the k values are usually dissolved in slightly acid solutions containing carriers and only a fraction is taken for activity measurements. The counting sources are in the form of thin layers of 25-mm. diameter placed 13 mm. from the top of a 3 × 3 inch NaI(Tl) detector (*10*). The cobalt wires are left to decay for at least one day to eliminate the interfering short-lived radioisotopes produced from impurities in the alloy; then they are counted.

All the activity measurements are made with a γ-ray spectrometer which has been described (*10*). The photopeak counting rate is evaluated graphically (*17*) or mathematically by a procedure derived from the method proposed by Covell (*6*) and modified for use with the IBM 7090 computer (*3*).

The irradiations and countings for the assessment of k are often done together with the analysis by the relative method. In this case a new standard is irradiated each time, together with the unknown sample and the cobalt wire. The ratio of the photopeak activity of unknown and standard is used for analysis by the relative method; the ratio of the activity of standard and single comparator is used to determine k. The experimental parameters (irradiation and decay times, amount of standard, chemical form, dilution, etc.) are changed whenever possible to minimize systematic errors. When the values of k determined lead to a statistically acceptable average, the standards are no longer irradiated and the weight of the element is calculated from the ratio of the photopeak counting rates of unknown and single comparator.

To be certain that no mistake has been made in the experimental determinations of k values, the theoretical values of k are also calculated from Equation 4 (when nuclear constants are known) and compared with the experi-

Table I. Theoretical and Experimental *k* Values

Element	Isotope	γ-ray energy, m.e.v.	*k* values Theor.	*k* values Exptl.
Arsenic	As^{76}	0.56	14	10.55
Barium	Ba^{139}	0.16	228.5	208
Chlorine	Cl^{38}	1.64 2.15	879 860	749 885
Chromium	Cr^{51}	0.32	167.5	120
Cobalt	Co^{60}	1.17 1.33	1 1.11	1 1.103
Copper	Cu^{64}	0.51	15.42	14.95
Gallium	Ga^{72}	0.83 0.89	20	17.2
Hafnium	Hf^{181}	0.48	16.2	13.2
Iron	Fe^{59}	1.10 1.29	16,960 26,000	13,150 20,200
Manganese	Mn^{56}	0.85	1.98	1.815
Nickel	Ni^{65}	0.37 1.12 1.49		14.730 10,790 9,000
Scandium	Sc^{46}	0.89 1.12	0.965 1.205	0.745 0.97
Silver	Ag^{110m}	0.65 0.67 0.70	23.3	20.4
		0.81 0.88 0.93	37.3	31.1
Sodium	Na^{24}	1.37	32.3	31
Rubidium	Rb^{86}	2.75 1.08	60.2 845	62.8 1,465
Tin	Sn^{117m}	0.16	21,800	18,000
Zinc	Zn^{65}	1.11	377	152

mental values. This procedure is possible, as the activity measurements are made with a gamma detector whose efficiency *vs.* γ-ray energy is known *(10)*. In case of disagreement the origin of the discrepancy is briefly studied, but the experimental value of *k* is preferred, if the discrepancy remains unexplained.

When the analyses are carried on over extended periods of time, occasional controls on the constancy of the *k* values are done. Additional periodical controls on the constancy of neutron energy spectrum and the performances of the counting equipment are routinely done.

Table II. Determination of Chromium in Iron Samples[a]

Irradiation	Comparator	Per cent Cr Relative method	Per cent Cr Single comparator method
	Sample with 0.18% Cr		
1	$K_2Cr_2O_7$ solid	0.172	0.178
2	Cr metal	0.182	0.177
3	$K_2Cr_2O_7$ solid	0.208	0.176
		0.262	0.230
4	Cr metal	0.172	0.170
		0.162	0.166
		0.155	0.158
5	Cr metal	0.135	0.153
		0.150	0.167
		0.208	0.220
	Av.	0.181	0.179
	Std. dev. of av.	0.011	0.008
	Sample with 0.879% Cr		
1	$K_2Cr_2O_7$ solid	0.838	0.880
2	Cr metal	0.84	0.815
		0.885	0.845
3	$K_2Cr_2O_7$ solid	1.010	0.875
		0.940	0.940
4	Cr metal	0.890	0.875
		0.760	0.780
		0.810	0.820
5	Cr metal	0.770	0.870
		0.800	0.845
		0.810	0.860
	Av.	0.851	0.855
	Std. dev. of av.	0.023	0.012

[a] Samples from Bureau of Analysed Samples, Ltd.

RESULTS AND DISCUSSION

***k* Values of Elements.** Table I shows the *k* values obtained experimentally for 17 elements. The calculated values (Equation 4) are reported for comparison, when possible. They are generally higher than the experimental, but systematic differences between the photopeak surface measured experimentally and those theoretically obtained should be considered. If cobalt is used as single comparator, the measured surface of the 1.17-m.e.v. photopeak of Co^{60} is about 17% lower than the true value of the surface, because of peaks overlapping and coincidence losses, when the evaluation is made with the graphical or mathematical methods used by us.

These differences should be taken into account when comparing the experimental and theoretical *k* values of all the elements (except cobalt), although they have no effect in practical analysis, if the photopeak surfaces are always measured in the same way.

The *k* values reported in Table I are valid for only one counting geometry and this fact limits the applicability of the method when a large range of concentrations exists in the samples to be analyzed. Modern advances in nuclear instrumentation have considerably decreased this limitation, with the commercial availability of detectors and analyzers which can tolerate rather high counting rates.

The low source-detector geometries can be correlated to high source-detector geometries by means of correction factors which can be calculated theoreti-

Table III. Determination of Chlorine in Lake Water

Irradiation	Comparator[a]	Results, p.p.m. Relative method	Results, p.p.m. Single comparator method
1	1	1.94	1.94
	2	1.66	1.70
2	3	1.92	1.83
	4	1.92	1.92
	Av.	1.86	1.87
	Std. dev. of av.	0.07	0.055

[a] For each determination comparators were prepared by taking different weights of the same initial aqueous solution containing a known concentration of NH_4Cl. Sample and comparator activities have been measured at three different instants, then the initial activity has been deduced from the decay curves.

Table IV. Determination of Gallium and Copper in Aluminum

Irradiation	Comparator[a]	Results, p.p.m. Relative method	Results, p.p.m. Single comparator method
	GALLIUM		
1	1	83.2	81.3
2	2	82.8	83.6
3	3	80.3	81.8
	Av.	82.10	82.23
	Std. dev. of av.	1.29	0.70
	COPPER		
1	10	35.7	33.8
2	20	31.7	32.1
4	20	31.8	32.4
	Av.	33.07	32.77
	Std. dev. of av.	1.32	0.53

[a] Comparators prepared from aqueous solution containing known concentration of $Ga(NO_3)_3 \cdot 8H_2O$ for gallium and $CuSO_4 \cdot 5H_2O$ for copper.

cally or determined experimentally. In the high geometry in which the k values are determined, coincidence summing for isotopes which decay with emission of γ-ray cascades is not negligible. Care should then be taken in applying correction factors to these isotopes, as the change in the shape of the spectra, when a low geometry is used, might introduce errors.

Analytical Results. In Tables II, III, and IV some results obtained with the single comparator method are compared with those obtained with the relative method on three analytical problems: determination of chromium in iron samples, chlorine in lake water, and gallium and copper in aluminum.

Each set of analyses was done in a limited period of time (about 2 weeks) and the k values were calculated by averaging the individual values obtained with the comparators.

In the results reported no systematic error between the values obtained by the two methods is evident, but the k values were obtained at the same time in which the analyses were done, thus minimizing the effect of possible long-term variations.

Effect of Variation of Reactor Neutron Spectrum. Any change in the reactor neutron spectrum changes the effective activation cross section of the element to be determined and of the single comparator ($\hat{\sigma}$ and $\hat{\sigma}^*$ in Equation 4). If the change affects the two nuclides differently, the ratio of the cross sections and the A/A^* ratio vary. A systematic error is induced with the single comparator method if such a change occurs between the assessment of the k values and the analysis.

The error induced by a modification of the neutron energy distribution is discussed on the basis of the simplifying assumption that all the neutrons above thermal energy behave like a single group.

The relative importance of the epithermal flux, Φ_r, and the thermal neutron flux, Φ_o, in the irradiation position used, can be experimentally determined by measuring the cadmium ratio (CdR) or ratio of the activity induced in an uncovered flux monitor (cobalt in our case) to the activity induced when a cadmium shield is interposed to absorb thermal neutrons. We have:

$$CdR = \frac{\sigma_o^*\Phi_o + \sigma_r^*\Phi_r}{\sigma_r^*\Phi_r} = \frac{\sigma_o}{\sigma_r}\left(\frac{1}{f_e} - 1\right) + 1 \quad (5)$$

where $f_e = \dfrac{\Phi_r}{\Phi_o + \Phi_r}$ is the fraction of the epithermal neutrons in the spectrum, σ_o^* is the thermal activation cross section for the neutron flux monitor, and σ_r^* is its effective cross section for reactor neutrons above the cadmium cutoff, or resonance integral.

From Equation 5 it is possible to derive:

$$f_e = \frac{\sigma_o^*}{\sigma_r^*\,(CdR - 1) + \sigma_o^*} \quad (6)$$

The effective activation cross sections of the elements are given by:

$$\hat{\sigma} = \sigma_o \frac{\Phi_o}{\Phi_o + \Phi_r} + \sigma_r \frac{\Phi_r}{\Phi_o + \Phi_r} \quad (7)$$

The weight of elements determined in activation analysis is proportional to the ratio of the photopeak activities of element and flux monitor, and then to the ratio of their effective activation cross section. We have:

$$W = \alpha \frac{A_p}{A_p^*} = \beta \frac{\hat{\sigma}}{\hat{\sigma}^*} = \beta \frac{\sigma_r\,\Phi_r + \sigma_o\Phi_o}{\sigma_r^*\Phi_r + \sigma_o^*\Phi_o} \quad (8)$$

where α and β are constants.

In a flux of pure thermal neutrons $\hat{\sigma} = \sigma_o$ and W becomes:

$$W_o = \beta \frac{\sigma_o}{\sigma_o^*} \quad (9)$$

We can then write from Equations 8 and 9:

$$\frac{W}{W_o} = \frac{\sigma_o^*}{\sigma_o} \cdot \frac{\sigma_r\Phi_r + \sigma_o\Phi_o}{\sigma_r^*\Phi_r + \sigma_o^*\Phi_o} \quad (10)$$

Equation 10 can be written in terms of the fractional epithermal contribution, f_e, of the total flux; we then have:

$$\frac{W}{W_o} = \frac{\dfrac{\sigma_r}{\sigma_o} + \dfrac{1 - f_e}{f_e}}{\dfrac{\sigma_r^*}{\sigma_o^*} + \dfrac{1 - f_e}{f_e}} \quad (11)$$

In terms of cadmium ratio, Equation 11 becomes:

$$\frac{W}{W_o} = \frac{1}{CdR}\left(\frac{\dfrac{\sigma_r}{\sigma_o}}{\dfrac{\sigma_r^*}{\sigma_o^*}} - 1\right) + 1 \quad (12)$$

$\dfrac{\sigma_r}{\sigma_o}$ is a constant for any given nuclide. Table V shows the values of $\dfrac{\sigma_r}{\sigma_o}$ for 44 isotopes, calculated from thermal activation cross sections reported by Hughes, Harvey, and Magurno (*12*, *13*) and resonance integrals reported by Brume and Jirlow (*5*) and Macklin and Pomerance (*14*) except for chlorine, which was experimentally determined.

Figure 1 shows the variation of W/W_o *vs.* f_e and *vs.* CdR for a few selected values of $\dfrac{\sigma_r}{\sigma_o}$ when cobalt is used as single comparator in the range of neutron fluxes from an almost pure thermal flux (0.1% epithermal component) to a pure epithermal flux. Values of W/W_o of individual elements are also reported for only one value of f_e. The other values can be obtained by interpolating the curves of the graph. The figure shows also the fractional epithermal flux at the different irradiation positions of the Ispra I reactor.

The limits of applicability of the method are clearly shown in relation to the variations of the neutron energy spectrum. When the irradiation positions are well thermalized, variations of the epithermal contribution have negligible effect on most elements. This is the case for the Ispra I reactor. All three irradiation positions correspond to cadmium ratio for cobalt greater than 50 (f_e values lower than 1.5%). Most of the elements enumerated in Table I can be irradiated in any of the three irradiation positions without important error. Only for silver and arsenic a correction must be applied, if the irradiations are made in positions different from that used for the determination of the k value (pneumatic tube position).

When the epithermal component of the reactor flux increases, the number of elements to which the method can be applied decreases. The elements which can still be determined are those having $\dfrac{\sigma_r}{\sigma_o}$ values within a certain range from that of the single comparator, the amplitude of the range depending on the variations of f_e around the average value for the position and the precision requested from the analysis.

Table V. Values of σ_r/σ_o

Isotope	σ_r/σ_o	Isotopes	σ_r/σ_o	Isotopes	σ_r/σ_o	Isotopes	σ_r/σ_o
Na^{23}	0.457	Zn^{64}	1.425	In^{113}	18.1	Re^{185}	9.66
Al^{27}	0.76	Zn^{68}	1.72	In^{115}	12.75	Re^{187}	4.43
P^{31}	0.438	Ga^{69}	1.84	Sb^{121}	23.8	Ir^{191}	3.65
Cl^{37a}	0.402	Ga^{71}	3.00	Sb^{123}	53.9	Au^{197}	15.9
Sc^{45}	0.48	As^{75}	8.75	I^{127}	25.5	Ir^{193}	10.55
V^{51}	0.49	Br^{79}	12.9	Pr^{141}	1.045	Hg^{202}	0.55
Mn^{55}	0.88	Y^{89}	0.716	Sm^{152}	12.5	Tl^{203}	11.75
Fe^{58}	0.57	Nb^{93}	3.52	Eu^{153}	2.26	Tl^{205}	5.0
Co^{59}	1.58	Rh^{103}	4.32	Hf^{180}	2.18	Th^{232}	9.05
Cu^{63}	0.975	Ag^{107}	2.74	Ta^{181}	31.11	U^{235}	2.53
Cu^{65}	1.22	Ag^{109}	10.3	W^{186}	10.45	U^{238}	101.0

[a] σ_r/σ_0, for chlorine experimentally obtained.

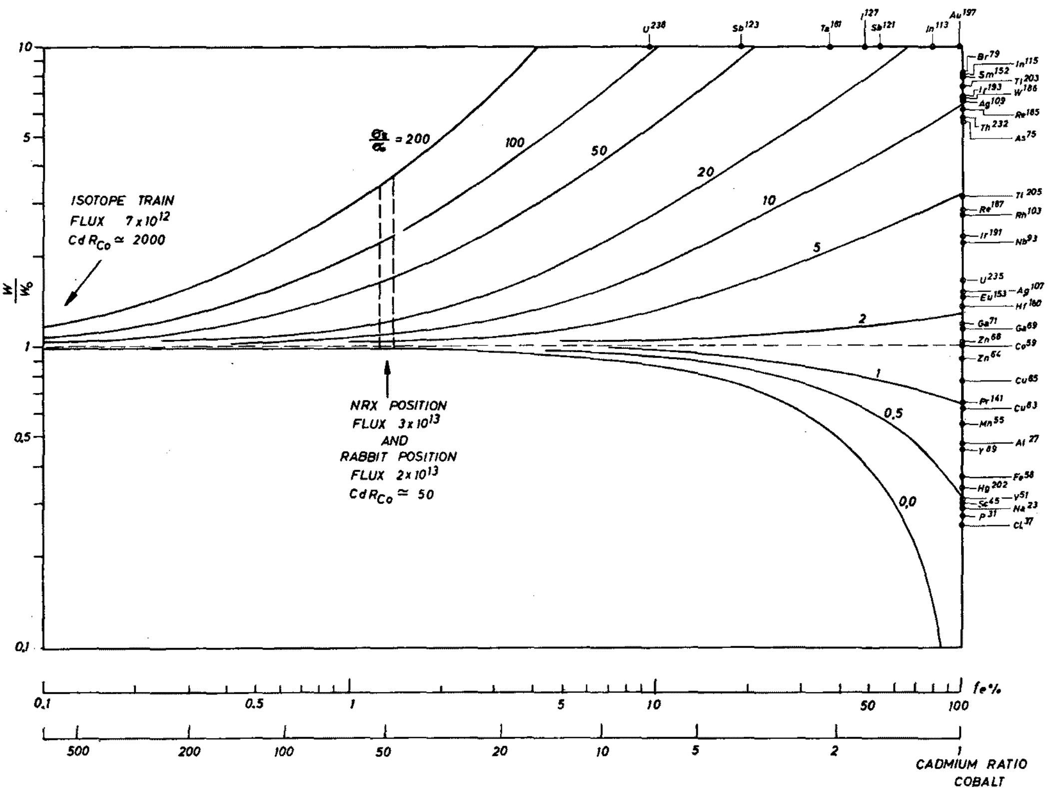

Figure 1. Variation of determined weights vs. fractional epithermal flux and cadmium ratio for different ratios between resonance integral and thermal activation cross section

Single comparator. Cobalt

The applicability of the method can be increased by an appropriate choice of the neutron flux monitor, in relation to the "quality" of the neutrons available and the nature of the problem under study.

There are, for example, some elements (Ta, Sb, I, In, Br, Sm, Tl, W, Ir, Ag, Re, Th, and As) having $\frac{\sigma_r}{\sigma_o}$ values between 8 and 26, for which gold is a better single comparator than cobalt. Figure 2 shows the W/W_o values for the same elements of Figure 1 when gold is used instead of cobalt as a single comparator, showing clearly the effect of the change of comparator.

Fluctuations of f_e for the irradiation positions used depend on parameters which are typical of the different reactor installations, such as stability of the reactor core configuration, influence of perturbing experiences near the irradiation positions, etc., which should be controlled carefully before confidence is placed on the single comparator method. Periodical controls of f_e are evidently necessary in any case, particularly when modifications take place in the reactor core.

The Ispra I reactor which is used for neutron irradiations by our laboratory is a heavy water moderated reactor. The epithermal flux never exceeds 1.5% of the thermal flux in the irradiation positions in the graphite reflector (*4*) which are used for activation analysis by the single comparator method. Cadmium ratios measured over periods of a few months never showed variations higher than 10%.

Figures 1 and 2 show that the single comparator method can be applied to almost any element with negligible errors. If cobalt is used as comparator, even for uranium for which $\frac{\sigma_r}{\sigma_o}$ is greatest, a variation of ±10% of the

Table VI. Relative Counting Rates of Photopeaks of La^{140}

Date of detn.	Energies, m.e.v., of photopeaks of La^{140}			
1962	0.33	0.49	0.82 + 0.93	1.6
March 13	0.76	1.42	0.89	1
May 21	0.71	1.46	0.91	1
1963				
July 10	0.70	1.35	0.86	1
Sept. 10	0.73	1.44	0.86	1
Nov. 19	0.73	1.44	0.95	1
1964				
Feb. 4	0.76	1.405	0.86	1
March 18	0.76	1.34	0.93	1
Av.	0.736	1.409	0.894	1
Std. dev. of single detn.	0.0204	0.0464	0.0369	
Std. dev. of av.	0.0077	0.0176	0.0139	

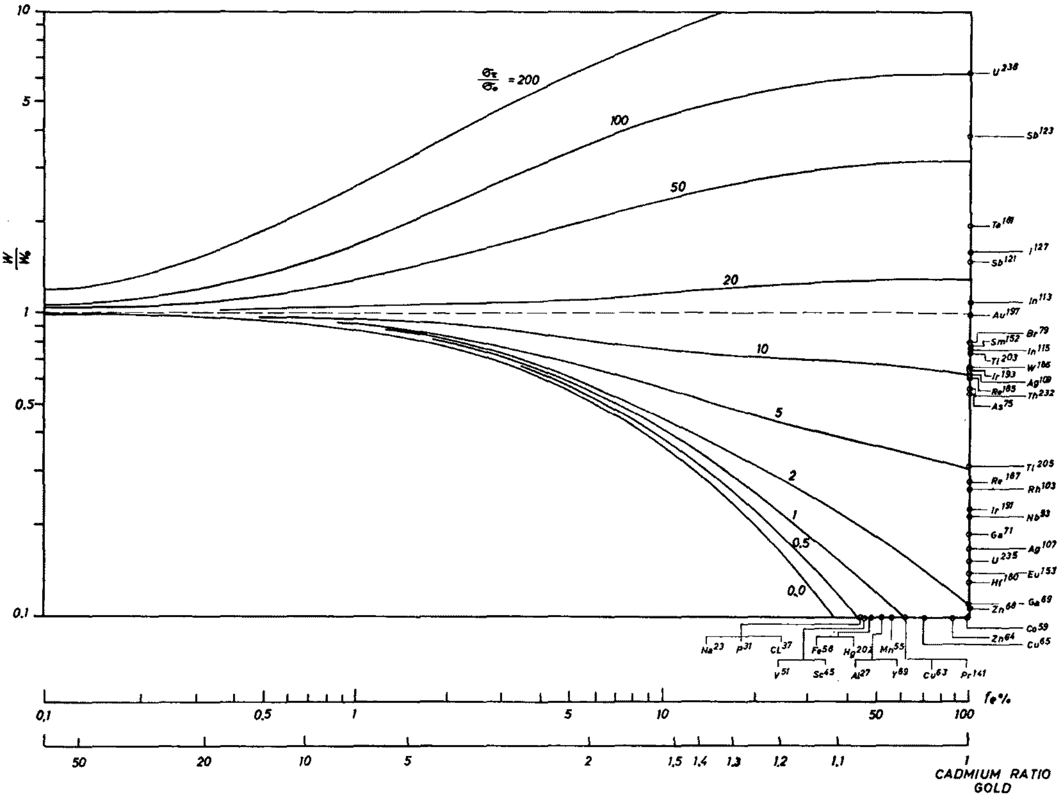

Figure 2. Variation of determined weights *vs.* fractional epithermal flux and cadmium ratio for different ratios of resonance integral and thermal activation cross section

Single comparator. Gold

fractional epithermal flux corresponds with an error of ±4.5% of the weight determined. For all the other elements this error will be smaller, less than 1%, and can be neglected therefore in most problems if the $\frac{\sigma_r}{\sigma_o}$ ratio is smaller than 12.

Errors Due to Counting Procedure. In the single comparator method the experimental quantity determined is the ratio of two photopeak activities, as in the relative method, with the only difference that the γ-ray energies of the two photopeaks are generally different. If the efficiency curve for different γ-ray energies does not vary, the two methods are identical for the counting problems concerned.

A variation of the curve of efficiency *vs.* γ-ray energy is very unlikely. It is nevertheless periodically controlled by counting a source with widely different γ-ray energies, La^{140}. In Table VI the results obtained over a period of 24 months show no evident trend.

Periodical controls of the counting equipment are important to keep high standards of quality in activation analysis, whatever method is used: relative, absolute, or by a single comparator. Variations of the counting rates can occur due to an unnoticed change in the counting geometry, or abnormal functioning of the timing unit or dead time correction unit. Variation in the resolving power of both detector and spectrometer can also affect the measurements of the photopeak surfaces.

Periodical control procedures to keep track of the performances of gamma spectrometers are reported in the literature (*7, 8*). We count a standard Co^{60} source at least once a day. Figure 3 shows the counting rates of the 1.17-m.e.v. gamma peak measured over a 9-month period.

Periodical checks are also done occasionally at different times of the day to control the absence of short-term drifts due to temperature excursion, which is not negligible in our particular setup.

The exactitude of the dead time correction is controlled periodically by measuring the stability of the counting rate of the 1.12-m.e.v., peak of Zn^{65} when a very active source of Cr^{51} (0.32-m.e.v. γ-ray) is brought step by step near the detector.

Influence of Variations of Neutron Flux during Irradiation. Since the half life of the radioisotopes to be measured is different from that of the 5.3 years of the Co^{60} comparator, an error can be introduced from a neutron flux variation during the activation. Its value can be estimated by comparing the activity, A_r, which is formed during the irradiation time, T, in a variable flux and the activity, A_c, formed at a constant average flux, $\bar{\Phi}$, which is the quantity indicated by the Co^{60} monitor. We have then

$$A_r = \sigma N \lambda \int_0^T \Phi(\tau) \cdot e^{-\lambda(T-\tau)} d\tau \quad (13)$$

$$A_c = \sigma N \bar{\Phi} (1 - e^{-\lambda T}) \quad (14)$$

The relative error is given by

$$\epsilon = \frac{A_r}{A_c} - 1 = \frac{\lambda e^{-\lambda T} \int_0^T \Phi(\tau) e^{\lambda \tau} d\tau}{\bar{\Phi}(1 - e^{-\lambda T})} - 1 \quad (15)$$

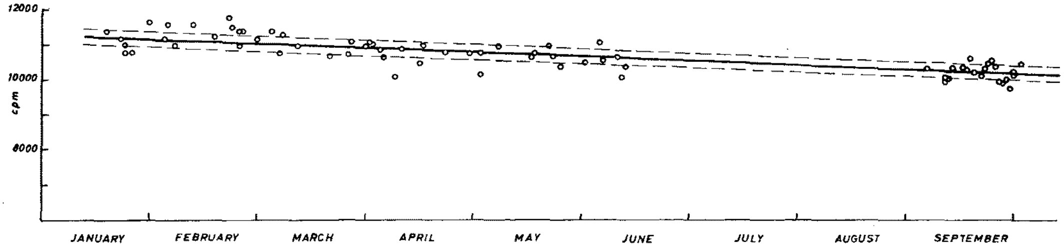

Figure 3. Counting rates obtained from Co^{60} source under 1.17-m.e.v. photopeak during 9 months of 1963

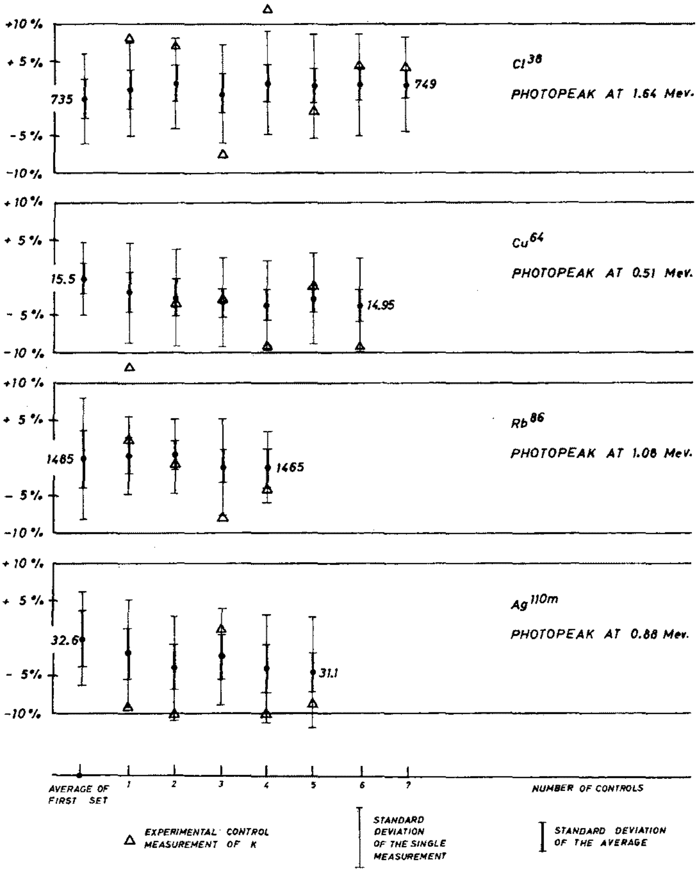

Figure 4. Fluctuations of k values for radioisotopes during periodical control

Equation 15 can be applied to the case in which a sudden change of the flux from $\Phi(1 - \Delta)$ to $\Phi(1 + \Delta)$ occurs at time $\tau = T/2$. It is easy to show that Equation 15 becomes:

$$\epsilon = \Delta \tanh (\lambda T/4)$$

It is then possible to show that if the sample is irradiated for a time of the order of one half life of the isotope formed or smaller, as is usually done to avoid the formation of long-lived interfering activities, the error is fairly small. Thus if the neutron flux varies by 20%, the error for $T = t_{1/2}$ is only 2%.

Matrix Effects. Self-shielding of neutrons within the matrix could be a source of error if the neutron-absorbing behavior of the sample analyzed is different from that of the specimens used for the assessment of the k factors. Various dilutions were used in these operations to make certain that the k factor determined is the one for infinitely thin specimens.

Direct use of these k values is possible only in the case of nonabsorbing matrices, which is our more general application. In other cases matrix effects should be treated in the same way as with the relative method—for example, by calculating the absorption coefficient from the knowledge of the matrix composition (*16*). With the single comparator method the empirical approach of inserting the monitor wire within the sample, as done by Anders (*2*), can lead in some cases to a satisfactory solution of the matrix problem, which cannot be reached so simply with the relative method.

Experimental Control of Constancy of k. There is no evident reason why k should vary with time, with the limitation produced by the variation of the reactor neutron spectrum. A periodical control of the k values is nevertheless necessary for the elements determined most frequently as an overall check of the correct performances of the entire analytical line.

The procedure adopted is the following: The k value is first determined by doing a certain number of irradiations within a limited period of time, and averaging the individual k values obtained. The standard deviations for the single measurement and for the average are then calculated. When a control of the k value is made, only one irradiation is done and the k value is determined. If its value falls within the limits of the standard deviation for the single measurement of the previously determined k, the value is accepted and a new average is derived including the last measurement. The new standard deviations are then calculated.

If the k value obtained with the control irradiation is largely outside the limits of the standard deviation, other irradiations are immediately repeated to determine eventual causes of errors.

Figure 4 shows the variations during periodical controls of the k values of Cl^{38}, Cu^{64}, Rb^{86}, and Ag^{110m}. The variations since the *k* value was determined for the first time are within the standard deviation of the average.

APPLICATIONS

The preference of a single comparator method over the more used relative method is mainly a matter of experimental facilities available and problems under study. Evidently if only a reactor with a high epithermal flux and nonsteady operation is available, the method cannot be used simply. A large variety of elements to be determined in a small series of samples may not warrant the preliminary assessment of *k* values and continuous control of the constancy of the experimental parameters.

The method is, on the contrary, ideally suited for large scale activation analysis by means of steady and well thermalized reactors. Under these conditions the method is as precise and accurate as the relative method and simplification of the analytical technique leads to a higher number of analyses per unit time, possible use of nonspecialized personnel for many operations, and possibility of establishing a standard routine procedure in which the chance of accidental errors is minimized. The coupling of this method with the evaluation of photopeak activity and calculation of weights by means of an electronic computer (the IBM 7090 in our case) (*11*), further enhances the possibility of a routine service on a semiautomated basis. This method has been used satisfactorily for routine analysis in our laboratory for more than a year. Applications include nondestructive determination of trace elements giving short-lived isotopes (Mn, Cl, Na, and Cu in terphenyls, Mn in biological materials) and destructive analysis of trace elements giving both short-lived and long-lived isotopes (Rb, Cs, Sr, Fe, Co, Zn, U, Th, Sc, Cr, Hg, etc., mainly in biological specimens).

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Determination of Oxalate in Beer by Cerate Oxidimetry and the Application of Isotopically-Derived Correction Factor

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▷ The oxalate content of most beers is below 20 mg. per liter and usually below 15 mg. The oxalate can be more readily and completely precipitated as calcium oxalate after a known amount of pure sodium oxalate is added to the beer sample. The precipitated calcium oxalate is determined by cerate titration in 1*N* perchloric acid. By use of oxalic–C^{14} acid, the best conditions for the precipitation of calcium oxalate have been established. From the radioactivity of the beer filtrates and the amount of precipitated oxalate found by cerate oxidimetry, a correction factor has been calculated for unprecipitated oxalate. The oxalate content of all beers, whether high or low in oxalate, can now be determined with an accuracy of ±0.5 mg. per liter.

The role of oxalate in relation to some of the problems encountered in the brewery has been reviewed by Burger and Becker (*5*) and by Brenner (*3*, *4*). The formation of calcium oxalate crystals in packaged beer contributes to haze, while the presence of microcrystalline nuclei of calcium oxalate promotes gushing and overfoaming. Hence, the oxalate content of beer has been of interest to the brewing industry for a long time.

The usual oxalate level, ca. 7–20 mg. per liter, is too low to be determined quantitatively by the conventional method of precipitation of calcium oxalate. In the method of Bau (*1*), which has been commonly used in the brewing industry, the beer sample, after the addition of calcium acetate, is allowed to stand for 40 hours in the refrigerator at approximately 4° C. Brenner (*3*) has shown by an isotope dilution technique that 19–60% of the oxalate failed to precipitate under these conditions from seven 4-liter beer samples, and 20–48% from eleven 300-ml. beer samples. Filtration of the precipitate and the determination of the recovered calcium oxalate by ashing or by titration with dilute permanganate present numerous problems to the most careful analyst. Finally, the correction factor (*5*) suggested to compensate for the oxalate remaining in the beer filtrate and wash water, based on the solubility of calcium oxalate in water, is meaningless and arbitrary since the solubility in beer is different from that in water and is further modified by excess of calcium ions from the precipitant.

The present method incorporates conditions for the precipitation of calcium oxalate which were established by the use of oxalic-C^{14} acid. In addition, improved filtration and washing techniques are used. From the radioactivity of the beer filtrate and the determination of precipitated calcium oxalate by cerate oxidimetry, a correction factor for unprecipitated oxalate has been calculated.

EXPERIMENTAL

Apparatus. For the filtration of calcium oxalate a filter tube with a 30-mm., porosity B, glass filter disk (Ace Glass, Inc., Vineland, N. J., catalog No. 8566) was most suitable. A slurry of medium-size asbestos fibers was added to the filter tube to give a 1-mm. asbestos pad which must be sucked down tightly with a vacuum filtration apparatus. A 1-liter filter flask is necessary to accommodate the 25- × 200-mm. test tubes used later in the procedure.

A Baird-Atomic Model 123 Abacus scaler with an EWH-108 Geiger-Müller tube (Atomic Accessories, Inc., Valley Stream, N. Y.) was used for counting the radioactivity. All samples for counting were plated on $1^1/_4 \times {}^1/_8$-inch stainless-steel planchets with concentric-ring bottoms.

Class A volumetric pipets were used and the cerate titrations were done with a class A microburet, graduated in 0.02-ml. subdivisions.

Reagents. A 2-mg./ml. solution of primary standard sodium oxalate from Thorn Smith (Royal Oak, Mich.) was used for addition to the beer samples and for standardization of the cerate solution. Cerate ammonium nitrate and nitro-ferroin indicator were from G. F. Smith Chemical Co. A 0.02*N* cerate solution in 1*N* $HClO_4$ was prepared according to the procedure of Diehl and Smith (*6*). This was standardized by adding 10 ml. of 2*N* $HClO_4$ to 10 ml. of the $Na_2C_2O_4$ solution, diluting with 50 ml. of 1*N* $HClO_4$, and titrating with the cerate solution as described under Recommended Procedure below.

The oxalic-C^{14} acid was supplied by the New England Nuclear Corp. and had a specific activity of 1.25 mc. per mmole. Solutions of the acid in distilled water were prepared as needed at a concentration of 0.36 mg. (5 μc.) per 3 ml. The gelatin used for plating the radioactive calcium oxalate was a bacteriological grade. Other chemicals were of reagent grade.

Wash water saturated with calcium oxalate (*7*) was prepared by suspending pure calcium oxalate powder in several liters of distilled water, in a suitable container for siphoning, and allowing the mixture to equilibrate for at least one day. After the calcium oxalate had settled, the wash water was filtered by suction through a sintered-glass filter tube containing an asbestos pad as described above. A siphoning arrangement was connected from the water reservoir to the filter tube. The calcium oxalate remaining in the reservoir was resuspended with distilled water for an additional supply of wash water. A cerate titration of a portion of the filtered wash water showed that it was saturated with calcium oxalate after 24 hours of equilibration with the solid phase.

Procedure. A. RECOMMENDED METHOD FOR DETERMINATION OF OXALATE IN BEER. Ten milliliters (20.0 mg.) of primary standard $Na_2C_2O_4$ solution is pipetted into 300 ml. of decarbonated beer contained in a 400-ml. beaker, and 5 ml. of 10% (w./v.) $Ca(OAc)_2 \cdot H_2O$ is slowly added with stirring. The beaker is covered with Parafilm and refrigerated for 4 days at 4° C. The calcium oxalate is then filtered off and the beaker, funnel, and precipitate are washed with calcium-oxalate-saturated wash water. The beer filtrate is discarded, a 25- × 200-mm. test tube is inserted into the filter flask, and the filter tube is replaced with its outlet in the mouth of the test tube. The calcium oxalate is then dissolved with hot 1*N* $HClO_4$ (wash bottle) by rinsing the beaker and filter tube and slurrying the asbestos in the filter tube. This procedure is repeated a number of times until about 50 ml. of solution has been collected. The contents of the test tube are transferred to a 150-ml. beaker, 3 drops of 0.0025*M* nitro-ferroin indicator is added, and the mixture is titrated with 0.02*N* cerate until the solution remains decolorized for at least 30 seconds. The asbestos in the filter tube is reslurried with distilled water, sucked down firmly, thoroughly washed, and is then ready for reuse.

$$\text{Apparent milligrams of } C_2O_4^{-2} \text{ per liter of beer} = \frac{(T - S) \times N \times 44 \times 1000}{\text{ml. beer}}$$

where T = ml. of cerate for beer sample containing 20 mg. of added $Na_2C_2O_4$
S = ml. of cerate equivalent to 20 mg. of $Na_2C_2O_4$
N = cerate normality

The amount of oxalate determined by the cerate oxidimetry is referred to as "apparent oxalate" since it does not include the unprecipitated oxalate ions remaining in the beer filtrate. For most beers the unprecipitated fraction represents a very substantial portion of the total oxalate. According to the radioisotope studies described below, this fraction amounts to 2.6 mg. of $C_2O_4^{-2}$ per liter of beer when the precipitation is carried out as specified above. Therefore:

Corrected milligrams of $C_2O_4^{-2}$ per liter of beer = 2.6 + apparent oxalate

B. EFFECT OF ADDED SODIUM OXALATE AND REFRIGERATION TIME. To conserve oxalic-C^{14} acid and to expedite the handling of a large number of samples in the experimental procedures below, the beer sample volume was reduced from the customary 300 ml. to 120 ml. The quantities of reagents were reduced proportionately and 150-ml. beakers were used.

A commercial beer known to be low in oxalate (Beer I) was used to investigate the completeness of calcium oxalate precipitation at four levels of added oxalate—equivalent to 0.54, 2.0, 4.0, and 8.0 mg. of $Na_2C_2O_4$ per 120 ml. of beer—after refrigeration periods of 2, 3, 4, 6, and 9 days—i.e., 20 samples in all.

To each of five samples was added 3 ml. of the oxalic-C^{14} acid solution and the solutions were thoroughly mixed. This set of samples represented the lowest level of added oxalate—i.e., 0.54 mg. (as $Na_2C_2O_4$) per 120 ml. Two milliliters of 10% $Ca(OAc)_2 \cdot H_2O$ was then mixed into each of these samples and three 1-ml. aliquots of each were immediately pipetted into planchets. No precipitation of calcium oxalate had occurred at this time. After 2 days of air-drying, the planchets were counted as described below. The observed counts, minus the background count, represented the initial radioactivity of all 20 samples.

To each of the remaining 15 samples, 3 ml. of oxalic-C^{14} acid solution was added with stirring and the 15 were divided into three sets of five each. To each sample was then added 2 ml. of a sodium oxalate solution of such concentration that the amount of $Na_2C_2O_4$ introduced was 1.46 mg. in the first set, 3.46 mg. in the second, and 7.46 mg. in the third. Then 2 ml. of 10% $Ca(OAc)_2 \cdot H_2O$ was added with stirring to each solution and all 20 beakers were covered with Parafilm and refrigerated at 4° C.

Four samples, one at each level of added oxalate, were filtered after each of the refrigeration periods indicated above. The first 100 ml. of filtrate was discarded, and the last portion was collected in a 25- × 200-mm. test tube. Three 1-ml. portions of each beer filtrate were plated on planchets for counting of residual radioactivity. The planchets, after air-drying, were counted for 10 minutes with 950 volts applied to the G-M tube. The planchet to Geiger tube distance was about 10 mm., and the counting efficiency of the scaler and G-M tube were frequently checked with a C^{14} reference source. A background count was made with a planchet containing the residue from 1 ml. of beer. No correction was made for coincidence loss because the counts were relatively low. The percentage of the initial radioactivity remaining in each beer filtrate was then calculated.

A second commercial beer (Beer II) was treated in the same manner with the exception that 24 samples were set up in order to include a 1-day refrigeration period.

C. CORRECTION FACTOR FOR UNPRECIPITATED OXALATE. From the data obtained in part B, the conditions selected as optimum for the precipitation of calcium oxalate in beer were first, the addition of 8 mg. of $Na_2C_2O_4$ per 120 ml. of beer (or 20 mg. per 300 ml.) and second, 4 days of refrigeration.

To determine the value of the correction factor, five different commercial beers were analyzed. The precipitated

Table I. Radioactivity of Beer Filtrates and Correction Factor for Unprecipitated Oxalate[a]

Beer sample[b]	Precipitated oxalate[c] mg./300 ml.	Per cent radioactivity in filtrate	Calcd. total oxalate[d] mg./300 ml.	Correction factor[e] mg./300 ml.
A-1	14.57	5.48	15.41	0.84
A-2	14.71	5.32	15.54	0.83
A-3	13.83	4.82	14.53	0.70
B-1	14.68	5.78	15.58	0.90
B-2	14.75	5.36	15.59	0.84
C-1	14.85	5.81	15.77	0.92
C-2	15.09	4.37	15.78	0.69
C-3	15.03	4.04	15.66	0.63
D-1	15.24	5.52	16.13	0.89
D-2	15.25	4.89	16.03	0.78
D-3	15.66	3.86	16.29	0.63
D-4	15.27	4.19	15.94	0.67
E-1	16.47	5.24	17.38	0.91
E-2	16.76	3.82	17.43	0.67
E-3	16.42	4.48	17.19	0.77
			Av.	0.78

[a] Refrigeration time 4 days; added $Na_2C_2O_4$, 20 mg./300 ml. beer.

[b] Letters designate different commercial beers and numbers indicate separate analyses. All analyses were in duplicate except for A-3 and D-4 which were single determinations.

[c] Determined by recommended procedure, part A, and including added $Na_2C_2O_4$. Values expressed in terms of $C_2O_4^{-2}$.

[d] (Precipitated oxalate × 100) ÷ (100 − % radioactivity in filtrate).

[e] Unprecipitated oxalate.

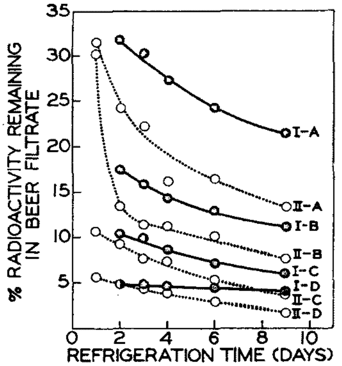

Figure 1. Radioactivity remaining in beer filtrate as function of refrigeration time

I and II are commercial beers. Beer I, ●—●; beer II, ○..○. 0.36 mg. (5 μc.) of oxalic–C^{14} acid added to all beer samples before precipitation of calcium oxalate. Total oxalate added to 120 ml. beer, expressed as $Na_2C_2O_4$:

I-A and II-A, 0.54 mg.
I-B and II-B, 2.0 mg.
I-C and II-C, 4.0 mg.
I-D and II-D, 8.0 mg.

Table II. Apparent Oxalate and Correction Factor

Refrigeration time: 2 days

	Milligrams $C_2O_4^{-2}$ per liter beer		
Beer sample	Apparent oxalate	Correction factor	Corrected oxalate[a]
A-2	3.9	3.4	7.1
B-2	3.6	3.4	6.8
C-2	5.6	3.7	8.8
D-2	6.1	2.8	9.3
E-2	11.4	2.8	14.6
	Av.	3.2	

[a] Apparent oxalate + 3.2. Beer samples designated as in Table I, footnote *b*.

Table III. Radioactivity in Calcium Oxalate Precipitates and in Beer Filtrates[a]

	Per cent radioactivity found		
Beer sample	CaC_2O_4 precipitate	Beer filtrate	Total
A-1	93.40	5.48	98.9
A-2	91.54	5.32	96.9
B-1	91.22	5.78	97.0
B-2	91.91	5.36	97.2
C-1	92.83	5.69	98.5
C-2	94.68	4.37	99.1
C-3	91.60	4.04	95.6
D-1	92.25	5.52	97.8
D-2	92.47	4.89	97.3
D-3	90.26	3.86	94.1
E-1	94.06	5.24	99.3
E-2	90.50	3.83	94.3
E-3	92.24	4.20	96.4
		Av.	97.1

[a] Conditions as in Table I, footnote *a*. All values are averages of duplicate determinations. Beer samples designated as in Table I, footnote *b*.

oxalate was first determined by the procedure in part A. Three additional samples of each decarbonated beer were then treated according to the radioisotope procedure of part B to determine the per cent of radioactivity remaining in the filtrates. From the precipitated oxalate values and the per cent radioactivity left in the filtrates, the total oxalate content of the different beers and the correction factor for unprecipitated oxalate were calculated.

D. RADIOACTIVITY IN CALCIUM OXALATE PRECIPITATES. As a check on the determination of radioactivity remaining in the beer filtrates, determinations of the radioactivity in the calcium oxalate precipitates were carried out. The precipitates from the filtrations in part C were washed with calcium-oxalate-saturated water and the washings were discarded. The precipitates were dissolved from their respective beakers and filter tubes with about 40 ml. of hot 0.2*N* $HClO_4$ in the general manner described in part A. The oxalate solutions were made to volume with 0.2*N* $HClO_4$ in 50-ml. volumetric flasks, and 15-ml. portions were transferred to 25-ml. volumetric flasks. A solution of 2.5% gelatin in 0.5*N* NaOH was added until the mixture became just pink to phenolphthalein and the mixture was then slightly acidified with 2 drops of 0.2*N* $HClO_4$. The solutions were diluted to 25 ml. with 2.5% gelatin in 0.02*N* NaOH (*2*). The resulting 1% gelatin solutions of the radioactive oxalate were mixed and immediately 1-ml. portions were plated in triplicate on planchets.

At the same time that the beer samples were set up in part C, a reference sample (containing the same amount of radioisotope as in each beer sample) was prepared as follows: 3 ml. of oxalic–C^{14} acid stock solution and 2 ml. (7.46 mg.) of $Na_2C_2O_4$ solution were pipetted into a 50-ml. volumetric flask. To precipitate the oxalate, 6 ml. of $CaCl_2$ solution (0.4 mg. Ca^{+2} per ml.) was added and the reference mixture was refrigerated. When the above calcium oxalate precipitates were dissolved and plated, 2.75 ml. of 1*N* $HClO_4$ was added to the reference mixture and the solution was made to volume with 0.2*N* $HClO_4$. Two 15-ml. aliquots were transferred to 25-ml. flasks and 1% gelatin solutions were prepared and plated as described above. The planchets from the beer and reference samples were counted for 5 minutes as previously described and the per cent activity in the calcium oxalate precipitate from each beer was calculated. No correction was made for coincidence loss.

RESULTS AND DISCUSSION

The rate and completeness of calcium oxalate precipitation in a beer sample after the addition of excess calcium acetate will depend on the amount of oxalate ions present and the refrigeration time. Figure 1 shows the results with two commercial beers after adding oxalic–C^{14} acid and unlabeled sodium oxalate and measuring the radioactivity of the beer filtrates after varying refrigeration periods. The two beers contained 3.5 and 7.0 mg. per liter of apparent oxalate. The pronounced and continued precipitation of calcium oxalate in samples I-*A* and II-*A* illustrate the importance of refrigeration time and the necessity for the addition of sodium oxalate. These results further emphasize the unreliability of the oxalate values obtained by the conventional methods (*1*, *5*). It should be noted that it is the change in slope of the curve in Figure 1 that is important and not the actual percentage of radioactivity remaining in the filtrate. The percentage of radioactivity will naturally decrease as more unlabeled sodium oxalate is added to the beer samples. The addition of 2 mg. of sodium oxalate per 120 ml. of beer was not very effective (Figure 1), but the higher levels, particularly 8 mg., caused most of the calcium oxalate to precipitate in 24 hours. Four days of refrigeration is preferred to ensure more reliable results when applying a common correction factor to oxalate values from beers that may vary somewhat in composition. Later results with five different beers showed that the steeper slope of curve II-*D* was more typical than that of curve I-*D*.

Table I presents the data for the calculation of the correction factor for oxalate ions remaining in the beer filtrate after the precipitation of calcium oxalate under the conditions specified. The residues from 1 ml. of beer filtrates gave an average count of 75 c.p.m. compared to an average of 1550 c.p.m. for the initial count of the treated beer samples. The assumption is made that the percentage of radioactivity remaining in the filtrate equals the percentage of the total oxalate not precipitated. The average correction factor was 0.78. mg. of $C_2O_4^{-2}$ per 300 ml. of beer (Table I), or 2.6 mg. per liter. The standard deviation was 0.11 mg. of $C_2O_4^{-2}$ per 300 ml., or 0.35 mg. per liter. A comparison of the correction factors for beers *A* and *E* (Table I) with the oxalate content of these two beers (Table IV) indicates that a common correction factor can be used regardless of the oxalate content of the beer.

Duplicate samples of the five beers were also analyzed exactly as described in part C except that the refrigeration time was reduced to 2 days. The results are summarized in Table II. A somewhat higher correction factor was found.

Table III shows the percentages of the added radioactivity which was found in the calcium oxalate precipitates. The planchets prepared from the reference samples (100% activity) and from the recovered calcium oxalates gave counts in the range of 3000 to 4000 c.p.m. The average total recovery of radioactivity from the precipitates plus the beer filtrates was 97.1%. The determination of the radioactivity from the precipitates is more complicated and subject to more errors than in the filtrates. For this reason the values obtained from the beer filtrate radioactivities were preferred in calculating the correction factors.

Table IV. Apparent and Corrected Oxalate Values of Five Beers[a]

Beer sample	Milliliters standard cerate: Total titration	Milliliters standard cerate: Standardization (20 mg. $Na_2C_2O_4$)	Milliliters standard cerate: Net titration	Milligrams $C_2O_4^{-2}$ per liter: Apparent	Milligrams $C_2O_4^{-2}$ per liter: Corrected[b]
A-1	17.05	15.39	1.66	4.7	
	17.12	15.39	1.73	4.9	7.4
A-2	17.73	15.84	1.89	5.2	
	17.75	15.84	1.91	5.3	7.9
B-1	17.18	15.39	1.79	5.1	
	17.22	15.39	1.83	5.2	7.8
B-2	17.39	15.43	1.96	5.6	
	17.24	15.43	1.81	5.2	8.0
C-1	17.34	15.39	1.95	5.5	
	17.46	15.39	2.07	5.9	8.3
C-2	17.71	15.43	2.28	6.5	
	17.72	15.43	2.29	6.5	9.1
D-1	17.82	15.39	2.43	6.9	
	17.90	15.39	2.51	7.1	9.6
D-2	18.40	15.84	2.56	7.1	
	18.38	15.84	2.54	7.0	9.7
E-1	19.34	15.39	3.95	11.2	
	19.26	15.39	3.87	11.0	13.7
E-2	19.64	15.43	4.21	12.0	
	19.70	15.43	4.27	12.2	14.7

[a] Conditions as in Table I, footnote *a*. Beer samples designated as in Table I, footnote *b*.

[b] Apparent mg. $C_2O_4^{-2}$/liter plus 2.6.

The addition of 20 mg. of $Na_2C_2O_4$ to 300 ml. of beer prior to the precipitation of the calcium oxalate may seem to be an unjustifiably large amount of oxalate ions (13.1 mg.) compared to the 2 to 5 mg. present in the beer itself. Nevertheless, as shown in Table IV, the replicate results of many beer samples are in close agreement. The following factors were important for securing satisfactory results using the method described. The filter tube with asbestos pad provided excellent retention of calcium oxalate and speed of filtration compared to other filtration methods tried. The calcium-oxalate-saturated wash water assured no loss of calcium oxalate during the washing procedure. The titration with cerate in 1*N* $HClO_4$ at room temperature using nitro-ferroin indicator gave easily recognizable end points.

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Spectrophotometric Determination of Vanadium(V) with 6-Hydroxy-1,7-Phenanthroline

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▶ A new spectrophotometric method for vanadium(V) employs 6-hydroxy-1,7-phenanthroline as a complexant. After development in aqueous solution containing 40% 1,2-propanediol, the colored complex is extracted into benzene for measurement at 480 mμ. The system is stable, conforms to Beer's law, and has a molar absorptivity of 5.8 × 10^3. Of the ions tested, chromium(VI), iron(III), tungsten (VI), and oxalate interfere seriously.

IN A RECENT PAPER (*6*) 6-hydroxy-1,7-phenanthroline was proposed as a new chromogenic reagent for the spectrophotometric determination of iron(III). As the presence of vanadium (V) caused serious interference in the determination of 0.1 mg. of iron, the present work was undertaken to study the feasibility of using the reagent for vanadium.

Because 6 - hydroxy - 1,7 - phenanthroline is closely related chemically to 8-quinolinol, prior references to the latter complexant seem relevant (*1–4, 7–10*). Vanadium(V) forms a water-insoluble chelate with 8-quinolinol (*7*) which, depending upon the method of preparation, may be dark purple, dark green, or yellow. At pH 5 to 6 the product has a very dark purple hue. An inert solvent, such as chloroform, gives a dark purple solution. Alcoholic solutions have reddish hues. Several of the papers cited deal with the nature of the chemical reactions involved.

In preliminary tests, Duswalt (*5*) observed that 6-hydroxy-1,7-phenanthroline reacted with vanadium(V), in the presence of an alcohol, to yield a reddish solution. Both water-soluble and water-insoluble alcohols reacted.

EXPERIMENTAL

Apparatus. The major apparatus consisted of a Cary spectrophotometer (Model 10-11) and a Beckman Zeromatic pH meter. The absorption cells were 1 cm.

Reagents. The stock solution of vanadium, containing 0.100 mg. of vanadium per ml., was prepared by dissolving 0.2296 gram of ammonium metavanadate (NH_4VO_3) in 25 ml. of 4*N* sulfuric acid and diluting to 1 liter with distilled water. It was standardized by the method of Willard and Young (*11*).

The buffer solutions were made 0.20 or 0.40*M* from reagent grade potassium hydrogen phthalate.

The chloroform was extracted four times with water to eliminate any alcohol. All other organic solvents were reagent grade. The redistilled benzene was free of thiophene.

The 6-hydroxy-1,7-phenanthroline was prepared by the method described previously (*6*). A 0.2% (w./v.) solution was prepared by adding enough 5*M* hydrochloric acid to dissolve the reagent and diluting to volume with water.

The Color Reaction. Possible use of 6-hydroxy-1,7-phenanthroline as a chromogenic complexant for vanadium(V) involved, first of all, a study of the effects of several variables upon the complex and its formation.

As a result of preliminary work, the following tentative experimental system was selected: 1.00 ml. of vanadium(V) solution (0.100 mg. V), 5.0 ml. of a 0.2% solution of 6-hydroxy-1,7-phenanthroline, 6.3 ml. of a 0.2*M* solution of potassium hydrogen phthalate, all diluted to 25 ml. with the desired solvent. The pH of the system, approximately 3.5 ± 0.2, was adjusted to 3.5 with a solution of hydrochloric acid or sodium hydroxide.

Table I. Data for Water-Miscible Solvents for Vanadium(V)–6-Hydroxy-1,7-Phenanthroline Chelate

Solvent	Wavelength of absorption maximum, mμ	Absorbance
Diethylene glycol	490	0.140
Dipropylene glycol	480	0.310
1,2-Ethanediol	490	0.290
Ethanol	475	0.350
Ethylene glycol dimethyl ether	510	0.220
Glycol monobutyl ethyl	480	0.335
2-Methyl-2-propanol	475	0.300
1,2-Propanediol	490	0.300
1-Propanol	470	0.365
2-Propanol	470	0.350

All solutions were adjusted to pH 3.5 except glycol monobutyl ether, which was 3.0.

EFFECT OF SOLVENT. A 0.2% (w./v.) aqueous solution of the reagent absorbs strongly from 400 to 460 mμ, as shown in Figure 1. Also shown therein is the absorption spectrum for the vanadium–6 - hydroxy - 1,7 - phenanthroline chelate in 50% 1-propanol the solvent, used in early work.

To find another solvent which would shift the absorption band of the chelate to longer wavelengths, and at the same time yield a system of high absorptivity, a number of solvents were used. Table I lists the data for selected water-miscible solvents. Because of the characteristics shown here, together with the ease of handling, 1,2-propanediol seemed to be the best. Other alcohols gave cloudy benzene extracts which did not clear readily. No reddish complex was formed with diethylene glycol monomethyl ether, mannitol, 1,2,3-propanetriol, or tetrahydrofurfuryl alcohol.

In studying water-immiscible solvents, 15.0 ml. of the phthalate buffer was used, and the solution was diluted to approximately 50 ml. with water. After adjusting the pH to 3.5, the solution was poured into a separatory funnel and shaken with two 10-ml. portions of the solvent. When the layers separated, the solvent was drained into a 25-ml. volumetric flask and diluted to the mark with more solvent. The solvents tested included 1-pentanol, 2-pentanol, 1-hexanol, 1-heptanol, 2-octanol, cyclohexanol, benzyl alcohol, and chloroform. Although one of these compounds could be used, none has any particular merit.

The possibility of using 1,2-propanediol was then investigated further. For the formation of the reddish complex between vanadium and 8-quinolinol, Blair, Pantony, and Minkoff (*3*) postulated the equilibrium,

$$\text{Dark acid chelate} + \text{ROH} \rightleftharpoons \text{reddish adduct}$$

A large excess of alcohol is necessary to shift the reaction to the right. Extraction of the reddish species into an immiscible solvent should facilitate formation of this species.

To test this possibility the solvents used included benzene, carbon tetrachloride, chloroform, ethyl acetate,

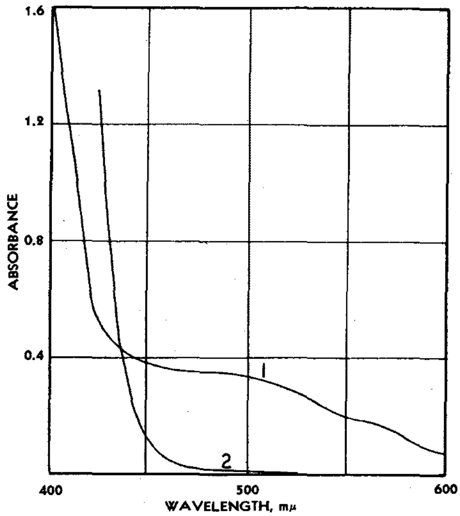

Figure 1. Absorption spectra of 6-hydroxy-1,7-phenanthroline: (1) vanadium chelate in 1-propanol; (2) reagent in water

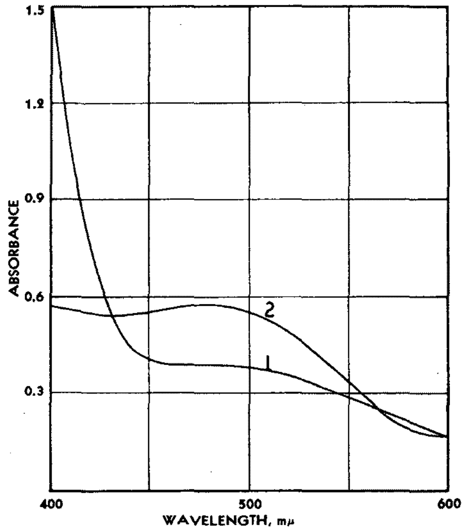

Figure 2. Absorption spectra of vanadium(V)–6-hydroxy-1,7-phenanthroline chelate: (1) aqueous 1,2-propanediol solution; (2) benzene solution

1,2-dichlorobenzene, and trichloroethylene. Of these, benzene was selected. It gives a rapid, clean separation of layers, and it yields a nearly colorless solution with the reagent. Figure 2 shows two absorption spectra. Curve 1 is for a solution containing 0.050 mg. of vanadium, 2.0 ml. of reagent solution, 1.3 ml. of 0.4*M* buffer solution, and 5.0 ml. of 1,2-propanediol, all diluted to 10.0 ml. Curve 2 is for the same system after extraction of the reddish complex into benzene.

EFFECT OF pH. A series of solutions was made, each containing 0.100 mg. of vanadium, 5.0 ml. of reagent solution, and 6.3 ml. of 0.2*M* buffer solution. After adjustment to the different pH values shown in Figure 3, the solutions were diluted to 25 ml. with 1-propanol and the absorbance was measured at 470 mμ against a reagent blank.

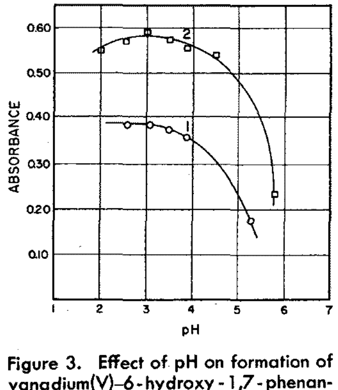

Figure 3. Effect of pH on formation of vanadium(V)–6-hydroxy-1,7-phenanthroline chelate: (1) in 1-propanol; (2) benzene

In a second series 1,2-propanediol was used. After adjustment to a specific pH value, the complex was extracted into benzene with two 10-ml. portions of benzene, and the combined extractates were diluted to 25.0 ml. with benzene. Absorbances were measured at 480 mμ against a reagent blank.

The data in Figure 3 show that the optimum pH range for maximum sensitivity for each system is between 2.5 and 3.5.

EFFECT OF AMOUNT OF REAGENT. The systems used to study the effect of amount of reagent contained 0.050 mg. of vanadium, 1.3 ml. of 0.4*M* buffer solution, 4.0 ml. of 1,2-propanediol, and different amounts of the reagent. All were adjusted to pH 3.0 and the complex was extracted into 9.0 ml. of benzene and diluted to 10.0 ml. with benzene for measurement. The data obtained for a range of concentrations showed that a molar ratio of reagent to vanadium of at least 30:1 is required.

EFFECT OF CONCENTRATION OF 1,2-PROPANEDIOL. Solutions used to study the effect of concentration of alcohol contained 0.050 mg. of vanadium, 1.3 ml. of 0.4*M* buffer solution, 2.0 ml. of 0.2% reagent solution, and different amounts of 1,2-propanediol. The pH was adjusted to 3.0. After extraction into 9.0 ml. of benzene, and subsequent dilution of the extractate to 10.0 ml. with benzene, the absorbance was measured at 480 mμ. The results showed that the percentage (v./v.) of 1,2-propanediol may vary between 30 and 60.

EFFECT OF TIME. The previous experiments were repeated using 40% 1,2-propanediol. After preparation, the solutions were shaken with 9.0 ml. of benzene for one minute and allowed to stand different periods of time before removal and measurement of the extracts. No significant increase in absorbance occurred after 30 minutes. The benzene layer clears at once, but the aqueous layer needs about 30 minutes to clear.

In another time study the absorbance of the extractate from one of these experiments was substantially constant for 48 hours.

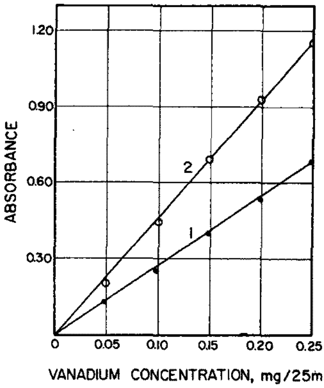

Figure 4. Beer's law plots for vanadium chelates: (1) with 8-quinolinol; (2) with 6-hydroxy-1,7-phenanthroline

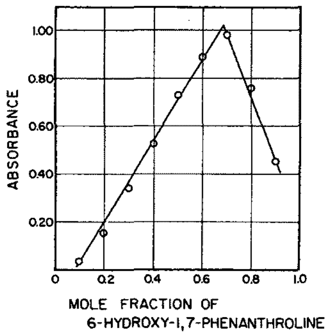

Figure 5. Data for continuous variation study of the vanadium(V)–6-hydroxy-1,7-phenanthroline chelate

CONFORMITY TO BEER'S LAW. To determine the effect of vanadium concentration, the following study was made. Both 6-hydroxy-1,7-phenanthroline and 8-quinolinol were used to compare the sensitivities of the two reagents.

To a series of beakers containing 0, 0.050, 0.100, 0.150, 0.200, and 0.250 mg. of vanadium, 2.0 ml. of a 0.2% solution of reagent was added for each 0.050 mg. of vanadium present. To each solution, 6.0 ml. of 0.4*M* buffer solution and 5.0 ml. of 1,2-propanediol were added. After adjusting the pH to 3.0, the reddish species was extracted by shaking with two 10-ml. portions of benzene. In each case the system was allowed to clear. The extractates were combined in a 25-ml. volumetric flask, diluted to volume with benzene, mixed, and the absorbance measured at 480 mμ against a reagent blank. The data, plotted in Figure 4, show that 6-hydroxy-1,7-phenanthroline is the more sensitive of the two reagents, and that each system conforms to Beer's law. The molar absorptivity calculated from these data for the new reagent is 5.8×10^3.

INTERFERENCES. To investigate the effect of various possible interfering species, a solution containing the ion in question was pipetted into a 10.0-ml. volumetric flask containing 0.050 mg. of vanadium. Two milliliters of a 0.2% solution of the reagent, 1.3 ml. of 0.4*M* buffer solution, and 4.0 ml. of 1,2-propanediol were added. After adjusting the pH to 3.0, the solution was extracted with 9.0 ml. of benzene. When the system cleared, the extractate was drained into a 10.0-ml. volumetric flask, diluted to volume with benzene, mixed, and the absorbance measured at 480 mμ.

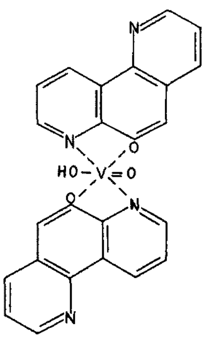

Figure 6. Suggested structure for the vanadium(V)–6-hydroxy-1,7-phenanthroline chelate

Table II. Effect of Various Metal Ions on Vanadium(V)–6-Hydroxy-1,7-Phenanthroline System

Absorbance of the chelate alone at the concn. of vanadium employed was 0.545

Ion	Added as	Amount added mg./10 ml.	Absorbance 480 mμ	Amount permissible mg./10 ml.
Al^{+3}	$Al(NO_3)_3$	0.5	0.520	0.2
AsO_4^{-3}	Na_2HAsO_4	5	0.550	5
Ba^{+2}	$BaCl_2$	5	0.545	5
Bi^{+3}	$Bi(NO_3)_3$	0.2	0.570	0.2
Cd^{+2}	$Cd(NO_3)_2$	2	0.540	2
$Cr_2O_7^{-2}$	$K_2Cr_2O_7$	0.2	0.150	0
Cu^{+2}	$CuSO_4$	0.2	0.525	0.2
Fe^{+3}	$Fe(NO_3)_3$	0.5	1.385	0
K^{+}	KCl	5	0.555	5
Mg^{+2}	$MgSO_4$	5	0.550	5
Mn^{+2}	$MnSO_4$	0.5	0.525	0.2
MoO_4^{-2}	Na_2MoO_4	0.2	0.525	0.2
Na^{+}	$NaCl$	5	0.545	5
Ni^{+2}	$NiCl_2$	0.2	0.535	0.2
Pb^{+2}	$Pb(NO_3)_2$	5	0.580	2
UO_2^{+2}	$UO_2(C_2H_3O_2)_2$	5	0.590	1
WO_4^{-2}	Na_2WO_4	0.2	0.505	0
Zn^{+2}	$ZnSO_4$	0.5	0.560	0.2

Table III. Effect of Various Nonmetal Ions on Vanadium(V)–6-Hydroxy-1,7-Phenanthroline System

Absorbance of the chelate alone at the concn. of vanadium employed was 0.545

Ion	Added as	Amount added mg./10 ml.	Absorbance 480 mμ	Amount permissible mg./10 ml.
Citrate	$Na_3C_6H_5O_7$	5	0.535	5
Cl^{-}	$NaCl$	5	0.545	5
ClO_3^{-}	$KClO_3$	5	0.560	3
CN^{-}	KCN	0.5	0.580	0.2
F^{-}	NaF	0.5	0.570	0.2
NO_3^{-}	$NaNO_3$	5	0.550	5
Oxalate	$Na_2C_2O_4$	0.2	0.435	0
PO_4^{-3}	KH_2PO_4	5	0.520	2
SiO_3^{-2}	Na_2SiO_3	5	0.560	3
SO_4^{-2}	Na_2SO_4	5	0.550	5
Tartrate	$Na_2C_4H_4O_6$	5	0.525	3

Tables II and III list the ions tested and indicate the amount of each which may be present without causing an error of more than 2%.

Barium, lead, copper(II), chromium (VI), molybdenum(VI), and nickel formed precipitates which had to be filtered off before extraction. Arsenic (V), barium, magnesium, sodium, potassium, citrate, sulfate, nitrate, and chloride may be present up to 100 times the concentration of vanadium. Chromium(VI), iron(III), tungsten(VI), or oxalate must not be present.

NATURE OF THE CHELATE. The method of continuous variations was employed to determine the ratio in which 6-hydroxy-1,7-phenanthroline combines with vanadium(V). Solutions containing various mole fractions of the reagent were prepared. The molar concentration of vanadium plus reagent was maintained at $2 \times 10^{-2}M$. The color was developed by addition of potassium hydrogen phthalate, 1,2-propanediol, and adjustment of the pH to 3.0. After extracting the chelate into two 10-ml. portions of benzene and diluting the extractates to 25 ml. with benzene, the absorbance was measured at 480 mμ.

The data of Figure 5, which show a peak at 0.69 mole of reagent, indicate a ratio of 2:1 for the combination of reagent with vanadium. In line with the structure proposed by Blair, Pantony, and Minkoff (*3*) for the vanadium-8-quinolinol complex, the structure shown in Figure 6 is suggested for the chelate of vanadium with 6-hydroxy-1,7-phenanthroline.

RECOMMENDED PROCEDURE

The following procedure is recommended for determining vanadium(V) with 6-hydroxy-1,7-phenanthroline.

Sample. Procure a representative sample and subject it to any necessary preparative treatment to obtain a usable solution. If necessary, remove any interfering ions to bring them within the tolerance limits listed in Tables II and III. The solution should be sufficiently acidic to prevent precipitation of hydrous oxides or hydroxides.

Calibration Curve. With a pipet transfer 0, 0.50, 0.75, 1.00, 1.25, and 1.50 ml. of stock vanadium solution, containing 0.100 mg. of vanadium per ml., to a series of 100-ml. beakers. To each beaker add 7.0 ml. of 0.2% (w./v.) solution of reagent, 6.0 ml. of 0.4*M* potassium hydrogen phthalate buffer solution, and 10.0 ml. of 1,2-propanediol. Adjust the pH to 3.0 with a solution of hydrochloric acid or sodium hydroxide, pour the solution into a separatory funnel, and extract the colored complex with two 10-ml. portions of benzene. Allow the system to stand until clear each time. Drain the benzene layers into a 25-ml. volumetric flask, dilute to volume with benzene, and mix.

Measure the absorbance of each solution at 480 mμ against a reagent blank. Plot a calibration curve with absorbances as ordinate and wavelengths as abscissa.

Procedure. To 2.0 ml. of the prepared solution, containing not more than 0.15 mg. of vanadium, develop the color as already described. Extract the reddish complex in the same way with benzene, and measure the absorbance of the extract at 480 mμ against a reagent blank. Determine the amount of vanadium from the calibration curve.

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Mass Analysis of Subnanogram Quantities of Iodine

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▶ A mass spectrometric method employing an ion source that generates ions by sputtering has been used in obtaining the isotopic abundance analysis from nanogram quantities of iodine. Negative iodine ions are mass analyzed in a spectrometer composed of two magnetic sectors followed by an electrostatic analyzer. The high abundance sensitivity ($>10^7$:1) permits one to measure minute quantities of I^{129} in the presence of large amounts of normal I^{127}. This method has direct application in studies utilizing I^{129} tracer. The sensitivity of the method is sufficiently high that 10^{-13} gram of a given iodine isotope can be detected in a sample.

WITH THE INCREASED INTEREST in I^{129} as a tracer (*1, 3*), the need for simple and sensitive detection capabilities for iodine has become evident. The existing activation analysis technique for I^{127} and I^{129}, although quite sensitive, is a rather lengthy procedure, and one that requires convenient access to a high flux reactor.

A mass spectrometric method utilizing an ion impact solids source (*2*) has been used in obtaining the isotopic abundance analyses of nanogram iodine samples. Negative iodine ions are generated in the source through bombardment of an iodine sample with an energetic positive gas–ion beam. The secondary negative ions are accelerated, mass analyzed, and detected. The lower limit for detection of any iodine isotope, based on the observed ion intensities from known samples, is 10^{-13} gram.

EXPERIMENTAL

A detailed description of the ion-impact-solids source is being prepared for publication (*2*). This source, henceforth referred to as Source I, is shown schematically in Figure 1. The primary ions are generated by electron bombardment of Hg vapor in S_1. The ion beam follows the path indicated, and is focused onto the sample filament S_2. Typical primary ion currents to S_2 are in the range of 10^{-8} to 10^{-9} A. The secondary ions produced from the sample (in this case I^-) by the primary ion beam are extracted, focused, and mass analyzed.

A second source, henceforth referred to as Source II, has been developed exclusively for the production of negative ions. A schematic of Source II is shown in Figure 2. Positive ions generated from the gas molecules in the ionization chamber are drawn out and bombard the sample at *S*. The negative secondary ions are accelerated and focused by the lens system. The negative ions pass through the region where the positive ions are generated, through the collimators, and into the mass analyzer. Source II has the advantage of being much simpler than Source I, and thus is preferred for negative ion production.

The ion detectors employed in the mass spectrometers were electron multipliers operated with the first dynode at ground potential and the collector at positive high voltage (this eliminates the loss in energy the I^- would experience when impinging on a conventionally operated electron multiplier). The pulses are taken off through a high voltage capacitor, amplified, and fed to a high speed counting system. In order to obtain a chart recording of a spectrum, a count rate meter is used in conjunction with the high speed counter. The output of the count rate meter drives a strip chart recorder.

DISCUSSION

The first attempt at obtaining an I^- beam was with Source I and a 12-inch radius, 60°-sector, single-direction focusing mass spectrometer. One microgram of I^{127} was evaporated onto a flat *W* ribbon filament from an aqueous solution of KI. A large negative I^{127} ion beam was observed. In addition low intensity negative ion beams of other masses, due mainly to hydrocarbons and oxygen-containing species, were observed. Large beams of WO_3^- are observed from the W sample filament.

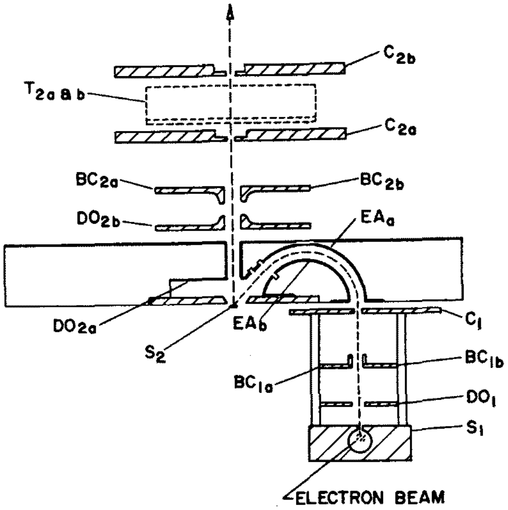

Figure 1. Schematic diagram of ion impact solids Source I

A heavy line on the main block indicates a conducting coating. Source electrodes have been designated as follows: *DO* - drawing out, *BC* - beam centering, *C* - collimator, *EA* - electrostatic deflector-analyzer, and *T* - the tilt plates

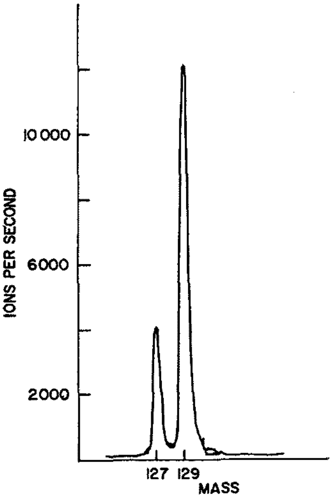

Figure 3. Mass spectrum of an iodine sample containing 4×10^{-9} gram of fission product I^{129}

Spectrum taken with Source I in single-stage, 12-inch radius, mass spectrometer

The sensitivity of this source for iodine was demonstrated by analyzing an iodine sample which contained 4×10^{-9} gram of fission product I^{129}. A spectrum taken from this sample is shown in Figure 3. For a primary ion current of 5×10^{-9}A. we observed a counting rate in excess of 10,000 counts per second for the I^{129}. Based on this observation one should be able to achieve a detection capability of 10^{-13} gram for the non-natural-occurring I^{129}, or for that matter, any other iodine isotope.

The successful demonstration showing the high efficiency this source has for iodine warranted installation of this source in a mass spectrometer which is capable of measuring large isotope ratios ($>10^6:1$). With our source in such a machine, it becomes possible to measure small quantities of one isotope in the presence of quite large quantities of another isotope. This feature is required if one is to successfully use I^{129} as a tracer. One can foresee instances when large quantities of normal I^{127} will be present in the iodine sample.

The mass spectrometer used in the remainder of this work possesses two stages of magnetic analysis arranged in a C-configuration, followed by a 90°, 12-inch radius, electrostatic sector which precedes the electron multiplier detector. A schematic layout of the instrument is shown in Figure 4. Source II has been installed in this spectrometer, and the results that follow will be for this source. Comparable results were obtained with Source I.

The ability to control sample contaminants will ultimately set the limiting sensitivity of this method. The sputtering process is not as highly selective as the thermal or surface ionization process, and thus it is possible to generate ions from many different materials residing in or on the sample surface. There is selectivity, though, in that the electronic structure of sample atoms, or the atomic composition of sample molecules determines the ratio of positive to negative secondary ions produced. Because of this selection, the negative secondary ion mass spectra are freer of contaminant peaks than the corresponding positive ion spectra. This is because the major contaminants encountered are from hydrocarbons present as residual gases in the spectrometer vacuum system. Pure hydrocarbons produce a greater preponderance of positive ion species. However, contaminants containing oxygen or any highly electronegative species generally will yield appreciable negative ions.

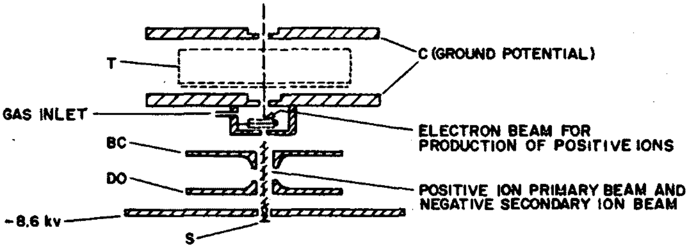

Figure 2. Schematic diagram of Source II

Refer to Figure 1 for electrode designations

We have observed what appears to be an oxygen-containing hydrocarbon of mass 129. It has been observed in all analyses to date. Figure 5 shows a spectrum taken from an analysis of a sample containing 3×10^{-11} gram of I^{129}. The impurity peak is quite large. The resolution of the spectrometer is sufficient to detect and make an accurate measurement of the $I^{129}:I^{127}$ ratio in the presence of 100 times more impurity. The contaminant comes mainly from the vacuum system environment. This conclusion is reached from our observations that the ratio of hydrocarbon-129 to I^{129} can be changed (and reduced considerably) by raising the temperature of the sample and by pro-

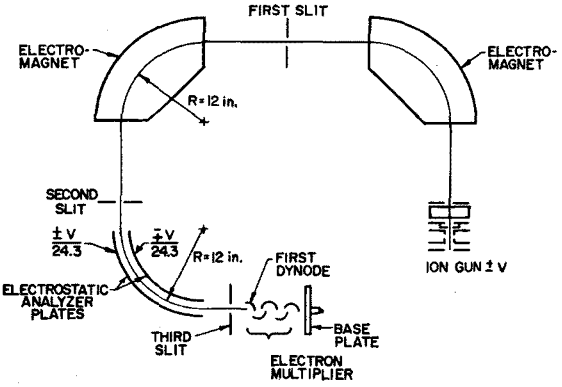

Figure 4. Schematic layout of 3-stage mass spectrometer

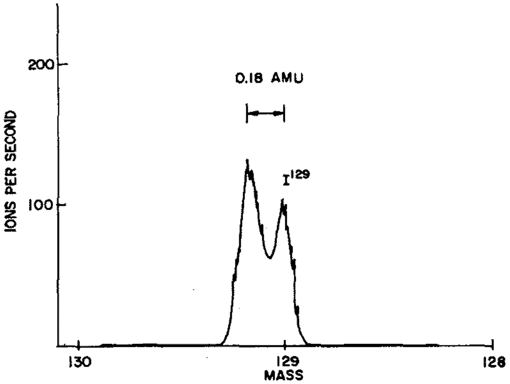

Figure 5. Spectrum taken from analysis of a sample containing 3×10^{-11} gram I^{129}

Impurity peak (a hydrocarbon containing oxygen) is reduced to 1/5 the I^{129} peak by heating and prolonged bombardment of the sample

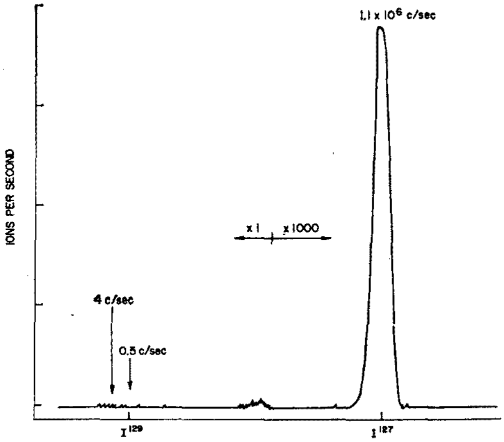

Figure 6. Spectrum taken for a 1-μg. sample of natural iodine

Source II and the 3-stage mass spectrometer employed

longed bombardment of the sample with a large primary ion beam. The contaminants are either vaporized or sputtered from the surface with this treatment. Control and elimination of vacuum system contamination can be achieved through the use of ultra-high vacuum techniques—all metal systems, metal gaskets, bake-outs, etc.

The abundance sensitivity of the mass spectrometer is such that large isotope ratios can be measured without any interference from the more abundant isotope. Ratios of adjacent mass isotopes exceeding 10^7:1 can be measured. The mass peak produced by an ion impact source tails to the high mass side because some ions of that mass possess more energy than the average. The three-stage spectrometer (magnetic, magnetic, electrostatic) eliminated the interference at the adjacent higher masses caused by this tail. A spectrum taken for a 1-μg. natural iodine sample is shown in Figure 6. The I^{127} beam intensity was in excess of 10^6 counts/second (beams in excess of 10^7 counts/second have been obtained for I samples of 1 to 5 μg.) and at the I^{129} mass position the intensity was 0.5 count per second. This intensity at the 129 position corresponds to slightly less than 10^{-12} gram of I^{129}. Whether this is I^{129} contamination of the natural sample, or an impurity of the same mass, has not yet been ascertained. Ions like $C_2Cl_3^-$, BrO_3^-, and H_2I^{127-} could not be differentiated from I^{129}. To date, experiments designed to prove that the small peak at I^{129} is due to molecular species have yielded negative results.

Most of our later discussions concerned the detection, and the problems encountered with the detection, of very small iodine samples, $<10^{-12}$ gram. One must not lose sight of the fact that 10^{-9}- to 10^{-10}-gram iodine samples can be handled easily and without any modifications to the spectrometer vacuum system. To our knowledge, no other mass spectrometric method exists which can handle iodine samples at this level and with the ease offered by the ion impact source.

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Pulse Polarographic Determination of Nickel and Vanadium

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▶ The increased sensitivity for reducible species obtained by pulse polarography, in contrast to direct-current polarography, allows microgram amounts of both nickel and vanadium to be determined with a single polarogram. Considerable time is saved over conventional polarographic or two different colorimetric procedures. The method has been successfully applied to petroleum stocks containing 0.5 to 50 p.p.m. of either metal; lower levels can be determined with larger sample sizes and higher available instrumental sensitivity.

Pulse polarography has an inherently higher sensitivity for both reversible and irreversible reductions and yields better resolution between two electroactive species than conventional direct-current polarography (*1*, *2*, *7*). These characteristics have been applied advantageously to the determination of nickel and vanadium in petroleum stocks. The two metals are well known catalyst poisons, and rapid analytical methods are continually sought for them. The high sensitivity of pulse polarography allows a relatively small sample to be taken for decomposition, considerably reducing the elapsed time over a conventional polarographic analysis. Since both metals can be determined from one pulse polarogram, the analyses can be completed in less than one half the time necessary for most colorimetric methods.

EXPERIMENTAL

Apparatus. The peak or "derivative" mode of the Southern-Harwell Mark II Pulse Polarotrace (Southern Analytical, Ltd., Camberley, Surrey, England) was used to obtain all pulse polarograms. In this mode a single, 40-millisecond, 35-mv. voltage pulse is superimposed on an increasingly negative d.c. ramp once during the life of each mercury drop. At the conclusion of the pulse, the drop is automatically knocked from the capillary; and there is a 1-second delay with the new drop until the next pulse is applied. The cycle repeats itself throughout a 1-volt d.c. potential sweep. Current measurements are taken during the last 20 milliseconds of the applied 40-millisecond pulse. Background current from the d.c. ramp is filtered out, and only the change in current resulting from the pulse is measured. All data were obtained with a 7.5-minute, 1-volt sweep. The signal-to-noise ratio was enhanced by using a smoothing circuit with an output voltage that was a function of the last three drop lives. A sensitivity was used such that the recorder deflection was 11×10^{-9} ampere per inch. The over-all sensitivity of the instrument can be increased by 20-fold. Cells with a mercury pool anode were thermostated at 25° ± 0.3° C.

Reagents. Nitrogen for deaeration was passed through a two-stage purification train, the first containing lead wool and an alkaline 1,2-naphthoquinone-4-sulfonic acid solution and the second a sulfuric acid solution of chromous sulfate over amalgamated zinc. The unit is designed to regenerate chromous ion continuously in the second scrubber.

Standard solutions were prepared from Fisher Certified ammonium metavanadate and Matthey nickel sponge. Distilled water was used after passing through a mixed bed ion exchanger.

Procedure. Petroleum stocks, containing about 5 to 10 µg. each of nickel and vanadium, were first evaporated on a hot plate and then decarbonized in a muffle furnace at 600° C. There was no evidence of the volatilization of nickel or vanadium when compared to previous analyses using a sulfuric-nitric acid digestion. Volatile nickel or vanadium compounds may be present in samples from other sources, in which case a wet-ashing or acid-digestion decomposition of the hydrocarbon would be preferable. Residues were treated with aqua regia, taken to dryness, and redissolved in 10 ml. of $0.1N$ hydrochloric acid. After quantitative transfer to a 25-ml. glass-stoppered cylinder, water was added to about 20 ml. and ammonium hydroxide (28 to 30%) added until the solution was pH 8 to 9 (pH paper). The solution was diluted to a final volume of 25 ml. with water. After a 5-minute deaeration, the peak or "derivative" mode pulse polarogram was obtained.

RESULTS AND DISCUSSION

Figure 1 is a typical polarogram of a hydrocarbon sample taken through the procedure (upper curve). The current peaks at about −0.78 and −1.20 volts (*vs.* Hg pool) are reductions of nickel and vanadium, respectively. The lower curve is that obtained with the reagents used to dissolve and treat the decarbonized sample. Over a period of time, the base lines of the polarograms begin to slope, and small periodic oscillations appear in the curves. These two effects present no problem in determining nickel or vanadium at 0.08 µg. per ml.; but at lower concentrations, both effects must be minimized before higher instrumental sensitivities can be used. This is readily done by installing a new capillary.

The magnitude of the current at its peak value, above that of the reagent-supporting electrolyte background, is proportional to the concentration of the nickel or vanadium. Measurements are made from the tops of the two curves. The spike between current measurements is just a discharge of a portion of the current that was stored in the measuring circuit before the next measurement is recorded. Linear calibration curves are obtained for both

Table I. Typical Nickel and Vanadium Determinations

Sample	Metal	Colorimetric[a]	Emission spectroscopic	Pulse polarographic
1	Ni	0.53, 0.48	0.65, 0.55	0.52, 0.40, 0.56
	V	2.1, 2.5	2.3, 2.1	2.0, 2.4, 1.9
2	Ni	2.8, 2.9	1.9	2.6, 3.0, 2.7
	V	13, 14	13	13, 14, 13
3	Ni	...	59	58, 53
	V	...	50	49, 45

[a] Modified procedure of Forrester and Jones (*4*).

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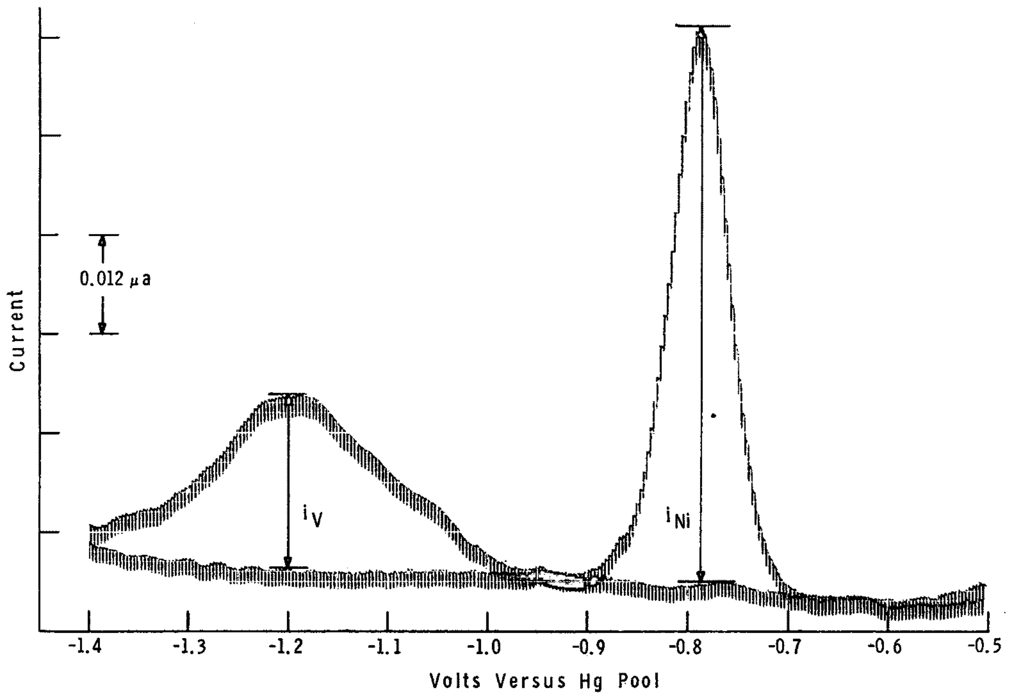

Figure 1. Typical pulse polarographic data

Upper. Sample taken through procedure, $5.7 \times 10^{-6}M$ Ni^{+2}, $4.3 \times 10^{-6}M$ V^{+5}
Lower. Electrolyte-reagents blank

nickel and vanadium between 0 and 0.4 μg. of Ni per ml. and 0 and 0.8 μg. of V per ml. with maximum currents of 80 and 75 nanoamperes, respectively. The linear relationship holds for even higher concentrations of these metals, but they are of no interest in this work.

Typical results for three different samples are shown in Table I. There is good agreement with colorimetric and emission spectroscopic analyses. Sample 3 was analyzed for both nickel and vanadium, pulse polarographically, in about 90 minutes using 0.1 gram of sample. No. 1 required 10 grams of sample and about 4 hours; solution volumes can be decreased and instrumental sensitivity increased so that less than 2 grams would be sufficient, reducing the elapsed time to less than 2 hours. No interference has been encountered from metals ordinarily present in petroleum stocks.

The interpretation of many peak-type pulse polarograms is rather difficult because the shapes of the curves are a function of the electrode process kinetic parameters (*2*). The reduction of vanadium at the dropping mercury electrode in an ammoniacal medium is particularly complex (*3*, *6*), and no attempt has been made in this work to determine the electrode process. Only one peak is observed for the vanadium reduction, in about $0.01M$ NH_3–$0.01M$ NH_4Cl, up to a concentration of $3 \times 10^{-5}M$ vanadium(V) with a linear relation between peak current and concentration. Higher concentrations were not studied. The vanadium pulse polarogram does not change after the solution is heated. Evidently, equilibrium between the various vanadium(V) species is established rapidly at these concentrations, whereas millimolar vanadium(V) solutions must be heated for a short time to hasten equilibrium before obtaining a polarogram (*5*).

The use of a dilute ammonia–ammonium chloride supporting electrolyte is beneficial on two counts. First, there is an increased separation between the nickel and vanadium peaks, in contrast to a solution of $1M$ ammonia and $1M$ ammonium chloride (470 mv. *vs.* 110 mv.). This is particularly advantageous should there be a high ratio of nickel to vanadium, in which case the vanadium could be easily determined. Very high ratios of one metal to the other were not encountered in this work. The second advantage of the more dilute supporting electrolyte is the minimization of contamination from reagents.

ACKNOWLEDGMENT

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Tracer Techniques in Sulfur Dioxide–Air Pollution Studies

Apparatus and Studies of Sulfur Dioxide Colorimetric and Conductometric Methods

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▶ Analytical tracer techniques for studying the role of sulfur dioxide in air pollution problems were developed. An apparatus was built which made it possible to measure directly microgram quantities of sulfur dioxide tagged with S^{35}. The tagged sulfur dioxide was followed from its original pure state to its mixture at high dilution in purified air, to the sampling medium, and finally to the quantitation step, and was measured by proportional tube counting and scintillation solution counting techniques. Colorimetric and conductometric methods for determination of sulfur dioxide were evaluated by radiochemical tracer techniques. Colorimetric standards prepared from measured quantities of gaseous SO_2 gave greater color intensities than standards prepared from equivalent amounts of standardized bisulfite solutions. Tracer techniques showed that conductometric methods became unreliable at concentrations below 1 p.p.m., even though purified diluting air was used, and sampling methods lost efficiency below 0.1 p.p.m. for both colorimetric and the conductometric methods. A second bubbler in series was not able to capture the $S^{35}O_2$ lost by the first bubbler. This indicates that series bubblers cannot be used for evidence of absorbing solution efficiencies. Correlation of colorimetric and radiochemical analytical techniques can give useful supplementary information on the reactions of SO_2 in controlled atmospheres.

Many chemical and physical methods of analysis have been proposed for studying the role of sulfur dioxide as one of the more common air pollutants (*2*, *4*, *5*, *8–10*). In general, quantitation of the actual pollutant has depended upon the comparison of the over-all chemical resultant of the air sample with the equivalent reaction of a carefully controlled laboratory "standard." In question are the efficiencies of the sampling processes and the effects of concentrating the pollutant by many orders of magnitude into a liquid or solid medium in the presence of equally concentrated cocontaminants.

Radiochemical techniques furnish a powerful tool for studying these effects, and sulfur dioxide readily lends itself to this type of analysis. Radioactive $S^{35}O_2$ is easily handled, has a convenient half life of 87.1 days, and is a weak beta emitter with an energy of 0.167 m.e.v. It is commercially available in high specific activity, ordinary glassware contains its radiation, and its air path is only a few inches. Using vacuum techniques, it can be readily purified, measured, and transferred from one vessel to another.

Because of the weakness of the β-ray emitted, the quantitative measurement of $S^{35}O_2$ requires special techniques. The techniques are similar to those used for the measurement of C^{14}, and in practice both internal proportional gas and liquid scintillation counting have been successfully used for S^{35} determinations (*3*, *6*).

EXPERIMENTAL

Apparatus. Figure 1 shows the apparatus used to purify, measure, and mix sulfur dioxide with any desired amounts of air in one, two, or three stages. The mixtures could be stored in an intermediate or final stage, or could be sampled at will. The Microvol (*7*) permitted the direct measurement of microgram quantities of sulfur dioxide with an accuracy of 1% or better. Essentially, it is a McLeod gauge containing a trap in which liquid nitrogen is placed. When the system is under vacuum, a condensable gas released into the system will collect on the trap. The mercury is allowed to rise to the neck of the collection chamber, and the liquid nitrogen is then removed by blowing warm air into the trap. After the condensable gas evaporates, the mercury is allowed to rise further, compressing the gas into the calibrated measuring capillaries. Mercury levels for the pressure-volume measurement were determined with a telescope mounted on a cathetometer.

A tube containing the radioactive sulfur dioxide (Nuclear-Chicago Corp., 30 mc. per mmole) was sealed into position (upper right, Figure 1). With the system closed but under vacuum of less than 1 micron, one or more aliquots were transferred to any one of several freeze-out points. The transfers were to the Microvol for volumetric measurement and then to the working flask, or to one of the bulbs for sealing off for scintillation counting, to the P_2O_5 tube for drying, or to the proportional tube for counting, etc. The transfers were quantitative, and were complete in less than 10 minutes, providing that air leaks were not present.

The working flask (Figure 1) was used to dilute the highly active $S^{35}O_2$ with untagged sulfur dioxide, so that larger quantities of sulfur dioxide could be used without involving excessive counting rates. The volume of the flask was calibrated and found to be 1082.1 ± 0.1 ml. at 25° C. The side arm for manometrically measuring the pressure in the flask had a volume of 0.347 ml. per cm. After evacuation, the working flask was charged with approximately 200 mm. of SO_2. This was purified by a freezing and pumping technique at liquid nitrogen and dry ice temperatures. Enough aliquots of the $S^{35}O_2$ were then transferred to the flask to give adequate count rates for the planned experiments.

Two 20-liter Mylar bags (G. T. Schjeldahl Co., Northfield, Minn.) were attached to the gas-air mixing portion of the apparatus with Teflon connections. SO_2-air mixtures were made either from aliquots taken directly from the $S^{35}O_2$ reserve or from the working flask. The sampling ports were used for filling additional sampling bags or containers. The S^{35} activity of the bag mixtures was checked frequently by transferring an aliquot from the gas pipet to the evacuated proportional tube connected to the sampling port. Purified air was used to flush the lines leading to the proportional tube.

A glass injection port sealed with a silicone rubber septum was built into the air stream for the injection of hydro-

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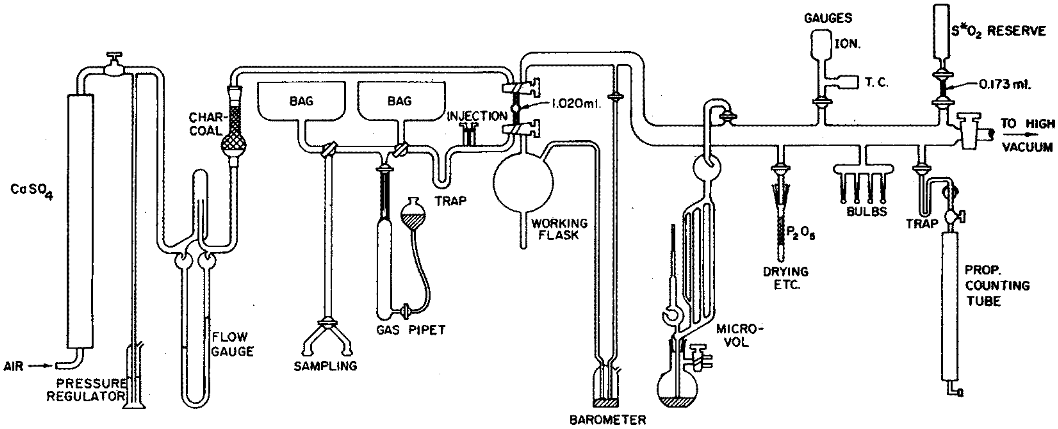

Figure 1. Apparatus for making $S^{35}O_2$-air mixtures

carbons or other compounds of interest by means of a microsyringe.

For simplicity, the diluting air train is shown in an abbreviated schematic form. Pressurized air is passed through a large anhydrous calcium sulfate column, followed by passage through indicating silica gel, activated charcoal, and Molecular Sieve 5A. Two flowmeters were used to measure either inlet or outlet flow rates for the mixing and sampling processes. Each flowmeter had several replaceable capillary restrictions, each of which was calibrated with a wet-test meter, water, or mercury displacement from calibrated glassware as needed. All connections were fused glass or glass to glass. All stopcocks were greased with Apiezon lubricants.

The gas pipet was calibrated, and its volume was 44.37 ml. at 25° C. With it a known volume of the bag mixtures could be repeatedly and reproducibly taken for consecutive sample studies. For preparing dynamic flow mixtures, an aliquot in the pipet was bled into an air stream at rates ranging from a few minutes to more than 4 hours by controlling the flow of mercury from the leveling bulb by means of the stopcock at the lower end of the pipet. The mercury head, or level, was manually adjusted to keep the same height. The long capillary neck prevented turbulent mixing of the air stream with the contents of the pipet.

The sampling ports were equipped with standard tapered ball joints for midget bubblers, the proportional counting tube, or vacuum for flushing out the system.

Procedures. COLORIMETRIC. Solutions were prepared according to the West-Gaeke and the Helwig-Gordon methods (*2*, *4*, *5*, *10*). For the West-Gaeke method, the gaseous samples were collected in 15.0 ml. of the Na_2HgCl_4 (TCM) solution in a fritted-glass midget bubbler. Sampling rates ranged from 300 to 450 ml. per minute. To 10.0 ml. of the absorbing solution, 1.0 ml. each of the pararosaniline and formaldehyde solutions were added. The color was allowed to develop for 30 minutes (to its maximum color) in a water bath at 25.0° ± 0.1° C. The absorbance was measured at 560 $m\mu$ with a Beckman Model DU spectrophotometer using 1-cm. cells. The remainder of the sampling solution was used for scintillation counting.

For the Helwig-Gordon method, 15.0 ml. of the reagent solution were used for sampling. Color development was completed in a water bath at 25.0° C.

CONDUCTOMETRIC. Solutions were prepared according to Thomas (*8*). The sample was collected in 15.0 ml. of the H_2O_2-H_2SO_4 absorbing solution in a midget bubbler as above. Ten milliliters of this solution were diluted to 25.0 ml. with more absorbing solution to give a sufficient volume to cover the electrodes. The remainder of the undiluted absorbing solution was used for scintillation counting. Conductance was measured at 25.0° C. with an Industrial Instruments Model RC-16B1 bridge, using a dip-type cell with 0.1 cell constant.

PROPORTIONAL TUBE COUNTING. Samples were transferred to the evacuated proportional counting tube (Nancy Wood Counter Laboratory, Chicago) at the position shown in Figure 1 or at one of the sampling ports. Samples were taken either directly from the Microvol or from the bag mixtures by means of the gas pipet. The proportional tube was designed for counting the $S^{35}O_2$ in the air samples without use of a counting gas. The tube was made of stainless steel, 16 inches long by 1-inch o.d. Its internal volume was approximately 200 ml. The potential on the tube was carefully controlled at approximately 2300 volts to give a constant counting rate with a standardized reference counting tube. The counting efficiency increased linearly with the log of the applied potential. The potential selected was 50 to 100 volts below the continuous discharge limit and resulted in approximately 80% counting efficiency. The tube was evacuated and flushed with clean air several times before final evacuation and filling with the sample. If background counts tended to build up, they were reduced with evacuation and flushing or with isotopic exchange using nonradioactive SO_2. All samples were adjusted to barometric pressure (ca. 630 mm. at this altitude) with clean air if needed.

SCINTILLATION COUNTING. The scintillation solution was made as follows: 75 grams of naphthalene, 7.0 grams of PPO (2,5-diphenyloxazole), 300 mg. of dimethyl POPOP [1,4-bis-(4-methyl-5-phenyloxazolyl)-benzene], and 1000 ml. of 1,4-dioxane. The dioxane was purified by passing it through activated alumina, and the naphthalene was recrystallized.

To 18 ml. of scintillator solution in a counting vial 2 ml. of aqueous sample (conductometric solution, TCM, or other) were added. The samples were counted with a Packard Tri-Carb liquid scintillation spectrometer, Model 3003. The counting chamber was kept at 2° C., and counting periods were sufficient to give 10,000 counts or for a minimum of 10 minutes. Counting efficiencies were 72% for S^{35} in TCM solutions and 77% for S^{35} in conductometric solutions.

Foil-lined screw caps react with TCM solutions and cannot be used. White plastic snap caps and ordinary glass vials were found satisfactory. Difficulties due to freezing or phase separation of samples were not encountered. With TCM solutions, the range of miscibility with the scintillator solution was between 10 and 22% by volume of TCM; with aqueous samples, 0 to 21% was miscible.

STUDIES OF COLORIMETRIC METHODS OF ANALYSIS

To prepare for the radiochemical study, nonradiochemical studies were made of the pararosaniline-formaldehyde–sulfur dioxide color reaction in both the West-Gaeke and Helwig-Gordon solutions. Bisulfite solutions were prepared and standardized with iodine-thiosulfate in the usual manner. Colorimetric absorption

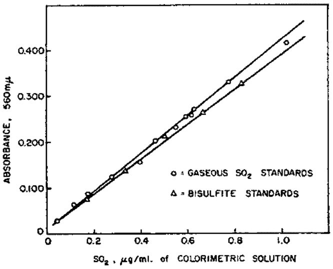

Figure 2. Comparison of standard curves obtained from gaseous SO_2 samples and bisulfite standard solutions

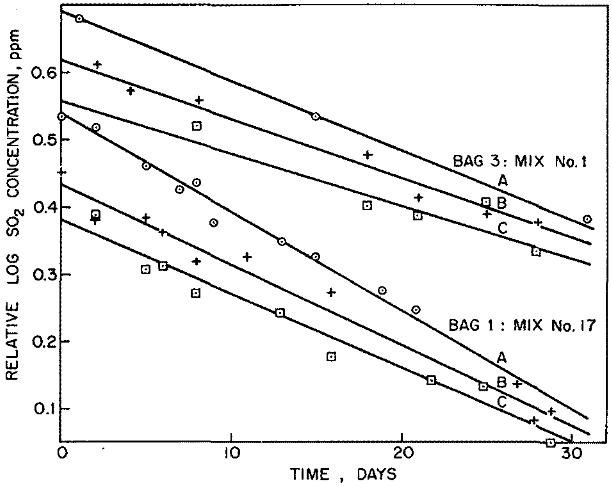

Figure 3. Comparison of concentration changes of SO_2-air mixtures in Mylar bags

All counts corrected for radioactive decay and all lines displaced for slope comparison
A. Proportional tube counting
B. Colorimetric analysis
C. Scintillation counting

curves were prepared by diluting the standardized bisulfite solutions with sodium tetrachloromercurato (TCM) solutions. In addition a standard colorimetric curve was prepared from gaseous sulfur dioxide samples measured with the Microvol and transferred to tetrachloromercurato (TCM) absorbing solutions by means of the small gas transfer bulbs of the vacuum apparatus.

Figure 2 compares the colorimetric absorption curves obtained by the two methods. The color reactions for the gaseous SO_2 samples have higher absorption values than those for the bisulfite solutions. Apparently, the lower color intensities are due to loss of sulfite activity in the dilution process despite the use of reagent chemicals and fresh double-distilled water.

Bag Mixtures. Bag mixtures of sulfur dioxide and air were made with both nonradioactive and radioactive sulfur dioxide. The concentrations in the bags were followed for long periods of time using colorimetric, proportional tube, and scintillation counting techniques. Figure 3 shows the rate of loss of sulfur dioxide above radioactive decay in two Mylar bags as measured by the different techniques used. The rate of loss for each of the bags is relatively consistent and amounts to approximately 2.5% per day. Proportional tube techniques indicate greater SO_2 losses than the colorimetric or scintillation techniques. It is not known whether this is real or due to some change in the proportional gas counting tube.

When mixtures of air and sulfur dioxide were made in a new bag there was an initial rapid loss of sulfur dioxide which settled down to the rates noted above. As a consequence, all new bags were treated with an approximately 500-p.p.m. mixture for a few days before use. At this time it is not known what happens to the sulfur dioxide that is lost from the bags. No counts were obtained from air taken from a bag one month after its last use. When pieces of a used bag were soaked in TCM solution, no color and less than 0.1 c.p.m. per sq. cm. were obtained when the solution was analyzed. When pieces of the bag were suspended in scintillation solution and placed in the counting chamber, as many as 17 c.p.m. per sq. cm. were observed. There may be some diffusion through the bag walls, but the preceding facts plus the fact that new bags cause a more rapid loss of SO_2, indicate that at least part of the sulfur reacts with the bag (*1*).

Sampling Efficiency. The sampling efficiency of the tetrachloromercurato sampling method for the colorimetric determination of sulfur dioxide (*4*, *10*) was checked in the following manner:

First 10 to 15 liters of air-$S^{35}O_2$ mixtures were prepared by taking a calculated number of aliquots of the sulfur dioxide from the working flask and flushing them into the Mylar bag. The concentration of sulfur dioxide in the bag was adjusted so that one gas pipet aliquot (44.37 ml.) of the mixture contained enough sulfur dioxide to give an absorbance of approximately 0.200 when sampled and analyzed colorimetrically. This amounted to having approximately 75 to 100 p.p.m. of SO_2 in the bag.

An aliquot from the bag was quantitatively transferred to the gas pipet. The upper stopcock was closed and the air lines were flushed with filtered air. A midget fritted-glass bubbler containing 15.0 ml. of the tetrachloromercurato absorbing solution was connected to one of the sampling port outlets. The air flow was adjusted between 300 and 450 ml. per minute and measured. The upper stopcock of the gas pipet was opened, and the mercury from the leveling bulb was allowed to displace the SO_2 mixture in the air stream. The time for the transfer was measured with an electric timer. The volume of air passing through the bubbler from the beginning to the end of the displacement period was calculated, and the concentration of the SO_2 in the sampled air was found by multiplying the bag concentration by the pipet-air stream volume ratio. All glass lines were carefully flushed until no radioactivity could be detected in test samples. Low concentration samples were run before higher concentration samples to prevent contamination from adsorption effects. Reproducible results were obtained at all but the very low concentrations, where some loss was observed. For these low concentrations a second midget fritted-glass bubbler connected in series with all-glass connections was used.

Table I summarizes the findings from colorimetric and scintillation analyses of the samples prepared in the above manner. Judging from both the colorimetric absorbance values and the scintillation counts, the colorimetric sampling method becomes relatively inefficient in concentration ranges below 0.1 p.p.m. Oxidation, or other chemical interference, of the SO_2 is ruled out because of the simultaneous drop in the color and the scintillation counts. The tracer technique definitely establishes a loss due to the sampling method rather than a chemical interference.

Also indicated is the fact that once a concentration is too low for efficient sampling, a second bubbler in series is unable to capture the lost SO_2 effectively. For example, samples 187 and 188 (Table I) were exposed to the same

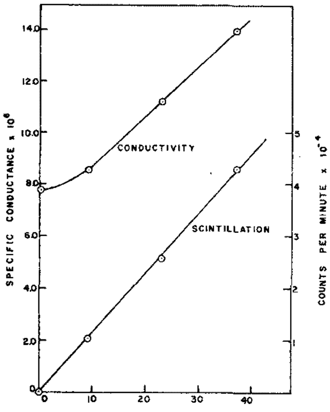

Figure 4. Standardization curves for typical batch of conductivity sampling solution

Table I. Colorimetric and Scintillation Analyses of Comparable Air Samples Taken at High and Low SO_2 Concentrations

Sample Number	Taken, µg. SO_2	Calcd., p.p.m.	Absorbance 1st bubbler	Absorbance 2nd bubbler	Scintillation, c.p.m. 1st bubbler	Scintillation, c.p.m. 2nd bubbler
187	5.5	0.033	0.116	0.000	2176 ± 13	65 ± 6
188	5.5	1.16	0.136	. . .	2533 ± 14	. . .
189	5.3	0.023	0.117	0.000	2183 ± 14	93 ± 7
190	5.3	2.3	0.132	. . .	2443 ± 15	. . .
191	5.3	0.018	0.109	0.000	2098 ± 13	2 ± 0.5
192	5.3	1.5	0.131	. . .	2440 ± 18	. . .
193	3.9	0.067	0.098	. . .	1636 ± 14	. . .
195	3.9	0.72	0.099	. . .	1802 ± 14	. . .
194	3.9	1.45	0.099	. . .	1794 ± 14	. . .

Table II. Efficiency of Conductometric Method for Measurement of Atmospheric Sulfur Dioxide

(16.4-µg. SO_2 samples at increasing dilution)

Sample	Total air vol., ml.	SO_2, p.p.m.	Specific conductance	Scintillation, c.p.m.
264	3,430	1.8	2.57×10^{-5}	1203
261	26,700	0.23	2.55×10^{-5}	1219
262	44,700	0.14	2.69×10^{-5}	1207
263	82,600	0.08	2.81×10^{-5}	1037

total amount of SO_2 (5.5 µg.), but sample 187 which was diluted with air to 0.033 p.p.m. showed a drop of 15% in absorbance and 14% in scintillation counts. A second bubbler in series with the first bubbler captured only 65 of the 357 c.p.m. lost by sample 187.

Helwig and Gordon (*2*) also used the formaldehyde-pararosaniline reagent but omitted the sodium tetrachloromercurate from the sampling solution, since they found that greater color response was obtained without it. They were adapting the colorimetric method to continuous recording analysis, which did not require prolonged stability of the dissolved sulfur dioxide. Their method in fact gave a greater color response, but the color was less stable and reproducible than that of the West method.

CONDUCTOMETRIC METHODS

Sulfur dioxide may be determined by capturing it in an acidified hydrogen peroxide solution, which oxidizes it to sulfuric acid, and measuring the conductance of the resulting solution (*8*). This method was less satisfactory than the colorimetric methods. More sulfur dioxide was required per sample to give sufficient precision, and reproducibility was only fair. The method is, of course, not specific for sulfur dioxide, since any atmospheric component which dissolves in the absorbing solution to give ions will also increase conductivity and consequently be measured as sulfur dioxide. It is convenient for automatic instrumentation, however, and is a popular method of analysis.

Analytical methods were developed for the determination of known quantities of sulfur dioxide in air using a conductometric method and a correlating scintillation counting method. Various known volumes of an analyzed SO_2-air mixture stored in one of the Mylar bags were passed directly and slowly through a fritted-glass midget bubbler containing conductometric absorbing solution. The conductance of each solution was measured and then the solution was analyzed by the developed scintillation method. Figure 4 shows the results obtained from a typical batch of conductometric absorbing solution and a high activity $S^{35}O_2$-air mixture. A nearly linear relationship was obtained between the conductivity of a given solution and the sulfur dioxide concentration. The scintillation method gave a linear relationship and extrapolated to zero.

Sampling Efficiency. The efficiency of the absorbing solution for conductometric analysis was comparable to that of the tetrachloromercurato solution of the West method (*10*). For samples to be analyzed by scintillation counting, the conductometric solution is to be preferred. A greater range of volumes of the solution can be used, and there is no interference from the tetrachloromercurato ion.

Table II compares the data obtained from a series of samples wherein a constant amount (16.5 µg.) of sulfur dioxide was diluted with increasing volumes of air. The sampling method was that described above, except that a conductometric absorbing solution was used. The absorbing solution was the one used for Figure 4 but from a different batch.

Since the amount of sulfur dioxide was the same in each of the samples (Table II), the specific conductance should have remained the same. However, samples diluted with air to 0.14 and 0.08 p.p.m., respectively, showed increasing conductivity. The scintillation counts, on the other hand, showed little change in efficiency down to 0.14 p.p.m. and a definite loss of sulfur dioxide when the sample was diluted to 0.08 p.p.m.

To reflect the loss of sulfur dioxide, the conductivity of the absorbing solution should have dropped. Instead it increased. This indicated that the conductometric method was subject to interference by substances other than sulfur dioxide. Consequently, under practical air pollution situations, the determination of sulfur dioxide by the conductometric method should be evaluated with caution because of the nonspecificity of the method as demonstrated in this case.

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Accelerated Automatic Chromatographic Analysis of Amino Acids on a Spherical Resin

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▶ Acceleration of analysis of amino acids by ion exchange chromatography has been facilitated in the Beckman amino acid analyzer by the use of a spherical particle resin. The acidic and neutral amino acids are analyzed on a 57- by 0.90-cm. resin column at a buffer volumetric input of 68 ml./hour (linear flow rate of 106 cm./hour). The basic amino acids are analyzed on a 5.0- by 0.90-cm. resin column at the same buffer flow rate. This system reduces the total analysis time to 4 hours, 5 minutes; (3 hours, 10 minutes for the acidic and neutral amino acids and 55 minutes for the basic amino acids). With the proper analysis sequence, three analyses can be completed in an 8-hour day.

We REPORT the performance of a newly available Styrene–divinylbenzene fully sulfonated nominal 8% cross-linked spherical particle ion exchange resin suitable for the chromatography of amino acids in column procedures patterned after, or similar to, the method of Spackman, Stein, and Moore (*7*). With this resin, and by modification of the accelerated system of Spackman (*8*), used in this work as a base line, the time of analysis of a protein hydrolysate was reduced to 4 hours, 5 minutes. With proper analysis sequence, three analyses can be completed in an 8-hour day.

The decreased time of analysis was achieved by an increased flow rate through a 0.9- by 57-cm. resin column; at a volumetric input of 68 ml./hour (equivalent to a linear flow rate of 106 cm./hour) the acidic and neutral amino acids were analyzed at the same flow rate on a 0.9- by 5.0-cm. resin column in 55 minutes. The 69-cm. column was packed with Beckman custom research resin, mean diameter 22 ± 6 microns, and the 23-cm. column was packed with similar resin of 15 ± 6 microns diameter. Column size employed and narrow particle diameter range helped keep pressures below 250 p.s.i., consistent with standard Beckman equipment, and resulted in improved resolution compared to our base line.

EXPERIMENTAL

Apparatus. A standard Beckman Model 120B amino acid analyzer was used.

Resin and Reagents. Beckman Custom Research Resin. For analysis of acidic and neutral amino acids, Type AA-15 with spherical particles having a mean diameter of 22 ± 6 microns was used. For analysis of basic amino acids, Type AA-27 with spherical particles having a mean diameter of 15 ± 6 microns was used.

Buffers. For analysis of acidic and neutral amino acids, pH 3.28 ($0.20N$) and pH 4.25 ($0.20N$) sodium citrate buffers were used. For analysis of basic amino acids, pH 5.28 ($0.35N$) sodium citrate buffer was used. All buffers were prepared with reagent grade sodium citrate (*2*), as shown in Table I.

Ninhydrin Reagent. Prepared according to the method of Spackman, Stein, and Moore (*7*).

Preparation of Ion Exchange Columns. A 69- by 0.9-cm. column was used for the analysis of the acidic and neutral amino acids and a 23- by 0.9-cm. column for the basic amino acids.

The resin without pretreatment was slurried with 2 volumes of buffer. The pH 4.25, $0.20N$ buffer was used to pack the long column and the pH 5.28, $0.35N$ buffer was used for the short column. Brij-35 and thiodiglycol were not present in these column packing buffers. Before pouring the column, about 10 ml. of buffer was forced, with air pressure, through the disk in the bottom of the column to remove any trapped air. About 1 cm. of liquid was left above the disk. The bottom of the column was capped. The resin slurry was stirred just before pouring and the column was filled. After 5 minutes the bottom cap was removed, and the column effluent line was connected. A buffer flow rate of 68 ml./hour was used to pack the column.

Table I. Sodium Citrate Buffers

pH	3.28 ± 0.01	4.25 ± 0.02	5.28 ± 0.02
Sodium concentration	$0.20N$	$0.20N$	$0.35N$
Sodium citrate · 2 H_2O	784.3 grams	784.3 grams	1372.6 grams
Concentrated HCl	493 ml.	335 ml.	260 ml.
Thiodiglycol (TG)	200 ml.	200 ml.	. . .
Brij-35 solution (50 g./100 ml.)	80 ml.	80 ml.	80 ml.
Caprylic acid	4 ml.	4 ml.	4 ml.
Final volume	40 liters	40 liters	40 liters

When the resin bed had packed, excess buffer was aspirated and the column was again filled with the resin slurry, taking care that the previously packed section was not disturbed. Several additional packings were necessary to fill the long column. The long column was packed to a height of 57 cm. The short column was packed to a height of 5.0 cm.

Each column was regenerated with $0.2N$ NaOH after which they were equilibrated with the appropriate buffer.

ANALYSIS OF AMINO ACIDS AND RESULTS

Figure 1 illustrates the resolution of a standard calibration mixture of basic, acidic, and neutral amino acids obtained at a buffer flow rate of 68 ml./hour. Both analyses were carried out at 55° C. The back pressure on the long column was 130 p.s.i. and on the short column, 50 p.s.i.

The sample (0.5 ml.) placed on each column contained 0.25 μmole of each amino acid. Recorder chart speed was 6 inches per hour with 1 dot/2 seconds printing speed. To prevent the recorder dots from cluttering on the chromatogram, the alternate 570-mμ Helipot potentiometer was adjusted so that the pen printed on the left side of the chart. For the analysis on the short column (basic amino acids) at the flow rates indicated above, the total analysis time was 55 minutes. The total analysis time for the long column (acidic and neutral amino acids) was 3 hours, 10 minutes. The buffer change was made at 85 minutes to take effect just before valine. The hexosamines, glucosamine, and galactosamine were present in the sample to indicate their lack of interference with the amino acid elution

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[1] Consultant to Beckman Instruments, Inc.

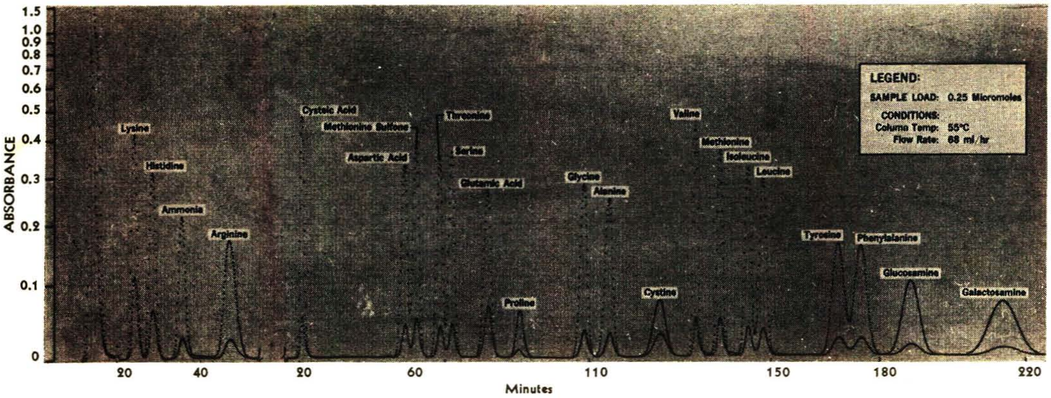

Figure 1. Chromatogram of an amino acid calibration mixture containing 0.25 μmole of each amino acid

Basic amino acids and ammonia (shorter curve at far left) sepd. on 5.0-cm. col. Acidic and neutral amino acids (longer curve) sepd. on 57-cm. col.

pattern; they are resolved well in this system. Cysteic acid, if present, is eluted at approximately 20 minutes and methionine sulfone emerges between aspartic acid and threonine. Citrulline, if present in the sample, would be eluted between glutamic acid and proline. Alpha-amino adipic acid is eluted just ahead of glycine and homocitrulline just after cystine.

Glucosamine, if present in the sample, would be eluted off the short column just before lysine.

Chlorotyrosine and an acid degradation product of tryptophan are also eluted early in the analysis. If the resin column is increased in height from 5 to 10 cm., the distance between these two peaks will then increase from 5 minutes to 11 minutes, with other separations increasing proportionally. Total analysis time will then be 1 hour, 35 minutes through the elution of arginine.

A typical daily schedule for the complete analysis of amino acid analyses is summarized in Table II. To obtain the same linear flow rate in a 0.9-cm. column as in the 0.6-cm. column employed by Spackman (*8*) at a volumetric input of 30 ml./hour, it was necessary to increase the volumetric input to the former column to 68 ml./hour. With these rates, a reaction coil was used which was twice the standard length (22.50-ml. volume instead of 11.25 ml.). Recovery determinations on various sample concentrations indicated that Beer's law was obeyed (*1*). A standard length reaction coil was also tried (11.25-ml. volume), and recovery values obtained over a sample concentration range of 0.1 to 0.5 μmole indicated that Beer's law was still obeyed.

To determine statistical accuracy and precision, 11 analyses were performed at the 0.25-μmole level to be used as a calibration point for the analyzer. The results at the 0.5- and 0.1-μmole load levels are shown in Table III, using a

Table II. Typical Daily Schedule

Time	Lapsed time (min.)	Operational changes
Short col. analysis		
8:30 a.m.	0	Start buffer pump (pH 5.28, 0.35*N*) and ninhydrin pump
8:38 a.m.	8	Turn on recorder
8:43 a.m.	13	Lysine peak emerges
9:25 a.m.	55	Analysis is complete
Long col. analysis		
8:55 a.m.[a]	0	Start buffer pump (pH 3.28, 0.20*N*) to drain
9:25 a.m.	30	Turn column effluent to coil and ninhydrin to coil
10:20 a.m.	85	Buffer change takes place to pH (4.25, 0.20*N*)
12:00 Noon		Start second short column analysis
12:05 p.m.	250	Analysis is complete
12:20 p.m.[a]		Start second long column analysis
12:50 p.m.		End second short column analysis
3:25 p.m.		Start third short column analysis
3:30 p.m.		End second long column analysis
3:50 p.m.[a]		Start third long column analysis
4:20 p.m.		End third short column analysis
7:00 p.m.		End third long column analysis using automatic shut-down timer

[a] These indicated times should be adjusted by 22 minutes if cysteic acid is to be determined.

Table III. Recoveries from 0.50- and 0.10-μmole Samples

(One standard length reaction coil, 11.25-ml. volume, and buffer flow rate of 68 ml./hour)

	0.5 μmoles (5 runs)		0.10 μmoles (6 runs)	
	Range	Av.	Range	Av.
Lysine	99–100	99	100	100
Histidine	100	100	100	100
Ammonia	98	98	101–102	102
Arginine	98	98	100–101	101
Aspartic acid	101–102	102	102	102
Threonine	100–101	101	100	100
Serine	101–102	102	99–103	103
Glutamic acid	101–102	102	99–103	103
Proline	100–104	100	96–115	100
Glycine	100	100	98–102	102
Alanine	100–102	100	98–102	102
Half cystine	100–101	100	92–100	100
Valine	100–102	102	94–103	98
Methionine	101–102	101	97–101	101
Isoleucine	102–103	102	99–103	100
Leucine	100–101	100	96–100	100
Tyrosine	100–102	100	98–102	102
Phenylalanine	101–102	101	98–102	98
Av.		100		101
Std. dev.		1.37		1.49
2 × Std. dev.		3.0		3.0

standard length reaction coil (11.25-ml. volume).

The results are expressed in terms of two standard deviations (95% probability). Thus, the average accuracy and precision in the 0.1- to 0.5-μmole sample range is 100 ± 3% and 100 ± 3%, respectively.

To determine the resolution at higher flow rates, the 57.0-cm. column was operated (using the same buffer and ninhydrin system previously mentioned) at 120 ml./hour for the buffer and 60 ml./hour for the ninhydrin reagent. The operating back pressure was 210 p.s.i. A sample load of a synthetic amino acid mixture containing 0.25 μmole (0.50-ml. volume) of each amino acid was tested. The analysis was conducted at 55° C. and a buffer change from the pH 3.28, 0.20*N* to the pH 4.25, 0.20*N* sodium citrate buffer occurred at 41 minutes. A slight loss of resolution was experienced. However, it is possible to quantitate accurately (height-width method) those peaks affected; namely, the threonine–serine and tyrosine–phenylalanine doublets. If the standard length reaction coil (*7*) is used, reproducibility of recoveries will be 100 ± 6%. With a double-length reaction coil, normal reproducibility of recoveries will be 100 ± 3%. An analysis time of 1 hour, 35 minutes for the analysis of the acidic and neutral amino acids is possible.

DISCUSSION

The goal of this work has been the optimization of resin, column length, column diameter, and flow rate to achieve the complete analysis of a protein hydrolysate in the minimum time. Limiting conditions imposed were; maintenance of precision and accuracy, operation at reasonable pressures, with maximal resolution and a minimum of change of existing equipment. We found no commercially available ion exchange resin that would allow us to meet these specifications using the conditions described above. In the accomplishment of these aims, the geometry and chemical composition of the resin column packing is crucial. The resin was designed specifically to meet the above goals. That these aims have been met adequately is demonstrated by the results obtained. The results with this resin are also in agreement with expectation indicated for the hydraulic characteristics of narrowly graded spherical column packing material (*3*, *6*). The good resolution with fine particles that has been previously obtained with other systems (*4*, *5*) is also confirmed for this system.

Because of rigid control in the manufacture of the resin to ensure constancy of cross-linking, spherical shape, and predetermined particle diameter range, the results shown here are typical; identical results have been consistently obtained from batch to batch.

Another resin system has been developed which will allow two complete analyses of physiological fluids in 24 hours; the details of this analysis are to be reported later.

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Ion Exchange Separation of Americium and Cerium

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▶ Tracer quantities of americium-241 (10^5 disintegrations per minute) and 30 mg. of cerium have been separated quantitatively using Dowex 50W X12, 100- to 200-mesh, ion exchange resin and ammonium lactate as the eluant. In the present procedure small columns are used, and the use of a fraction collector is eliminated.

CERIUM can be separated from the rare earths by extraction (*3*) of Ce(IV) by diethylhexyl phosphoric acid; radiochemical analyses for fission product cerium have been developed using this property. Usually the cerium is back-extracted, precipitated as the oxalate, ignited, and weighed. In this case, there is a small amount of phosphate (either organic or inorganic) carried along with the cerium, which renders the composition of the ignited oxalate indefinite. To eliminate the contamination, the cerium is absorbed on cation exchange resin, washed well with dilute nitric acid, and eluted rapidly with ammonium lactate before the oxalate precipitation.

When the analysis is made from gram amounts of plutonium, there is, in addition, a large amount of Am^{241} (10^9 disintegrations per minute) present from the decay of Pu^{241}. The oxidation of Ce(III) to Ce(IV) with BrO_3^- in strong HNO_3 solutions will oxidize a small fraction ($\sim$0.1%) of the Am(III) to Am(V) which extracts into diethylhexyl phosphoric acid (*1*) and is not subsequently separated from the cerium. The radioactivity of the remaining Am^{241} is enough to interfere seriously with the measurement of Ce^{141} and Ce^{144} radioactivities. The object of this study is to find a rapid, simple separation of americium from 30 mg. of cerium that is compatible with the existing radiochemical procedures. The relatively large difference in cation exchange behavior between Ce(III) and Am(III) (*4*) suggested that the separation could be carried out using a variation of the ion exchange procedure already in use.

EXPERIMENTAL

Apparatus. The ion exchange column was 9 cm. long, 6 mm. in diameter, and had a reservoir 16 mm. in diameter. Solutions were added to the reservoir at the top of the resin column and allowed to flow by gravity into collection tubes. Gamma radiations from Am^{241} and Ce^{144}–Pr^{144} in the collection tubes were counted directly by a well-type NaI(Tl) scintillation crystal, a photomultiplier tube, an amplifier, and a scaling unit.

Reagents. The Dowex 50W X12 100- to 200-mesh resin used was purchased from the BioRad Co., Richmond, Calif., and was used without further treatment. Lactic acid was purchased from J. T. Baker and was used without further purification. Ammonium lactate solutions were prepared by diluting the

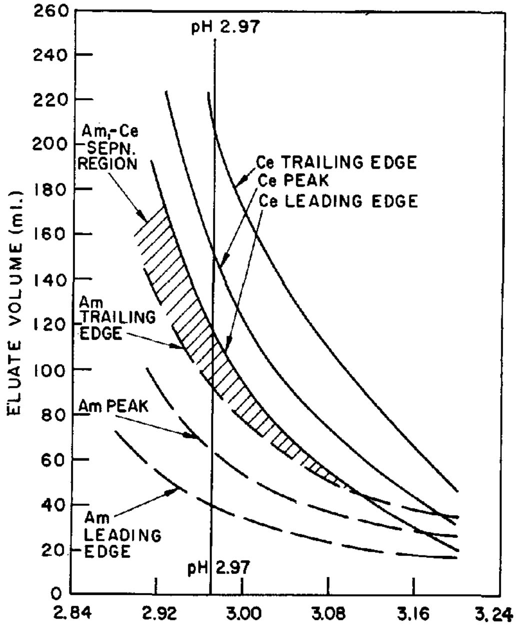

Figure 1. Position of Am(III) and Ce(III) elution peaks as a function of pH of a 1*M* initial lactic acid eluting solution

lactic acid with water to 1*M* and neutralizing with concentrated NH_4OH to the proper pH as measured with a Beckman pH meter. To retard bacterial degradation of the ammonium lactate solution, saturated aqueous phenol solution was added during dilution (5 ml. per liter of ammonium lactate solution).

Procedure. About 10^5 counts per minute of either Am^{241} or Ce^{144}–Pr^{144} were added to 30 mg. of inactive cerium in dilute acid. In general, only a single radioactive species was used in a given column elution to avoid ambiguity in the results; duplicate or triplicate experiments were performed to check reproducibility.

The $Ce(OH)_3$ was precipitated with NH_4OH, centrifuged, and washed with water. The hydroxides were dissolved in 15 ml. of 0.5*M* HNO_3 with 2 drops of 30% H_2O_2 added. The solution was heated to reduce Ce(IV) formed by air oxidation of the hydroxides because Ce(IV) elutes with Am(III) under the conditions of these experiments. The solution was then transferred to the resin column which had previously been equilibrated by passing about 10 ml. of 0.5*M* HNO_3 through the column. After the solution containing the cerium and tracer had passed through the column, 5 ml. of H_2O was added as a wash. Then the collection tube was changed and 5 ml. of the ammonium lactate eluant was added to the top of the column. When the solution had passed through the column the collection tube was changed, and the procedure was repeated. Each portion of eluate was counted separately to measure the elution curve. The initial flow rate of 20 drops per minute (obtained by adding 5 ml. of ammonium lactate solution to the reservoir) was the maximum flow rate which maintained chemical equilibrium in the system.

Initial conditions were chosen rather arbitrarily, based on previous experience with rare earth separations (*2*); i.e., a resin column 9 cm. in length and an initial lactic acid concentration before neutralization of 1*M*. Other concentrations of initial lactic acid were used (0.5*M* and 2.0*M*), but no significant difference in separation or eluate volumes was found.

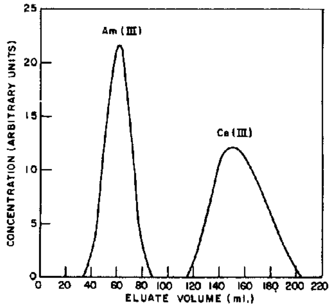

Figure 2. Elution of Am(III) and Ce (III) using 1*M* initial lactic acid adjusted to pH 2.97 with NH_4OH

RESULTS AND DISCUSSION

Elution curves were made at pH values of 2.85, 2.93, 2.95, 2.97, 3.03, 3.06, 3.10, and 3.20. The results are summarized in Figure 1. The leading edge of the elution band was taken to be the point at which the radioactivity in the collection tube rose over 100 counts per minute above a counter background of 150 counts per minute, or roughly 0.1% of the total radioactivity. The trailing edge was taken to be when the activity fell to the same value. Separation was considered adequate when there were at least two collection tubes (10 ml.) between the trailing edge of the americium band and the leading edge of the cerium band. The condition for optimum separation was taken to be the pH at which there was a minimum of ammonium lactate to effect adequate separation. Under the conditions of the experiment, the optimum pH was 2.97 for 1*M* initial lactic acid concentrations; there was less than 0.01% of the Am^{241} in the cerium subsequently eluted from the column by 15 ml. of pH 5 ammonium lactate solution. In one experiment, both Am^{241} and Ce^{144}–Pr^{144} were

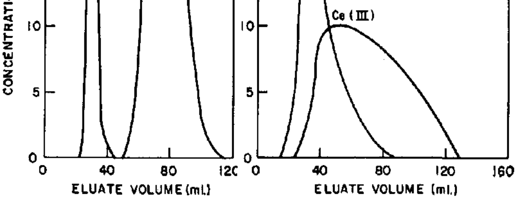

Figure 3. Comparison of separation of Am(III) and Ce(III) using Dowex 50W X12 and Dowex 50W X8 with a 1*M* initial lactic acid eluting solution adjusted to pH 3.10 with NH_4OH

added to 30 mg. of cerium, and the elution was made with ammonium lactate made by adjusting 1*M* lactic acid to pH 2.97. The elution curve is shown in Figure 2.

In the course of the work, experiments were made with resins of lower crosslinkage to check the possibility of faster separations. In general, under the conditions of our experiments, the results were unsatisfactory. Figure 3 shows a comparison between experiments made with Dowex 50W X12 and Dowex 50W X8, both 100- to 200-mesh, with pH 3.10 ammonium lactate.

Interference of any diverse ions, except phosphate, was not checked because the prior extraction of the cerium into diethylhexyl phosphoric acid had eliminated them all. Phosphate does not interfere.

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Determination of Strontium in Environmental Media Using Neutron Activation

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▶ A neutron activation procedure for the determination of strontium in environmental media is described. The method presented simplifies the handling and flux monitoring problems associated with activation analyses. Prior to irradiation, the strontium is separated from the sample by oxalate and nitrate precipitations using the calcium present in the sample as a carrier. Copper is then added to the purified strontium as in internal monitor and the sample is irradiated in a thermal neutron flux of 10^{12} neutrons per square centimeter per second. After irradiation, strontium carrier is added and the strontium further purified by nitrate and chromate precipitations. Copper is separated by dithizone extraction and the strontium is then calculated from the induced activities of strontium-87m and copper-64. Strontium-85 is used to measure the strontium recovery. This method has been applied to the determination of strontium in food, milk, bone, hair, and blood.

Strontium occurs in low concentrations in foods and in the human body. Considerable interest has been shown in the concentrations of this element in these media because of the presence of its radioisotopes in the environment due to nuclear weapons testing and development of atomic energy programs. Several studies are being carried on at this laboratory to develop a better understanding of the behavior of strontium in man. Associated with these programs was a need for a method of analysis of trace quantities of stable strontium in environmental and biological media.

Trace quantities of stable strontium in environmental media have been measured by emission spectrometry (*1*, *12*), x-ray spectrometry (*3*, *6*, *8*), flame photometry (*4*, *7*, *13*), absorption spectrometry (*10*), and by neutron activation (*2*, *5*, *9*, *11*).

Although neutron activation is a reliable and extremely sensitive method for the analysis of strontium, it has not been routinely applied to the analysis of environmental or biological samples. This has probably been due to the lack of availability of a source of neutrons; but also contributing have been problems associated with handling the large amounts of induced activities produced in these samples and the care required to assure proper flux monitoring. With neutron generators now commercially available and nuclear reactors more readily accessible, neutron activation for the determination of strontium should find wider application. A method is presented which simplifies the handling procedures and flux monitoring problems associated with this technique and allows it to be applied on a routine basis.

In previous applications of neutron activation for the determination of strontium in environmental media, direct irradiation of the sample was made so that large quantities of induced activities were produced. Because of the resulting high dose rates, the handling of these samples required considerable care. To avoid this problem, an extension of Harrison's (*5*) technique of concentrating the strontium in blood and urine prior to irradiation was used. The strontium was separated by oxalate and nitrate precipitations using the calcium naturally present in the sample as a carrier. Strontium-85 tracer, added to the original sample and measured simultaneously with the induced activity of strontium-87m, was used to measure strontium recoveries during these separations. This pretreatment reduces the induced activity of the irradiated sample such that the radiation level is <1 mr./hour at 10 cm. The sample can then be handled using the precautions normally applied to tracer quantities of radioactivity.

Because pertinent nuclear data are usually not accurately known, it is a standard procedure to use a comparative method in activation analysis. A standard sample of the element of interest, or a thin foil of copper or gold as a flux monitor, is irradiated simultaneously with the sample. Care must be taken to ensure that the standard or monitor receive the same neutron flux as the sample or that a constant relationship exists between the flux received by the sample and that received by the comparator. This is sometimes difficult to accomplish when significant flux gradients occur along the length of the irradiation container. It is also important that no significant self-shielding occur in the comparator or the sample. The method described simplifies the comparator technique by mixing a monitor homogeneously with the sample. This allows greater flexibility in the conditions under which the sample is irradiated. The type of irradiation facility, the gradient or variability of the neutron flux, and the positioning of the sample within an irradiation container are no longer of concern. Together with the reduction of the radiation level as a result of sample purification before irradiation, this technique lends itself readily to routine analysis.

EXPERIMENTAL

Apparatus. Samples were irradiated in sealed polyethylene vials, $2^1/_8$ inches × $^3/_4$ inch in a slant tube facility of the Army Materials Research Reactor at the Watertown Arsenal, Watertown, Mass. This system permits irradiation in a thermal neutron flux of about 10^{12}n./cm.²/second. Gamma activities were measured using a 4- × 4-inch NaI (Tl) crystal in conjunction with a 400-channel pulse height analyzer.

Reagents. Strontium-85 Tracer, Carrier Free, Nuclear Science and Engineering Corp., was diluted to a concentration of 0.05 µc./ml. with 0.1*M* HCl.

Preirradiation Separation. After suitable pretreatment to reduce the sample to an ash, dissolve a weighed portion of the ash estimated to contain 25–50 mg. of calcium in 20 ml. of 4*M* HCl in a centrifuge tube. Add 0.05 µc. of Sr^{85} tracer and 5 ml. of 1*M* $H_2C_2O_4$. Adjust the pH to 4 with concentrated NH_4OH and digest in a hot water bath for 10 minutes. Cool, centrifuge, and discard the supernatant. Wash the precipitate with 30 ml. of water. Dissolve the precipitate in 5 ml. of concentrated HNO_3 and add 35 ml. of fuming HNO_3. Cool in an ice bath for 10 minutes, centrifuge, and discard the supernatant. Repeat this step and again discard the supernatant. Dissolve the precipitate in water, transfer to a 10-ml. volumetric flask containing 40 µg. of copper and dilute to volume. Transfer the solution to a 4-dram polyethylene vial and heat-seal. Irradiate the vial in a neutron flux of 10^{12} n./cm.²/second for 60 minutes. Record the time of removal from neutron flux. Allow the sample to decay for 30 minutes.

Measurement of Strontium Activity. To a 5.0-ml. aliquot of the solution add 100 mg. of strontium carrier and 30 ml. of fuming HNO_3. Cool in an ice bath for 10 minutes, centrifuge, and discard the supernatant. Dissolve the precipitate in 5 ml. of water, add 30 ml. of fuming HNO_3, cool in an ice bath for 10 minutes, centrifuge, and discard the supernatant. Dissolve the precipitate in 10 ml. of water and add concentrated NH_4OH to a methyl red end point. Add 5 ml. of pH 5 ammonium acetate buffer and 1 ml. of 0.5*N* $Na_2Cr_2O_7$. Add 10 mg. of barium carrier and digest in a water bath for 10 minutes. Cool, centrifuge, and measure the gamma activity of the supernatant. Record the time of counting. Measure the gamma activity of an aliquot of the strontium-85 tracer identical to that added to the sample.

Measurement of Copper Activity. Add 1.0 ml. of the irradiated solution to a separatory funnel containing 10 ml. of water. Add 15 ml. of 0.01% of dithizone in CCl_4 and shake for 3 minutes. Drain the CCl_4 layer into a counting container. Add 10 ml. of 0.01% dithizone in CCl_4 to the separatory funnel and shake for 3 minutes. Combine the CCl_4 layer with the above and measure the gamma activity. Record the time of counting.

Table I. Induced Activities of Standard Solutions of Strontium and Copper Placed in Various Neutron Fluxes

Solution comp., µg./ml.		Induced activities				Activity ratio
Sr	Cu	Sr^{87m}[a] c.p.m./ml.	Cu^{64}[a] c.p.m./ml.	Sr^{87m} c.p.m./µg.	Cu^{64} c.p.m./µg.	$\frac{Sr^{87m}\text{ c.p.m./µg.}}{Cu^{64}\text{ c.p.m./µg.}}$
20.0	4	47,677	42,000	2384	10,500	0.227
20.0	4	21,941	19,910	1097	4,978	0.220
10.0	4	18,699	33,125	1870	8,281	0.226
10.0	4	14,482	26,296	1448	6,574	0.220
4.0	4	7,219	31,848	1805	7,962	0.227
4.0	4	5,817	26,042	1454	6,512	0.223
2.0	4	4,100	36,480	2050	9,120	0.225
2.0	4	3,150	28,000	1575	7,000	0.225
0.5	4	1,153	40,800	2306	10,200	0.226
0.5	4	584	20,820	1168	5,205	0.224
						av. = 0.224

[a] Activities are corrected to time of removal from neutron flux.

Calculations. Strontium, p.p.m. = $\frac{A\,(B - CD)\,DEF}{GHIJKL}$

A = µg. of copper in aliquot counted (*4*)
B = Net counts per minute in strontium aliquot in Sr^{87m} spectral region (0.34–0.43 m.e.v.)
C = Fractional coefficient of Sr^{85} in Sr^{87m} spectral region
D = Net counts per minute in strontium aliquot in Sr^{85} spectral region (0.47–0.56 m.e.v.)
E = Volume to which sample is diluted prior to irradiation in milliliters (*10*)
F = Cu^{64} decay factor from end of irradiation to time of counting
G = Calibration factor
H = Net counts per minute in copper aliquot in Cu^{64} spectral region (0.47–0.56 m.e.v.)
I = Sr^{87m} decay factor from end of irradiation to time of counting
J = Net counts per minute in Sr^{85} tracer added to sample in spectral region (0.47–0.56 m.e.v.)
K = Aliquot taken for strontium measurement in milliliters
L = Ash weight in grams

RESULTS AND DISCUSSION

Calibration. The calibration factor was determined by irradiating synthetic solutions containing known amounts of strontium and copper. The strontium content was varied over a range of 0.5–20 µg./ml. while the copper concentration was held constant at 4.0 µg./ml. This amount of copper produced the desired activity of copper-64.

Two slant-tube facilities were used for sample irradiation. Previous experience (*11*) had shown a steep flux gradient within these tubes and a significant flux difference between tubes. The standard solutions were placed in various positions within the two tubes. After irradiation these solutions were carried through the post irradiation chemistry described in the procedure. The activities induced in these solutions are presented in Table I. These results show, as expected, significant variations in the specific activity of strontium-87m but a constant ratio between the specific activities of strontium-87m and copper-64.

The calibration factor is calculated as follows:

$$\text{Calibration Factor, } G = \frac{ABF}{HIK}$$

A = µg. of copper in aliquot counted
B = Net counts per minute in strontium aliquot in Sr^{87m} spectral region (0.34–0.43 m.e.v.)
F = Cu^{64} decay factor from end of irradiation to time of counting
H = Net counts per minute in copper aliquot in Cu^{64} spectral region (0.47–0.56 m.e.v.)
I = Sr^{87m} decay factor from end of irradiation to time of counting
K = µg. of strontium in aliquot counted

The calibration factor, G, was 0.224 ± 0.003. Although this factor is independent of the irradiation conditions, it is dependent on the counter geometry and crystal size.

Strontium Recoveries. Strontium recoveries were measured by adding 0.05 µc. of strontium-85 tracer to the original sample. The production of strontium-85 during the irradiation from the reaction strontium-84 (n, γ) was negligible compared to the amount of tracer originally added. Strontium yields of 85–98% have been obtained on environmental samples analyzed by

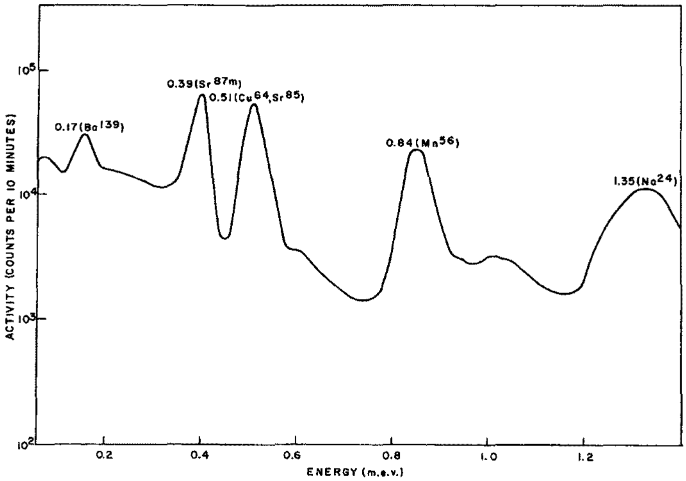

Figure 1. Gamma spectrum of hair sample No. 263 prior to purification

this procedure. The preirradiation chemistry, the calcium oxalate precipitation step in particular, accounts for most of the strontium loss. The loss of strontium during the post irradiation chemistry was approximately 1%. Table II shows loss of strontium-85 tracer during the various separation steps of the procedure on a diet sample.

Table II. Loss of Sr^{85} Tracer during Separation Procedure

Separation	Loss Sr^{85}, %
Preirradiation	
Oxalate precipitation and wash	6.2
1st Calcium nitrate precipitation	0.5
2nd Calcium nitrate precipitation	0.3
Postirradiation	
1st Strontium nitrate precipitation	0.1
2nd Strontium nitrate precipitation	0.1
Barium chromate precipitation	0.8
Total loss	8.0%

Table III. Copper Content of Samples after Preirradiation Separations

Type of sample	Cu^{64} in aliquot, c.p.m.	Cu in total sample, μg.
Bone	95	0.18
Hair	106	0.20
Food	85	0.16
Limestone	91	0.17

Copper Decontamination. Since copper is added to the purified sample as a neutron flux monitor, it is necessary that any copper in the original sample be removed, or at least greatly reduced, during the preirradiation chemistry. To test the effectiveness of the procedure for removing copper, a diet sample to which copper-64 had been added was carried through the preirradiation chemistry. The copper-64 activity was reduced by a factor of about 10 during the calcium oxalate precipitation step and by an additional factor of 10^3 during the two calcium nitrate precipitations. The overall decontamination factor was 10^4. This indicates that up to 10 mg. of copper may be present in the sample taken for analysis without constituting a serious interference in the method. It is unlikely that this amount of copper would be present in any of the environmental samples to be analyzed. As a further check on the copper removal, a series of typical environmental samples were carried through the procedure without the addition of the copper monitor. Table III shows the copper-64 activity measured in these samples. In all cases the amount of copper present in the sample after the preirradiation chemistry was 0.2 μg. or less; this is a negligible amount in comparison to the 40 μg. added as a monitor.

Sample Spectrum. Figure 1 shows the spectrum of an irradiated hair sample prior to the postirradiation purification. It was hoped originally that the sample would be sufficiently pure to allow the direct measurement of the copper and strontium activities simultaneously on the irradiated sample. Strontium-85 tracer would not have been added and a constant yield factor would be applied. However, in addition to the 0.39-m.e.v. and 0.51-m.e.v. peaks from strontium-87m and copper-64, peaks from barium-139 (0.17-m.e.v.), manganese-56 (0.84-m.e.v.) and sodium-24 (1.35-m.e.v.) were also observed. The magnitude of these impurities were such that the spectrum could not be resolved with sufficient accuracy to allow direct measurement. Figures 2 and 3 show the spectra obtained for the purified strontium-87m and copper-64. The copper-64 spectrum is identical to that obtained from the

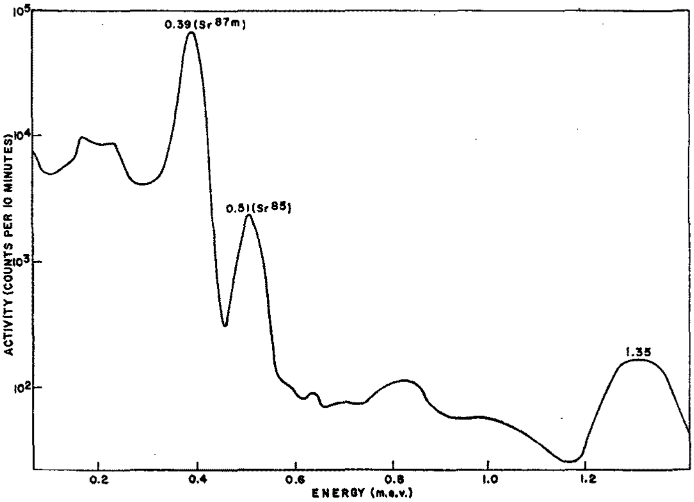

Figure 2. Gamma spectrum of strontium activity separated from hair sample No. 263

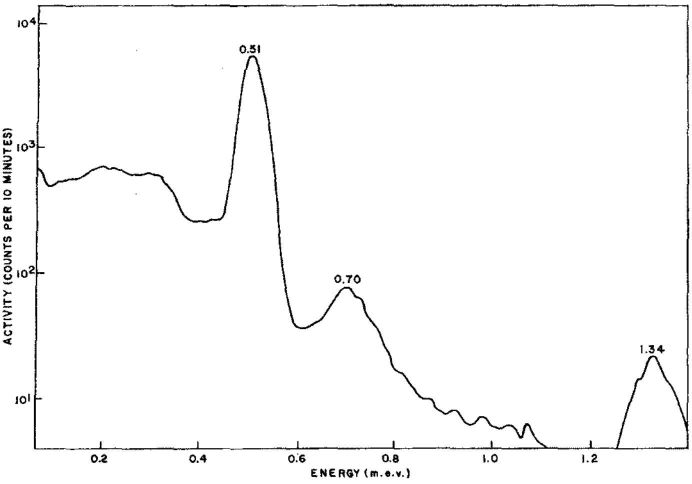

Figure 3. Gamma spectrum of copper activity separated from hair sample No. 263

irradiation of a solution of $Cu(NO_3)_2$. The strontium-87m spectrum, with the exception of a slight broad peak from 1.3–1.4 m.e.v. (probably due to sodium-24) is almost identical with the spectrum obtained from the irradiation of a solution of $Sr(NO_3)_2$.

As a further check on the purity of the strontium fraction, decay measurements were made on the strontium activity from a food sample in the 0.34–0.43-m.e.v. spectral region. The sample decayed with the 2.8-hour half life of strontium-87m.

Since copper-64 and strontium-85 both have gamma photopeaks at the same energy (0.51-m.e.v.), it is necessary that the procedure separate these nuclides with a high degree of purity. The decontamination factor for strontium-85 in the dithizone extraction was $>10^3$.

Table IV. Analyses of N.B.S. Samples

Sample number	Per cent SrO Reported	Per cent SrO Found
1011	0.11	0.108
1014	0.26	0.254

Reagent Blank. A strontium reagent blank was measured for those reagents used for sample preparation prior to irradiation. This blank was determined to be 0.08 μg. of strontium. Oxalic acid was the principal contributor to this blank. At the concentration levels of strontium in environmental and biological samples, this contribution from the reagents is small. If, however, the samples to be analyzed contain less than 5 μg. of strontium, a reagent blank should be determined and the appropriate correction applied.

Accuracy and Recovery. Since samples of known strontium content of the type to be analyzed are not available, National Bureau of Standards cement samples were analyzed to evaluate the accuracy of the method. The results of the analyses of two of these samples are presented in Table IV. In addition, previously analyzed samples were spiked with known amounts of strontium and the accuracy with which the method measured the added strontium was evaluated. Table V shows the results obtained when 100 μg. of strontium were added to samples of calcium carbonate, hair, food, and blood.

Table V. Recovery of Added Strontium

Type of sample	Strontium, μg. Present	Strontium, μg. Added	Strontium, μg. Found	Error, %
Calcium carbonate	13.2	100	115	+1.5
Blood-220	18.1	100	120	+1.6
Food-104	95	100	191	−2.1
Hair-380	376	100	462	−3.0

ACKNOWLEDGMENT

The authors express their appreciation to John O'Connor, Eugene Zagarella, and John Balian of the Army Materials Research Reactor, Watertown, Mass., for assistance in sample irradiations.

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Correction

Radiochemical Determination of Carbon–Lithium Bonds in Lithium-Terminated Polymers Using Tritiated Alcohols

In this article by D. R. Campbell and W. C. Warner [Anal. Chem. **37**, 276 (1965)] on page 277, column 2, line 15, "thymolphthalein" should be "thymolsulfonephthalein."

Determination of Mixtures of Hydrazine and Monomethylhydrazine by Reaction with Salicylaldehyde

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▶Mixtures of hydrazine and monomethylhydrazine are resolved in glacial acetic acid by reaction with salicylaldehyde in the presence of excess perchloric acid. In this system any hydrazone formed by the reaction of salicylaldehyde and monomethylhydrazine is hydrolyzed back to the original substances. However, the excess perchloric acid does not inhibit the formation of the azine. The perchloric acid neutralized by the sample is a direct measure of monomethylhydrazine. The hydrazine content is then determined by difference from a total base titration.

Experimental work involving samples containing monomethylhydrazine (MMH) and hydrazine (N_2H_4) prompted an analytical investigation to develop a method of analysis to quantitatively differentiate these components.

At the inception of our investigation the method of Clark and Smith (*3*) was the only one available for the analysis of such mixtures. Their method, which employs oxidation with Chloramine-T and sodium hypochlorite to differentiate MMH and N_2H_4, was tried initially on the experimental system; however, high, erratic results were usually obtained. A recent publication by Sutton (*6*), which utilizes gas chromatographic and wet analysis for the analysis of this mixture was not tested on the experimental system.

Malone (*4*) analyzed mixtures of N_2H_4 and 1,1-dimethylhydrazine (UDMH) based on the reactions of these compounds with salicylaldehyde in acetic acid to form what was termed the neutral azine and the basic hydrazone, respectively. The basicity of the system was then determined and calculated as a measure of the UDMH and the N_2H_4 content was obtained by difference from a total base titration. Malone attempted this method on the N_2H_4-MMH system and concluded that it was not successful because the reaction producing the hydrazone was incomplete. The evidence presented in the present study shows that the species actually titrated are the free MMH and the free UDMH and that low recoveries are the result of incomplete hydrolysis of any hydrazone present during the titration. When an excess of perchloric acid is included in the salicylaldehyde reaction mixture, hydrolysis is complete and MMH can be determined.

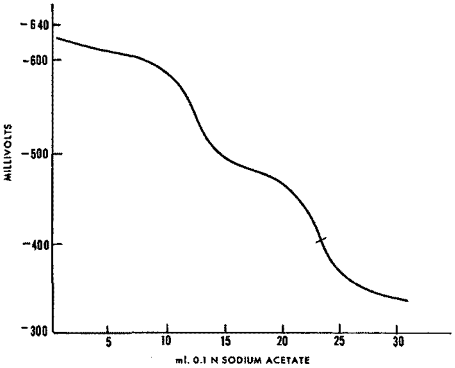

Figure 1. Hydrazine reacted with salicylaldehyde and excess perchloric acid titrated with 0.1*N* sodium acetate

EXPERIMENTAL

Reagents. Perchloric acid, 0.1*N* in glacial acetic acid. Acetic anhydride is omitted in the preparation to avoid any acetylation of the hydrazines.

The samples of hydrazine and monomethylhydrazine used in the study were obtained from the Chemicals Division of the Olin Mathieson Chemical Corp. and were employed without purification.

Preparation of Sample. About 0.4 gram of N_2H_4 and/or MMH is weighed to the nearest 0.1 mg. and added to approximately 35 ml. of chilled acetic acid in a 50-ml. volumetric flask. After equilibration to room temperature, the samples are diluted to 50 ml. with acetic acid and mixed thoroughly.

Determination of Total Alkalinity. Titration A. A 5-ml. aliquot is dissolved in 50 ml. of acetic acid, to which 25 ml. of 0.1*N* perchloric acid in acetic acid is added. The solution is then titrated potentiometrically with 0.1*N* sodium acetate in acetic acid. The amount of perchloric acid consumed in Titration A by the sample is a measure of the total hydrazine content (substituted and unsubstituted).

Determination of Monomethylhydrazine. Titration B. To a second 5-ml. aliquot dissolved in 50 ml. of acetic acid, 25 ml. of 0.1*N* perchloric acid is added, followed by 2 ml. of salicylaldehyde. The solution is stirred on a magnetic stirrer for 4 to 5 minutes, and is titrated as above with 0.1*N* sodium acetate. The amount of perchloric acid neutralized by the sample is a direct measure of monomethylhydrazine.

Blanks are run in both titrations, omitting only the sample.

CALCULATIONS

$$\%\ \text{MMH} = \frac{(\text{meq. NaOAc Blank Titration B} - \text{meq. NaOAc Titration B})\ 46.075}{\text{sample wt.}}$$

$$\%\ N_2H_4 = \frac{(\text{meq. NaOAc Blank Titration A} - \text{meq. NaOAc Titration A}) - (\text{meq. NaOAc Blank Titration B} - \text{meq. NaOAc Titration B})\ 32.05}{\text{sample wt.}}$$

The determinations should be made immediately on dilution of the sample with acetic acid to minimize hydrazide formation. A definite decrease in basic equivalents was noted for diluted samples which were permitted to stand longer than two hours at room temperature.

DISCUSSION AND RESULTS

Effect of Concentrations of Hydrazine and Monomethylhydrazine. In the analysis of mixtures of N_2H_4 and MMH with the above procedure, two distinct inflections are observed when the hydrazine concentration is greater than 50%; the first inflection is the excess perchloric acid, and the second inflection is the azine perchlorate salt (Figure 1).

However, with less than 50% hydrazine in the mixture, only one distinct inflection is observed, but a second constituent is very evident from the shape of the titration curve.

Visual end point detection was not used in this system; however, the system should be amenable to an indicator such as crystal violet.

The procedure was tested by analyzing synthetic mixtures of N_2H_4 and MMH from 0–100% of each component. The data are tabulated in Table I and are corrected for N_2H_4 found in the MMH sample.

Mechanism of the Reaction. The azine and hydrazone reactions are reversible and dependent on hydrogen ion concentration (*1, 2, 5*).

In glacial acetic acid in the presence of perchloric acid, the equilibrium is displaced completely in the direction of azine formation. However, the reaction of MMH and the formation of the hydrazone is not complete in the same medium. This was established by the following experiments:

The salicylaldazine and the salicylaldehyde hydrazones of MMH and UDMH were prepared in benzene and analyzed quantitatively by nonaqueous titrimetry in pyridine. UDMH was included in this study for purposes of comparison.

The azine assayed 101% and the hydrazones 100%. The infrared spectra of these materials were consistent with that expected of the azine and the hydrazones. These materials were then dissolved in acetic acid and titrated with 0.1*N* perchloric acid in acetic acid. The azine titrated as a very weak base and was quantitatively recovered, whereas the hydrazones titrated as relatively strong bases, of which the UDMH hydrazone was quantitatively recovered while the MMH was only 60–70% recovered. The potentiometric plots obtained in the titrations of the MMH and UDMH hydrazones are almost superimposable on the plots of MMH and UDMH. However, the basicity of these hydrazones should be weaker than MMH and UDMH becouse of the decrease in electron density of the nitrogen atoms.

Therefore, it was concluded that perchloric acid shifted the equilibrium such that the MMH and UDMH were actually titrated and not the weakly basic hydrazones. The low recovery of MMH could be attributed to incomplete acid hydrolysis of the hydrazone. It was established that the azine is stable, the MMH hydrazone is somewhat stable, while the UDMH hydrazone is entirely unstable in acetic acid–perchloric acid media.

Additional data confirming the above conclusions were obtained by agitating the azine and hydrazones in excess aqueous hydrochloric acid. The solution was extracted with benzene to remove any liberated salicylaldehyde, free azine, and hydrazones. The aqueous phase was then evaporated to a residue which was identified by infrared as the hydrochloride salts of MMH and UDMH in the case of the hydrazones, whereas no hydrazine hydrochloride was detected in the azine experiment—i.e., the azine was recovered as such in the benzene layer.

Table I. Analysis of Hydrazine–Monomethylhydrazine Mixtures

% MMH		% N_2H_4	
Present	Found	Present	Found
100.0	100.2	0	0.9
89.1	90.4	10.9	11.1
79.2	80.5	20.8	21.1
73.4	73.0	26.6	26.3
65.1	66.3	34.9	35.0
49.6	50.9	50.4	49.6
37.8	38.9	62.2	62.0
29.3	28.4	70.7	69.5
19.3	19.2	80.7	82.2
13.0	13.1	87.1	87.5
0	0	100.0	99.3

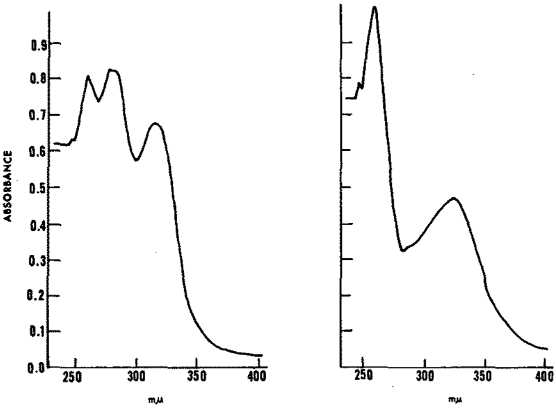

Figure 2. Ultraviolet spectrum of monomethylhydrazone of salicylaldehyde before and after addition of perchloric acid

Left. Before addition of perchloric acid
Right. After addition of perchloric acid

More definite proof was obtained on this system by observing the ultraviolet spectral changes of the azine and the hydrazones in acetic acid and in the presence of excess perchloric acid.

Figure 2 illustrates the ultraviolet spectrum of the MMH hydrazone before addition of excess perchloric acid, and immediately after the addition of excess perchloric acid. About 94% of the hydrazone has hydrolyzed to MMH and salicylaldehyde. The spectrum after addition of excess perchloric acid is practically identical to that of free salicylaldehyde in acetic acid, with the exception of the small amount of material at approximately 288 mμ which could be attributed to N_2H_4 present in the original MMH since this absorption is still evident after 70 minutes, and it was established that the azine is stable for this length of time in this system.

UDMH was also tested as above, and it was established that the UDMH hydrazone is also unstable to perchloric acid in acetic acid—i.e., the equilibrium is shifted completely in favor of free UDMH and free salicylaldehyde.

The ultraviolet spectrum of the azine before addition of perchloric acid and immediately after the addition of perchloric acid shows a shift in the spectrum, but no free aldehyde is present immediately as shown by absence of the salicylaldehyde peak at 256 mμ. After 24 hours in the presence of excess perchloric acid the azine begins to hydrolyze as indicated by the formation of the salicylaldehyde peak at 256 mμ. After 24 hours, 80% of the azine is hydrolyzed back to hydrazone and salicylaldehyde.

Therefore, the conclusion arrived at by Malone—i.e., that the UDMH hydrazone of salicylaldehyde is as basic as UDMH—is incorrect. Under the conditions employed by Malone, the UDMH hydrazone is hydrolyzed rapidly to UDMH and salicylaldehyde upon addition of perchloric acid, whereas, the azine is stable and therefore not titrated as a moderate base in glacial acetic acid.

ACKNOWLEDGMENT

The authors gratefully thank Irene Cowern, Warren Harple, and George Hurt who performed the infrared and ultraviolet determinations.

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Separation of Protium and Deuterium Forms of Carbohydrates by Gas Chromatography

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▶ Gas liquid chromatography on 15- to 25-meter, narrow-bore packed columns of SE-30 and other liquid phases brought about the complete separation of trimethylsilyl derivatives of β-glucose from β-glucose-d_7. Partial separations were achieved with the α anomers of glucose and glucose-d_7, and with the α and β anomers of other pairs of protium and deuterium sugars. Structural factors appear to play a significant role in these separations. It is calculated that columns with 200,000 theoretical plates would give complete resolution of all the protium-deuterium pairs studied (ribose, xylose, fucose, rhamnose, mannose, and glucose).

The possibility of fractionation in compounds containing isotopes of hydrogen has received considerable attention, particularly with the advent of high resolution chromatographic methods. (The term "fractionation" rather than "isotope effect" is used to describe the separations discussed here since the latter term is usually reserved for chemical reactions). One of the earliest studies of such a fractionation in a gas liquid partition chromatographic system was that by Wilzbach and Riesz in 1957 (*20*), in which cyclohexane and its completely deuterated form (C_6D_{12}) were partially separated. More recently, Lee and Rowland (*8*) have demonstrated a partial resolution of monotritiated butene on a 160-foot column packed with silver nitrate–ethylene glycol. Root, Lee, and Rowland (*12*) have described an effective recycling technique for the separation of butane from deuterated butane, and methane from deuterated methane. Van Hook and Kelly (*17*) separated deuterated ethanes by gas chromatography, using methylcyclopentane as the liquid phase; subambient operating temperatures in the range 273° to 158° K. were employed.

Other chromatographic techniques have also been shown to lead to fractionation. For example, Gant and Yang (*4*) have partially separated all of the tritium-substituted methanes and deuterium-substituted methanes by gas-solid adsorption chromatography on a 50-foot column packed with charcoal. A great many observations have been reported on the separation of molecular hydrogen, deuterium, and tritium from each other and from mixed forms such as HD and DT [for a review of this work, see Akhtar and Smith (*1*)]. Liquid-solid chromatography has been used by Klein, Simborg, and Szczepanik (*7*) to achieve some isotope fractionation of C^{14}- and H^3-labeled cholesterol acetates on silica gel columns. In this case, a measurable effect was noted with one tritium atom in the presence of 47 hydrogen atoms, in a compound of molecular weight 430. Similarly, Sgoutas and Kummerow (*14*) have shown small differences in C^{14}- and H^3-labeled fatty acids on chromatography with silica gel–silver nitrate columns. Piez and Eagle (*11*) observed a slight fractionation on ion exchange chromatography of C^{14}-labeled amino acids, and obtained evidence that the effect of the C^{14} atom on chromatographic behavior was dependent on its position in the molecule, rather than solely on the basis of a difference in mass. Similarly, Marshall and Cook (*10*) noted that small differences in countercurrent distribution of arabinose-1-C^{14} and other labeled pentoses were not related to differences in mass only.

These effects have generally been demonstrated in gas chromatography with compounds of relatively low molecular weight, in which the isotope-labeled species differed in mass from the protium form by from 5 to 10%. The only exception has been the recent report by Kirschner and Lipsett (*6*) of a slight separation of H^3- and C^{14}-labeled steroids on short packed columns. If complete separations were possible with isotope-containing compounds of higher molecular weight, chromatographic techniques might be used in the biomedical field for direct determinations of isotope abundance following metabolic tracer experiments. A direct chromatographic procedure would obviate the necessity of converting compounds to a form suitable for isotope analysis by classical methods of mass spectrometry, and would be less complex, instrumentally, than recently described techniques for continuous mass spectrometric analysis of gas chromatographic effluent streams (*13*, *18*).

Deuterated hexoses, in which all of the carbon-bound hydrogen is replaced by deuterium, are now commercially available. Since we had developed a rapid method for the preparation of *O*-trimethylsilyl (TMS) derivatives of polyhydroxy compounds, and had studied the gas chromatographic behavior of many of these compounds (*3*, *16*, *19*), we undertook an investigation of the chromatographic separation of deuterated hexoses (and other sugars) from the protium forms. For a compound such as glucose, with seven carbon-bound deuterium atoms, the mass difference for the TMS derivative is 7 in 547, or 1.3%. This paper reports the complete separation of glucose and glucose-d_7, and partial separations with other carbohydrates, using gas liquid chromatographic columns with efficiencies of from 40,000 to 60,000 plates.

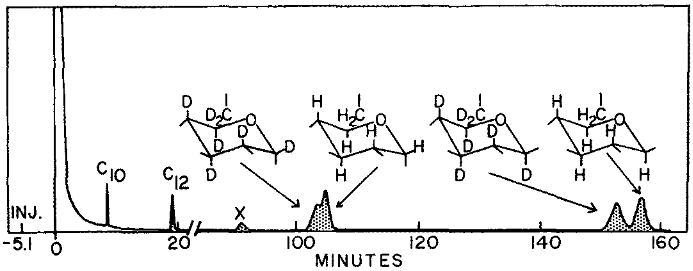

Figure 1. Separation of protium and heptadeutero forms of α- and β-glucose penta-TMS derivatives

Column. 3% SE-30, 15 meters, operated at 175° C.
Peaks. Left to right, solvent peak, 5.1 minutes after sample injection (inj.); C_{10}, reference methyl decanoate; C_{12}, reference methyl dodecanoate; X, impurity in glucose-d_7 sample (plates = 35,000); α anomers of glucose-d_7 and glucose; β anomer of glucose-d_7 (plates = 31,000); β anomer of glucose (plates = 40,000)
In formula showing chair conformations of glucose, substituent —$OSi(CH_3)_3$ groups omitted in interests of clarity

EXPERIMENTAL

Materials. Throughout this paper, we are concerned only with compounds containing deuterium atoms linked to carbon in a stable bond. D-Glucose and D-mannose containing seven atoms of deuterium were purchased from Merck, Sharp and Dohme of Canada, Ltd., Montreal, Canada. These compounds, in their aqueous equilibrium form, had been obtained by cultivation of *Scenedesmus obliquus* in deuterium oxide of 99.7% isotopic purity. In both cases, the isotopic purity of the sugar, as determined by nuclear magnetic resonance spectroscopy, was greater than 95%. D-Glucose-1-*d* was prepared as described by Bentley and Bhate (*2*). The TMS derivatives of all compounds were prepared by methods which have been used routinely for gas chromatography of carbohydrates (*16*).

Apparatus. An F & M Model 400 gas chromatograph, equipped with a flame ionization detector, was used for this work. Gas chromatography of the common type was performed on a glass, U-shaped column 2 meters in length and 3 mm. in internal diameter. The column was packed with 3% methylsilicone gum (SE-30) on acid-washed, silanized 100- to 120-mesh Gas Chrom S (Applied Science Laboratories, Inc., State College, Pa.), using the solution coating technique (*5*) to prepare the material. This column exhibited efficiencies which ranged from 3500 to 4500 plates with TMS derivatives of hexoses.

Special columns used to separate deuterated sugars from their protium forms consisted of 15 to 25 meters of 1.74-mm. internal diameter (1/8-inch o.d.) copper tubing. Long lengths (15 meters) of the tubing were given preliminary washes with methanol and chloroform, after which the tubing was dried thoroughly with a stream of nitrogen. Long packed columns were prepared in sections, essentially according to techniques of Spencer (*15*), as follows: Short lengths (3 meters) of washed tubing, bent into a U-shape, were filled from a funnel with a measured amount of packing (9.5 ± 0.5 ml.) by tapping the sides of the tubing until both sides were completely full. The ends of the sections were packed loosely with borosilicate glass wool, after which the tubing was bent into a 7-inch coil. Sections were joined with Swagelok unions to a desired total length and the column was inserted into the oven of the F & M Model 400, connecting the inlet side to a 4-inch length of 4-mm.-i.d. stainless steel tubing which served as an injection port. Injections were made in the usual manner through a silicone septum with a 10-μl. Hamilton syringe.

A 15-meter column packed with 3% SE-30 on acid-washed, silanized 100- to 120-mesh Gas Chrom S was used for most of the studies herein reported. This column was operated isothermally with helium as the carrier gas. An inlet pressure of 150 p.s.i. gave an average linear gas velocity of 4.8 cm. per second, which was equivalent to an outlet flow of 30 ml. per minute (measured with a soap bubble flowmeter). A 25-meter column, packed with the material described above, was operated at 195° C. and required an inlet pressure of 210 p.s.i. to maintain the optimal helium flow rate of 30 ml. per minute. The average of several *H* values for nondeuterated sugars, chromatographed on 15- and 25-meter columns as described above, was 0.425 mm.

Some studies were also made with 15-meter columns packed with 2.2% Apiezon M or 5% Carbowax 20M.

RESULTS

In a preliminary investigation of the behavior of deuterated and protium forms of sugars on short conventional packed columns, it was observed that TMS derivatives of the α anomers of glucose-d_7 had essentially identical retention times with SE-30 as the liquid phase. With the β anomers, however, a consistent but very slight difference was observed in separate runs of the deuterium and protium forms, the deuterated derivative having the lower retention time. An average separation factor, calculated from these chromatograms, was 1.013. It was not possible to measure the resolution (*R*) of this pair, which was so slight that mixtures of the TMS β anomers gave one symmetrical peak.

From these results obtained with short packed columns, it was calculated that the β anomeric forms could be completely separated with a column developing an efficiency of about 50,000 plates. Trial separations were made with a number of types of long packed columns, varying the geometry of the columns, the material of their construction, and their internal diameters; the best separations up to the present time have been obtained with narrow-bore packed columns 15 meters or more in length.

Figure 1 shows a typical chromatogram of TMS α and β anomers of approximately equal amounts of glucose and glucose-d_7, obtained with 15 meters of 3% SE-30. The separation

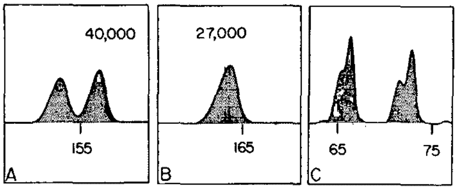

Figure 2. Separation of protium and deuterium forms of TMS carbohydrates

Column and conditions same as in Figure 1. Portions of complete chromatograms shown with retention times in minutes and, where calculable, theoretical plates above peaks
A. First peak, β-glucopyranose-d_7 TMS; second peak, β-glucopyranose TMS (plates = 40,000)
B. Mixture of β-glucopyranose-1-*d* and β-glucopyranose TMS (plates = 27,000)
C. First double peak, methyl α-glucopyranoside-d_7 and methyl α-glucopyranoside TMS; second double peak, methyl β-glucopyranoside-d_7 and methyl β-glucopyranoside TMS

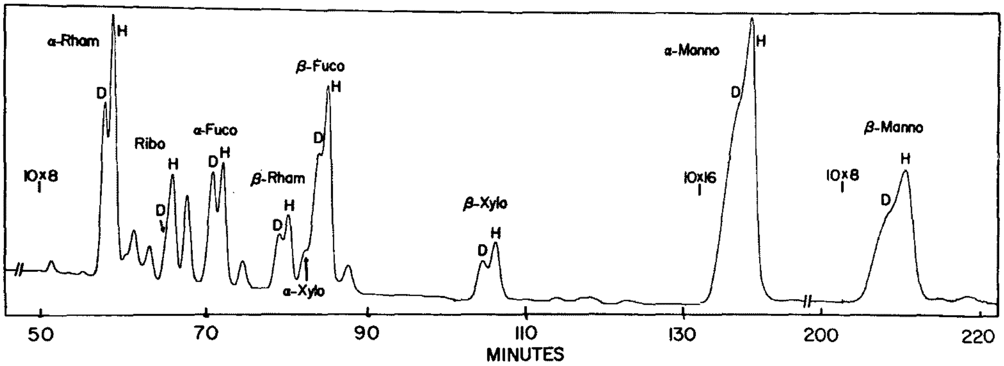

Figure 3. Separation of protium and deuterium forms of mixed TMS monosaccharides

Column and conditions same as in Figure 1 but temperature 165° C. Instrument sensitivities shown as 10 × 8 and 10 × 16. Deuterium and protium forms distinguished by D and H, respectively. Peaks between α-rhamnose, H, and ribose, D, are other ribose forms. Precise structural assignments of ribose forms cannot be made. Other unmarked peaks are unidentified components of deuterated sirup

factor for the β anomers was 1.026; R for this separation was 1.16. The α anomeric forms were not so well resolved; the observed separation factor for this pair was 1.015. Compared with the separation obtained with glucose-d_7, results with glucose-1-d were disappointing. The TMS derivatives of the β anomers were eluted from the 15-meter SE-30 column at essentially the same retention time. A definite band broadening was observed (Figure 2, B), however, which suggested that a slight separation may have been achieved. The TMS derivatives of methyl glucopyranosides prepared from glucose and glucose-d_7 were not as well resolved as were the TMS derivatives of the free sugars, as shown in Figure 2, C.

Table I. Relative Retention Times of Trimethylsilyl Derivatives of Deuterated and Nondeuterated Carbohydrates[a]

Sugar	Deuterium	Protium
Ribose (minor)	2.037	2.070
Ribose (major)	2.124	2.156
β-Xylose	3.456	3.509
α-Rhamnose	1.871	1.906
β-Rhamnose	2.589	2.627
α-Fucose	2.311	2.357
β-Fucose	2.755	2.789
α-Mannose	4.518	4.563
β-Mannose	6.962	7.030
α-Glucose	5.385	5.469
β-Glucose	7.964	8.177

[a] Retention times, relative to methyl dodecanoate, were taken from chromatograms with 15 meters of 3% SE-30.

Table II. Separation Factors for Deuterium and Protium Carbohydrates[a]

Sugar	Separation factor	Standard deviation	$n^{b}_{\text{req}} \times 10^{-3}$
Ribose (minor)	1.0132	0.0022	111
Ribose (major)	1.0131	0.0013	112
β-Xylose	1.0189	0.0006	51
α-Rhamnose	1.0182	0.0006	60
β-Rhamnose	1.0142	0.0016	93
α-Fucose	1.0190	0.0012	53
β-Fucose	1.0127	0.0016	115
α-Mannose	1.0103	0.0007	166
β-Mannose	1.0093	0.0007	198
α-Glucose	1.0150	0.0006	81
β-Glucose	1.0262	0.0005	26

[a] Data obtained with 15 meters of 3% SE-30, conditions in text.
[b] Calculated for 98% resolution ($R = 1$).

A sirup consisting of several fully deuterated carbohydrates was first examined on the 2-meter SE-30 column. Twelve distinct peaks were attributed to anomeric mixtures of mannose (the major component), ribose, xylose, fucose, and rhamnose. A detailed analysis of this mixture on the 15-meter SE-30 column revealed at least 22 separate peaks, from which the following composition was calculated: unidentified (triose ?), 11.5%; ribose, 2.8%; xylose, 4.6%; fucose, 12.2%; rhamnose, 10.8%; mannose, 48.9%; other unidentified materials, 9.2%. On the basis of this analysis, a mixture was prepared, containing the deuterated sugars and the hydrogen forms of ribose, xylose, fucose, rhamnose, and mannose in approximately the same proportions as those in the deuterated mixture. On the 15-meter column of SE-30, the chromatogram shown in Figure 3 was obtained. Clearly separate peaks were observed for the protium and deuterium forms of α- and β-fucose, α- and β-rhamnose, β-xylose, and α- and β-mannose. In addition, a shoulder was distinguished on the major ribose peak. With xylose, the α anomeric form was partially obscured by the much larger adjacent β-fucose peak, so that no separation of protium and deuterium forms of this sugar was observed. The relative retention times determined from several chromatograms of the mixture as well as from pure mannose-d_7 and various pure protium forms are tabulated in Table I. In Table II are shown the separation factors for individual protium-deuterium pairs and required plates for 98% resolution, all calculated from analyses of the mixed forms.

Experiments were undertaken to evaluate the possible assay of mixtures of glucose and glucose-d_7 by the gas chromatographic method, involving area measurements of the separated forms. Three mixtures were prepared, containing, respectively, 50% glucose-d_7, 5.7% glucose-d_7, and 0.57% glucose-d_7. The TMS derivatives were examined on the 15-meter SE-30 column in the usual way, with particular attention to the β peaks in view of the completeness of their separation. With the 50% mixture, both peaks were measured at the same attenuation of the electrometer, whereas changes were made in the attenuation with the other mixtures, to accommodate the much larger glucose peaks. Tracings of the actual results are shown in Figure 4. The observed compositions of the mixtures, as determined by measurements of the areas, were 48.4, 4.6, and 0.55%, in good agreement with the known values. The ultimate practical limit of detection by this method is dependent on the sensitivity of the detector and the complete separation of the two forms; it is expected that this limit will be about 0.1% by weight.

Extension of the length of the SE-30 column from 15 to 25 meters resulted in an appreciable increase in pressure drop through the column (from 150 to 210 p.s.i.) and a 50% increase in column efficiency. From a chromatogram of the mixture of glucose and glucose-d_7, it was calculated that the β anomeric forms were >98% resolved; the plate efficiency for the protium form of β glucose was, in this case, 60,000. Although the increase in length resulted in some added inconvenience as far as high pressure operation was concerned, the added efficiency actually allowed equivalent or better separations to be made in considerably less time, as compared with 15-meter columns.

Comparisons were made of the retention behavior of deuterated sugars on other types of liquid phases. Of the three phases tested so far, SE-30, Apiezon M, and Carbowax 20M, the best separation factors for protium and deuterium mixtures were achieved with Apiezon M, while the lowest H values were obtained with SE-30. The resolution of the β anomers of glucose and glucose-d_7 was 1.13 with 15 meters of 2.2% Apiezon at 165° C.; the value of H measured on β-glucose was 0.709 mm. Our results are in agreement with those of Liberti, Cartoni, and Bruner (*9*), who found that nonpolar liquid phases were more effective than polar ones for separation of benzene and perdeuterobenzene on capillary columns.

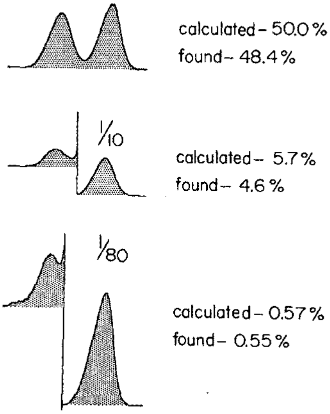

Figure 4. Measurement of deuterium abundance in β-glucose by gas chromatography

Column and conditions same as in Figure 1. Instrument sensitivities shown as 1/10 and 1/80

DISCUSSION

Although the separation of β-glucose and β-glucose-d_7 was excellent on narrow-bore packed columns 15 meters or more in length, our results support the generalization that isotope separations of high molecular weight compounds are not routinely a function of differences in mass. For example, the α anomeric pair in glucose was less well resolved and will require at least 80,000 plates for complete separation. The range of separation factors found with various sugar pairs indicates that several factors must govern retention behavior in the carbohydrate series.

The pronounced difference in behavior of the α and β anomers of the glucose-glucose-d_7 pair suggested that the placement of one TMS group in an axial position in the α anomers diminished the degree of separation. This was to some extent confirmed by the fact that the mannose anomers were not as well resolved as those of glucose (α-mannose in the Cl conformation has two axial groups; β-mannose in the same conformation, one axial group). On the other hand, when glucose and glucose-d_7 were chromatographed in the form of TMS methyl glucosides, the separation of the deuterium from the protium forms was incomplete for the β as well as the α anomers. These observations are consistent with a growing body of evidence indicating that structural features have an important role in such isotopic fractionations. In their studies of isotope separations of C^{14}-labeled amino acids on ion exchange chromatography, Piez and Eagle in 1955 found that the effect depended to some extent on the position of the C^{14} in the molecule, rather than solely on the mass difference (*11*). Similarly, a fractionation was observed during the countercurrent distribution of arabinose-1-C^{14}, but not with arabinose-5-C^{14}, xylose-1-C^{14}, and ribose-1-C^{14} (*10*). Klein *et al.* have also pointed out that with doubly labeled cholesterol or dihydrolanosterol acetates, the relative location of the two isotopes in the same structure was a strong determinant of the observed displacement in adsorption chromatography (*7*). In our work with mannose and glucose, both compounds have the same number of deuterium atoms at the same carbon atoms of the pyranose ring. The differences we have observed in the behavior of various anomeric and epimeric forms of sugars cannot, therefore, be attributed to positional variations, but more likely must depend on the over-all structure or conformation of the molecule. It may be that in the work of Marshall and Cook (*10*) with pentoses, both positional and structural effects were operative.

No easily proved mechanism can be invoked to account for the fact that the deuterium forms were always eluted earlier than the protium forms in these partition studies—that is, a "negative isotope effect"; our results agree in this respect with the frequent though not invariable observation of a negative effect in other partition systems (*6, 9, 10, 12, 17, 20*). By contrast, the isotope-labeled species generally have greater elution volumes than the normal forms in gas- or liquid-solid adsorption systems (*1, 14*) and ion exchange chromatography (*11*), although again exceptions are known (*4, 8*). An interesting finding of this study, which may be implicated in the mechanism which leads to negative isotope effects in partition systems, was that the deuterated carbohydrate derivatives always showed appreciably more band broadening than the corresponding protium forms. For example, β-glucose-d_7 gave a plate value of 31,000 on the 15-meter SE-30 column, whereas 40,000 plates were calculated for the adjacent β-glucose on the same chromatogram (see Figures 1 and 2, *A*). This characteristic difference in plate efficiency for deuterium and protium forms, which was independent of the nature of the liquid phase, cannot be accounted for by differences in retention time. It is possible that the observed band broadening is caused by differences in gaseous diffusion of the protium *vs.* the deuterium forms.

The separation factors (Table II) for various protium-deuterium pairs in the carbohydrates studied thus far are extremely low in some instances but do not necessarily preclude the possibility that gas chromatography might eventually be of some use for isotope abundance measurements of mixtures containing the fully carbon-substituted deuterium forms. Present evidence suggests that a column of either SE-30 or Apiezon M will be effective with most of the carbohydrates tested, provided its column efficiency is at least 200,000 plates. Spencer (*15*) has reported that plates increase relatively linearly with length in narrow-bore packed columns; he has obtained slightly more than 10^6 plates with a column 460 meters in length.

The factors which affect retention behavior of deuterated sugars are not applicable to isotope-labeled compounds in general. For example, the best column for resolving β-glucose and β-glucose-d_7 was completely ineffective with a mixture of glucose and uniformly labeled glucose-C^{13}. A mass difference of 6 parts in 546 in this case, as compared with 7 parts in 547 with the deuterium compound, made little difference between the apparent partition coefficients of glucose and glucose-U-C^{13}. Furthermore, no separation of the N-trifluoroacetyl n-butyl esters of glycine-N^{14} and glycine-N^{15} could be demonstrated on the 15-meter SE-30 column.

NOMENCLATURE

Glucose-d_7 = D-glucose-1,2,3,4,5,6,6-d_7
Mannose-d_7 = D-mannose-1,2,3,4,5,6,6-d_7
H = height of theoretical plates
k = partition ratio = t_R'/t_S
n_{req} = theoretical plates required to achieve 98% resolution of a given component pair = $16 \times \left(\frac{\alpha}{\alpha - 1}\right)^2 \left(\frac{k+1}{k}\right)^2$
R = peak resolution = $\frac{t_R'{}_{(H)} - t_R'{}_{(D)}}{{}^1/_2[w_{b(D)} + w_{b(H)}]}$

t_R' = adjusted retention time, measured from solvent peak

t_S = retention time of solvent, from injection

w_b = peak width at base

α = relative volatility = $\frac{t_R'{}_{(H)}}{t_R'{}_{(D)}}$

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Use of Binomial Probability Distribution Tables for Calculation of Withdrawn Series of Countercurrent Distribution

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▶ The application of the Pascal distribution to the single withdrawal, simultaneous withdrawal, and diamond pattern in countercurrent distribution is discussed. The Pascal distribution equation is converted to the binomial with changed *n* and *r*. This makes it possible to calculate the theoretical distribution of solute in a withdrawn series of either phase from standard Binomial Probability Distribution tables or from more recent tables of the Negative Binomial Probability Distribution.

THE WITHDRAWN SERIES of the single withdrawal procedure in countercurrent distribution (CCD) follows a Pascal distribution (*11*), the *r*th term of which may be represented as (*6*)

$$T_{u,r} = \frac{(u+r)!}{r!\,u!}\left(\frac{K}{K+1}\right)^{u+1}\left(\frac{1}{K+1}\right)^{r} \quad (1)$$

$T_{u,r}$ in Equation 1 is the fraction of the total solute emerging in the *r*th withdrawal from the distribution apparatus having number of tubes equal to u, and K is the partition coefficient. By substituting different values of r starting from 0, the entire withdrawal pattern can be calculated from the equation. Hence, Equation 1 is analogous to the equation presented by Williamson and Craig (*15*) for the calculation of the "binomial" distribution.

Equation 1 also holds good in case of a withdrawal procedure where, the fundamental distribution being completed, both the upper and lower phases are simultaneously withdrawn from both sides of the apparatus after each transfer without adding further solvent. This type of withdrawal procedure will subsequently be referred to as simultaneous withdrawal to differentiate it from Craig's double withdrawal (*4*) where the phases emerge on every second transfer. However, it was referred to as double withdrawal by one of the present authors (*6*) after Karlson and Hecker (*7*), whose "Zweiphasige Entnahme" should have been correctly translated to "Two Phase Withdrawal." The upper phase series withdrawn from one side of the apparatus should follow Equation 1. By interchanging $K/(K+1)$ and $1/(K+1)$, Equation 1 becomes applicable to the series of the lower phases simultaneously withdrawn from the other side of the apparatus.

The Pascal distribution is also applicable to the "diamond pattern" distribution (*2*), as this is a form of simultaneous withdrawal procedure where the transfers are continued until all the upper phases have been equilibrated with all the lower phases. The equations of Karlson and Hecker (*7*) and of Newton and Abraham (*9*, *10*) regarding the distribution pattern of the single withdrawn series are readily obtainable from the Pascal distribution.

In a laboratory where Craig's automatic countercurrent distribution apparatus with hundreds of tubes (*3*, *5*) is not available, a series of separatory funnels or a manually driven apparatus with a comparatively small number of tubes can be more profitably applied if withdrawal procedures are adopted (*2*). A more detailed application of the Pascal distribution than has heretofore been made should facilitate the withdrawal procedures.

In a previous communication (*6*), one of the present authors has presented an equation relating partition coefficient of the distributed material with the peak of the Pascal distribution curve. Karlson and Hecker (*7*) have reduced their equation to a form adaptable to a calculating machine, as did Lieberman (*8*) for the binomial distribution.

Though much trouble can be avoided by use of a calculating machine, considerable "manual" computation is still necessary. Moreover, the method suffers the disadvantage that any initial error will affect all subsequent calculations. Since the binomial is a statistical distribution, Way and Bennett (*14*) suggested the use of the B.P.D. tables (*12*) for calculating the distribution pattern of a fundamental CCD procedure. They used tables of n from 2 to 49 and referred to similar tables having a range of n up to 150.

Recently Alderton (*1*) presented a method of calculating distribution patterns from the tables of cumulative binomial distribution (*13*) in which values of n are given up to 1000. We will now discuss the relationship between the Pascal and the binomial distribution and how the B.P.D. tables can be used for the calculation of the distribution of solute in a withdrawn series.

Equation 1 can be represented in terms of p and q as

$$T_{u,r} = \frac{(u+r)!}{r!\,u!}\,p^{u+1}q^{r} \qquad (2)$$

which can be written as

$$T_{u,r} = p\left[\binom{u+r}{u}p^{u}q^{r}\right] \qquad (3)$$

The expression within the brackets of the right hand side of Equation 3 is essentially the uth term of a binomial distribution having number of transfers $(u + r)$. The terms p and q generally used in extraction procedures (*2*, *11*) mean the fraction of solute transferred to the upper phase and that remaining in the lower phase, respectively, and $p + q = 1$. In terms of partition coefficient they can be represented as $K/(K + 1)$ and $1/(K + 1)$ only when the volume ratio of the solvents used equals unity. In case of unequal volumes, $p = KV_x/(KV_x + V_y)$ and $q = 1 - p = V_y/(KV_x + V_y)$, respectively (*2*).

By interchanging p and q in Equation 2, the terms for the lower phase series withdrawn from the apparatus can be evaluated in an analogous manner

$$T'_{u,r} = \frac{(u+r)!}{r!\,u!}\,p^{r}q^{u+1} \qquad (4)$$

Equation 4 can be rearranged as

$$T'_{u,r} = q\left[\binom{u+r}{r}p^{r}q^{u}\right] \qquad (5)$$

Equation 5 also involves the rth term of a binomial distribution having number of transfers $(u + r)$.

Now to evaluate the terms of a Pascal distribution, the corresponding values of the binomial distribution with modified n and r values should be found from the B.P.D. tables and multiplied by p or q (cf. Equations 3 and 5). For example, when $u = 5$ and $p = 0.4$, to find the fraction of solute distributed in the fourth withdrawal of the upper phase—i.e., at $r = 4$—B.P.D. tables should be consulted for a value having $n = 9$ and $r = 5$ and $p = 0.4$—viz., 0.1672151. (The terms n and r of the B.P.D. tables should not be confused with those in the present context.) This fraction when multiplied by 0.4 (= p) gives the required result—viz., 0.06688604. The corresponding value presented by Bush and Densen (*2*) is 0.0666, for their fraction 5. The former value should be more accurate as it was calculated from the figure of the B.P.D. tables correct to the 7th decimal place.

The B.P.D. tables should be consulted for both the changed n and r values to evaluate the upper phase withdrawn series, but in case of evaluating the lower phase withdrawn series r remains unchanged. Thus, to calculate the distribution of the lower phase series at $r = 4$, having $u = 5$ and $p = 0.4$, B.P.D. tables should be consulted for a value having $n = 9, r = 4$, and $p = 0.4$—viz., 0.2508226. This multiplied by 0.6 (= q) gives the required value, 0.15049356. Bush and Densen (*2*) showed the corresponding value to be 0.1507 for their fraction 8.

In order to obtain the corresponding $T_{u,r}$ values for p greater than 0.5 it is only necessary to interchange the values of p and q and those of the r and $(n - r)$ terms. Equations 3 and 5 are reduced to (3a) and (5a), respectively.

$$T_{u,r} = q\left[\binom{u+r}{r}q^{r}p^{u}\right] \qquad (3a)$$

$$T_{u,r} = p\left[\binom{u+r}{u}q^{u}p^{r}\right] \qquad (5a)$$

The B.P.D. tables can now be referred to with these revised values. Thus to calculate the $T_{u,r}$ value of $u = 19, r = 11$, and $p = 0.52$, the binomial term for $n = 30, r = 11$, and $p = 1 - 0.52 = 0.48$ should be found and multiplied by 0.48 (see Equation 3a).

Since the range of values of p and q in the table is from 0.01 to 0.5 at intervals of 0.01, it provides a wide range of values for p and allows accurate plotting of theoretical distribution patterns of a withdrawn series of either phase.

Alternatively, Equation 1 may be rearranged to make use of recent and extensive tables of the negative binomial distribution by Williamson and Bretherton (*16*).

$$T_{u,r} = \binom{u+r}{u}p^{u+1}q^{r} = \binom{k+r-1}{k-1}p^{u}q^{r} \qquad (6)$$

where $k = u + 1$. The right hand side of Equation 6 is given in these tables to 6 decimals for various n, k, and p. Using these tables eliminates the single multiplication necessary when using standard B.P.D. tables.

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Fluorometric Microdetermination of Heme Protein

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▶ A fluorometric method is described for the measurement of as little as 0.01 μg. of heme protein in animal tissues. The method is based upon conversion of the protein's heme moiety to its fluorescent porphyrin derivative by incubation with oxalic acid. The relative standard deviation with the proposed procedure is about 2%. The simplicity of the procedure and the stability of the fluorescence facilitate the measurement of a large number of samples. The determination of heme proteins in biopsy material from several organs has been shown to be primarily dependent on the hemoglobin concentration.

IN QUANTITATIVE histochemical studies of tissues, a method was needed for measuring as little as 0.01 μg. of heme protein in biopsy specimens in order to estimate the contribution of whole blood to other biochemical measurements. In a simple procedure which has the required sensitivity when used with a photomultiplier-type fluorometer, the heme moiety of heme proteins is converted into a stable porphyrin derivative.

Zade-Oppen (*5*) reported an adaptation of the colorimetric method of Drabkin (*2*) which measures dilute solutions of cyanmethemoglobin prepared from washed red blood cells. By modifying this procedure to measure the cyanmethemoglobin formed in microcuvettes with a final volume of 50 μl., as little as 0.5 μg. of hemoglobin could be measured. However, because of the development of turbidity due to protein in the final reaction mixture, this method is not satisfactory for analysis of hemoglobin in tissues other than whole blood where the ratio of heme protein to total protein is high. The fluorometric procedure described has the advantage of a greater ultimate sensitivity and can be used to measure tissues which have a low ratio of heme protein to total protein.

EXPERIMENTAL

Reagents and Equipment. Oxalic acid, analytical grade, is washed with redistilled water, 100 ml. of water per 50 grams of oxalic acid, at 4° C. A saturated solution of oxalic acid is then made up at room temperature in order to obtain a solution which is approximately 2 molar.

Standard hemoglobin solutions with concentrations between 0.005 and 0.05 mg. per ml. are prepared in $0.1M$ phosphate buffer, pH 7.4, containing 0.05% bovine plasma albumin (Sigma Co., St. Louis). In the absence of added albumin, dilute hemoglobin standards cannot be stored and even fresh standards give erratic results. The hemoglobin for these standards is obtained from red blood cells which are washed in isotonic saline and lysed in 100 volumes of redistilled water. The solution is centrifuged to remove erythrocyte ghosts. This concentrated preparation of hemoglobin is standardized spectrophotometrically after conversion to cyanomethemoglobin (*1*). Dilute standards are stable for at least two months when stored at −20° C.

Solutions with 0.1 to 1.0 μg. per ml. of coproporphyrin-1-tetramethyl ester (Sigma Co., St. Louis) are prepared in $0.1N$ hydrochloric acid. These standards are not essential, but may be convenient to control instrument settings during fluorescence measurements.

Lang-Levy pipets (*3*, *4*) are used throughout.

Fluorometer tubes are selected from 7.5 × 50 mm. shell vials (Kimax, No. 60935-L, A. S. Aloe Co., St. Louis) and for larger samples from 10 × 75 mm. serological tubes (Corning No. 9820, A. S. Aloe Co., St. Louis). Tolerances are kept within 1 or 2% for the outer diameter. The fluorometer tubes must be very carefully cleaned before use. The following procedure is recommended: two rinses with detergent, two with water followed by heating in half concentrated nitric acid at 100° C. for 30 minutes, and then three rinses with distilled water.

The Farrand fluorometer is suitable for measuring the fluorescence. An adapter is necessary to hold tubes of 7.5 × 50 mm. in size.

A small autoclave was most convenient for incubation of samples. However, tubes may be placed in a water bath at 100° C. if care is taken to ensure uniform heating to be certain that evaporation is equal from each tube. This is best accomplished in a circular pan with a circular rack made to hold tubes equidistant from the center of the pan where the source of heat is applied. Covering the pan and the rack with aluminum foil but leaving the upper two thirds of each tube exposed allows the temperature of the boiling water to approach 100° C. and decreases evaporation from the exposed portion of the uncovered tubes.

Procedure. The description given below is applicable to tissues containing 0.01 to 0.10 μg. of heme protein. Frozen dried sections of tissue are weighed on a quartz beam balance. Sections weighing 1.0 to 20.0 μg. are placed along the bottom rim of 1-ml. fluorometer tubes, 7.5 × 50 mm. Into each tube are pipetted 5 μl. of $0.02N$ NaOH in such a manner that the solution flows over the section. The tubes are kept at room temperature for 15 minutes to allow the proteins to solubilize after which 200 μl. of $2M$ oxalic acid solution are added. If homogenates are used, NaOH treatment is not necessary and 5 μl. of homogenate are pipetted into the 1-ml. fluorometer tubes before adding the oxalic acid solution. When handling a large number of tubes it is necessary to add the oxalic acid solution rapidly by using an automatic syringe. Solutions may be thoroughly and rapidly mixed by use of a mechanical "buzzer" (*3*). Within 10 minutes of adding the oxalic acid, the rack of tubes is loosely covered by a sheet of aluminum foil and placed in an autoclave which has been preheated so that the tubes can be exposed to a temperature of over 100° C. without delay. The tubes are autoclaved for 30 minutes at about 120° C. (15 lb. per square inch) after which the heating unit of the autoclave is shut off. In order to minimize changes in volume, the inner chamber of the autoclave is opened only after the autoclave has cooled for about 30 minutes and the pressure of the inner chamber has fallen considerably. The samples may be read in a fluorometer after cooling for 15 minutes at room temperature. The fluorescence of solutions is stable for over 24 hours at room temperature in daylight.

Standards are prepared by adding 5 μl. of standard hemoglobin solutions to 1-ml. fluorometer tubes. Standard blanks are prepared by adding 5 μl. of phosphate buffer with bovine plasma albumin to 1-ml. fluorometer tubes. Blanks for dried sections contain 5 μl. of $0.02N$ NaOH and for homogenates, 5 μl. of the solution in which homogenates are prepared. The standards, standard blanks, and tissue blanks are carried through the entire analytical procedure. The above tissue blanks are satisfactory for measurement of total tissue heme protein but if the procedure is to be utilized to measure accurately total tissue hemoglobin, tissue blanks may be prepared which contain appropriate amounts of tissue from organs which have been perfused with saline to remove circulating red blood cells.

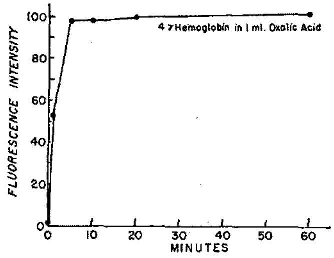

Figure 1. Rate of fluorescence development at 120° C.

The λ 410-mμ mercury line, isolated with Corning filter No. 5113, is used as the exciting source. The secondary filter is Corning No. 2424, a cutoff filter with 50% transmittance at about λ 600 mμ. All samples may be read against one of the standards or against a coproporphyrin I solution in 0.1*N* HCl.

The procedure may be readily adapted to larger samples by appropriate selection of tube size and reagent volumes. In making such changes, it should be remembered that the ratio of homogenate or dilute NaOH volume to oxalic acid volume should be less than 1 to 20 and that over 0.5 μg. heme protein per ml. of oxalic acid solution produces quenching of the fluorescent solution. For example, 0.05 to 1.50 μg. of heme protein in dry sections weighing 5 to 100 μg. may be treated with 25 μl. of 0.02*N* NaOH and incubated in 1 ml. of 2*M* oxalic acid using standard 10 × 75 mm. fluorometer tubes which can be used in the Farrand fluorometer without a special adapter.

DISCUSSION AND RESULTS

The details of the proposed fluorometric procedure were worked out in studies using hemoglobin while the validity of the method was evaluated using tissue from several organs and purified heme proteins.

Upon treatment of heme proteins with certain acids, the iron is removed from the heme moiety with the result that fluorescence of the porphyrin derivative develops. Of several acids studied, hypophosphoric acid and oxalic acid were found most capable of developing the fluorescence of hemoglobin. Oxalic acid was superior to hypophosphoric acid for microanalyses because it gives a higher ratio of porphyrin fluorescence to reagent blank fluorescence. The fluorescence intensity increases markedly with increasing acid concentration. The concentrations of oxalic acid solution most effective in developing the fluoresence of hemoglobin are between 1.8 and 2.0 molar. Consequently, the volume of 2*M* oxalic acid utilized in a reaction should be at least 20 times greater than either the volume of homogenate utilized or the volume of 0.02*N* NaOH added to solubilize the protein in dried tissue.

Concentrated solutions of heme protein were used to study the rate of development of fluorescence in oxalic acid. Incubating at temperatures between 98° C. and 125° C., fluorescence of 4 μg. of hemoglobin in 1 ml. of oxalic acid is fully developed after 30 minutes and additional incubation does not lead to a change in fluorescence (Figure 1). Following incubation, the fluorescence of the final solution is stable at room temperature in daylight for over 24 hours and upon exposure to ultraviolet light loses fluorescence very slowly.

A critical point in the procedure is the interval between the addition of 2*M* oxalic acid to fluorometer tubes containing solutions of heme protein and the onset of incubation. The longer this interval at room temperature, the lower the fluorescence of the final incubated solution. The loss in ultimate fluorescence of the pre-incubation mixture of heme protein and oxalic acid is almost linear during the first 30 minutes at room temperature and amounts to approximately 15% but thereafter the rate of loss becomes progressively less rapid. Consequently, it is important to add oxalic acid solution rapidly to tubes containing heme protein so that the mixed solutions remain at room temperature for less than 10 minutes before incubation is begun. In view of the stability of fluorescence between 30 and 60 minutes at 120° C. (Figure 1) and for at least 24 hours at room temperature after incubation, this preincubation effect is difficult to explain. It is not related to alterations in protein produced by 2*M* oxalic acid inasmuch as the effect was also observed in the absence of protein by using solutions of crystalline hemin or acid hematin prepared from blood which had been treated with 3:1 ethyl acetate and glacial acetic acid to remove the protein.

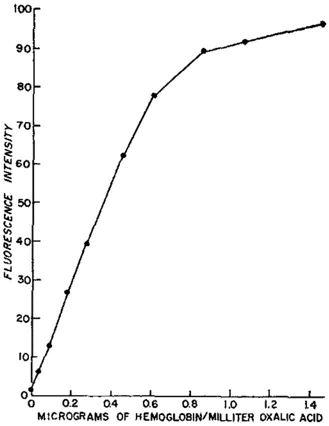

Figure 2. Standard curve for hemoglobin

Slight turbidity appears after incubation of oxalic acid solutions containing large amounts of brain, liver, pancreas, and kidney. This does not appear to interfere with fluorometric readings inasmuch as the turbidity can be largely removed without altering fluorescence by "buzzing" the oxalic acid solution with a small amount (10 μl. per 200 μl. of oxalic acid solution) of ether.

Filters for the fluorometer were chosen which produced the highest ratio of porphyrin fluorescence to reagent blank fluorescence. The primary filter isolates the Sorêt band, λ 410 mμ, which is the exciting wavelength giving the maximum red fluorescence of porphyrins. The secondary filter permits transmission of the red fluorescent bands, all of which are above λ 600 mμ. The loss of sensitivity entailed by measuring only the red fluorescence is compensated by a greater specificity.

Quenching becomes marked at concentrations of hemoglobin greater than 1.0 μg. per ml. of oxalic acid solution but

Table I. Precision and Recovery

	Heme protein found, mμg.				Heme protein found, mμg.		
	Tissue[a] alone	Tissue plus Hgb[a]	Calculated[b] total		Tissue[a] alone	Tissue plus Hgb[a]	Calculated[b] total
Testes	9.8	43.7	47.8	Kidney	44.9	83.8	83.0
	10.0	41.5	47.8		44.9	82.7	83.0
	10.0	44.7	47.8		45.7	82.8	83.0
	9.7	42.8	47.8		45.1	83.2	83.0
Brain	16.6	54.1	54.5	Liver	100.1	131.6	134.8
	16.5	53.1	54.5		96.2	130.0	134.8
	16.5	52.4	54.5		97.7	131.0	134.8
	16.8	50.1	54.5		93.5	134.1	134.8
Pancreas	26.1	66.9	64.2	No tissue	...	37.6	37.8
	26.1	66.2	64.2		...	38.4	37.8
	26.9	65.4	64.2		...	37.6	37.8
	26.0	65.3	64.2		...	38.1	37.8

[a] 13.1 μg. of each tissue was used as a homogenate either alone or mixed with 0.0378 μg. hemoglobin (Hgb) as indicated.
[b] Calculated using average of tissue alone values.

the fluorescence-concentration curve is linear up to 0.5 μg. per ml. (Figure 2).

Validation of Method. The relative standard deviation with the proposed procedure is about 2% with quantities as small as a few hundredths of a microgram of hemoglobin (Table I.) Even with 0.01 μg. hemoglobin in 200 μl. of final volume it is only about 5%. Fresh specimens of testes, brain, pancreas, kidney, and liver from rats sacrificed by decapitation were analyzed with and without amounts of added hemoglobin. Recovery of 0.0378 μg. of hemoglobin added to 13.1 μg. of the different tissues as homogenates is satisfactory (Table I).

A comparison was made between the proposed fluorometric procedure and the colorimetric method of Zade-Oppen (*5*) for the determination of dilute hemoglobin solutions by means of parallel determinations of the total hemoglobin in ten samples of whole blood collected in heparinized tubes. Dilute solutions of each sample containing about 5 mg.% hemoglobin were prepared by mxiging 35 μl. of whole blood with 100 ml. of redistilled water. This dilution reduces the concentration of plasma proteins to a level which will not create turbidity that is a problem in the colorimetric procedure. For the colorimetric procedure, 4 ml. of each dilute hemoglobin solution was mixed with 0.1 ml. of a freshly prepared solution containing 0.08 gram $NaNO_3$, 2.08 mg. KCN, and 0.04 gram $NaHCO_3$ per ml. Twenty minutes after mixing of these solutions, absorbance at λ 420 mμ was measured. The fluorometric analyses were performed on 3-μl. aliquots of each dilute hemoglobin solution mixed with 1 ml. of $2M$ oxalic acid immediately before incubating in an autoclave. The paired *t* test revealed no significant difference between values obtained by the two methods; $0.1 < p < 0.2$ (Table II).

Table II. Comparison of Fluorometric and Colorimetric Methods on Ten Blood Samples

Hemoglobin per 100 ml. of water, mg.

	Fluorimetric	Colorimetric	Difference
	2.91	3.08	+0.17
	3.02	2.97	−0.05
	3.24	3.20	−0.04
	4.11	4.01	−0.10
	4.54	4.41	−0.13
	4.83	5.02	+0.19
	5.44	5.42	−0.02
	5.51	5.63	+0.12
	5.69	5.83	+0.14
	6.37	6.42	+0.05
Av.	4.57	4.60	+0.03 ± 0.019[a]

[a] Standard error of difference.

Table III. Comparison of Heme Proteins in Unperfused and Saline Perfused Organs

	μg. of Heme protein per mg. fresh weight		Heme protein removed by perfusing organs with saline, %
	Unperfused biopsy	Perfused organ	
Pancreas	4.26	0.41	90.5
Brain	2.91	0.29	90.4
Psoas muscle	4.56	0.47	89.7
Testes	1.73	0.20	88.4
Lung	5.34	0.87	83.7
Kidney	4.53	0.89	80.3
Liver	7.37	2.53	65.7
Heart	5.48	2.30	58.9

The heme proteins in tissues which can be expected to contribute to the fluorescence of incubated oxalic acid solutions with the proposed fluorometric procedure include the hemoglobins, myoglobins, cytochromes, catalases, and the perioxidases. Unless tissues are perfused with solutions containing anti coagulants to remove circulating erythrocytes, the major heme protein measured upon analysis of all tissues will be hemoglobin. In order to determine to what extent hemoglobin contributes to the fluorescence of tissue analyses, heme protein determinations were made of various tissue biopsies taken from four rats under ether anesthesia and from four rats which had been heparinized, sacrificed under anesthesia by cardiac excision, and perfused through the ascending aorta with 500 ml. of normal saline containing heparin. Perfused tissues were blotted free of excess water prior to weighing. As demonstrated in Table III where the average of total heme proteins in various organs from the four unperfused rats are compared with those from the four perfused rats, the major heme protein in unperfused tissues is hemoglobin. Consequently, in tissue biopsies, the proposed fluorometric procedure is primarily a determination of hemoglobin in the tissues. This is especially true for lung, brain, kidney, testes, skeletal muscle, and pancreas in which it was revealed that over 80% of the heme protein present in the unperfused organ is hemoglobin.

The relative fluorescence of several heme proteins incubated in $2M$ oxalic acid differs quantitatively. The fluorescence with different filter combinations may be of interest (Table IV). The secondary filter in all cases was Corning No. 2424. The fluorescences are recorded as per cent of that obtained with the same weight of heme protein (0.4 μl. per 1 ml. of $2M$ oxalic acid) and are expressed relative to hemoglobin with the same filter combination. The filter combination in the first column is that recommended in the proposed procedure. Data are to be considered only approximate. Except for cytochrome C, the relative fluorescent values which were determined compare reasonably well with values calculated on the basis of molecular weights and atoms of iron per mole of heme protein. Bilirubin produces about one four-hundredth the fluorescence of an equal weight of hemoglobin.

By substituting fluorometry for colorimetry in the measurement of heme proteins it is easy to obtain high sensitivity without sacrifice of precision. No attempt has been made to attain maximal sensitivity. Merely reducing the volumes fourfold—a completely feasible change—would increase the useful sensitivity four times (since the reagent blank is the present limiting factor and is equivalent to 0.01 μg. of heme protein per ml. of oxalic acid).

Table IV. Fluorescence of Heme Proteins Relative to That of Hemoglobin

Primary filter[a]	5113	4010 + 5120	5860	Calculated relative fluorescence[b]
Exciting wave length	436 mμ	546 mμ	365 mμ	
Hemoglobin	100	100	100	100
Myoglobin	93	108	87	100
Peroxidase	45	49	38	39
Catalase	26	25	22	30
Cytochrome C	27	27	19	131

[a] Corning filter numbers.

[b] Based upon molecular weight and atoms of Fe per mole of heme protein.

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Application of Lithium-Drifted Germanium Gamma-Ray Detectors to Neutron Activation Analysis

Nondestructive Analysis of Aluminum

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▶ A lithium - drifted germanium gamma-ray spectrometer has been utilized for the nondestructive analysis of aluminum by the method of neutron activation. Because of the much higher resolving power of these semiconductor detectors in comparison to the widely used sodium iodide scintillators, a marked simplification is achieved in the analysis of samples yielding complex gamma-ray spectra. In this work, fractional parts-per-million concentrations of Mn, Sc, Hf, and Cr were readily detected and analyzed nondestructively in 99.9999% aluminum.

IN RECENT years, the technique of activation analysis utilizing gamma-ray detection has received considerable attention and has been shown to have important applications to a wide variety of analytical problems. Of the many features tending to make the technique attractive, perhaps the most important are: very high sensitivity for many elements, elimination of need for reagent blanks common to many other analytical techniques, and lack of interference from neighboring elements (since the decay properties of radioactive isotopes are unrelated to their chemical properties). With the development of large sodium iodide scintillation detectors and lower-cost multichannel pulse-height analyzers, the technique has been put within reach of most laboratories.

However, in many practical situations, the use of activation analysis has not been attractive because of the laborious procedures that are required, for example, for the simultaneous determination of several elements in the same sample. Practical samples containing a number of readily activated elements generally yield complicated gamma-ray spectra, because of the production of several radioactive isotopes each of which may have a number of gamma-rays in its characteristic spectrum. Because of the poor intrinsic resolving power of sodium iodide scintillation detectors, there results a considerable overlap of gamma lines in the spectrum. In order to sort out and identify the component gamma-ray lines, it is necessary either to employ elaborate and time consuming chemical separations or to resort to indirect methods such as the "synthetic analysis" of the spectrum with use of complex computer programs (*2*).

Recently, a significant advance in the field of gamma-ray spectroscopy has taken place, with the development of semiconductor detectors that have very much higher resolving power than the widely-used NaI scintillators and yet are moderately sensitive to gamma rays. It is possible with the use of these lithium-drifted germanium [Ge(Li)] detectors to distinguish gamma rays differing in energy by as little as 2 to 4 k.e.v. in complex gamma-ray spectra, and to determine their absolute energies to better than 0.5 k.e.v. Because of the high resolution, individual photopeaks stand out more distinctly over background radiations, and thus it is possible to detect relatively weaker gamma lines in a spectrum than can be done with scintillation detectors.

These properties have aroused our interest in the application of Ge(Li) detectors to problems in activation analysis, especially to nondestructive analysis, where the high available resolution would appear to allow wider application of the technique as well as an improvement in sensitivity.

To investigate these possibilities, we have considered the analysis of high-purity aluminum by neutron activation, a problem that has been given considerable attention. For a review of previous activation analyses of high-purity aluminum, the reader is referred to the paper by Chinaglia and Malvano (*3*) on a nondestructive analysis and that of Gaittet and Albert (*5*) on a destructive analysis. In this report we discuss and compare the results of our nondestructive analysis using Ge(Li) detectors with previously reported nondestructive analyses.

EXPERIMENTAL

The detector used in the present study was prepared in this laboratory and has dimensions 6 sq. cm. × 9 mm. (active thickness). The detector is operated in vacuum at approximately 77° K., with a bias voltage of 720 volts. For a comprehensive description of the characteristics and fabrication of lithium-drifted germanium detector systems, the reader is referred to the reports of Ewan and Tavendale (*4*), Goulding (*6*), Goulding and Hansen (*7*), Hansen and Jarrett (*9*), and Miner (*12*).

A sectional view of a typical detector assembly is shown in Figure 1 and a picture is reproduced in Figure 2. The detector is mounted on a copper plate that makes thermal contact with a liquid nitrogen reservoir cryostat. A Varian VacIon pump is used to provide a pressure of approximately 2×10^{-5} micron in the detector chamber. The front window of the detector chamber is aluminum, of thickness 0.020 inch (137 mg./sq. cm.). The associated electronics consists of a low-noise, low capacity preamplifier and biased amplifier system designed by Goulding and Landis (*8*) and constructed at this laboratory. Pulses from this system are routed to an RIDL 400 channel pulse-height analyzer for sorting.

The photopeak efficiency function of the detector for gamma rays of various energies was obtained by counting standardized sources of Hg^{203}, Na^{22} Na^{24}, and Au^{198} under the experimental conditions used for the activation analysis samples. The absolute disintegration rates of these standard sources were obtained by a coincidence method (*1*). The resulting experimental photopeak efficiency curve is shown in Figure 3 along with the corresponding curve for a 3 × 3 inch (diameter) NaI(Tl) crystal. The latter curve was constructed from the data given by Heath (*10*). In the case of the Hg^{203} 279-k.e.v. line, the efficiency of the Ge(Li) detector relative to that of the NaI(Tl) detector (with the source located at a distance of approximately 2.5 cm. from the face of the detector) was 1.3×10^{-2}.

In Figure 4 are shown curves relating the observed line widths of gamma rays as a function of gamma-ray energy for a Ge(Li) detector of dimensions 2 sq. cm. × 7 mm. (active layer) and a 3 × 3 inch (diameter) NaI(Tl) crystal. The larger Ge(Li) detector used in the present work showed a line width of about 4 k.e.v. (full width at half maximum) for the 122-k.e.v. gamma ray of Co^{57}, as compared to about 2 k.e.v. for the smaller detector.

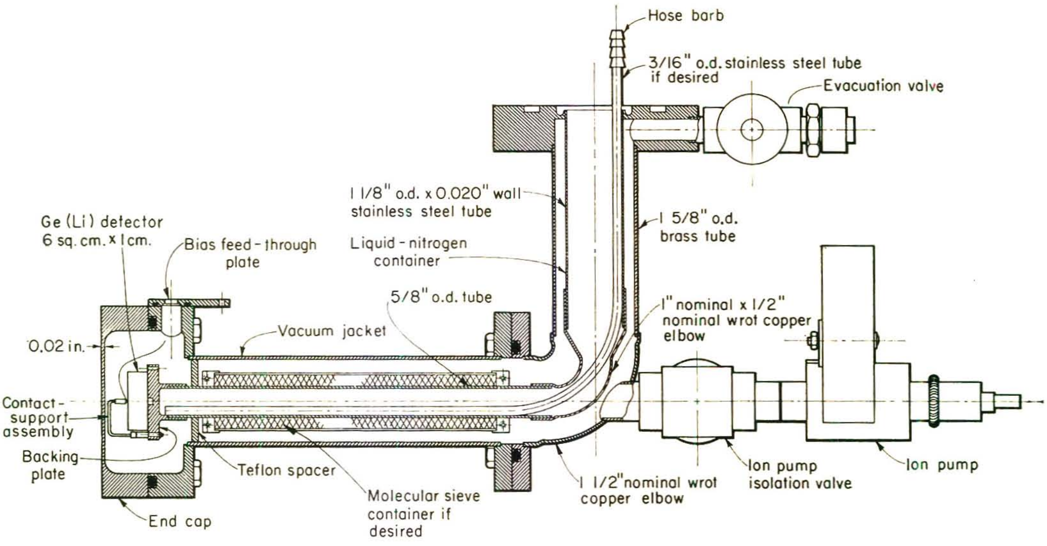

Figure 1. Schematic diagram of Ge(Li) detector assembly

Table I. Characteristics of LPTR Reactor Irradiation Positions

Position	Thermal flux	Cadmium ratio	Flux, $E_n >$ 3.3 m.e.v.
S-1	5.1×10^{12} n/sq. cm. sec.	11	1×10^{11} n/sq. cm. sec.
S-2	3.4×10^{12}	8.3	$2-3 \times 10^{10}$

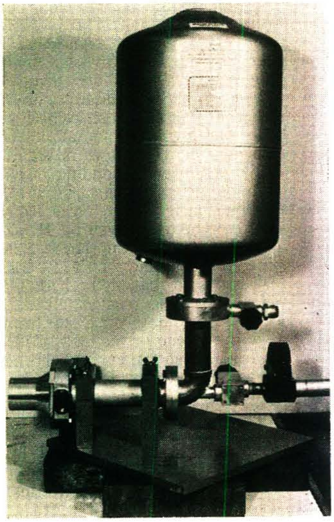

Figure 2. Photograph of Ge(Li) detector assembly

These line widths are to be compared with a width of about 20 k.e.v. typical of the response of NaI(Tl) detectors at this energy.

The aluminum samples, which ranged from aluminum wire of unspecified purity to 99.9999% aluminum ingots, were prepared for irradiation by etching in concentrated HCl to remove surface contamination. The samples were then packaged in polyethylene film or sealed in quartz tubes along with the appropriate standards. Neutron irradiations were carried out in the Livermore LPTR reactor. Irradiation periods ranged from 2 hours to 90 hours. After irradiation the samples were again cleaned by etching in concentrated HCl and then mounted on aluminum planchets for counting. Samples were generally available for counting within 3 hours after the end of irradiation. In order to prevent the detection of beta rays and internal conversion electrons, the samples were counted through a 675 mg./sq. cm. aluminum absorber.

The pertinent characteristics of the reactor irradiation positions used in these studies are given in Table I.

RESULTS AND DISCUSSION

Short Irradiations: Analysis of Copper, Manganese, and Gallium in Aluminum. In order to determine impurities in the aluminum giving rise to short-lived activities, several samples of aluminum of different purities were irradiated for 2-hour periods in the LPTR reactor. The gamma-ray spectra of these samples indicated the presence of Cu^{64}, Mn^{56}, Ga^{72}, and Na^{24}.

Examples of gamma-ray spectra obtained from the 2-hour irradiation of aluminum wire of unspecified purity in position S-1 of the reactor are shown in Figure 5. Spectra *A* and *B* were obtained with the Ge(Li) detector and spectrum *C* with a good 3 × 3 inch (diameter) NaI(Tl) detector.

The energy range used in the spectra of Figure 5 is 2500 k.e.v. Although most of the gamma rays are well resolved it is important to note that the full resolving power of the detector is not apparent because of this large energy range. In particular, it appears that the 834-

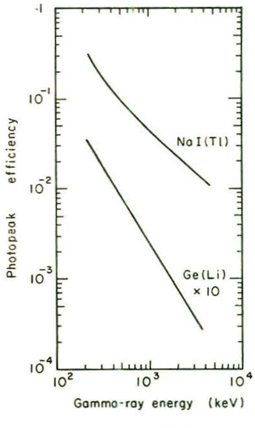

Figure 3. Photopeak efficiency curves for the Ge(Li) gamma-ray detector and a 3 × 3 inch (diameter) NaI(Tl) scintillator

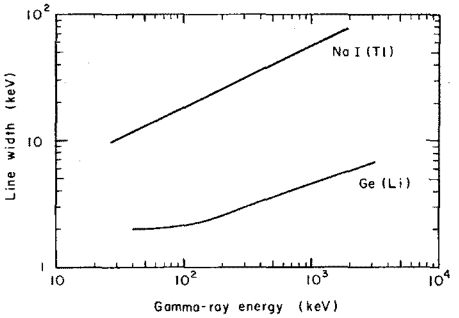

Figure 4. Comparison of gamma-ray line widths as a function of gamma-ray energy for a Ge(Li) detector and a 3 × 3 inch NaI(Tl) detector

k.e.v. line from Ga^{72} is not resolved from the 845-k.e.v. from Mn^{56}; that the detector is capable of resolving these lines is demonstrated in the insert to this figure in which a smaller energy interval is analyzed. This illustrates the practical point that although a 400-channel analyzer provides a sufficient number of channels for the low-resolution sodium iodide spectrum of an energy range as great as 2500 k.e.v., it is not adequate for a high-resolution spectrum. We normally use a maximum energy increment of 1.0 k.e.v. per channel with germanium systems in order to take full advantage of the available detector resolution.

Note also that the relatively weak line from Mn^{56} at 1815 k.e.v. is cleanly resolved from the 1729 k.e.v. "double escape peak" from Na^{24} in the Ge(Li) spectrum. The many resolved lines of Ga^{72}, although weak, illustrate the benefits of the improved resolution.

The results of the analysis of copper, manganese, and gallium in aluminum samples of four different grades are given in Table II. These were obtained by comparision of the intensities of the 511-k.e.v. line (Cu), 834-k.e.v. line (Ga), and the 849-k.e.v. line (Mn) in the spectra of the aluminum samples with the corresponding intensities obtained from standards that were irradiated simultaneously. Included in the table are the apparent concentrations of sodium impurity in two of the aluminum samples, as determined from the induced Na^{24} activity. The decay of these gamma-ray lines gave half-lives in good agreement with values reported in the literature for the decay of Cu^{64}, Ga^{72}, Mn^{56} (*13*). In this case a major fraction of the observed Na^{24} is actually due to the secondary reaction, $Al^{27}(n,\alpha)Na^{24}$. In the case of the sample of 99.9999% aluminum, this reaction accounts for more than 90% of the observed Na^{24}.

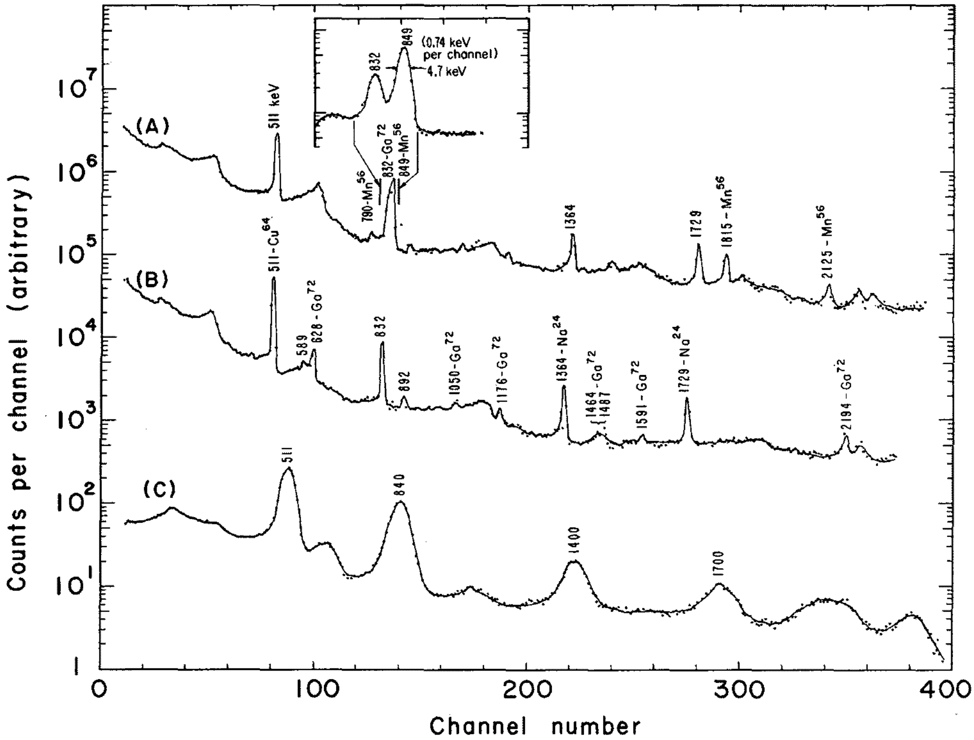

Figure 5. Gamma-ray spectra of activated aluminum wire

Spectra A and B were obtained with the Ge (Li) detector and spectrum C with a 3 × 3 inch (diameter) NaI(Tl) scintillator. Spectra taken at the following times after a 2-hour irradiation: A, 5.2 hr.; B, 54.7 hr.; C, 5.7 hr.

Long Irradiations: Analysis of Iron, Cobalt, Chromium, Hafnium, and Scandium in Aluminum. Samples of the aluminum wire and 99.9999% aluminum were irradiated for 90-hour periods in position S-1 of the LPTR reactor to enhance the longer-lived activities induced in the aluminum. After a decay period of about 10 days essentially all of the Na^{24}, Cu^{64}, and Ga^{72} had decayed and it was possible to observe gamma rays from Fe^{59}, Co^{60}, Cr^{51}, Hf^{181}, and Sc^{46} in the activated aluminum wire. The gamma-ray spectrum of the wire sample, taken two weeks after the end of irradiation, is shown in Figure 6. The spectrum shown in the upper part of this figure was taken with an analyzer setting of 3.6 k.e.v. per channel. For more detail, the various energy regions were also examined with a setting of 0.8–1.0 k.e.v. per channel; two such regions are shown in the lower part of the figure.

The gamma-ray spectra of the wire sample obtained with the smaller energy

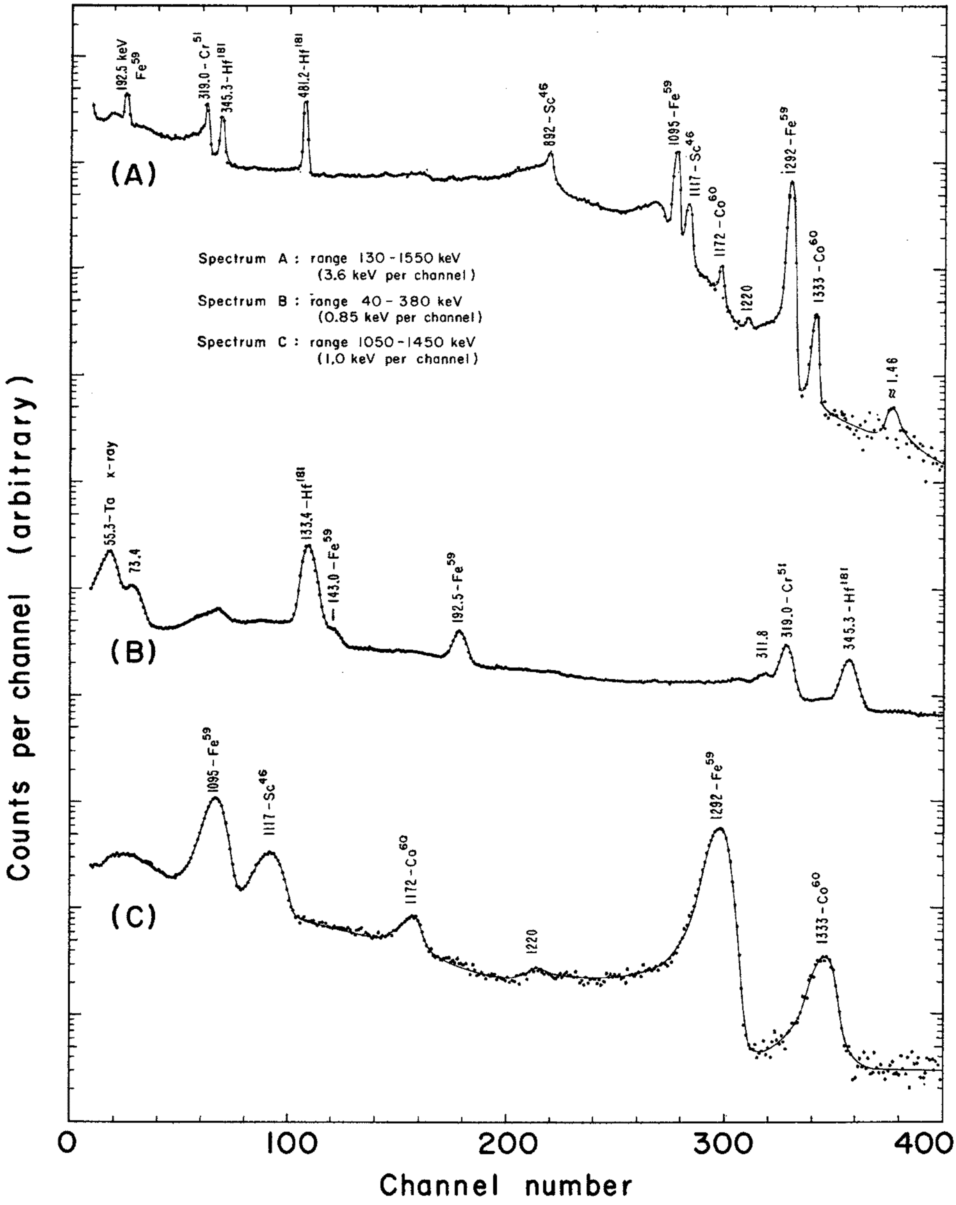

Figure 6. Gamma-ray spectra of the activated aluminum wire showing long-lived activities induced in sample

Spectra obtained with the Ge(Li) detector 16.4 days after end of a 90-hour irradiation

Table II. Results of Nondestructive Activation Analysis for Copper, Manganese, and Gallium in Four Grades of Aluminum

Sample	Sample weight	Irradiation position	Copper		Manganese		Gallium		Sodium	
			μg.	p.p.m.	μg.	p.p.m.	μg.	p.p.m.	μg.	p.p.m.
Al wire[a]	0.0714g	S-1	68	950[b]	0.26	3.7	14	200	15	210[c]
99.99% Al[d]	0.133	S-2	1.7	13[b]	0.029	0.22		<1.4[e]		...[f]
	0.5050	S-2	5.2	10[b]	0.12	0.25		<3.4[e]		...[f]
99.999% Al[d]	0.6918	S-2	0.79	1.1[b]	0.22	0.32		<0.14[e]	11	16[c]
	0.3706	S-2	0.39	1.1[b]	0.080	0.22		<0.19[b]	7.4	20[c]
99.9999% Al[d]	0.6072	S-2		<0.30[e]	0.13	0.22		<0.14[e]		...[f]
	0.5024	S-2		<0.40[e]	0.084	0.17		...[f]		...[f]

[a] Sample of unspecified purity.

[b] Calculations of copper concentrations have been corrected for contribution to the 511-k.e.v. photopeak from Na^{24}.

[c] Sodium concentrations are uncorrected for contribution from the reaction $Al^{27}(n,\alpha)Na^{24}$.

[d] Obtained with spectrographic analysis in the form of ingots from Cominco Products, Inc., Spokane, Wash.

[e] Upper limits correspond to the maximum concentration allowed by statistics (2σ limits) of the total counts in the region of the analyzed photopeak.

[f] Not determined.

interval per channel permitted the precise determination of the photon energies. These values are compared with literature values in Table III. Also apparent in the expanded spectra were a number of weak lines whose presence aided in the qualitative identification of several isotopes. Thus the 55.3-k.e.v. line (Ta K x-ray) and 133.4-k.e.v. line, as well as the prominent lines at 345.3 and 481.2 k.e.v., were readily assigned to the decay of Hf^{181} from their energies and relative intensities. Similarly, in the case of Fe^{59}, the assignments of the 1095-k.e.v. and 1292-k.e.v. lines to the decay of this isotope were confirmed by the observation of the weaker lines at 143.0 and 192.5 k.e.v. with the correct relative intensities. In addition to the impurities noted above, a weak line at 412 k.e.v. was observed in the earlier spectra and was assigned to the decay of Au^{198}. The gamma-ray spectra of the 99.9999% aluminum sample showed the presence of Cr^{51}, Hf^{181}, Au^{198}, and Sc^{46}. In Table IV we give the concentrations of the observed impurities calculated from the data described above.

It is interesting to note here a problem associated with the early use of the new Ge(Li) detectors that, from the point of view of analysis, is somewhat troublesome. Because of the high resolution one often observes gamma-ray lines that have not been reported previously because of their low intensities or because they were not resolved from other lines. In the experiment reported here we have observed lines at 73.4, 311.8, and 1220 k.e.v. which at present are unassigned.

Sensitivity Limits. It would naturally be of interest to place on a quantitative basis the sensitivity limits for various impurity elements in aluminum obtained by use of the Ge(Li) detectors and compare these with sensitivity limits obtained with use of sodium iodide scintillators. As yet no direct comparison has been attempted. Comparison between the results of this study with those reported in the literature (*3*, *11*, *15*) would not be justified because of possible differences in experimental conditions in the various studies (sample preparation, irradiation conditions, etc.). This is particularly true in the case of aluminum since the detectable limits of Cu^{64}, Mn^{56}, and Ga^{72} are dependent upon the Na^{24} activity induced by the reaction $Al^{27}(n,\alpha)Na^{24}$. Since the threshold energy for this reaction is 3.3 M.e.v., variations in the ratio of fast neutrons ($En > 3.3$ M.e.v.) to thermal neutrons in different reactors can significantly alter the sensitivity limits for these elements.

With the specific experimental conditions utilized in the present experiments, the estimated sensitivity limits for copper, manganese, and gallium in high-purity aluminum are 0.5, 0.05, and 0.3 p.p.m., respectively.

Table III. Gamma-Ray Energies and Isotope Assignments

Isotope	E_γ (exp) (k.e.v.)	E_γ (literature) (k.e.v.)
Ta K x-ray	55.3	55.8
Hf^{181}	133.4	133.0[a]
	345.3	345.8
	481.2	482.0
Fe^{59}	143.0	145
	192.5	192
	1095	1100
	1292	1290
Cr^{51}	319.0	319.8[b]
Sc^{46}	1117	1119
	892	885–892
Co^{60}	1172	1173
	1333	1333

[a] All values have been taken from the Nuclear Data Sheets (*13*) unless otherwise noted.

[b] Reference 14.

CONCLUSIONS

The results of our analyses of high-purity aluminum demonstrate the power of lithium-drifted germanium gamma-ray detectors as a tool in activation analysis. Their high resolution relative to that of NaI(Tl) scintillators is particularly significant for nondestructive analysis. Because the need for extensive chemical separations is reduced when analysis of many elements in the same sample is required, the use of the nondestructive techniques can be extended to a greater variety of systems. In those systems presently studied by nondestructive analyses, the high resolution may improve significantly the detection sensitivity and may also permit the determination of more elements. The ease with which gamma-ray energies can be measured precisely and the enhanced ability to observe weak spectral lines facilitates the qualitative identification of radioactive isotopes, as shown here in the cases of Fe^{59} and Hf^{181}. The tedious procedure of decomposition and analysis of complex photopeaks, common to the scintillation technique, is generally unnecessary with the use of germanium detectors.

Although the experiments reported here were performed on a matrix that does not of itself produce interfering long-lived activities, the arguments presented here should be valid in most

Table IV. Concentrations of Impurity Elements in Aluminum Giving Rise to Long Lived Activities

Sample	Sample wt., gram	Concentrations in p.p.m.				
		Fe	Sc	Hf	Co	Cr
Al wire	0.1216	5300	0.58	2.6	0.88	57
99.9999% Al	1.029	...	0.17	0.48	...	0.47

experimental situations. In some cases it may still be necessary to perform a primary separation from the bulk material, but there should be no need for individual separations of all elements of interest. The analyses of minerals and rare earth element mixtures are particularly interesting in this regard, and experiments are now in progress to investigate these systems.

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Application of Anodic Dissolution Technique to Automated Analysis of Metals

Determination of Phosphorus in Copper

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▷ A novel, rapid, and automated method for phosphorus is described which eliminates the need for weighing the samples and carrying out the usual acid dissolution. It consists of anodic dissolution of copper samples against an inert cathode by applying a fixed current for periods of time ranging from 45 to 70 seconds. As the current shuts off automatically, a solenoid valve located at the bottom of the electrolysis cell opens to release the liquid which descends by gravity into a sample cup placed on a rotating sampler plate. From there the solution moves by the action of a pump, and after being combined with the molybdovanadate reagent, passes through a flow cell inside the colorimeter. The resulting signal is either recorded on a strip-chart recorder or printed directly on a tape as per cent phosphorus. The total time of analysis from metallic sample to recorded phosphorus signal is 3 minutes. The new sample dissolution technique is applicable to the analysis of other metals for other elements.

Numerous automated procedures based on color development and redox titrations have been reported in literature in recent years. The basic requirement of these automated techniques is that the elements to be determined be present in solution. Obviously, wherever the analysis of metals is involved, the automation can not start before the samples have been weighed, dissolved, excess acid eliminated, and the solution brought to a fixed volume. On occasions, the dissolution step alone may take longer than all the rest of the procedure. It was the purpose of this investigation to develop a technique allowing the handling of metallic samples from the beginning to the end of the analysis in a fully automated manner. The specific need for such development arose in connection with the analysis of phosphorus in copper.

In the copper industry, phosphorus is added to the molten copper for its deoxidizing properties. However, phosphorus is highly volatile and its losses are unpredictable. As a result, appreciable quantities of cast deoxidized copper have to be scrapped because the phosphorus content is outside the specifications. These copper losses could be substantially reduced if the information relative to the phosphorus content of the melt could be obtained shortly before casting, in time to effect the necessary corrections.

A rapid instrumental method for phosphorus is available (*3*), based on the sharp drop in conductivity proportional to the phosphorus concentration. Unfortunately, this method is applicable only where pure copper is used. The generally accepted method of analysis of phosphorus in deoxidized copper and phosphorized bronzes is the ASTM Method E 62-60 (*1*). It is based on the formation of the yellow-colored molybdivanadophosphoric acid (MVP) when molybdate solution is added to an acidic solution containing orthophosphate and vanadate ions. This is a proven method, unaffected by most impurities. However, the analysis of a single sample takes about half an hour. We needed a method which would give a phosphorus analysis within less than 10 minutes after taking the samples of molten copper.

Ferretti and Hoffman (*2*) reported an automated procedure for phosphorus in fertilizer materials after the sample dissolution in mixed nitric-hydrochloric acid. In using a 9-minute time-delay coil and two double-length mixing coils, the total time of the automated portion of the procedure, apart from the sample dissolution, must have been very close to 15 minutes. A similar automated procedure for the determination of phosphorus in iron- and steel-making slags was described by Scholes and

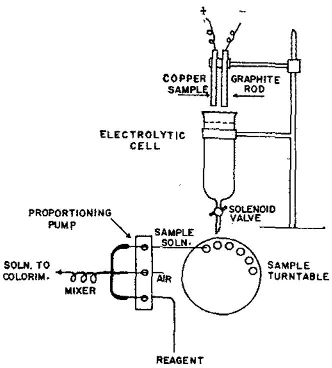

Figure 1. Schematic diagram of automated phosphorus analysis

Thulbourne (*4*). Apparently, the time factor was not considered critical in either paper since the time of sample digestion and dissolution was substantial.

In the present work, an entirely new technique of bringing solid, metallic samples into solution rapidly by anodic dissolution is described. In accordance with this technique, weighing of samples is not required and the push-button dissolution takes no longer than 70 seconds. The anodic dissolution is fully integrated with the color development procedure which has been time-optimized to be completed in 1 minute and 50 seconds. Thus the total time of analysis from metallic sample to recorded phosphorus signal is 3 minutes.

EXPERIMENTAL

Apparatus. Technicon *Auto*Analyzer, laboratory model consisting of a Sampler II module, a two-speed proportioning pump, a heating bath with adjustable thermo regulator, a tubular flowcell colorimeter and a Bristol Dynamaster 560 recorder.

Harrison Laboratories power supply unit, Model 6266, providing a maximum of 5 amperes, 36 volts.

Labindustries Repipet, 10-ml., for fast dispensing of any desired volume from 5 to 10 ml. of electrolyte solution.

Hoke solenoid valve, stainless steel, Series 90, 2-way normally closed.

Electrolytic Cell. In applying a current of 4 amperes to the electrodes immersed about 1 inch deep into the electrolyte solution, the heating of the solution is appreciable. To avoid boiling, the volume of the electrolyte should be at least 8 ml. In this case a simple separatory funnel of suitable dimensions will do for electrolysis cell. When it is desirable to handle smaller volumes for greater sensitivity or even larger volumes for greater accuracy, the cell should be provided with a water-jacket.

Flow Diagram. The automated system developed for the analysis of phosphorus in copper is shown schematically in Figure 1. After the completion of the electrolysis, the contents of the cell are emptied automatically through the solenoid valve into the sample cup. The sample solution and the vanadomolybdic acid are then drawn each through polyvinyl tubes 0.08-inch i.d. at an approximate rate of 2.5 ml. per minute. Air is drawn through a polyvinyl tube of 0.045-inch i.d. The two solutions and the air stream are combined into one by means of a three-pronged glass connector (*G2*) and mixed in a single-length mixing coil of approximately 3 feet in total path. Finally, the solution from which the air bubbles have been removed in an F-shaped debubbler enters a 15-mm. flow cell for absorption measurement.

Reagents. Molybdovanadate Solution. Dissolve in a 600-ml. beaker 20 grams of ammonium heptamolybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in 300 ml. of hot water, and cool. In another 1000-ml. beaker dissolve 1 gram of ammonium metavanadate, NH_4VO_3, in 200 ml. of hot water. Cool and add 120 ml. of 70% perchloric acid. After cooling, transfer the molybdate solution to the vanadate solution while stirring and adjust to the mark in a 2000-ml. volumetric flask.

Standard Phosphorus Solution, 25 p.p.m. of phosphorus. Dissolve 0.1146 gram of disodium phosphate, Na_2HPO_4, in about 200 ml. of water. Add 20 ml. of nitric acid and dilute to 1 liter in a volumetric flask.

Electrolyte Solution. Fifty grams of ammonium persulfate, $(NH_4)_2S_2O_8$, in 8 volume % nitric acid made up to a liter with the same acid.

Calibration. *Conventional Dissolution:* Dissolve six 1.25-gram portions of pure copper containing less than 2 p.p.m. phosphorus in 7.5 ml. nitric acid. Boil to expel brown nitrogen oxide fumes, then cool and transfer each solution to a 50-ml. volumetric flask. Carry one solution through as a blank and to the others add 2, 5, 10, 20, and 30 ml. of the standard phosphorus solution corresponding to 0.004, 0.01, 0.02, 0.04, and 0.06% phosphorus. Adjust to the mark with distilled water. Run portions of these solutions on the *Auto*Analyzer using 420 mμ filters. For greater accuracy use carefully analyzed samples for the preparation of the calibration graph.

Anodic Dissolution: Select five accurately analyzed samples in the form of 0.25-inch rods covering the same concentration range from 0.004 to 0.06% phosphorus. For the blank use a rod of pure copper. Effect anodic dissolution of each rod by placing it into the electrolytic cell containing 5 ml. of electrolytic solution against a graphite cathode. Apply 4 amperes for a period of anywhere from 45 to 70 seconds and run the resulting solutions on the *Auto*Analyzer using 420 mμ filters.

Procedure. Carry out the analysis in accordance with the previous section on Calibration. Calibration graphs for analysis by conventional dissolution using synthetic standards and actual samples, and anodic dissolution using actual samples are shown in Figure 2.

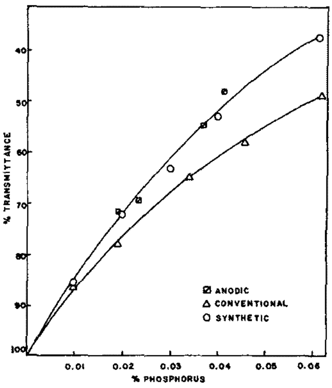

Figure 2. Calibration curves for conventional and anodic dissolution

Sequencing of Samples. To allow the detection of very low phosphorus signals coming immediately after very high signals, the filling of intermediate sample cups with wash water between successive samples is recommended. In setting the sampling rate at 60 samples per hour, 30 samples per hour will actually be analyzed. If 70 seconds are allowed for anodic dissolution, the operator will have 50 seconds remaining in which to pull out the used sample electrode from the pressure clip and insert a new one. The total capacity of the system could easily be twice as much by eliminating wash water cups and by either slightly reducing the electrolysis time or by operating with two electrolytic cells. The indicated power supply unit is more than adequate to provide current to two cells simultaneously.

DISCUSSION

The experimental work covered in this investigation centered around the optimization of the MVP color development, and the anodic dissolution. The discussion concerning the factors affecting the two items will be presented to the same logical order.

Color Development. EFFECT OF PERMANGANATE AND HYDROGEN PEROXIDE. In accordance with the ASTM Method E 60-62, potassium permanganate is added to the hot sample solution to oxidize any suboxides of phosphorus to orthophosphate which is the only form in which phosphorus reacts with molybdovanadate to form the yellow MVP complex. The excess permanganate is then destroyed with hydrogen peroxide which in its turn is subsequently decomposed by boiling. Since the MVP method, as used in the analysis of phosphorus in copper, is based on the method originally applied to iron and steels containing varying amounts of carbon, it was felt that the

Table I. Effect of Time on MPV Color

Total time cycle,[a] seconds	Time color develop.,[b] seconds	Absorbance
418	378	0.261
375	335	0.260
277	256	0.260
122	78	0.261
90	45	0.261
51	5	0.187

[a] Total time cycle is the time from aspirating the sample solution to obtaining the recorded signal.

[b] Time of color development is the time elapsed after the sample solution combined with the reagent leaves the three-pronged glass connector and before it enters the flow cell.

addition of permanganate and hydrogen peroxide, mandatory in the analysis of the latter materials, might be dispensed with in the analysis of copper. To corroborate this hypothesis, three portions of a sample containing 0.029% phosphorus were run by the ASTM method—i.e., adding $KMnO_4$ and H_2O_2; by omitting $KMnO_4$ but adding H_2O_2; and by omitting the additions of both $KMnO_4$ and H_2O_2. The absorbances read were 0.32, 0.31, and 0.30, respectively, indicating some but not significant drop in sensitivity. As a result, the additions of $KMnO_4$ and H_2O_2 were omitted in all subsequent tests.

EFFECT OF TEMPERATURE. To establish the effect of temperature on the color development of the MVP complex six portions of a sample solution assaying 0.040% phosphorus were run on the *Auto*Analyzer with the thermostat set at 26°, 40°, 61°, 76°, 90°, and 100° C., respectively. The absorbances recorded at 420 mμ did not vary from the mean by more than 0.01 corresponding to 0.001% phosphorus, which is insignificant. As a result all subsequent tests were carried out at room temperature.

Other experimental conditions were as follows: the MVP reagents were prepared as per Reference (*2*); the sampling rate was 40 samples per hour; the sample solution, after being combined with the color reagent was passed first through two single-length mixing coils, then through a 40-ft coil in the thermostat. The total time for each sample solution from aspiration from the sample cup to recording the transmission peak was 7 minutes.

EFFECT OF TIME. The effect of time on the color development of the yellow MVP complex was established by comparing the absorbances of portions of the same sample solution passing through coils of various lengths before entering the colorimeter. The pertinent data are shown in Table I.

The data presented show clearly that nothing is gained by extending the time of color development beyond 45 seconds. This is the time required for the solution to pass through a single-length mixing coil.

EFFECT OF REAGENT CONCENTRATION. A reagent solution containing 2 grams of ammonium vanadate, 40 grams of ammonium molybdate, and 450 ml. of perchloric acid per liter was prepared. Stepwise dilutions from this solution were made down to $^1/_{32}$nd of the original concentration. No loss in signal was experienced in the analysis of deoxidized copper samples in using the reagent solutions that were as low as one-sixteenth of the original reagent concentration. Signal, however, was reduced by about 17% for the solution that was diluted by a factor of 32.

Subsequently, solutions were prepared to contain 10 grams of ammonium molybdate and 0.5 gram of ammonium vanadate per liter. The perchloric acid concentration of these solutions was adjusted to be 1.2, 2.5, 5.0, 7.5, 11.25, 15.0, 17.5, and 20.0 volume %. In trying each of these reagents in a sequential manner with the same sample solution, it was observed (Figure 3) that for the two reagent solutions that were the lowest in acid content, the recordings were of a peculiar shape not amenable to easy measurement. This behavior is due to the surprising fact that the absorption of the copper blank solutions comprising the reagents turned out to be far less that that of the reagents alone. The best performance was realized with the reagents containing 5.0 and 7.5 volume % of perchloric acid. For solutions of higher acid concentration, the signals obtained decreased as the acid concentration was increased.

Finally, reagent solutions were prepared to contain 6.0 volume % of perchloric acid and increasing amounts of the two chromogenic reagents. The highest sensitivity resulted for the regent solutions containing 0.5 and 1 gram of ammonium vanadate and 10 and 20 grams of ammonium molybdate per liter.

Anodic Dissolution. GENERAL CONSIDERATIONS. Anodic dissolution accompanied by cathodic deposition is an old and well-established practice in the electrolytic purification of numerous metals. The novelty of this application consists in effecting the anodic dissolution of the sample presented in the form of a rod or tube without the undesirable deposition at the cathode. To this end, a spectrographic graphite rod was selected for inert cathode. The hydrogen evolution at this electrode replaced the undesirable metal deposition.

However, for the purposes of a more general application of the anodic dissolution technique to the analysis of metals for a number of elements, the absence of cathodic deposition of the main constituent is not a prerequisite. For as long as the element to be determined does not deposit on the cathode or deposits only partially in a reproducible manner, one could safely use as cathode a rod of the sample material.

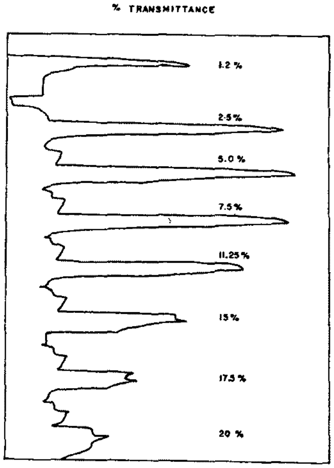

Figure 3. Effect of perchloric acid on absorbance

Based on the Faraday's Law, the amount of copper dissolved at the anode can be calculated as follows:

$$\text{Cu (dissolved)} = \frac{Ite}{96{,}500}$$

where I is the current in amperes, t time in seconds, and e the copper equivalent of 31.79 grams.

In setting the maximum operating current at 4 amperes, it can be easily calculated that the dissolution of from approximately 60 to approximately 90 mg. of copper needed for the phosphorus analysis of deoxidized copper will take from 45 to 70 seconds of electrolysis.

If the electrolysis is carried out for longer periods of time, trace amounts of dissolved copper will tend to deposit on the graphite electrode. These trace quantities of copper dissolve promptly in the nitric acid electrolyte solution by stirring it with the graphite rod after completion of the electrolysis. By slightly greasing the graphite electrode with silicone stopcock grease, the deposition of copper at the cathode can be either prevented altogether or at least delayed.

EFFECT OF AMMONIUM PERSULFATE. In the beginning of this work, anodic dissolution was carried out in an 8 volume % nitric acid solution containing no ammonium persulfate. The phosphorus signals obtained were some 20% less than when the dissolution was carried out as per the ASTM method. Moreover, the reproducibility was not too satisfactory. In the area surrounding the anode, one could observe in the course of the electrolysis some yellowish substance forming and promptly disappearing in the solution. This might have been phosphorus hydride of the type $(P_2H)_n$ (*5*). In one instance electrolysis was performed in a solution containing the molybdovanadate solution as the electrolyte. The solution became a deep blue, a clear indication that strongly reducing conditions prevailed in the course of the electrolysis. Obviously, in the course of the anodic dissolution in nitric acid electrolyte solution at least some lower valent phosphorus compound formed which did not react with molybdovanadate to form the MVP complex. Attempts made to remedy this situation by adding some potassium permanganate to the electrolyte solution were not successful. However, when ammonium persulfate was added no yellow substance could be seen during the dissolution. The phosphorus signals obtained on the recorder were larger than obtainable by the conventional dissolution of phosphorized copper and equal to signals obtained when pure standard phosphorus solution was allowed to react with molybdovanadate (Figure 2). This indicates a complete recovery of phosphorus present in copper as orthophosphate. The slightly weaker signals obtained following the conventional ASTM dissolution technique are caused by the presence of some residual nitrogen oxide which has the effect of depressing the MVP color.

Table II. Precision of Automated Analysis Using Conventional and Anodic Dissolution

Each sample contained 0.036% phosphorus

Conventional, 25 mg. Cu/ml.			Anodic, 15.4 mg. Cu/ml.		
Absorbance	P, %	Deviation from mean	Absorbance	P, %	Deviation from mean
0.275	0.036	0.000	0.205	0.036	0.000
0.290	0.038	0.002	0.200	0.035	0.001
0.280	0.037	0.001	0.200	0.035	0.001
0.255	0.034	0.002	0.195	0.034	0.002
0.250	0.033	0.003	0.203	0.036	0.000
0.275	0.036	0.000	0.200	0.035	0.001
0.270	0.036	0.000	0.210	0.037	0.001
			0.210	0.037	0.001
Mean	0.036	0.0011		0.036	0.0009
Std. dev.		0.0017			0.0011

Anodic *vs.* Conventional Dissolution. Precision studies were carried out by the automated phosphorus procedure on a sample of deoxidized copper containing 0.036% phosphorus starting with conventional and anodic dissolution. In the case of conventional dissolution 2.5-gram portions were dissolved in nitric acid and made up to 100-ml. in a volumetric flask. In the case of anodic dissolution, a copper rod of the same sample was repeatedly electrolyzed at 4 amperes for 70 seconds in 6 ml. of electrolyte solution. The data obtained are shown in Table II.

The superiority of the method involving the anodic dissolution does not lie so much in improved precision as in the elimination of the skill from the analysis. Any inexperienced technician following the automated anodic dissolution technique will get from the very first run results as good as those obtained by the most experienced technician following the ASTM method. Anodic dissolution is a highly reproducible push-button technique. Conventional dissolution requires full attention of the operator in the dissolution of the samples and elimination of excess acid. A comparison of the results from the two methods is given in Table III.

Table III. Comparative Results by ASTM and Automated Methods Using Anodic Dissolution

Phosphorus, %		
ASTM	Automated	Difference
0.036	0.038	0.002
0.020	0.018	0.002
0.036	0.036	0.000
0.019	0.019	0.000
0.038	0.038	0.000
0.037	0.035	0.002
0.037	0.034	0.003
0.023	0.024	0.001
0.037	0.036	0.001
0.042	0.039	0.003
0.020	0.018	0.002
0.036	0.034	0.002
0.022	0.024	0.002
0.037	0.037	0.000
0.019	0.018	0.001
	Mean	0.0014
	Std. dev.	0.0018

The difference between the results by the two methods is no larger than between the duplicate analyses by the same method. A typical series of recordings displaying the sequence of high (0.07%) and low (0.005%) phosphorus values is shown in Figure 4.

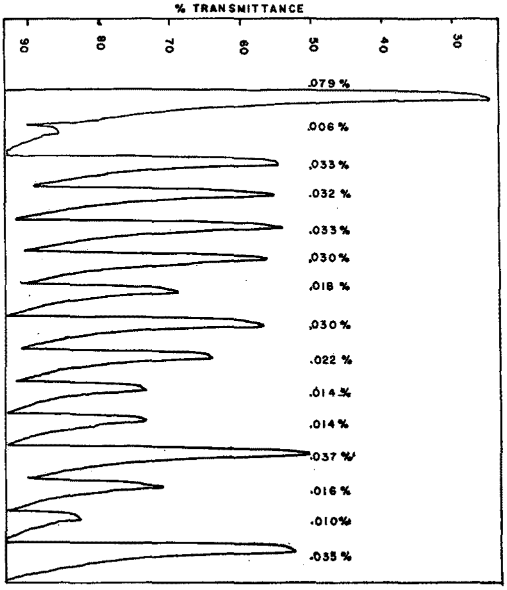

Figure 4. Typical strip chart recordings of phosphorus in copper

ACKNOWLEDGMENT

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Solvent Extraction of Metal Ions with Trifluoroacetylacetone

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▶ Copper, iron, and aluminum can be quickly, cleanly, and effectively extracted from aqueous media (acetate-buffered) with chloroform which is 0.10*M* with respect to trifluoroacetylacetone. At an equilibrium pH of 4.5 to about 5.5, 99.0% copper, 99.7% aluminum, and 99.9% iron can be removed from aqueous media containing initially 0.5 mmole of the metal ion (equal phase volumes). Iron is also extracted at lower pH values, but the efficiency of the extraction is a function of pH and of equilibration time. Manganese, nickel, zinc, and magnesium are extracted with only poor efficiency (1 to 3%) in the acetate-buffered region, hence separations of iron and other metals from bulk quantities of these metals are possible. Iron, copper, and aluminum in a National Bureau of Standards reference sample were extracted and examined by gas liquid chromatography to demonstrate practical applications of solvent extraction with chloroform–trifluoroacetylacetone.

GAS LIQUID chromatographic elution of trifluoroacetylacetone chelates of Be(II), Al(III), In(III), Cr(III), Fe(III), Cu(II), Rh(III), Zr(IV), and Hf(IV) has been reported by Moshier, Sievers, and others (*17*, *27*). Certain multicomponent mixtures were quickly and efficiently resolved. The quantitative aspects of the GLC analysis of metal–trifluoroacetylacetone or metal–hexafluoroacetylacetone chelates have been studied by Hill and Gesser (*11*), by Ross and coworkers (*20–22*), and by Schwarberg, Moshier, and Walsh (*24*).

These studies suggest that GLC might be employed for the rapid analysis of metals and metal mixtures. The utility of the method would be greatly enhanced if practical means could be found for converting inorganic samples into organic solutions of the metal chelates. One approach is solvent extraction of an aqueous solution of the sample by an organic solution of the fluoroacetylacetone. Brandt and Heveran have combined solvent extraction and gas chromatography for the determination of trace amounts of chromium using acetylacetone (*1*).

Trifluoroacetylacetone has been studied for the solvent extraction of plutonium(IV) (*3*, *5*), zirconium (*4*), separation of zirconium from hafnium (*14*, *23*), separation of actinides from fission products (*31*), actinium from radium and decay products (*9*), neptunium from plutonium, uranium, and fission products (*15*), and protactinium from uranium and thorium (*29*). The distribution coefficient of scandium trifluoroacetylacetone has been reported recently (*18*).

This report presents the results of a program to study the solvent extraction properties and solution chemistry of metal trifluoroacetylacetonates, the objective of which is to define conditions favoring the rapid, quantitative extraction of metals or groups of metals.

The following conditions were selected. Metal ions studied were those known to form trifluoroacetylacetonates amenable to gas liquid chromatographic elution and detection. Other metal ions were also examined to demonstrate separation by solvent extraction. Chelating agent concentration was initially 0.100*M*. The pH was varied by the addition of noncomplexing acids or bases, although auxiliary complexing agents were added when needed to prevent hydroxide formation. Chloroform was employed as the principal solvent because it had been successfully used for GLC studies. Equilibration time was 10 minutes. Influence of equilibration time was studied when necessary. All experiments were performed at ambient temperature, and equal volumes of organic and aqueous phases were employed.

After equilibration, the concentration of metal ion remaining in the aqueous layer was determined by an appropriate method for which the noninterference of trifluoroacetylacetone was demonstrated.

Data resulting from the above studies were employed to plot per cent extraction *vs.* pH for various metal ions. Reference to these graphs permits selection of a pH range over which a metal or groups of metals will be quantitatively extracted by the trifluoroacetylacetone–chloroform system.

EXPERIMENTAL

Apparatus. Absorbance measurements were made with Beckman Model B and IR-4 spectrophotometers. A Leeds and Northrup pH indicator was used for pH measurements, employing a Beckman 39183 combination electrode and a Leeds and Northrup standard 1199 BA plug. A Burrell wrist action shaker was used for equilibration of aqueous and organic phases.

Reagents. Commercial trifluoroacetylacetone (Columbia Organic Chemicals) was distilled (2- × 45-cm. heated column, helices packed, 80° C.), and the fraction boiling between 105° and 106° C. was taken (740 mm.). The infrared spectrum of distilled material was transparent at 1800 cm.$^{-1}$; $n_D^{25} = 1.3864$. This material has now been stored for 8 months at −20° C. and has retained its clarity and water-white appearance.

Trifluoroacetylacetone from some suppliers contains an acidic impurity absorbing at 1800 cm.$^{-1}$ which cannot be removed by a simple distillation.

A chloroform solution of the reagent (0.100*M*) was prepared in a manner which tended to minimize errors due to the high volatility of trifluoroacetylacetone. A clean, dry, 50-ml. Erlenmeyer flask fitted with a ₸ 16 stopper was weighed. Twelve milliliters of trifluoroacetylacetone were added (graduate), and the flask and stopper were placed on the balance pan. Additional trifluoroacetylacetone was added dropwise until the flask and contents weighed 15.41 grams more than the tare weight. The flask was quickly closed, and a final weight was obtained. The flask was then filled with chloroform, and the mixture was transferred with copious chloroform washings into a 1-liter volumetric flask half-filled with chloroform. Contents were diluted to the mark and mixed well. Chloroform used for this solution was distilled from phosphorus pentoxide to remove ethanol.

The chloroform–trifluoroacetylacetone was stored in a vessel that had been sprayed with flat black enamel and which was fitted with a 10/30 ₮ joint with side arm and stopcock. The latter assembly permitted the filling of a pipet via nitrogen pressure, thereby minimizing introduction of air every time the vessel was opened.

Approximately 0.05M solutions of copper, iron, aluminum, zinc, nickel, manganese, and chromium were prepared from reagent grade salts or high purity metals. The iron solution was prepared from iron nitrate, 9-hydrate; perchloric acid (25 meq./liter) was added to prevent hydrolysis. Solutions were standardized by titration with (ethylenedinitrilo)tetraacetate, EDTA.

Extraction Procedure. Generally, the following procedure was employed. To a 125-ml. separatory funnel with Teflon (DuPont) stopcock were added 10.00 ml. of 0.05M metal ion, varying amounts of 2.5 or 0.25N perchloric acid, 0.10N sodium hydroxide, or 1M sodium acetate, and sufficient water from a buret so that the total volume of the aqueous phase was 25.00 ml. An equal volume of chloroform–trifluoroacetylacetone was then added. The mixture was shaken for 10 minutes, using the Burrell shaker set at position 9 (about 300 vibrations per minute).

After equilibration, the mixture was allowed to stand for a few minutes to permit the phases to separate. The equilibrium pH of the aqueous phase was measured, and the amount of metal ion remaining in the aqueous phase was determined titrimetrically or spectrophotometrically.

Analysis Methods. For all methods it was necessary to prove the noninterference of up to 0.75 mmole of free trifluoroacetylacetone which could be present in the aqueous phase after equilibration. The possibility of this interference was studied by adding an aliquot of a standard solution of the metal ion to water which had been equilibrated with chloroform–trifluoroacetylacetone. The pH was then adjusted, and EDTA titrations were completed or spectrophotometric measurements were made after addition of color-forming reagents.

EDTA titrations of manganese and magnesium with Eriochrome Black T indicator (*12*, *25*), of nickel with copper–PAN indicator (*8*), of zinc with xylenol orange indicator (*13*), of aluminum with Alizarin Red S as indicator and thorium (IV) as back-titrant (*7*), and of copper with PAN indicator (*2*) were employed. Also for copper, a few points in the pH region of highly efficient extractions were checked using the sensitive zinc dibenzyldithiocarbamate method (*16*).

Bathophenanthroline (*6*) and orthophenanthroline (*28*) were used to determine iron remaining in the aqueous phase after extractions of high efficiency and moderate efficiency, respectively. For extractions of poor efficiency, the absorbance of the chloroform phase was measured at 438 mμ. This absorbance is caused by the intrinsic color of iron (III) trifluoroacetylacetonate in chloroform (ϵ = 3500). A slightly more intense, but sharper, peak exists at 368 mμ.

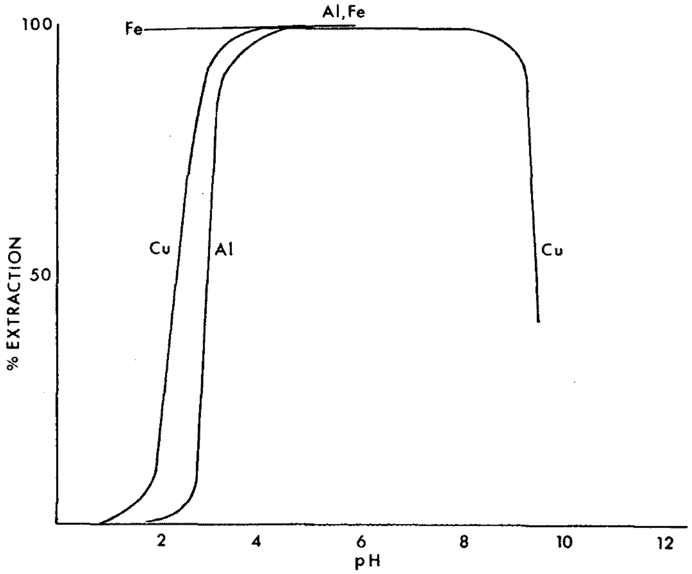

Figure 1. Effect of pH on extractability of copper, iron, and aluminum with chloroform–trifluoroacetylacetone

RESULTS AND DISCUSSION

Distribution of Trifluoroacetylacetone between Chloroform and Water. Factors which favor a high distribution constant of metal in favor of the organic phase include a fairly high acid dissociation constant of the chelating agent and a relatively high solubility of the chelating agent in the aqueous phase. It is important, therefore, to study the distribution of chelating agent between the organic phase and water as a function of pH.

An infrared spectrum of the chloroform–trifluoroacetylacetone solution was obtained using a 0.162-mm. cell. A comparision of this spectrum with that of chloroform indicated the presence of a strong absorption at 9.02 microns, which would be useful for measuring the amount of trifluoroacetylacetone remaining in chloroform after equilibration with water. The base line absorbance method was used for all measurements by subtracting absorbance at 9.20 microns from values at 9.02 microns.

Solutions of 0.100, 0.060, 0.010M yielded net absorbances of 0.628, 0.373, and 0.065. Beer's law is obeyed to within 1 or 2%.

The distribution of trifluoroacetylacetone between chloroform and water was determined by equilibrating chloroform–trifluoroacetylacetone and an equal volume of water containing various amounts of perchloric acid or potassium hydroxide. After equilibration, the mixture was allowed to stand for 1 minute to permit the phases to separate. The pH of the aqueous phase was measured and an infrared spectrum of the chloroform layer was obtained using the fixed thickness cell.

Data are summarized in Table I and indicate that the trifluoroacetylacetone–chloroform system should be useful for extractions over a wide pH range.

Distribution data also permit an approximation of log P_r, the organic/aqueous partition constant (*26*), and pK$_a$, the acid ionization constant. The pK$_a$ value, 6.6, compares somewhat favorably with a literature value of 6.3 (*19*).

Table I. Distribution of Trifluoroacetylacetone between Chloroform and Water ($D_{o/w}$)

Equilibration time, min.	Equilibrium pH	$D_{o/w}$
10	−0.5	2.9
10	0.17	2.4
10	1.16	2.0
10	2.09	2.0
10	3.25	2.2
10	6.29	1.4
10	6.68	0.9
10	7.78	0.2
10	12.79	0.0
1	3.25	6.8
5	3.25	2.3
10	3.25	1.9
20	3.25	1.8

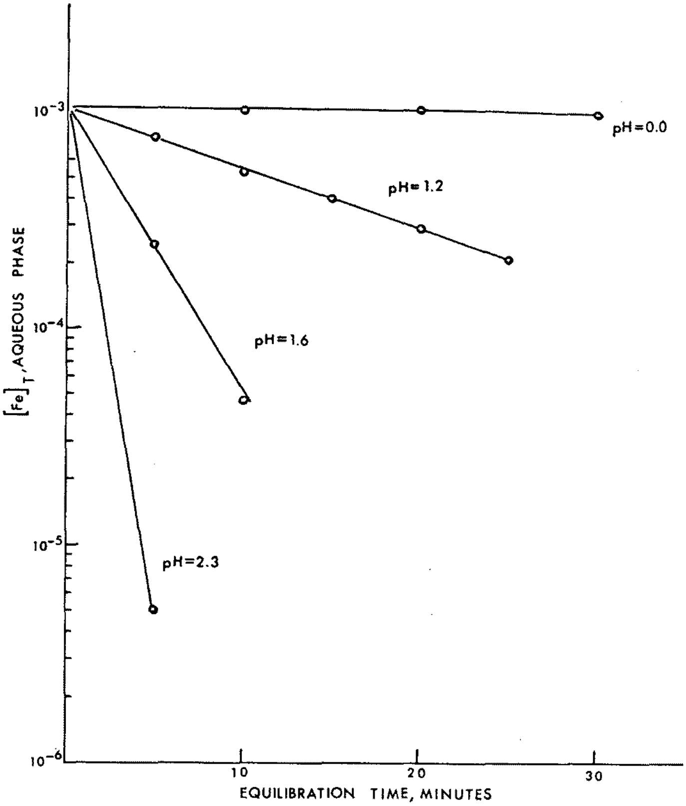

Figure 2. Influence of equilibration time and pH on extractability of iron with chloroform–trifluoroacetylacetone

The value of log P_r from these data, 0.30, agrees with the figure 0.289 recently reported (*30*).

The distribution of trifluoroacetylacetone between chloroform and water was also studied as a function of equilibration time. Results presented in Table I show that for all practical purposes equilibrium was reached after 5 minutes and that there was only a small decrease in trifluoroacetylacetone concentration (in chloroform) upon further equilibration up to 20 minutes.

The stability of the chloroform–trifluoroacetylacetone solution appears to be good. There was no significant change in the magnitude of the absorbance at 9.02 microns after 1 month, although there was a slight increase in background absorption at 9.20 microns.

COPPER. From pH 4 to 8, copper is rapidly and effectively removed (99%) from aqueous medium in a single extraction (Figure 1). No significant difference in extractability was observed after 1, 10, and 30 minutes of shaking (pH 5).

The extraction occurs even though copper is initially present as a hydroxide precipitate. The aqueous phase under these conditions, however, tended to be cloudy immediately after equilibration. No cloudiness was observed when equilibrium pH values were 5 or below.

Because the ultimate objective of this program is to develop practical procedures for the extraction of metal ions, a study of the influence of weak auxiliary complexing agents to provide clean solutions prior to equilibration was indicated. Acetate ion was selected because it not only forms weak complexes with copper, iron, aluminum, etc., but buffers in the region where copper is extracted with the highest efficiency. Several experiments were performed where the extractability of copper was studied in the presence of varying amounts of sodium acetate and/or acetic acid. The data revealed that the extraction of copper was not influenced even by the presence of a total acetate concentration of 30 mmoles.

These data are of key importance for they now provide a simple means for overcoming a potentially serious hindrance to the practical use of trifluoroacetylacetone as an extraction reagent. The intrinsic acidity of trifluoroacetylacetone can now be compensated for by the addition of sufficient acetate so that equilibration will result in the desired pH. Thus, hydroxide formation can be avoided by employing this weakly basic substance.

Use of ammonium hydroxide to achieve still higher equilibrium pH values, coupled with clear solutions prior to extractions, did not result in effective extractions. Efficiency dropped sharply from 95 to 45% from pH 9 to 9.5 in the presence of 3 to 15 mmoles of ammonia/ammonium ion. In the absence of ammonia, efficiency was 88% at pH 11.

Because copper forms a highly stable aqueous chelate with EDTA (log K = 18.8), it was felt that EDTA would prevent the formation of copper trifluoroacetylacetonate and therefore prevent the extraction of copper by trifluoroacetylacetone. Two experiments were performed at equilibrium pH values of 4.6 and 5.2 where sufficient EDTA was added to react with the copper present and to provide a 0.005 mmole excess. No extraction of copper was observed as evidenced by the lack of color in the organic phase after equilibration. Excess EDTA in the aqueous layer after equilibration was back-titrated with copper to the PAN end point. These titrations verified the visual observations and permit the claim that no titratable copper was extracted. In a final experiment, a chloroform solution of copper trifluoroacetylacetonate was shaken with an aqueous, acetate-buffered solution of EDTA. The color in the organic layer was discharged quickly and the aqueous layer assumed the pale blue color characteristic of copper–EDTA. This powerful chelating agent is therefore not only capable of preventing the extraction of copper, but will remove extracted copper from the organic phase. These observations permit the derivation of schemes for selective extraction or selective back-washing.

IRON. Preliminary experiments on the extraction of iron (0.001*M*) indicated the efficiency of the extraction to be markedly influenced by pH and by equilibration time. A plot of the logarithm of the total concentration of all iron species (remaining in the aqueous phase) as a function of equilibration time is shown for four pH values in Figure 2. Notice that at an equilibrium pH value of 2.30, iron is extracted nearly quantitatively in only 5 minutes, whereas at pH 1.60 quantitative extraction would require about 20 minutes. Estimated time for quantitative extraction at pH 1.18 is 110 minutes, while at pH 0, quantitative extraction, if thermodynamically possible, would be prohibitively time-consuming.

Because a plot of log[Fe] *vs.* time yields a straight line, one concludes that a pseudo first-order reaction is occurring. The rate of this reaction is dramatically pH dependent. The pseudo rate constant was calculated to be 0.065 min.$^{-1}$ at pH 1.18 and 0.31 min.$^{-1}$ at pH 1.60. Strict attention must therefore be paid to pH values and equilibration time when attempting to extract iron with chloroform–trifluoroacetylacetone.

In contrast with copper, iron was not cleanly extracted when initially present as a hydroxide. However, when sodium acetate solution was added after prior equilibration of an acid iron solution and chloroform–trifluoroacetylacetone, rapid, clean, efficient extraction of iron resulted. Up to 0.5 mmole of iron could be extracted with 99.9% efficiency, pH 4.5 to 6.1.

The chloroform solution of iron trifluoroacetylacetonate was evaporated, and an infrared spectrum was obtained. The spectrum was identical to one obtained on iron trifluoroacetylacetonate prepared in the absence of acetate, thereby demonstrating that a mixed acetate–trifluoroacetylacetone chelate is not the extracted species in the above studies.

EDTA not only prevented the immediate extraction of iron with chloroform–trifluoroacetylacetone but also failed to remove the iron from chloroform once it was extracted. Advantage can be taken of this unusual phenomenon to achieve a separation of iron from copper. Extract both in the usual manner, discard the aqueous layer, then backwash the organic layer with aqueous EDTA. Copper is almost instantly removed while iron remains in the chloroform.

As previously indicated, the color of iron trifluoroacetylacetonate in chloroform is useful for the spectrophotometric determination of iron(III). The suggested method is rapid, moderately sensitive, and can be made highly selective via removal of colored interferences by backwashing with EDTA and by pH control.

Aluminum. In the absence of auxiliary complexing agents, 0.05 mmole of aluminum was extracted (98%) from pH 5 to 7, but an equilibration time of 1 hour was necessary because of a slow reaction of aluminum hydroxide with trifluoroacetylacetone. These extractions were accompanied by a trace of aluminum hydroxide which prevented the extractions from being as clean as possible.

To expand the scope of the method, these additional experiments were performed using 0.5 mmole of aluminum. The pH was varied by employing 2M acetic acid and 1M sodium acetate. Equilibration time was 10 minutes. The use of acetate resulted in these improvements: clean separations, improved efficiency, and decreased equilibration time. The useful range was also demonstrated by excellent extractions of 0.5 mmole of aluminum.

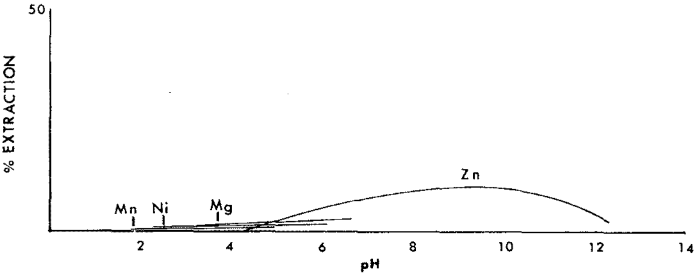

Figure 3. Effect of pH on extractability of magnesium, magnanese, nickel, and zinc with chloroform–trifluoroacetylacetone

Results are presented in Figure 1. Notice that the sharp rise in extractability as a function of pH in the region of pH 3 is typical behavior for a trivalent metal ion. There is virtually no extraction at pH 2.1, and nearly quantitative extraction at pH 5 to at least 7

Extraction of aluminum at pH 2.1 did not occur even after equilibration time of 1 hour. One may conclude from previous studies, then, that the separation of iron from aluminum will readily and easily occur at this pH, provided a 10-minute equilibration time is established. At pH 5 to 7, both copper and aluminum will be extracted together. Data above pH 7.2 were not obtained.

Zinc. The extremely poor efficiency of the zinc extraction is immediately apparent from Figure 3. Notice that no detectable extraction occurred at pH 2.9 or below and that less than 1% of the zinc was extracted at pH 4.1. Efficiency was somewhat higher from pH 5 to 9, but never exceeded 10.5%.

The extraction of zinc was accompanied by a cloudy aqueous layer when the equilibrium pH was about 7. This layer cleared, however, upon standing or when purged with nitrogen, so the turbidity was not caused by a zinc-containing precipitate.

To evaluate the influence of equilibration time, a single experiment was performed (equilibrium pH, 6.3). Efficiency was 5.95%, and, consequently, little improvement resulted at longer equilibration times (1 hour).

An examination of prior extraction data will show that a highly efficient separation of iron from zinc will occur at pH 2.3. No significant amount of zinc is extracted at this pH while more than 99% of the iron is extracted in 5 minutes. Aluminum and/or copper can also be separated from zinc by employing an equilibrium pH of 4.0. More than 98% of aluminum or copper would be removed from 99% of the zinc present.

Efficiency of the extraction of zinc might be enhanced by the use of an adduct-forming agent such as isobutylamine. Experiments to determine this are planned.

Manganese. Less than 3% manganese is extracted in the acetate-buffered region. In some cases, the aqueous layer was light green after equilibration. Because the presence of manganese(III) by air oxidation was expected, hydroxylamine hydrochloride was added prior to addition of the reagent. The light green color was still present after equilibration; apparently it is caused by manganese(II) trifluoroacetylacetonate. No precipitate was observed. Clean separations of iron (III), copper, and aluminum from manganese(II) should occur from pH 4 to 6, although some manganese will be co-extracted.

In marked contrast to the clean separations reported above, experiments in ammonia-buffered media resulted in the formation of precipitates or dark yellow solutions and/or emulsions. When no reducing agent was present, a brown precipitate formed which was not completely removed by the addition of hydroxylamine hydrochloride. Analysis by titration indicated that approximately 50% of the manganese was still dissolved in the aqueous layer. Prior addition of hydroxylamine hydrochloride prevented precipitation formation, but after equilibration, both layers were yellow. At higher ammonia concentrations (pH 10), a yellow emulsion formed which could not be avoided by prior addition of hydroxylamine hydrochloride. Quantitative results are shown in Figure 3.

Efficient extraction of manganese(II) might be possible if another solvent or mixed solvent system were employed, or if manganese(II) were extracted in the absence of oxygen.

Nickel. A nominal amount of nickel (~1%) was extracted at pH 2 to

4.7 from unbuffered media (Figure 3). Actual presence of nickel trifluoroacetylacetonate in the chloroform layer was verified (pH 4.9) by isolation of a residue and examination by infrared spectrophotometry. At higher pH values (6.6), a precipitate formed which did not disappear with long equilibration times. This precipitate was also isolated and examined by infrared spectrophotometry. A characteristic pattern of a divalent metal–trifluoroacetylacetone chelate was obtained.

Nickel trifluoroacetylacetonate could not be eluted by gas liquid chromatography, so co-extraction of some nickel with iron, copper, etc., at pH 5 will not influence the gas liquid chromatographic analyses of those metals.

MAGNESIUM. In a preliminary experiment, clear aqueous and organic layers resulted when 0.5 mmole of magnesium was studied (pH 6.5). A trace of white precipitate was visible at the interface. Titration indicates that about 3% of the magnesium had been removed.

The experiment was repeated with more base being added after initial equilibration of aqueous layer and the reagent. After 10 minutes, the aqueous layer (pH 6.8) was cloudy, and the organic layer contained traces of a white precipitate which adhered to the walls of the vessel. The chloroform layer was filtered and allowed to evaporate. A trace (0.0003 gram) of residue resulted which, nevertheless, was sufficient for an infrared analysis. A weak spectrum resulted which was consistent with the general pattern of a divalent metal–trifluoroacetylacetone chelate. The aqueous layer was also filtered, and titration of the filtrate indicated that about 55% of the magnesium had been precipitated.

When ammonia buffer was employed (pH 9.4), a fine suspension resulted. Titration of the filtered aqueous layer showed that 69% of the magnesium had been removed by both precipitation and extraction. Elemental analysis of the dried precipitate was consistent with the formula $Mg(C_5H_4F_3O_2)_2 \cdot H_2O$. Efficiency-pH data are presented in Figure 3.

For practical applications, the important result of this quick survey is that only a small percentage of magnesium will be extracted in the analytically useful pH range. That which is extracted is not eluted from a gas chromatograph under the conditions studied.

CHROMIUM. Because the conditions for the gas liquid chromatographic elution of chromium(III) trifluoroacetylacetonate are well established, the development of a scheme for the solvent extraction of chromium trifluoroacetylacetonate would be highly desired. Difficulties were expected, however, because of the unique solution chemistry of chromium(III).

The slow reaction of chromium(III) with chelating agents such as EDTA and acetylacetone, etc., is well known. Frequently, quantitative reaction occurs in boiling aqueous media if an excess of reagent is present. This approach, however, would be somewhat unwieldly for extraction purposes. Another route to the formation of chelates that has been successful is to reduce chromium (VI) in the presence of the reagent. By this means, formation of inert chromium polynuclear hydroxy complexes is avoided.

Because practical applications of extractions would most conveniently be applied on solutions of chromium(III), experiments were performed on a 0.05*M* solution prepared from chromium chloride 6-hydrate, to assess its behavior. At pH 2.4, no apparent extraction occurred, but at pH 6.1, the chloroform layer had assumed a green color of considerable intensity after an overnight equilibration. The aqueous layer was clear, although there was a trace of precipitate present. A similar experiment at pH 6.8 yielded more precipitate than at pH 6.1, but at pH 12.2 no color appeared in the organic layer nor was there a precipitate in the aqueous layer.

This initial survey suggested that additional experiments in the region pH 6.1 or below were desirable. At pH 5.8, the mixture was shaken for 4.5 hours while the aqueous and organic layers were periodically observed. After 1 hour, the aqueous layer was light green. The organic layer was also green with traces of an emulsion. After 2 hours, the organic layer was darker, but a scum was present on the sides of the vessel. After 3 hours, the aqueous

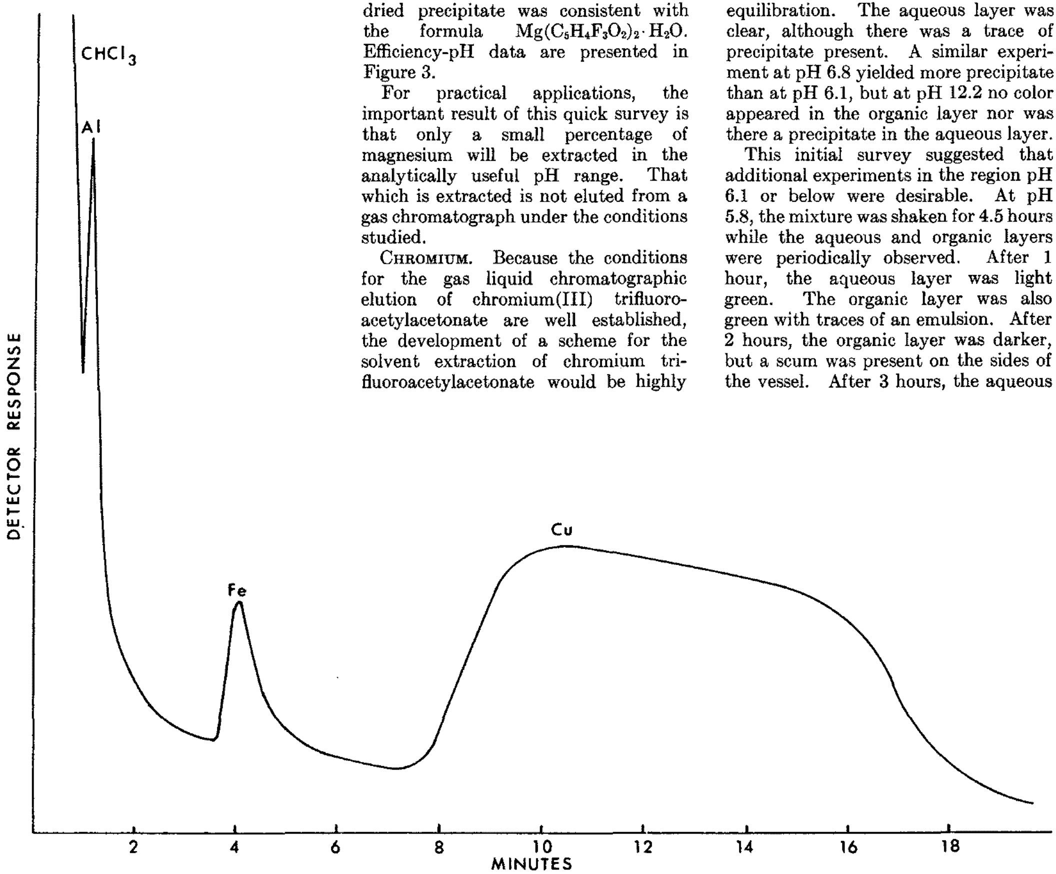

Figure 4. Gas liquid chromatogram of chloroform–trifluoroacetylacetone extract of NBS 162a

Equilibrium pH, 4.5.

layer was clear, but slightly green, while the organic layer was dark green. The precipitate was still present after 4.5 hours.

Mixtures of butyl alcohol and chloroform did not result in clean separations after 3 hours (pH 5.5 and 6.2), nor did mixtures with ether and carbon tetrachloride.

Although conditions for the clean, rapid separation of chromium(III) were not derived, the above experiments permit two important conclusions. No extraction occurs at pH 2.2. Iron, aluminum, and copper can be separated from chromium at pH 5 to 6 in 10 minutes, although some chromium might be extracted.

Additional work is definitely warranted, for the possibilities have by no means been exhausted. Reduction of chromium(VI) under more acidic conditions followed by the addition of acetate is suggested. Formation of chromium trifluoroacetylacetonate via chromium(II) may also be fruitful (*10*).

PRACTICAL APPLICATIONS: SEPARATION OF METALS IN NATIONAL BUREAU OF STANDARD SAMPLES

Data on the solvent extraction behavior of a sufficient number of metals permitted a firm test of the methods by an examination of a standard material.

A sample of nickel-copper alloy, NBS 162a (2.5097 grams) was treated with 6-ml. nitric acid-18-ml. hydrochloric acid mixture in the cold for 30 minutes and was then heated. The solution was filtered (to remove silica) and diluted to 250 ml. (pH 1.3). The standard contains 63.95% nickel, 30.61% copper, 2.19% iron, 1.60% manganese, 0.93% silicon, 0.50% aluminum, 0.076% cobalt, 0.042% chromium, and 0.005% titanium. A 10-ml. aliquot of the above solution should contain 30.73 mg. of copper, 2.20 mg. of iron, 0.50 mg. of aluminum, 64.2 mg. of nickel, 1.61 mg. of manganese, and traces of chromium, cobalt, and titanium.

A turbid emulsion was observed after equilibration when sodium acetate was added before the solvent-reagent mixture (pH 4.5, 4.9, 5.4). When the order of addition was reversed, however, clean separations resulted (pH 4.5) via this scheme: 10 ml. of the alloy solution were treated with 20 ml. of water and 25 ml. of chloroform-trifluoroacetylacetone. After it was shaken for 10 minutes, 5 ml. of sodium acetate (1*M*) were added. After an additional 10 minutes of shaking, the organic layer was isolated and evaporated. The residue contained (by emission analysis) > 1% copper, 0.5% aluminum, 1.0% iron, 0.6% sodium, 0.3% nickel, 0.007% manganese. The amount of nickel carried over is that expected for 1% extraction of nickel at this pH, in keeping with the survey data.

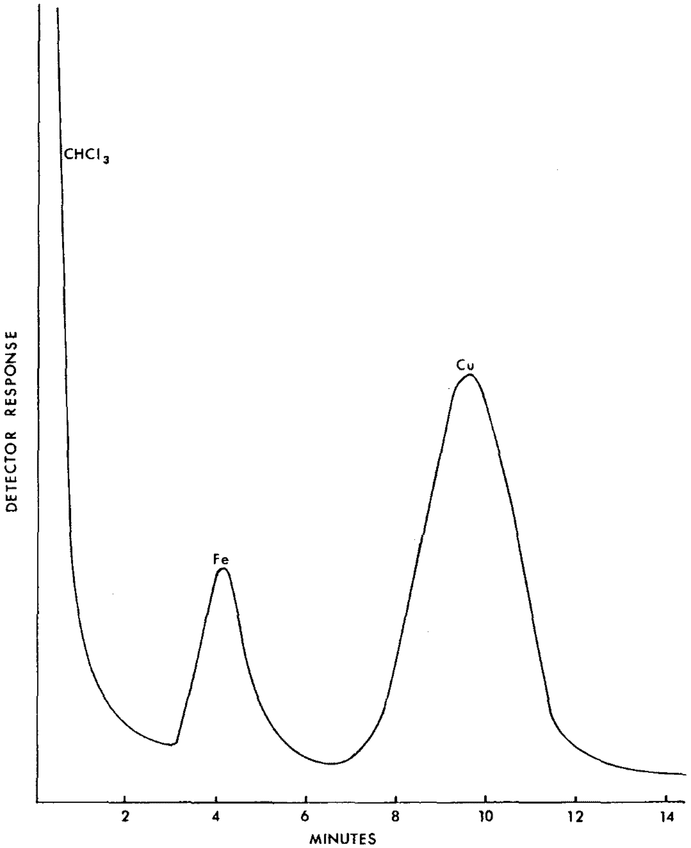

Figure 5. Gas liquid chromatogram of chloroform-trifluoroacetylacetone extract of NBS 162a

Equilibrium pH, 2.1

The extraction was repeated, and an aliquot of the organic layer was concentrated from 10 ml. to 2 ml. for GLC examination (polyethylene wax column, 2 ft. × 4-mm. i.d., 0.5% polyethylene wax on glass beads, with a thermal conductivity detector, column temperature, 92° C.). The resulting chromatogram (Figure 4) shows excellent resolution of aluminum and iron peaks. The relative areas of the iron and aluminum peaks were consistent with the known concentration of these metals in the alloy, and retention times matched those previously determined for aluminum, iron, and copper trifluoroacetylacetonates.

Figure 4 indicates that there was such a high concentration of copper that the column was overloaded.

To provide a solution free from aluminum and the bulk of the copper, the extraction was repeated at a higher equilibrium acidity (pH 2.1). A 10-ml. aliquot of the chloroform layer was concentrated to 1 ml., and a 9-µl. sample of the concentrate was examined by gas liquid chromatography (Figure 5). As expected, no evidence for the presence of aluminum was obtained. The amount of copper was greatly but not completely reduced. At pH 2.1, about 13% of the copper was extracted (Figure 1). This scheme nevertheless should provide an excellent means for the gas liquid chromatographic analysis of iron after solvent extraction separation from aluminum, most of the copper, nickel, and other metals.

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Variable Angle Reflection Attachment for the Ultraviolet, Visible, and Infrared

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▶ A variable angle reflection attachment which operates in the ultraviolet, visible, and infrared regions has been developed for spectrometers. The design is simple, especially as an internal reflection unit, in which case it comprises a right angled mirror and a right angled prism. The sample is placed in contact with one short face of the prism at which various angles of incidence are obtained by rotating the mirror. The attachment is useful to obtain attenuated total reflection spectra, to obtain indices of refraction directly by a single reflectivity measurement at less than critical angle or by determining the critical angle itself, or to obtain reflectivity data at two polarizations or two angles from which both optical constants can be calculated.

INTERNAL REFLECTION SPECTROMETRY has a number of unique advantages, and the methodology and apparatus exploiting these advantages have developed over the past few years (*3, 4*).

A simple reflection attachment is described here which can be used to convert almost any ultraviolet, visible, or infrared absorption spectrometer into an internal reflection spectrometer. This device can be used as an ATR unit to obtain transmission-like spectra.

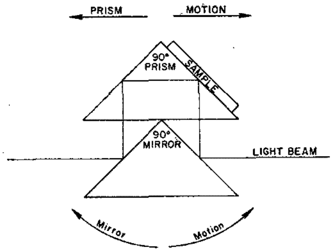

Figure 1. Arrangement of prism and mirror of variable angle reflection unit for a 45° angle of incidence at sample

Indices of refraction of substances which are not too absorbing can be obtained as a function of wavelength by measurements of reflectivity at angles less than the critical angle or by the critical angle method itself at any wavelength. Both optical constants—i.e., the refractive index and the absorption coefficient—can be calculated by using the device to obtain reflectivities at two angles or two polarizations (*1, 2*).

APPARATUS

General Description. The device comprises a right angled prism and a right angled mirror arranged as shown in Figure 1. The mirror is rotatable about a line through its 90° apex, and the prism can be translated in a direction parallel to its long face. A simple geometrical analysis shows that the direction of a light ray is not changed by having passed through the device, regardless of the original direction of the ray. There will in general be a parallel displacement, but this is readily eliminated by sliding the prism as indicated. Thus, any angle of incidence, θ, on the sample face can be obtained at will, within certain limits. (The angles obtainable are limited only by the net "window width" of the unit—i.e., as θ approaches normal or grazing, the width of beam that can be accommodated approaches zero).

Figure 2 shows the relative prism, mirror, and beam positions for $\theta = 70°$. Note that at other than $\theta = 45°$ for an isosceles prism, there will be refraction. Despite the value of θ and the refraction, the beam direction is still the same after leaving the device as it was before entering it. To see this it is helpful to note that the beam entering the prism face is parallel to the beam leaving the prism face, both inside the prism and outside the prism. Also note that as the unit as a whole is translated perpendicular to the light beam (see Figure 3) the direction of the beam is unchanged. The distance traveled by the beam in air and the distance traveled in the prism are also unchanged. In fact the distance traveled in air by any ray is exactly the same as if the unit were not there.

For prisms with low indices it is

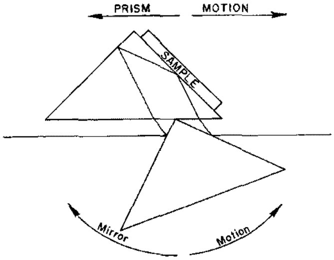

Figure 2. Relative position of prism and mirror for an angle of incidence at the sample of 70°

Refraction is shown for a prism of index 1.5

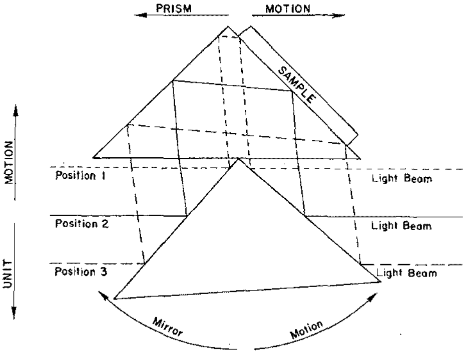

Figure 3. Schematic illustrates how point of reflection scans across sample as the unit as a whole is moved perpendicular to the incoming light beam

Here the angle of incidence is fixed at 50°

necessary to silver the short face not contacting the sample to prevent loss of light when the reflection is nontotal at this face. For prisms with high indices, like silicon and germanium, it is advantageous to use a nonisosceles shape in order to permit a wider range in θ.

Special Features. A reflection unit of this simple design can be used in virtually any spectrophotometer with sample compartment large enough to accommodate it. (Of course, if polarized light is to be used a polarizer must also be provided.) From the general description given above several features can be seen: (1) Known angles of incidence are easily obtained, provided an appropriate angular scale is fastened to the mirror. (2) The beam collimation is usually n_1 times as good as that of the original beam in the plane of incidence, where n_1 is the refractive index of the prism. This is the best collimation that it is possible to obtain in a practical way. More specifically, consider a light beam of rectangular cross section with its short dimension in the plane of incidence (the usual arrangement). An angular spread of δ in the plane of incidence outside the prism will give rise to a spread of δ/n_1 in the angle of incidence, θ, on the sample inside the prism. The angular spread of the beam perpendicular to the plane of incidence may be much larger than δ without increasing the spread of δ/n_1 in θ. A geometrical analysis shows that a perpendicular angular spread of $n_1\beta$ outside the prism gives a spread of β inside and a spread of $\theta - \sin^{-1}(\sin \theta \cos \beta)$ in θ. For example, if θ is *ca.* 45°, a beam spread of 9° outside a prism of index 3.0 would give a spread in θ of only 0.08°. For small θ (near normal incidence) this difference in the effect on θ of beam spread parallel and perpendicular to the plane of incidence will tend to disappear. At small θ, however, reflectivity is in general insensitive to angle, and θ need not be so well defined. The practical way, therefore, to collimate the beam further, if needed, for reflectivity measurements is simply to mask it to reduce the angular spread in the plane of incidence. Well defined angles of incidence are therefore easily realized. (3) Because all working surfaces have their normals in a common plane, the plane of incidence, light polarized either parallel or perpendicular to this plane will remain so, provided the prism is homogeneous. (4) Since the path length of any ray in air is the same with and without the unit present there is absolutely no appearance of atmospheric absorption bands when the unit is used in an unpurged double beam spectrometer. (5) The fact that the unit as a whole can be shifted back and forth perpendicular to the beam without changing any parameters permits the sample surface to be scanned by the beam. A constant reading with scan indicates a uniform sample. Or the sample may cover only part of the sample face, and the other part be bare or covered by a standard substance like silver. By merely moving the unit slightly a direct comparison can be had between the sample reflectivity and that of the standard, independent of instrument drift, etc. Within obvious angular limits, the standard can be total reflection, the very best standard available.

The unit can also serve as a convenient variable angle *external* reflection unit. For this purpose the prism is removed, a mirror takes the place of one short prism face and a flat sample alone replaces the prism-sample inter-

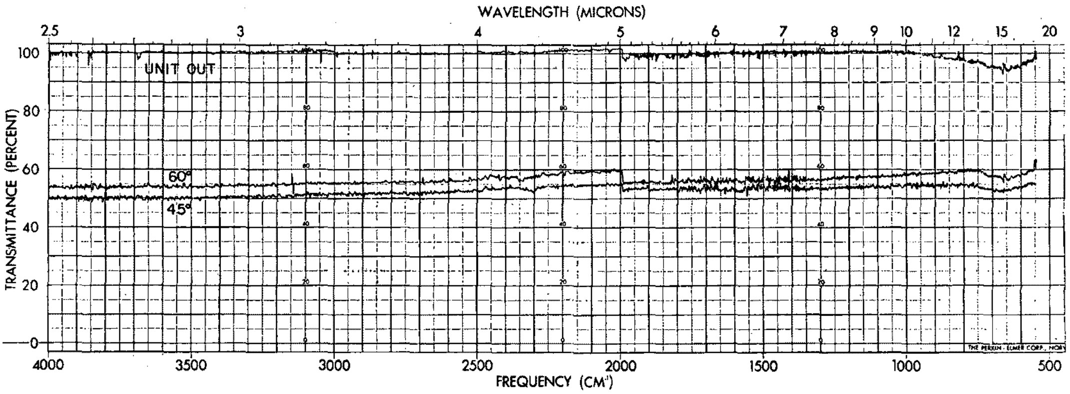

Figure 4. Base lines (no sample present) for variable angle unit with KRS-5 prism at two different angles of incidence in a Perkin-Elmer 421 spectrophotometer

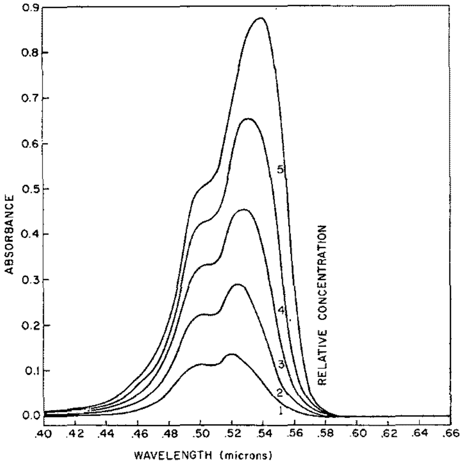

Figure 5. ATR spectra for aqueous eosin-Y solutions

Relative concentration of 1.0 corresponds to 50 grams/liter
ATR prism has $n_D = 1.787$. $\theta = 55°$

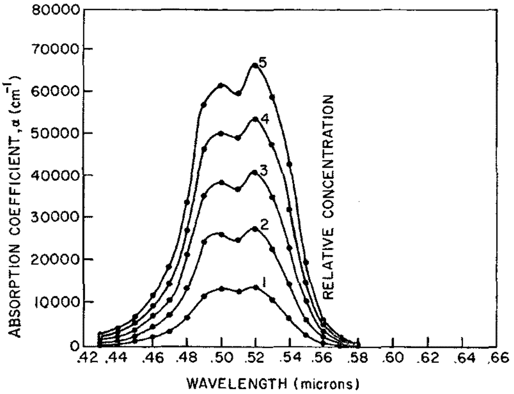

Figure 6. Absorption coefficient, α, of eosin-Y solutions calc. from reflectivity data

face. All of the above mentioned features except (4) and the total reflection part of (5) still obtain. If desired, feature (4) can be restored by enclosing the space ordinarily occupied by the prism (using an appropriate window instead of the long face) and filling the space with a nonabsorbing gas. This space can be filled with a transparent liquid and all of the above listed features of the prism case will be restored. An advantage of the liquid prism is easy optical contact with hard solids.

RESULTS AND DISCUSSION

Performance as an ATR Unit. One of the uses of the reflection unit is to obtain transmission-like spectra by means of ATR. We have used the unit for this purpose in the ultraviolet, visible, and infrared. Figure 4 shows the performance of the unit in the infrared with no sample present; a Perkin-Elmer 421 spectrometer was used. The prism was KRS-5. The mirrors were aluminum evaporated onto the faces of a right angled prism. The 100% trace (unit out) and traces for the unit set at $\theta = 45°$ and $\theta = 60°$ are shown. Note that because the sample can be placed on either short face of the prism, the 60° trace is also a 30° trace. Several features are noteworthy: (1) The efficiency--i.e., the transmittance of the unit without sample—is close to that theoretically possible considering the reflection losses at two KRS-5 surfaces plus losses at the two aluminum mirrors. This is true despite the fact that the Perkin-Elmer 421 has a short focal length and large angular spread of the beam (small f value), a fact which emphasizes any effects of defocusing caused by the unit. Of course, some defocusing does occur. The high efficiency throughout, however, proves that defocusing by the unit is unimportant. (2) The efficiency of the unit is maintained over a wide choice of θ, traces for all angles between *ca.* 27° and 63° lying between the two shown. A wider angular range can be used for KRS-5. However, for $\theta < 25°$ or $\theta > 65°$ one short face of the prism must be silvered. (3) Atmospheric absorption causes no more noise than with the unit out, even though the instrument was unpurged. (4) The traces at all angles are nearly as flat as the regular 100% line of the instrument permitting drift-free ATR spectra. The slight increase in the break at 2000 cm.$^{-1}$ for the 60° trace is due to the slight polarization of the beam by the beam entering and leaving the KRS-5 prism at non-normal incidence.

The case cited above was chosen because it was about the most unfavorable encountered or expected. In the UV-VIS-NIR range, using optical glass prisms, the energy losses are generally found to be less than the case cited. Because of the lower prism index there is less lost by reflection; however, this is partly offset since the aluminum mirrors are less efficient. Defocusing contributes to the loss, but only the divergent rays are lost in this fashion, improving the net collimation of the beam. With ordinary optical glass prisms the easily obtainable range in θ is *ca.* 15° to 75°.

As examples of ATR spectra in the visible region the results of measurements on a series of aqueous eosin-Y solutions of regularly varying concentration are presented. The observed ATR spectra are shown in Figure 5. The ordinate here is "reflection absorbance," defined as $A = \log_{10} I°/I$ where I is the intensity of light reflected from the sample and $I°$ is the intensity reflected when no sample is present (total reflection). This special absorbance is read directly on the absorbance scale of standard spectrometers if the scale is adjusted such that the absorbance given without the sample present (total reflection) is zero. Unit relative concentration represents 50 grams per liter. The prism index varied from 1.816 at 0.43 micron to 1.781 at 0.66 micron. The angle of incidence was 55° with a total spread of 0.5°. The polarization was parallel to the plane of incidence. To the extent that ATR spectra are transmission-like, they are a direct measure of the variation of the absorption coefficient, α, with wavelength. The spectra can be compared directly with plots of α shown later in Figure 6. When this comparision is made it will be seen that only at the lowest concentrations do the relative heights of the two peaks compare closely in the two figures. This type of deviation of the ATR spectra from the transmission spectra has been called "distortion." It can readily be understood by considering what is happening to the index of refraction as shown in Figure 7. In the 0.54-micron region, especially, n_2, the real part of the refractive index of the sample is increasing appreciably, causing considerable increase in the intensity of the ATR spectrum in this region. The ATR spectra are, however, similar to the transmission spectra, especially at low concentrations.

Direct Measurement of Refractive Index. If θ is chosen smaller than the critical angle, the reflection measurement gives a rather direct measure of n_2. Reflection spectra for the above eosin-Y solutions but with θ smaller than critical, are given in Figure 8. From these data, in regions where α is

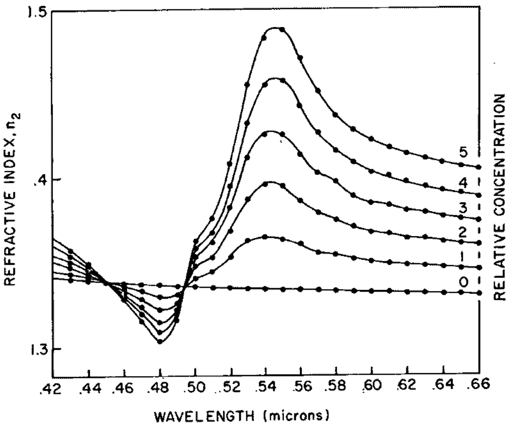

Figure 7. Real index of refraction, n_2, of eosin-Y solutions calcd. from reflectivity data

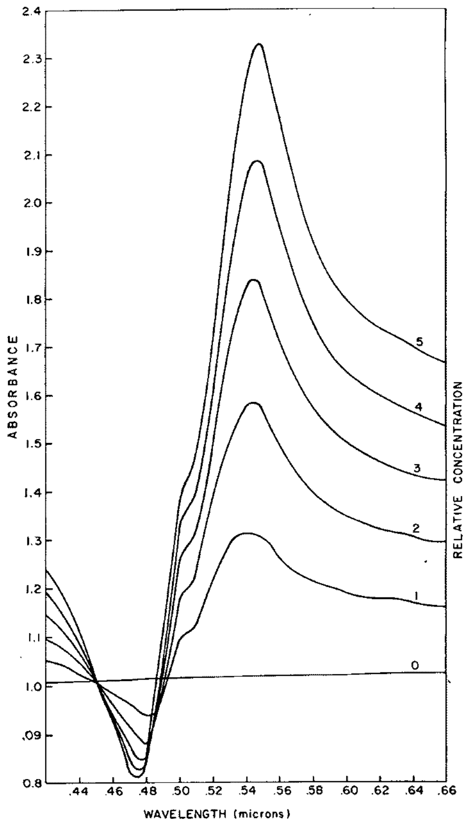

Figure 8. Reflection spectra at less than critical angle for eosin-Y solutions

Relative concn. of 1.0 corresponds to 50 grams/liter. The prism n_D = 1.787. θ = 45°

not too large, n_2 can easily be calculated (*2*). The equation is

$$\frac{n_2}{n_1} = \left[\cos^2\theta\left(\frac{1 \mp \sqrt{R_\perp}}{1 \pm \sqrt{R_\perp}}\right)^2 + \sin^2\theta\right]^{1/2}$$

where $R_\perp$ is the reflectivity measured at less than critical angle. An analogous equation will be found for parallel polarization in reference (*2*). The angle θ should be enough less than the critical angle so that it is out of the region where reflectivity changes so rapidly with θ that error is introduced by the uncertainty in θ. The similarity between A and n_2 as a function of wavelength can be seen by comparing Figures 7 and 8.

The reflection unit also makes it easy to determine n_2 by the critical angle method wherever α is not too large. The 90° mirror is rotated until the critical angle, θ_c, is reached as evidenced by a sudden shift in the indicated energy. It will be recalled that $n = \sin\theta_c$ where $n = n_2/n_1$. This method is convenient at any wavelength. When no sample is present—i.e., when the second phase is air—this method can be used to determine the index of the prism itself. Thus, it is not necessary to know the dispersion curve of the prism before measurements can be made.

As an example of the use of the above methods, the index of water was measured. The results agreed with the zero concentration (pure water) curve of Figure 7.

Determination of Both Optical Constants. From complex Fresnel formulas for reflectivity at a plane boundary, R is a function of n, α, θ, and P where P is a measure of the polarization. The variables θ and P are subject to choice. It is possible to invert the reflectivity equations and solve for n and α in terms of R_1 and R_2, reflectivities measured at two different polarizations or two different angles. The reflection unit described above was designed to permit convenient and accurate measurement of R_1 and R_2 using a standard automatic scanning spectrophotometer.

As an example of this usage of the reflection device the optical constants n_2 and α have been calculated as a function of wavelength for eosin-Y solutions from the reflectivity data given in Figures 5 and 8. For these calculations a computer program is used which inverts the reflectivity equations for parallel polarization at two different angles—i.e., solves for n and α from A at two θ's. The resultant optical constants are plotted in Figures 6 and 7.

The reflection unit has also been used to determine optical constants of metals, for which the method proves to be extremely useful (*1*).

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Radio Release Determination of Dichromate Ion in Natural Waters

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▶ A radio release procedure is presented for the measurement of dichromate ion concentrations in natural waters. On reacting the acidified sample with radioactive silver metal, silver ions are stoichiometrically produced in the sample. The resulting count rate of the solution is directly proportional to the original dichromate concentration. The two commonly occurring ions which interfere with the reaction, Fe^{+3} and Cl^- are easily accommodated in the reaction system. The limit of sensitivity of the procedure, with the radio silver used for these studies, is 10 μg. of Cr(VI) per liter.

SODIUM DICHROMATE is used routinely in France to measure the volume flow rate of streams. The technique is standard and straightforward: a concentrated solution of sodium dichromate is injected into a stream at a known rate. The waters are sampled downstream where the dichromate concentration has reached a uniform concentration. Heretofore, the concentration of dichromate in the injected solution and in the collected samples has been determined by colorimetry. Knowing these concentrations and the injection rate of the dichromate solution, the volume flow rate can be calculated.

The quantity of sodium dichromate injected usually is 1–2 kg. of the salt per each cubic meter per second estimated flow rate for mountain rivers tested in France, and for flow rates below 50 cubic meters per second. Dichromate concentrations are then of the order of 1 mg. of the ion per liter in the collected samples. This concentration is about the minimum one can measure conveniently by present colorimetric methods. The size or flow rate of the stream which can be measured by the colorimetric technique is limited, however, by both the cost of the dichromate and the logistic problems of getting large quantities of sodium dichromate to a difficultly accessible injection point. A more sensitive technique for measuring dichromate ion concentrations in natural waters is described here.

The method of measuring dichromate concentrations in natural waters described here makes use of the "radio release" technique. In this technique, nonradioactive ions (or elements) of interest are caused to react with an insoluble radioactive compound (*1*, *2*). The radioactive compound is chosen such that its reaction with the ion of interest releases a stoichiometric quantity of the radioactive species into solution. Measurement of the radioactivity of the solution is then a measure of the concentration of the nonradioactive ion of interest. The technique is useful for measuring very small concentrations of ions by the radioactive species.

The chemical reaction employed in the work reported here is that between dichromate ion and silver metal. The following equation describes the reaction in acid solution.

$$Cr_2O_7^{-2} + 6Ag + 14H^+ \rightarrow 6Ag^+ + 2Cr^{+3} + 7H_2O$$

The radioactive isotope Ag^{110m} (half life = 253 days) which emits a mixture of beta and gamma rays, is desirable for this work. If solutions containing dichromate ion are made acidic and then reacted with metallic silver-110m, the solution will contain silver-110m ions in direct proportion to the original concentration of the dichromate ion. Counting a portion of the solution enables the concentration of the dichromate to be determined.

EXPERIMENTAL

Apparatus and Reagents. A scintillation counter having a 2- × 2-inch sodium iodide crystal is used for counting samples.

The radioactive silver is 50-mesh gauze in the form of a rectangular stirrer paddle. A central hole is made in a 0.5- × 3-cm. piece of the gauze so that it can be affixed to the end of a threaded polystyrene stirring shaft by means of two small polystyrene nuts. The gauze is then irradiated in a nuclear reactor. (The silver used for this work was irradiated in the Grenoble reactor "Melusine" for 48 hours at a flux of approximately 10^{12} neutrons per square centimeter-second. This should produce a specific activity of Ag^{110m} of 1 mc. per gram, but because of the neutron distribution in Melusine, and the absorption spectrum of Ag^{109}, the specific activity of the Ag^{110m} is approximately 10 mc. per gram.) After irradiation, the gauze is attached to the shaft which can be rotated at 250–300 r.p.m. by a small motor.

The $NH_4F{\cdot}HF$ solution was the reagent grade salt with a concentration of 300 mg./ml.

The H_2SO_4 and NH_4OH used were concentrated, analytical grade reagents.

Procedure. Measure 100 ml. of the sample to be analyzed into a 250-ml. beaker of Teflon. Add by pipets 1 ml. of $NH_4F{\cdot}HF$ solution and 1 ml. of concentrated H_2SO_4. Stir the solution with the silver stirrer for 1 hour. At the end of this time, add by pipet 5 ml. of concentrated NH_4OH, stir for 1 minute, and then remove the solution from the stirrer. Place the solution, or a known portion of it, on the scintillation counter and record the counting rate. For absolute measurements, run a standard solution of dichromate under the same conditions. For measuring the flow rate of streams, if the concentrations of the collected sample and the (diluted) injection sample are similar, only the ratio of the concentrations (counting rates) is necessary. It is more accurate, however, for this latter application, to run a sample of the stream water collected before the dichromate injection and use this (counting rate) as a blank.

RESULTS AND DISCUSSION

In the development of this procedure for dichromate, simplicity of manipulations was deemed desirable so that it could be used routinely by unskilled technicians. At the same time, it was desired to measure dichromate ion at very small concentrations. Since there are many other ions in natural water, the two goals seem at first too incompatible. However, preliminary work had shown that there are usually only three ions in unpolluted streams which may interfere with the dichromate–silver reaction: chloride ion, ferric ion, and nitrate ion. Following is a discussion of the reasons for choosing the particular reagents given above to minimize these potentially interfering ions.

Chloride Ion. Chloride ion can cause difficulties in the radio release procedure for dichromate ion by precipitating silver chloride. If the silver chloride were to remain suspended

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in the solution, there would be no problem because the sample of solution taken for counting would be representative of the original dichromate ion concentration. If, on the other hand, the silver chloride were to remain on the stirrer, or on the walls of the vessel, then a sample of the solution would not be a measure of the initial dichromate concentration. This latter situation is the one which occurs so it is necessary to complex the silver so that it remains in the solution.

There are two approaches to keeping silver in solution: (1) To complex it as soon as it is formed (thus, silver chloride is never precipitated) (2) To allow the reaction to go to completion after which the precipitated silver chloride is dissolved by a suitable reagent. For the first approach, many reagents were tried, but only two commercially available compounds were successful: thiosinamine and 1,3-diethyl-2-thiourea. These can keep silver complexed in acid chloride solutions. Unfortunately, dichromate in such solutions slowly oxidizes these compounds so that at lower pH values the results are not reproducible. It is necessary to adopt the second approach—that of allowing the reaction to be completed—then attempt to dissolve the silver chloride from the silver stirrer. Of the several reagents tried for this purpose, ammonia was the most successful. Thiosulfate may be satisfactory in basic solution, only if it is free of sulfide ion, while cyanide in basic solution tends to dissolve some of the silver metal, thus giving high blank values. Coating of the stirrer with a thin impervious layer of silver chloride so that remaining dichromate in the solution cannot react does not appear to be a problem, as quantitative results have always been obtained with solutions up to $0.5M$ in chloride ion.

Ferric Ion. Ferric ion can oxidize silver metal in acidic solutions. Most streams do not contain ferric ions as such because the pH values are above those at which ferric hydroxide precipitates. But when these waters are made acidic and ferric hydroxide may dissolve, or ferric ion may be leached from suspended matter, so that ferric ion may cause difficulties in this radio release technique. Since the solution is quite acidic, and because dichromate is a good oxidizing agent, many organic agents capable of complexing ferric ion are not useful in the solution. Of the inorganic ions capable of complexing ferric ion, only two are satisfactory: phosphate and fluoride. Both are satisfactory, but fluoride seems to be somewhat better than phosphate. For much of the early work in development of this procedure, phosphoric acid was used to make the solutions the desired pH values and at the same time complex the ferric ion in solution. When it later developed that the use of sulfuric acid was advantageous (discussed below), fluoride ion was added to the solutions to reduce the interference of ferric ion more than phosphate. In solutions prepared as described in the procedure, 10 mg. of Fe^{+3} per liter produce the same activity of silver-110m as does 50 μg. of Cr^{+6} per liter.

Nitrate Ion. Nitrate ion was thought to be a potential problem because it can oxidize silver metal in acidic solutions. It could be present in streams either from biological action or by having been leached from fertilized fields. Experiments using NH_4NO_3 solutions show that 5 mg. of NO_3^- per liter produce an activity of silver-110m equal to less than 3 μg. of Cr^{+6} per liter. Nitrate ion then does not interfere unless it appears in higher concentrations.

Organic Material. Suspended organic materials, such as algae, decayed plant material, etc., may interfere by reducing the Cr^{+6} ion. This interference is not serious except at very low levels of dichromate concentration or for extended delays between stream dosing and sample assaying. Methods of circumventing this problem are now being investigated in a separate study.

Effect of pH and Stirring Time. The reaction between dichromate ion and silver metal is complete in reasonably short times only if the pH is less than 3.0. Many experiments were carried out at pH 2.5, for which stirring times of 2.5 hours are required. These experiments were with H_3PO_4. Lower pH values required correspondingly larger amounts of the acid, for which volume corrections became necessary. With H_2SO_4, however, much smaller volumes of acid are required to achieve a given pH value. It was found that identical results are obtained for a given solution of dichromate ion in stream water from pH 2.5 down to pH 1.0 using either H_2SO_4 or H_3PO_4. It was further found convenient to add 1 ml. of H_2SO_4 to a 100-ml. volume of stream water (containing 300 mg. $NH_4F \cdot HF$), and the pH was then 1.5 ± 0.1 units. It is thus not necessary to use a pH meter. At 1.5, 1 hour of stirring time is sufficient for complete reaction.

Reproducibility, Precision, and Sensitivity. It is possible to present here details of the reproducibility and precision using samples of natural waters to which known quantities of dichromate ion have been added. Table I shows the counting rates obtained when 2 ml. of a standard solution of dichromate were diluted to 500 ml. with various natural waters, and 100 ml. of the resulting solution was then treated with H_2SO_4 and $NH_4F \cdot HF$ according to the method given in the procedure. These results were obtained over a period of several weeks, using both H_2SO_4 and H_3PO_4 in the pH range 1.0–2.5. Each run was made on a different standard solution made up at a different time with different water. Standard counting time was 100 seconds which represented a total of about 160,000 counts.

Table I. Reproducibility of Counting Rates for a Standard Dichromate Solution

Run No.	Counts per sec.
1	1620
2	1670
3	1670
4	1670
5	1640
Av.	1654

Table II. Reproducibility of Counting Rates for Blank Samples

Run No.	Counts per sec.
1	103
2	107
3	107
4	105
5	109
Av.	106

Table II shows the counting rates of various "acid blanks" (samples of stream waters containing $NH_4F \cdot HF$ made to pH 1.5–2.5 with H_2SO_4 or H_3PO_4 and with 1 to 3 hours of stirring. The counting rates for the blank samples are high. It must be mentioned that no attempt has been made to optimize the counting arrangement. The scintillation counter used for these studies is in a chemical laboratory in which are also other radioactive sources more or less well shielded in lead bricks. The counting rate of the instrument with no sample is about 60 counts per second; the net blank counting rate is therefore about 46 counts per second.

The numbers from Table I and Table II, together with the concentration of the standard dichromate solution used for obtaining data of Table I, enable one to calculate the sensitivity of the procedure: The dichromate solution is 0.0500 mg. of Cr(VI) per milliliter, 2 ml. of which diluted to 500 ml. gives a solution of 0.200 mg. of Cr(VI) per liter. This concentration of Cr(VI) produces a net counting rate of 1548 (= 1550) counts per second. A solution containing 0.01 mg. of Cr(VI) per liter therefore produces 77.5 counts per second above the acid blank. In one field experiment, the measured dichromate concentration was 0.03 mg. of Cr(VI) per liter, a concentration which, from calculation, gave a volume flow rate for the stream within 3% of that determined by colorimetric means. The stream flow was 7 cubic meters per second.

It is convenient to clean the silver gauze stirrer between experiments with a KCN solution. Stirring of the KCN (3 grams of the salt per 100 ml. of H_2O) for 1 or 2 minutes, followed by three 5-minute rinses with water, has always produced a bright, active stirrer which gives reproducible results. Actually, in the experiments described here, 2 pieces of gauze were irradiated simultaneously in the reactor. Their activities are identical and a sample and an "acid blank" can be carried out together. These stirrers show no signs of deterioration after having been used for more than 100 samples or blanks with KCN cleanings between each use.

ACKNOWLEDGMENT

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Solvent Extraction Studies with a Hydrochloric Acid–2-Ethylhexanol System

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▶ The distribution of 45 elements between 83% 2-ethylhexanol–17% petroleum ether and hydrochloric acid solutions has been determined. A graphic presentation of the extraction data as a function of acid concentration is given. Very efficient extraction of Ti(IV), V(V), Ru(VIII), Sn(IV), Pa(V), Nb(V), Ta(V), Ga(III), Fe(III), Sb(V), Au(III), As(III), Np(VI), and Mo(VI) was achieved. Of the remaining elements studied, only W(VI), Zn(II), U(VI), Tc(VII), Cd(II), Hg(II), and Pd(II) were appreciably extracted. Separations within the group of well extracted elements can be accomplished by back-extraction utilizing selective reduction, complexation, and variation of acid concentration. The extracted elements are readily stripped into dilute acid solution or water. A number of applications of the system to activation analysis as well as other radiochemical separations, including preparation of some carrier-free samples, are given.

IMMISCIBLE ALCOHOLS have not been widely applied as extractants for inorganic species as have ethers, ketones, and more basic extractants such as the high molecular weight amines. Alcohols are often used as diluents for other extractants (*2*) and as solvents for chelate extractions. Distribution studies between hydrochloric acid and an immiscible alcohol have been used to determine ionic species in hydrochloric acid solution (*1*, *3*).

In many analyses the samples are solubilized in strong mineral acid solution, while the optimum conditions for specific separations occur in the pH range 0–12 where masking and pH control are most effective. In radiochemical procedures, a preliminary separation step is often used to eliminate the bulk of interfering activity and consequent radiation hazard in a simple, remote operation. The hydrochloric acid–alcohol system to be described is very suitable for this type of separation because of the rapid equilibrium, ease of manipulation, and high solute capacity. In the case of sequential multielement analysis, the separated fractions are free in most cases of excess reagents and salts which may interfere in a following analytical step.

Many of the elements covered in the present study extract into various oxygenated solvents such as ethers and ketones, but 2-ethylhexanol is superior to these reagents in several respects. The low solubility (0.33% in concentrated HCl) of the alcohol is a distinct advantage over ether and ketone systems. Having a flash point of 85° C., and an azeotrope with water boiling at 99° C., gives the alcohol system stability as well as ease of evaporation. The low vapor pressure at room temperature permits one to carry on experiments without significant solvent loss and with low flammability hazard. The latter is of particular concern when working with highly radioactive samples.

Of some 45 elements studied, 14 were well extracted (75–99%) while nine were extracted in the 30–60% range and would be considered interferences. The alkali metals, alkaline earths, and rare earths were not extracted appreciably. Nickel, bismuth, indium, scandium, silver, and copper were extracted 10% and less; iridium (IV), ruthenium (III), chromium (III), manganese (II), and yttrium, 1% and less.

EXPERIMENTAL

Reagents. 2 Ethyl-1-hexanol (practical grade) was obtained from Matheson, Coleman, and Bell. This grade has an assay of 98% by gas chromatography, the remainder consisting of isomers. All other chemicals and solvents were reagent grade or equivalent except *n*-hexanol which was Eastman practical grade.

Procedure. Distributions were determined using purified radioactive tracers. All extractions and pre-equilibrations were carried out in 40-ml. centrifuge cones using battery-driven mechanical stirrers. Although phases separated well, centrifugation was employed to eliminate any suspended droplets in either phase. Aliquots were pipetted into small polyethylene bottles or dried on planchets for counting. Single channel and multichannel analyzers were used for gamma counting, and gas proportional detectors for alpha and beta counting.

Petroleum ether was used as diluent for all alcohols studied. The 2-ethylhexanol for all extractions was diluted to 83% by volume for ease of phase separation, unless otherwise noted.

A small amount of crystalline $KMnO_4$ (30–40 mg.) was added three times during the extraction of V, Ru, Np, Au, Mo, and Sb tracers in order to oxidize these elements to their higher oxidation states. Cr, Ce, Mn, and Bi could not be maintained in the maximum valence state in the alcohol-HCl system.

The organic phase was pre-equilibrated in all cases. Equal volumes (10 ml.) of organic and aqueous phases were used for the extractions. The distribution coefficients (*D*) given are the ratio of radioactive count rates of equal

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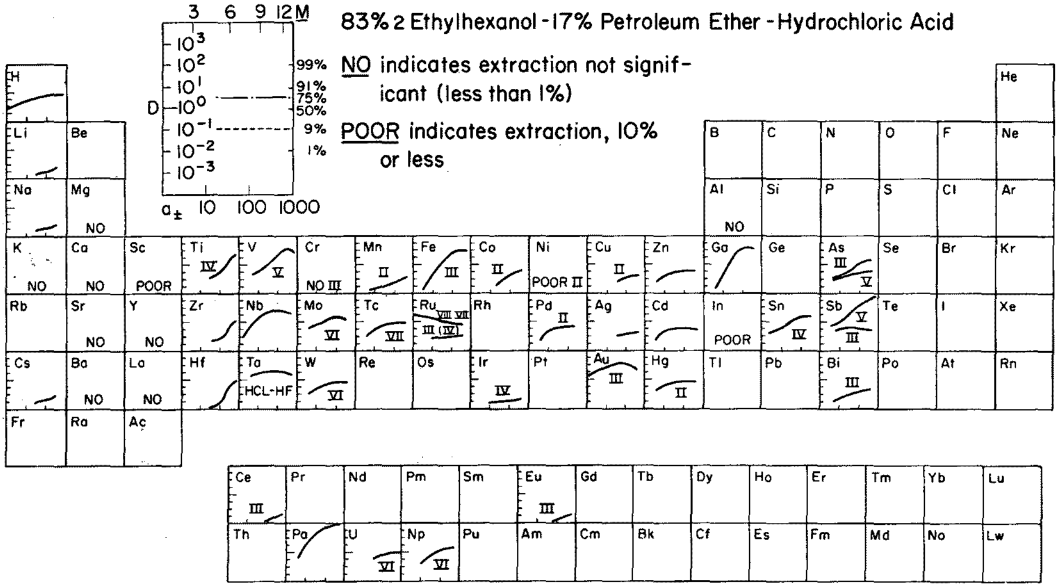

83% 2 Ethylhexanol-17% Petroleum Ether-Hydrochloric Acid

NO indicates extraction not significant (less than 1%)

POOR indicates extraction, 10% or less

Figure 1. Distribution coefficient *vs.* ionic activity of HCl

aliquots of organic and aqueous phases. Based on studies of extraction time dependence for several typical elements, a 10-minute equilibration time was used for all extractions.

RESULTS AND DISCUSSION

Figure 1 shows log-log plots of the extraction data. The main coordinates as shown on the model figure are distribution coefficient *D* and mean ionic activity $a_\pm$ as determined from molality and standard activity coefficients. Molarity and percent extraction are also indicated on the model. The alkali metals show no appreciable extraction. Less than 1% of Li, Na, and K was extracted from strong HCl. Ag(I) has a *D* about 10 times higher, 8% having been extracted from strong HCl. The distribution of HCl is included to indicate the significant extraction of H^+ from concentrated acid solution, giving an organic phase concentration equivalent to 4*M* HCl. This affects the distribution behavior of elements extracted from strong acid solutions.

Significant quantities of bivalent elements were extracted by this system. Zn, Cd, Hg, and Pd with maximum extractions between 40 and 50% are considered interferences over the useful range of acidities, whereas Co would be an interference at 9*M* HCl or higher. Cu and Mn can be easily removed from well extracted elements by organic phase scrubbing.

Of the trivalent elements Ga, Fe, Au, and As(III) show high distributions (>95%). Insignificant amounts of Al, In, and the rare earths were extracted. Ga and Fe were extracted together under oxidizing conditions; however, reduction of Fe(III) to Fe(II), which is poorly extracted, facilitates the separation from gallium. Gold was highly extracted (>90%) even in the lower acid range where distributions of most elements are low. Gold extractions were run in the presence of $KMnO_4$ because of the tendency of gold to be partially reduced in the simple system.

The high extraction of Ga and Fe makes possible separations from associated elements including Co, Cu, Mn, Ni, In, V, and Al.

The curves in Figure 2 represent the dependence of the distribution coefficient upon the concentration of the alcohol in the organic phase, with HCl concentration as a parameter. These curves are useful in maximizing differences in behavior for specific separations. Gallium and iron have similar alcohol dependence. The alcohol dependence for gold was studied at 6*M* HCl acid and found to be similar to Fe but with a higher range of distribution coefficients.

The family Ti, Zr, and Hf shows increasing extractability with decreasing ionic radius. Ti is well extracted (>91%) above 11*M* HCl. Separation factors in this subgroup of elements are not high. However, Sn(IV) shows a different dependence on acid strength, and separation factors between Sn and Hf, or Sn and Zr, at 8*M* HCl are good. Sn is also readily separated from In, Bi, and Cu which are poorly extracted in this system.

Germanium is not included because of its well known chloride extraction into a variety of organic solvents.

The alcohol dependence of Ti and Zr is unique among the elements studied

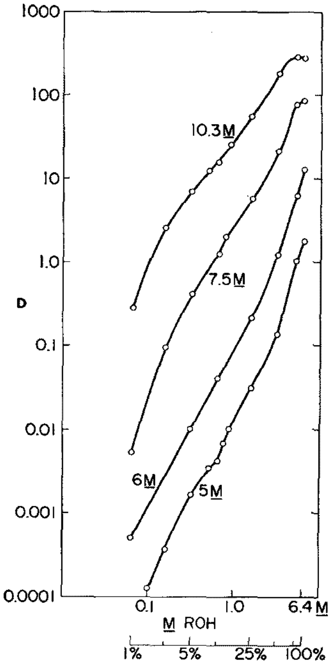

Figure 2. Distribution coefficient of Fe(III) *vs.* molarity of alcohol in organic phase

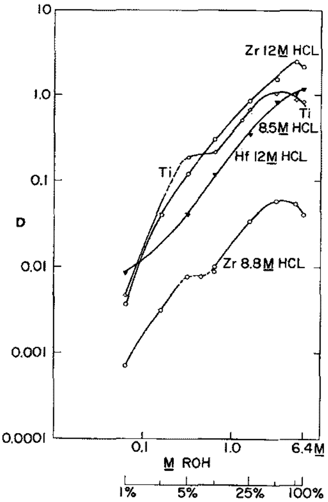

Figure 3. Distribution coefficient vs. molarity of alcohol in organic phase

because of the distinct shifts at 9*M* HCl (Figure 3). Zirconium goes through a transition in the alcohol dependence curves from 9 to 12*M* HCl. The maxima in the dependence curves for Ti and Zr at 50% alcohol suggests the use of this alcohol concentration rather than 83% strength. Sn(IV) shows a strong and also uniform alcohol dependence at all acidities.

Distribution coefficients of greater than 2000 for Sb(V) and 10,000 for Pa(V) were observed. The high distribution (>99%) for vanadium(V) contrasted to low distributions for vanadium(IV) and (III) enables ready separation of vanadium from well extracted elements, including group (V) elements.

Tantalum is not stable in hydrochloric acid and tends to be precipitated out of solution, and in the case of tracer concentrations is quantitatively adsorbed on the glass surroundings. The Ta curve in Figure 1 shows the extraction in the stated HCl concentrations with 0.2*M* HF present. Since Ta is well extracted from HF·HCl solutions the possibilities of separation from many elements is evident. This behavior has also been studied by Casey and Maddock (*1*).

Figure 4 shows the alcohol dependence curves for Sb(V), Nb(V), Pa(V), and V(V) at 12 and 5*M* HCl. Noteworthy is the overall low dependence of vanadium and the shift in the antimony curve in 5*M* HCl. A very efficient separation of Sb(V) and from Sn(IV) can be achieved on this basis. The distribution coefficient of antimony between 12*M* HCl and 0.32*M* (5%) alcohol in petroleum ether is 125 (99^{+} %) while distribution of Sn(IV) under these conditions is less than 0.1 or 9%.

Among the hexavalent and heptavalent elements Mo(VI) and Np(VI) have good distributions (75%) in strong HCl while Tc(VII) shows a maximum extraction of 67%. Tungsten with a maximum extraction of 57% is considered a high level interference. Np (VI) is easily reduced to lower oxidation states which are poorly extracted. Mo also is poorly extracted in its lower oxidation states and is readily reduced by stannous chloride. Cr(VI) has a tendency to be well extracted in this system. However, this element is rapidly reduced to the nonextractable Cr(III) even in the presence of $KMnO_4$ and may easily be separated from other well extracted elements such as V, Ti, Fe, Nb, and Sn.

Ru(III) and (IV) are not appreciably extracted from HCl, but in the presence of an oxidizing agent ($KMnO_4$) Ru extracts quite well (75–88%) from 1 to 3*M* HCl. At higher acidities the extraction falls off and remains between 50 and 70%. Extraction of Ru from dilute HCl offers the possibility of separating this element from many others.

Effect of Macro Amounts of Element on Distribution. Experiments were run to determine the effect of macro concentrations of an element upon its distribution. Examples are given in Figure 5. Distribution coefficients remain near maximum well into the range of analytical concentration for the elements shown. Noteworthy is the close similarity between Sn(IV) and Mo(VI) under these conditions. It was observed in the extraction of macro amounts of vanadium from 9–12*M* HCl that V(V) in the 2-ethylhexanol phase was notably more stable to reduction than V(V) in aqueous HCl.

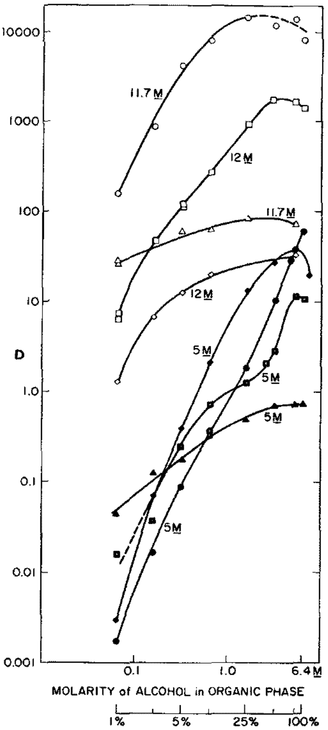

Figure 4. Distribution coefficient of pentavalent elements vs. molarity of alcohol in organic phase

Pa(V) —○—, —●—
Sb(V) —□—, —■—
V(V) —△—, —▲—
Nb(V) —◇—, —◆—

Table I. Ratio of Distribution Coefficient in Mixed Acids to Distribution Coefficient in HCl Alone

Element	8.2*M* HCl, 0.06*M* HF	8.2*M* HCl, 1.2*M* HNO_3	8.2*M* HCl, 1.3*M* H_2SO_4	Distribution Coefficient HCl 8.2*M* HCl
Zn(II)	1.0	0.56	1.63	0.42
Ga(III)	1.0	0.39	1.2	770
Fe(III)	0.63	0.34	1.14	270
Sn(IV)	1.0	0.39	1.34	2.89
Nb(V)	0.13	3.0	0.6	62
W(VI)	0.85	0.47	1.35	1.44
	9.6*M* HCl, 0.06*M* HF	9.6*M* HCl, 1.2*M* HNO_3	9.6*M* HCl, 1.3*M* H_2SO_4	9.6*M* HCl
Zr(IV)	0.02	1.0	0.03	0.46

Effect of Acids and Anions. The effect of HCl containing moderate amounts of hydrofluoric, nitric, and sulfuric acids upon the distribution coefficient was determined for a representative group of elements (Table I). Qualitatively, hydrofluoric acid lowers extractions with varying effectiveness. Hydrofluoric acid at 0.06*M* showed little effect upon Ga extraction but strongly decreased Zr extraction. Sulfuric acid strongly decreases Zr extraction at the acidity shown and could be used to enhance separation factors where Zr is an interference. Nitric acid triples the extraction of Nb(V) at 1.2*M* HNO_3, 8.2*M* HCl while decreasing Ga and Fe extraction at the same acidity.

An interesting extension of the HCl

Table II. Applications of 2-Ethylhexanol in Petroleum Ether as Extractant

Sample	Element	Separated from	Aqueous phase	Organic phase
Meteorites, steel	Fe(III)	Co, V, Mn, Cu, Sc, Ni, Cr, Al, Mg	6–8*M* HCl	2-Ethylhexanol–petroleum ether 83% ROH
	Ga	Fe	6–8*M* HCl reducing agent ($SnCl_2$)	"
Detn. of Zr in Hf using Nb^{97} daughter activity	Nb, Sb(V)	Zr, Hf	6–8*M* HCl	30% ROH
Purification of tracers	Nb	Sb	9–11*M* HCl reducing agent	"
	Nb	Fe, V	5*M* HCl mild reducing agent	50% ROH
Sepn. of V^{48} from Cyclotron irradiated Ti foils	V(V)	Ti, Cr, Al, Sc	6–8*M* HCl $KMNO_4$	83% ROH
	Ti(IV)	V, Sc	Warm 12*M* HCl	"
Trace analysis of Th, for Hf, Zr, Ta by neutron activation	Ta	Pa, Hf, Zr	3–5*M* HCl 0.5–1*M* HF	83% ROH
	Pa	Hf, Zr, Th	7–8*M* HCl	"
	Sn(IV)	Hf, Zr, Cu, In, Bi	7.5*M* HCl	100% ROH
	Au(III)	Many elements	3*M* HCl	83% ROH
	Ag (carrier free tracer)		1*M* HCl, KI	"
Detn. of trace Sb in metals and fission products	Sb(V)	Sn, Bi, Cu, Zn	12*M* HCl	2.5% ROH

system is the pronounced effect of KI on the extraction of Ag. Carrier free Ag tracer is extracted about 85% from 1*M* HCl containing a small amount of KI. At higher concentrations of Ag, the extraction is decreased.

Effect of Alcoholic Type. The alcohol dependence curves for the elements studied showed a complex distribution response to changes in the alcohol concentration. Contrasting behavior is noted between regions where the distribution coefficient is relatively insensitive to changes—e.g., Figure 3, Ti 8.5*M* HCl; Figure 2, Fe 10.3*M* HCl—and regions where extraction increases rapidly with moderate alcohol concentration changes (Figure 2, Fe(III) 6*M* HCl). Experiments using *n*-hexanol, *n*-heptanol, 2-ethylhexanol, *n*-octanol, and *n*-decanol indicate that significant differences are observed only in certain regions of high alcohol dependence. Fe(III) in 10.3*M* HCl was extracted to nearly the same extent by the five alcohols at 50% concentration. In 6*M* HCl and 50% alcohol, 2-ethylhexanol was least effective ($D = 1.7$) and *n*-hexanol most effective ($D = 11.5$). Similar behavior occurs with Sn(IV) in 5*M* HCl with 50% alcohols and with Ti in 12*M* HCl and 20% alcohol. A comparison of 2-ethylhexanol and *n*-hexanol in the extraction of Pa(V) from 5*M* HCl showed no difference over the range of 70–100% alcohol. The studies indicate that an alcohol-type effect may be observed where the 2-ethylhexanol concentration dependence curve exhibits linear regions. The use of different alcohols can enhance the separation of elements under certain conditions.

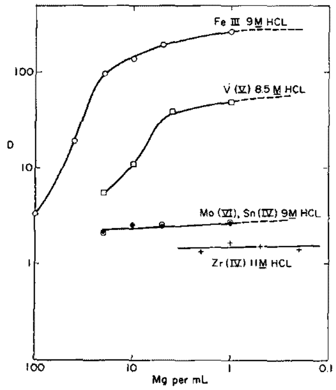

Figure 5. Distribution coefficient (*D*) vs. element concentration

Mo(VI) —○—
Sn(IV) —◆—

Typical Applications. Table II shows some typical applications using 2-ethylhexanol in petroleum ether as the extractant. For these radiochemical applications, milligram amounts of carrier for gravimetric measurement were not added since the separation could be made quantitative (> 98%). The use of inactive carriers is recommended to eliminate adsorption losses. By utilizing differences in distribution response to the various parameters, separations can be readily optimized for the particular sample material of interest.

A typical application of the 2-ethylhexanol–HCl system is the extraction of high levels of radioactive protactinium-233 from a thorium matrix in the determination of trace amounts of hafnium and zirconium by neutron activation.

Vanadium has been separated as carrier free V^{48} from deuteron irradiated titanium foils. This separation is performed in 7.5*M* HCl where in the presence of $KMnO_4$, 94% of the V(V) and about 13% of the Ti(IV) are extracted. The Ti(IV) is scrubbed out of the organic phase with 7.5*M* HCl. Alternatively, Ti(IV) may be extracted from vanadium in 12*M* HCl where vanadium is easily reduced to the poorly extracted IV state.

An example of separation of a three element combination is the case of processing zirconium–niobium tracer which contained antimony impurity. Niobium and antimony are readily extracted from zirconium in 7.5*M* HCl by 30% alcohol. The Nb–Sb combination is scrubbed once for removal of traces of zirconium, then antimony is back-extracted into a separate aqueous phase of 9*M* HCl containing a suitable reducing agent such as stannous chloride. The niobium is back-extracted into water containing H_2O_2.

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Gas Chromatographic Separation of Oxides of Nitrogen

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▷ By a unique arrangement of columns, combined with subambient temperature gas chromatography, a method has been developed for the determination of H_2, O_2, N_2, NO, CO, N_2O, CO_2, C_2H_6, C_2H_4 C_2H_2, and $NO_2(N_2O_4)$. The separation is accomplished using three columns in series. The first column temperature is subambient for the separation of $NO_2(N_2O_4)$ and water. The remaining two columns separate the other components in the gas sample. To obtain the complete analysis from one injection it is necessary to fabricate, or modify, a commercial gas chromatograph to accomodate two detectors and two columns. The schematic of a relatively cheap and simple gas chromatograph developed for this analysis is presented.

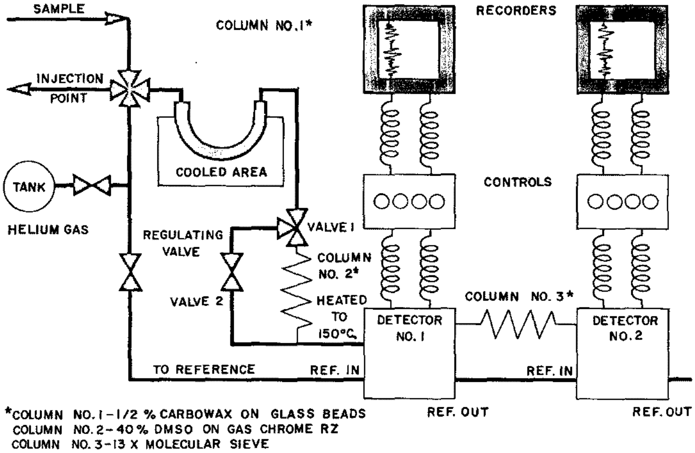

Figure 1. System schematic

Explosives and related industries have had a definite need for methods of analyzing nitrogen oxides. One analytical technique which has been extensively investigated is that of gas chromatography. However, the reported methods have been limited either to the determination of nitric and nitrous oxides with the exclusion of nitrogen dioxide, or to the determination of nitrogen dioxide with the exclusion of nitric and nitrous oxides. Two samples have therefore been required using gas chromatography methods of analysis. The more common methods reported have been at the exclusion of nitrogen dioxide. The work of Frazer and Ernst (*1*) is one of the more recent. They separated nitric oxide and nitrous oxide from a mixture of other gases by using a silica gel column in series with a molecular sieve column. Greene and Pust (*2*); and more recently Morrison, Rinker, and Corcoran (*3*), have reported the analysis of nitrogen dioxide in air. Greene and Pust used a wetted molecular sieve column for their analysis; Morrison *et al.*, used a packed column of SF-96 for the separation. A method for analyzing nitric oxide, nitrous oxide, and nitrogen dioxide in a mixture of other gases from a single sample has not been reported. This paper presents a gas chromatographic procedure for determining nitric oxide, nitrogen dioxide, carbon dioxide, carbon monoxide, oxygen, and nitrogen in a sample using series columns with dual detectors to complete the analysis.

EXPERIMENTAL

Apparatus. A gas chromatograph consisting of a series arrangement of three columns and two detectors was fabricated. The detectors were Gow-Mac Model TR11B thermal conductivity cells with W-2 filaments. The detector signal outputs were fed to a Varian two-pen recorder, 0–5 mv. full scale. The supply of helium was dried by passing it through a −76° C. cold trap packed with 13X molecular sieve. The system schematic is shown in Figure 1.

Columns. Column No. 1 was a 1-foot length of $^1/_8$-inch stainless-steel tubing packed with 0.5% Carbowax 1500 on 60- to 80-mesh silanized glass beads. The column was prepared using standard evaporation procedures. To treat the column, 1 cc. of nitrogen dioxide was passed through the tube. The column was then heated to 100° C. and purged with helium.

Column No. 2 was a 20-foot length of $^1/_4$-inch stainless-steel tubing packed with 40% dimethyl sulfoxide (DMSO) on 60- to 80-mesh Gas Chrom RZ. Evaporation procedures using acetone as the solvent were also used to prepare this column; however, Column 2 was packed using the Matronic XL300 pressurized column packer at a packing pressure of 50 p.s.i.g. As will be shown, this column was superior to a silica gel column for separating nitrous oxide and carbon dioxide.

Column No. 3 was an 8-foot length of $^1/_4$-inch stainless-steel tubing packed with 30- to 60-mesh 13X molecular sieve. This column was also packed using the Matronic XL300 pressurized column packer at a packing pressure of 50 p.s.i.g. To obtain optimum separation, the column was activated at 250° C. for 5 minutes with a rapid helium purge of approximately 200 cc. per minute. Overactivation resulted in considerable tailing of the nitric oxide peak. Molecular Sieve 5A was investigated as a possible packing for Column 3; however, a prohibitive amount of tailing was found with nitric oxide.

Procedure. A helium flow of 75 cc. per minute was established through the columns. Column 1 was controlled at a temperature of −76° C., and Columns 2 and 3 were maintained at 25° C. A gas sample was introduced into the system at point *A* (Figure 1). Injection can be made by an appropriate means; however, for this study a gas sampling valve was used. The sample volume varied with the type of sample under analysis. When analyzing for trace quantities of the nitrogen oxides, up to 25 cc. were injected with satisfactory results. The injected sample was carried by the helium through Column 1. This column removed the nitrogen dioxide and water vapor from the helium stream. The remainder of the sample was carried to Column 2 where nitrous oxide and carbon dioxide were separated and chromatographed. The exhaust of Detector No. 1 then passed through Column 3 where the order of

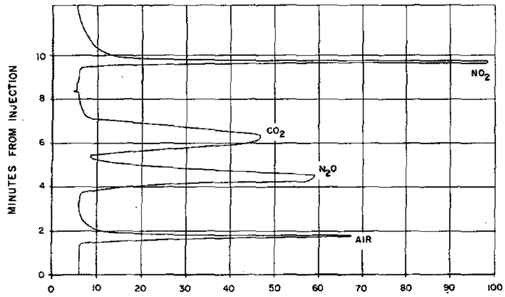

Figure 2. Gas chromatogram; air, N_2O, CO_2, and NO_2

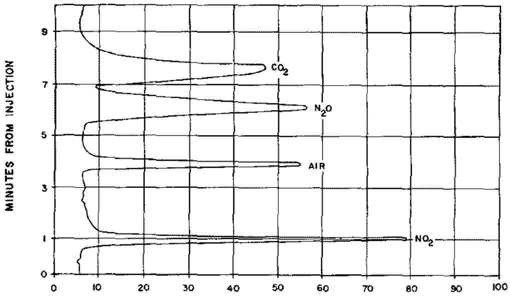

Figure 3. Gas chromatogram; air, N_2O, CO_2, and NO_2 (NO_2 peak position changed)

elution was hydrogen, oxygen, nitrogen, nitric oxide, and carbon monoxide. After elution of carbon dioxide from Column 2 and carbon monoxide from Column 3, the three-way valve No. 1 was turned to channel the helium flow past Column 2, thereby directing the helium flow through a second regulating valve, No. 2. Valve No. 2 reduced the helium flow from 75 cc. per minute to 30 cc. per minute. After the momentary upset due to the helium flow changes, Column 1 was rapidly heated to 70° C. The nitrogen dioxide and water were vaporized and carried directly to Detector 1. (If a measureable peak is desired for water, the column can be heated to 100° C. after elution of the nitrogen dioxide.) Following elution of the water, the three-way valve was returned to the original position. If the sample contained hydrocarbons, such as C_3's, C_4's, or acetylene, these components were then eluted from Column 2. The tubing connecting Columns 1 and 2 to the detector was kept at 150° C. by wrapping with a voltage-controlled heating tape.

RESULTS AND DISCUSSION

The principle of operation of Column 1 for the separation of nitrogen dioxide from the other gases was not unique. This technique has been used routinely in the past for the removal of unwanted or interfering materials in carrier gas and samples. However, in this analysis, the trapped components were of interest and were subsequently analyzed. The temperature of −76° C. was chosen because nitrogen dioxide would be adequately removed with very little chance of components freezing, other than water. Mass spectrometer and infrared analysis had shown that the remaining decomposition gases of explosives or double-base propellants would be unaffected at −76° C. The 0.5% Carbowax 1500 on glass beads was chosen as the column packing material to aid in the separation of the nitrogen dioxide from the water and certain other solvents, such as acetone and ethyl alcohol. In addition, this column minimized the interaction of nitrogen dioxide and water. A temperature gradient from 25° C. to −76° C. existed in the first two inches of the column. This removed the water from the sample prior to removing the nitrogen dioxide. Thus nitrogen dioxide and water were separated by a combination of temperature and column liquid phase. Therefore, any interaction of water with nitrogen dioxide must occur prior to injection in the instrument.

Increased load on the glass beads or a change in the column support of Column 1 to one of the fluorocarbon types resulted in nonreproducible results. If greater separation was desired between nitrogen dioxide and some component, other than water, the common tubing between Columns 1 and 2 could be packed and the temperature adjusted from 150° C. to yield the desired separation. A second method which was used for greater separation was to lengthen Column 1. The packing was changed to only glass beads and the column temperature was crudely programmed from −76° C. to 100° C. However, if any one of these modifications is incorporated, time must be allowed for the complete elution of water from the extra packed column. Any water remaining on the column will cause nonreproducible results.

A typical gas chromatogram of a mixture of air, nitrous oxide, carbon dioxide, and nitrogen dioxide is shown in Figure 2. There was slight tailing of the nitrogen dioxide peak. Another chromatogram of the same gases is shown in Figure 3; however, the position of the nitrogen dioxide peak was changed, from the last peak to the first peak. Figure 4 is similar to Figure 3, except the position of the nitrogen dioxide peak was changed to the second peak. The switching of the nitrogen dioxide peak's position was accomplished by simple manipulation of the bypass valves.

A tabulation of peak area *vs.* sample size of nitrogen dioxide is shown in

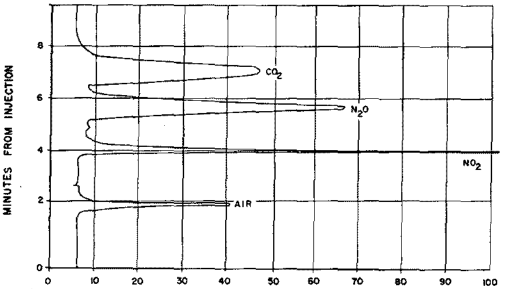

Figure 4. Gas chromatogram; air, N_2O, CO_2, and NO_2 (NO_2 peak position changed)

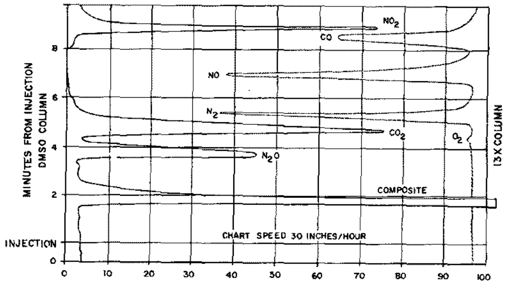

Figure 5. Chromatogram; gases obtained under optimum conditions

Table I. Linearity of NO_2 Results

Sample volume, mm. pressure	Peak area, sq. cm.
20	4.9
30	8.6
40	11.6
50	15.9
60	19.8
70	25.0
80	29.9
100	40.0
120	53.0

Table II. Method Reproducibility

Component added	Sample volume, mm. pressure	Peak height, mv.	Peak area, sq. cm.
N_2	25.0	0.605	0.443
N_2	25.0	0.607	0.442
N_2	25.0	0.606	0.443
N_2	25.0	0.607	0.442
CO_2	25.0	0.792	0.135
CO_2	25.0	0.800	0.132
CO_2	25.0	0.799	0.136
CO_2	25.0	0.804	0.131
NO_2	50.0	6.00	1.56
NO_2	50.0	5.65	1.51
NO_2	50.0	5.85	1.52
NO_2	50.0	6.15	1.60
NO_2	50.0	5.95	1.55

Table I. The sample size was expressed in millimeters (mm.) of mercury, since the sample injection was accomplished using a gas sample valve connected to a vacuum gauge. A sample size of 100 mm. would equal approximately 1 cc. of sample. The linearity of the data indicated the freeze-out technique was quantitative. The lower limit of detection for nitrogen dioxide was not determined. However, by increasing sample size or by making several injections it was found that trace quantities (p.p.m.) of nitrogen dioxide could be trapped in Column 1 and subsequently analyzed.

The Columns 2 and 3 and conditions were carefully chosen so that the DMSO column and the 13X column could be operated in series without multiple helium flows. Both of these columns gave optimum separation at a temperature of 25° C. with a helium flow of 75 cc. per minute.

A chromatogram of a mixture of gases obtained under optimum conditions is shown in Figure 5. Chart speed was 30 inches per hour. The separation of the nitrous oxide and carbon dioxide was essentially base line. Further, there was negligible tailing of either component. If ethane and ethylene had been present in the sample, the two peaks would have appeared between the composite and the nitrous oxide peak. Acetylene, if present, would appear 20 minutes after appearance of the nitrogen dioxide peak, as explained in the procedure. The separation obtained with the 13X column was equally satisfactory. Although the nitric oxide peak did exhibit tailing, the tailing was minimized by the stringent activation conditions. Increased activation of the 13X increased the difference in the retention times of the nitric oxide and carbon monoxide peaks; however, tailing of the nitric oxide peak was increased. The average useful life of the columns with continuous use was 3 months for the DMSO and 1 month for the 13X.

The life of the 13X column can be increased by placing a three-way valve between Detector 1 and Column 3. During the first part of the analysis the valve is turned to direct the exhaust of Detector 1 to Column 3. Following the elution of the carbon monoxide from Column 1, the valve is turned so as to vent the exhaust of Detector 1 to the atmosphere, thus avoiding the contamination of the 13X with nitrogen dioxide, water, and other components retained in Column 1.

A compilation of replicate analyses of carbon dioxide, nitrogen, and nitrogen dioxide is given in Table II. The data show the 95% confidence limit of the analysis of carbon dioxide and nitrogen to be ±0.70% per component at 100%, whereas the calculated 95% confidence limit for the nitrogen dioxide determination was ±2.6% at 100%. This reproducibility range was completely satisfactory for gas chromatographic analysis.

The Bacchus Laboratory of Hercules Powder Co. has used the gas chromatographic method for the analysis of nitrogen oxides routinely for over one year. The method has been applied to the analysis of thermal decomposition gases of explosives, double-base propellant firing gases, and effluent gas analysis coupled with differential thermal analysis of propellant. The samples have varied from trace concentrations to extremely high concentrations of various decomposition gases in both inert and air atmospheres; in all instances satisfactory results were obtained. To date, this laboratory has not experienced any interference in the subambient column used for the separation of the nitrogen dioxide.

ACKNOWLEDGMENT

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Spectrophotometric Determination of Gold with Azide

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▶ The formation of the tetraazidogold(III) ion is indicated by the mole ratio method and confirmed by an analysis for azide on an evaporated sample. A spectrophotometric method for the determination of gold is based on measuring the absorbance of the complex at 325 mμ in water, for gold alone, or at 330 mμ in an *n*-butyl alcohol extract. Factors which control color development, color stability, and extraction are discussed, and the effects of common foreign ions are noted. From 1.5 to 5.3 p.p.m. optimum absorbances are obtained although Beer's law is followed well beyond these limits.

In a previous investigation for the determination of palladium with azide (*1*), it was observed that gold was extracted from acidic azide solutions with *n*-butyl alcohol, but was not back-extracted by neutral aqueous azide solutions as was palladium. Further studies indicated that a spectrophotometric method for gold could be developed from this behavior, and that such a method had not been reported.

The optical absorbance of the tetraazidogold(III) ion is made the basis here for the determination of gold in the optimum ranges from 38 to 127 μg. in 25 ml. of water at 325 mμ, or from 15 to 53 μg. in an extract made with 10 ml. of *n*-butyl alcohol, at 330 mμ. The color is developed immediately and is stable for about 15 minutes in water and for about 8 minutes in the *n*-butyl alcohol extract. The color reagent, $1.0M$ sodium azide, is stable for months. The platinum metals, exclusive of ruthenium and osmium, do not interfere in milligram amounts if gold is extracted and the absorbance is read in the alcohol phase.

EXPERIMENTAL

Apparatus. All absorbance measurements and spectral scans were made with a Beckman DU spectrophotometer equipped with a photomultiplier tube, using 1.00-cm. silica cells and, when necessary, 0.90-cm. silica cell spacers. A Beckman Model 76 expanded scale pH meter was used for all pH measurements. Separatory funnels with stopcocks of Teflon were used to avoid grease contamination of the organic solvent.

Reagents. Weighed gold sheet, containing less than 0.02% copper as the only impurity (spectrographic analysis), was dissolved in aqua regia, boiled with concentrated hydrochloric acid, heated just to fumes with perchloric acid, cooled, and made to volume to give a $0.1000M$ gold stock solution. Aliquots of the stock solution were checked by weighing the gold formed by reduction with hydrogen peroxide; a solution $0.1001M$ in gold was found. The stock solution was $0.400M$ in chloride, as shown by titration of the filtrate by Fajan's method, and $0.417M$ in hydrogen ion, after allowing for the hydrogen ion formed by oxidation of the peroxide. Other gold solutions were prepared by dilution of the stock solution. The $10^{-4}M$ solution used in preparation of the calibration curves was made $0.12M$ in hydrochloric acid and was remade every 5 days. All gold solutions were kept in the dark.

Practical grade sodium azide (Eastman) having a purity of 99.2%, as determined from the hydrogen ion consumed on oxidation with nitrite (*2*), was used to make 1.00 and $0.1000M$ solutions. Initially, the solutions were slightly turbid and colored, but on standing for two weeks they cleared and precipitates settled out. Spectrographic analysis showed that the precipitates contained aluminum, calcium, magnesium, and iron, but that only traces of aluminum and calcium remained in the solutions. These aged solutions were used, and no attempt was made to purify the salt by recrystallization with organic solvents (*5*, *8*) since the metal impurities would probably follow. The azide concentrations remained constant during the precipitation, and are stable for at least three months.

A buffer was prepared by dissolving one mole of monosodium phosphate monohydrate (Baker and Adamson reagent) in 800 ml. of water, adjusting the pH to 6.00 with $10M$ sodium hydroxide, and diluting to 1 liter. The platinum metals used were described in a previous paper (*1*). Reagent grade mercuric and silver nitrates and purified tellurium metal (Fisher) were used in the interference tests.

Preliminary Tests. The tetraazidogold(III) ion, which forms immediately in water, was extracted from acid solutions into *n*-butyl alcohol, isoamyl alcohol, and diisopropyl ether; the complex is reduced to metallic gold at high pH. The *n*-butyl alcohol was selected because it permits the back-extraction of traces of the platinum metals which may accompany the gold. A high concentration of an indifferent salt, such as the phosphate buffer, prevents emulsification and effects a fast phase separation.

Procedure. Gold alone, in the optimum range from 38 to 127 μg., may be determined by reading the color directly in aqueous solution. Transfer to 25 ml. volumetric flasks an aliquot of the unknown and sufficient aliquots of the $10^{-4}M$ gold solution to define a calibration curve in the optimum absorption range. Add to each flask 2.5 ml. of $1.00M$ sodium azide and 12.5 ml. of the pH 6.00 buffer, and dilute to volume. Obtain the absorbance values within 15 minutes of preparation, at 325 mμ, against a blank containing all components but gold.

Gold in the presence of the tolerated platinum metals is determined by extraction. Add the sample solution to a 125-ml. separatory funnel; add 5 ml. of the pH 6.00 buffer and 2 ml. of $1.00M$ sodium azide and adjust the volume to 10 ml. Add 10.0 ml. of *n*-butyl alcohol and extract by shaking for 30 seconds. Discard the aqueous layer and wash the organic phase by shaking for 30 seconds with 10 ml. of solution containing 5 ml. of the buffer and 2 ml. of the azide. Withdraw 4 ml. of the *n*-butyl alcohol layer with a spitzer and expel it into a 1.00-cm. absorbance cell through asmall tuft of cotton supported on a microfunnel. Measure the absorbance within 8 minutes, at 330 mμ, against a blank which has been carried through the same procedure. Obtain a calibration curve by carrying aliquots containing 15 to 53 μg. of gold through the same procedure. If gold alone is determined by the extraction procedure, back-washing of the organic phase is unnecessary for both the sample and the calibration aliquots.

RESULTS AND DISCUSSION

Precision. Beer's law is obeyed by both the extracted and unextracted solutions; the quantities for the optimum absorption range are 38 to 127 μg. in 25 ml. of water and from 15 to 53 μg. in the alcohol extract for 1.00-cm. cells. The volume of the organic phase increases during the extraction from 10.0 ml. to 10.9 ml. The absorptivity, based on the initial 10.0 ml., is 0.1321 ± 0.0017 (std. dev.) p.p.m.$^{-1}$ cm.$^{-1}$ or 0.1440 p.p.m.$^{-1}$ cm.$^{-1}$ based on 10.9 ml. The volume returns to 10.0 ml. during back-washing and the absorptivity is then 0.01297 ± 0.0016 p.p.m.$^{-1}$ cm.$^{-1}$, indicating a loss of about 1.8% of the

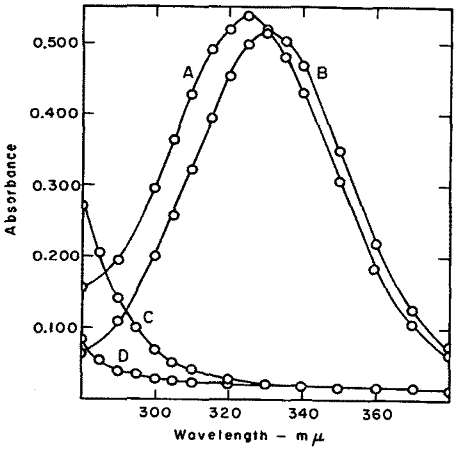

Figure 1. Absorption spectra of analytical species and blanks

(*A*) 2 × $10^{-5}M$ Au^{+3} in water; 0.10*M* N_3^-; 0.50*M* PO_4^{-3}; pH 6.00; readings vs. (*D*)
(*B*) *n*-butyl alcohol extract of solution as for (*A*) except 0.20*M* N_3^- readings vs. (C)
(C) *n*-butyl alcohol extract as for (*B*) without Au^{+3}; readings vs. solvent
(*D*) solution as for (*A*) without Au^{+3}; readings vs. water
All with 1.00-cm. cell

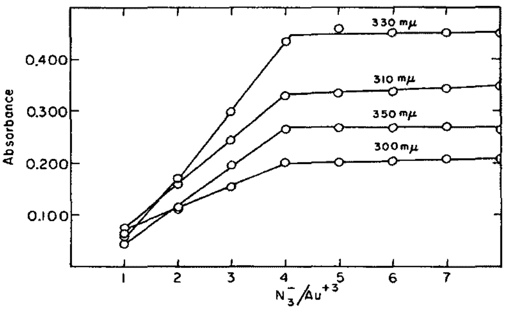

Figure 2. Mole ratio plots

2 × $10^{-4}M$ Au^{+3}
2 to 16 × $10^{-4}M$ N_3^-
Ionic strength 1:00
pH 4.07 ± 0.10
0.10-cm. cell.

gold. The absorptivity of the aqueous solution without extraction is 0.1368 ± 0.00020. When the aqueous to organic volume ratio is increased from 1:1 to 3:1, the absorbance of the extract increases linearly at the rate of 1% for each 15% increase in volume ratio, due to the increasing loss of alcohol into the aqueous phase which is not compensated by an increasing amount of water in the alcohol.

Statistical summaries of the results obtained for the three types of solutions are given in Table I.

Composition of the Complex. Figure 1 shows spectral scans in the near ultraviolet region of the gold azide complex in water and in *n*-butyl alcohol, taken against appropriate blanks. These blanks are, respectively, an aqueous solution containing all constituents except gold, and *n*-butyl alcohol equilibrated with such a solution. Scans of these blanks are also shown, read against the respective solvents. If the scans of the complex are continued into the visible region of the spectrum they show a gradual diminution in absorbance.

Table I. Reproducibility

No. of samples	μg. gold Added	Found	Range	Std. dev., μg.
		Extracted; not back-washed		
2	9.85	9.9(2)	9.8(5)–10.0(0)	. . .
3	19.70	19.9(5)	19.6(7)–20.1(7)	0.26
4	29.55	29.7(5)	29.4(5)–30.0(6)	0.28
5	39.40	39.0(4)	38.7(4)–39.2(7)	0.23
5	49.25	49.1(6)	48.7(1)–49.4(7)	0.34
4	59.10	58.6(8)	58.5(3)–58.9(1)	0.23
3	68.95	68.3(5)	68.3(5)–68.3(5)	0.00
2	78.80	78.9(2)	78.5(4)–79.2(2)	. . .
Std. dev. pooled, $\Sigma(n-1) = 20:0.30$ μg.				
		Extracted; back-washed		
5	19.70	19.5(8)	19.3(5)–19.9(7)	0.26
5	39.40	39.6(8)	38.5(5)–40.2(5)	0.73
5	59.10	58.9(0)	58.2(1)–59.2(1)	0.44
Std. dev. pooled, $\Sigma(n-1) = 12:0.33$ μg.				
		Not extracted		
5	39.40	39.1(0)	38.2(0)–40.0(0)	0.62
5	78.80	78.7(8)	78.5(0)–79.1(3)	0.26
5	137.9	138.(9)	138.(0)–138.(9)	0.30
Std. dev. pooled, $\Sigma(n-1) = 12:0.39$ μg.				

The mole ratio method of Yoe and Jones (*9*) was used at 2 × $10^{-4}M$ and 2 × $10^{-5}M$ gold and at azide to gold ratios from 1:1 to 8:1, in the region of maximum absorptivity. To suppress possible hydrolysis of the azido-gold ion, the pH was regulated with sodium hydroxide or perchloric acid to 4.07 ± 0.10 or 3.89 ± 0.14, respectively, for the two concentration levels. All solutions were made to 1.00*M* with sodium perchlorate to maintain constant ionic strength and were read against blanks containing gold(III) chloride and sodium perchlorate at the same concentration and pH levels. Sharp breaks at a ratio of 4:1 azide to gold are shown in Figure 2 at the 2 × $10^{-4}M$ gold level, indicating negligible dissociation of tetraazidogold(III) ion. A similar set of curves at the 2 × $10^{-5}M$ gold level also shows sharp breaks, but at a slightly higher than 4:1 ratio. This is probably explained by the slow oxidation of azide by gold(III), so that the apparent ratio of azide to gold is higher than the true ratio. At 2 × $10^{-5}M$, finely divided gold appears in less than half an hour at ratios greater than 4:1. At higher concentrations the solutions are more stable for the corresponding ratios. All of the foregoing results could be interpreted to indicate the primary formation of diazidogold(I) ion by the reaction

$$AuCl_4^- + 4N_3^- \rightarrow Au(N_3)_2^- + 4Cl^- + 3N_2$$

instead of the formation of tetraazidogold(III) ion.

The addition of sodium or potassium azide to gold(III) chloride has been reported to form explosive orange colored needles upon careful evaporation of the solution (*3*). No analysis was reported for the product, but it has been referred to as AuN$_3$ (*7*). Repetition of this preparation in the present work, using a ratio of 10:1 azide to gold, gave a similar product which readily redissolved in water. The solution had an absorption maximum at 325 mμ, indicating the presence of the same complex ion as above. Another preparation by evaporation at pH 7 using 4:1 azide to gold was analyzed for azide (*2*). Ratios of 1:3.89 and 1:3.98 were obtained indicating negligible oxidation of azide by gold(III). It appears that the earlier preparations gave sodium and potassium tetraazidogold(III) salts rather than gold(I) azide, and that the tetraazidogold(III) complex is the absorbing species used herein.

Color Development in Aqueous Solutions. In the following studies the pH, gold concentration, and azide concentration were held constant at 6.00, 39.4 μg. and $0.02M$, respectively, unless otherwise indicated. Absorbances were read at 325 mμ.

The color intensity is insensitive to changes in azide concentration at values greater than $6 \times 10^{-3}M$. On decreasing the azide concentration to $2 \times 10^{-4}M$ the color intensity decreases to 77% of its maximum value.

The pH was varied from 1 to 9 by adjusting with either sodium hydroxide or perchloric acid, while maintaining the ionic strength at 1.00 with sodium perchlorate. The color intensity remains constant in the pH interval from 4.35 to 7.00, but decreases slightly outside of these limits. For example, the intensity decreases to 93 and 97% of its maximum value at pH 1.00 and pH 9.00, respectively.

A study of absorbance versus time was made over a 70-minute interval while exposing the sample continuously to the fluorescent lights in the work area, except during the time necessary to obtain the absorbance values. The color intensity decreases at the rate of 2% per 15 minutes of exposure. For this reason more samples should not be prepared than can be read in 15 minutes. If the developed samples are kept in the dark, the decrease is less than 2% in 1 hour.

Extraction and Color Development in *n*-Butyl Alcohol. For the following studies conditions were held constant at pH 6.00, $0.5M$ phosphate buffer, 39.4 μg. gold, $0.2M$ azide, and phase volume ratio of 1:1, unless otherwise indicated. Absorbances were read at 330 mμ.

The color intensity in the extracted phase remains constant for $0.1M$ to $0.2M$ azide in the aqueous phase, but decreases from the maximum value by 7% and 86% upon decreasing the azide concentration to $10^{-2}M$ and $10^{-3}M$, respectively.

Spectrophotometric examination of the aqueous phase indicates that at least 99% of the gold is extracted at pH 6.00. The color intensity does not change, when corrected for blank absorbance, in the pH interval from 2.7 to 7.1. At pH values lower than 2.7 the absorbance decreases; e.g., 93% of the maximum absorbance is found at pH 1.90. At high pH values the gold is reduced. The extracted blank has an absorbance which varies from 0.074 at pH 1.85 to 0.010 at pH 7.90, presumably due to hydrazoic acid. Use of the buffer in preparing both sample and blank eliminates the effect of this variance.

The color intensity decreases at the rate of 2% per 8 minutes in light, as described above, and less than 2% in 1 hour in the dark.

Gold is easily reduced to the metal and this property serves well to separate macro to semimicro amounts from gross quantities of other metals. Reduction and coprecipitation with tellurium is used to isolate and concentrate micro amounts (*4*, *6*). Because of the ease of this separation, an extensive list of diverse ions was not studied. If sulfurous acid and hydrazine are used for the reduction (*4*) and the precipitate is redissolved in aqua regia, only tellurium, silver, mercury, palladium, and platinum will follow as impurities (*6*). None of these elements, in 1-mg. quantities, cause an error in excess of 2.8% in the determination of 39.4 μg. of gold, using the extraction procedure with back-washing, even through the silver is precipitated as chloride and the tellurium is present as the dioxide at pH 6.00. Table II summarizes these interferences. Gold is reduced to metal by azide in the presence of ruthenium as evidenced by a purple color, typical of colloidal gold, observed at the interface. Some ruthenium is also extracted, but the absorbance of the extract is a nonlinear function of the amount of ruthenium present, in the range from 0.3 to 1.8 mg., under the stated conditions. In the presence of 1 mg. of osmium only 25% of the expected color for gold is developed, and a blue-black powder appears at the phase interface. Ruthenium and osmium may be removed either by tellurium or by volatilization (*6*).

Table II. Interference in Determination of 39.4 μg. of Gold

No. of detns.	One mg. each of	Max. error, μg.
2	Te	0.4
2	Hg	1.1
4	Ag	0.4
2	Ir	0.4
2	Pd	0.7
2	Pt	0.7
2	Rh	0.7

The anions chloride, perchlorate, sulfate, and phosphate in $0.1M$ concentrations do not interfere in either the direct or extraction procedures. Cyanide, a strong complexing agent for gold, must be absent. Nitrate interferes with the direct procedure because it absorbs strongly in the ultraviolet spectral region, but it does not follow gold in the extraction procedure even when present in $0.1M$ concentration.

ACKNOWLEDGMENT

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Liquid-Liquid Extraction of Zirconium(IV) with Mesityl Oxide

SIR: Mesityl oxide (4-methyl-3-penten-2-one) has been used for the extraction of uranium(VI) (*2*). Extension of these studies to zirconium(IV) revealed that zirconium(IV) can be quantitatively extracted from solutions containing 4*M* nitric acid and 4*M* sodium nitrate. Zirconium(IV) is back-extracted from the organic phase with water and is spectrophotometrically determined in the aqueous phase with alizarin. This provides the basis for the liquid-liquid extraction of zirconium (IV) at the milligram level. The method, although not specific, is applicable for the rapid separation of zirconium(IV). Early work on the solvent extraction of zirconium(IV) has been summarized by Morrison and Freiser (*5*). A recent method includes the extraction of the alizarin complex of zirconium(IV) in butanol (*3*).

EXPERIMENTAL

Apparatus and Reagents. A Cambridge pH meter (Marshall Model) and a Russian Type Cϕ4 quartz spectrophotometer with 1-cm. cells were used.

A stock solution of zirconium nitrate (E. Merck and Co.) was prepared by dissolving 1.6024 grams of zirconium nitrate in 500 ml. of water containing 1% nitric acid. The solution was standardized gravimetrically as an oxide. It contained 1.08 mg. of zirconium per milliliter. The test solutions (10.8 μg. of zirconium per ml.) were prepared by 10-fold dilution.

Mesityl oxide (B.D.H., b.p. 128.7° C.) and alizarin (G. T. Gurr Ltd., London, 0.05% solutions) were used.

General Procedure. The experimental outline was similar to that reported earlier (*2*).

An aliquot of zirconium nitrate solution containing 130 μg. of zirconium(IV) was mixed with sodium nitrate and nitric acid to a volume of 25 ml. so that the concentration of the salting-out agent and acid would be 4*M*. It was then introduced into a separatory funnel and extracted with 10 ml. of 100% mesityl oxide.

For acidity studies, suitable nitric acid concentrations were used in place of 4*M* nitric acid, whereas for the study of the effect of salting-out and diverse ions, suitable concentrations of salting-out agent and foreign ion were added to the aqueous phase before extraction.

At the end of extraction the layers were allowed to settle and separate. The aqueous layer was removed first; then the zirconium(IV) was removed from the organic layer by back-extraction with two 20-ml. portions of water, and was spectrophotometrically determined with alizarin at 525 mμ (*6*).

Table I. Partition Coefficient as the Function of Acidity

Zirconium(IV), 130 μg.; salting agent $NaNO_3$, 4*M*

Mesityl oxide	HNO_3, *M*	Partition coefficient, *D*
19%, (1.62*M*)	1	0
	2	0
	3	0.132
	4	0.546
	5	1.42
50%, (4.35*M*)	1	0.063
	2	0.54
	3	1.42
	4	2.39
	5	4.66
75%, (6.53*M*)	1	0.132
	2	0.699
	3	4.66
	4	2.39
	5	7.40
100%, (8.70*M*)	1	0.137
	2	0.699
	3	7.4
	4	100
	5	7.4
100%, (8.70*M*) without salting agent	0.5	0.132
	1.0	0.416
	1.25	0.546
	1.5	0.546
	2.5	0.699
	4	1.12
	6	4.66

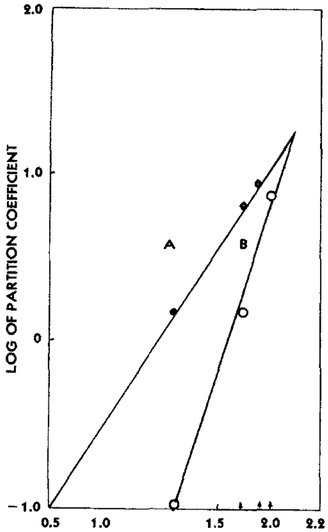

Figure 1. Partition coefficient as function of mesityl oxide concentration

A. Aqueous phase 5*M* HNO_3
B. Aqueous phase 3*M* HNO_3

RESULTS AND DISCUSSION

Effect of Acidity. The study of the extraction of zirconium(IV) with mesityl oxide from 0.5–6*M* nitric acid concentration showed that the maximum extraction occurs at 4*M* nitric acid concentration. The partition coefficient (*D*) was computed from the ratio of the concentration of zirconium(IV) in the organic phase to that in the aqueous phase. Zirconium(IV) content in the mesityl oxide phase was determined as described above, and that in the aqueous phase by difference from the total amount of zirconium(IV) initially taken. The maximum partition value was 100, corresponding to an acid concentration of 4*M* containing 4*M* sodium nitrate (Table I).

Salting-Out Agent. The effect of varying concentrations (1–4*M*) of ammonium and sodium nitrate as the

Table II. Diverse Ions

Zirconium(IV), 130 μg.

Foreign ion	Source	Tolerance limit, μg.
Hg^{+2}	$Hg(NO_3)_2$	20[a]
Pb^{+2}	$Pb(NO_3)_2 \cdot 2H_2O$	457
Tl^{+}	$Tl_2SO_4 \cdot 2H_2O$	510
Pt^{+2}	$H_2PtCl_6 . 2H_2O$	30[b]
Pd^{+2}	$PdCl_2$	150[a]
Cu^{+2}	$CuSO_4 \cdot 2H_2O$	20[b]
Cd^{+2}	$Cd(NO_3)_2$	500
Bi^{+3}	$Bi(NO_3)_3$	520
Sn^{+4}	$SnCl_4$	150[a]
Th^{+4}	$Th(NO_3)_4 \cdot 4H_2O$	500
Ce^{+4}	$Ce_2(SO_4)_3$	50[b]
Fe^{+3}	$Fe(NO_3)_3$	450
Cr^{+3}	$Cr_2(SO_4)_3$	150[b]
Al^{+3}	$Al(NO_3)_3$	230
U^{+6}	$UO_2(NO_3)_2 \cdot 6H_2O$	240
V^{+5}	NH_4VO_3	150[b]
Zn^{+2}	$ZnSO_4 \cdot 7H_2O$	750
Mn^{+2}	$MnSO_4 \cdot 4H_2O$	750
Co^{+2}	$CoSO_4$	640
Ni^{+2}	$NiCl_2$	500
MoO_4^{-2}	$(NH_4)_6Mo_7O_{24}$	150[c]
PO_4^{-3}	$NaH_2PO_4 \cdot 10H_2O$	None
SO_4^{-2}	$(NH_4)_2SO_4$	500
Cl^{-}	NaCl	250[c]
CN^{-}	KCN	50[c]
SCN^{-}	NH_4SCN	50[c]
Tartrate^{-4}	Tartaric acid	120
Citrate^{-3}	Citric acid	None
Oxalate^{-2}	Oxalic acid	None
CH_3COO^{-}	Acetic acid	50[c]
Ascorbate^{-2}	Ascorbic acid	None
EDTA^{-4}	EDTA (disodium salt)	None

[a] Foreign ion masked by sequestering agent as KI, H_2O_2
[b] Tolerance limit increased by preliminary extraction with TTA
[c] Anion removed by passing on anion exchange resin column

salting-out agent on extraction of zirconium(IV) with 100% mesityl oxide was studied in the acid range of 2.5–4*M*. Their presence in the aqueous phase increased the extraction of zirconium(IV), because less mesityl oxide is combined with acid and hence more of it is available for the extraction. The optimum concentration of salting-out agent is 4*M* sodium nitrate in 4*M* nitric acid. A higher concentration of nitric acid was avoided because of the slight dissolution of the mesityl oxide layer. The extraction of Zr(IV) with 100% mesityl oxide was also studied in the acid range of 2.5–4*M* to determine the effect of varying concentrations (1–4*M*) of NH_4NO_3 and $NaNO_3$ as the salting-out agent.

Mesityl Oxide Concentration. The concentration of mesityl oxide was varied from 19 to 100% with methyl isobutyl ketone as the diluent. The effect of the extraction was noted at different acidities (Table I) in the presence of 4*M* sodium nitrate. Dilution of mesityl oxide lowers the extraction. A plot of log *D* *vs.* log *C* mesityl oxide (Figure 1) at 3 and 5*M* nitric acid indicates slopes of 2.4 and 1.6, showing the extractable species to be $Zr(NO_3)_4 \cdot 2MeO$ and $H[Zr(NO_3)_4(MeO)_2]$, respectively. The system conforms to the limiting square law (*1*) in the case of zirconium(IV). The optimum reagent concentration is 100%.

Diverse Ions. A number of representative ions were tested for interference (Table II). Lead, thallium, cadmium, bismuth, iron, aluminum, zinc, manganese, cobalt, nickel, uranium, thorium, chloride, and sulfate do not interfere, even if present in the ratio of 1:5. Ions which can easily form anionic complexes with zirconium(IV)—e.g., oxalate, citrate, ascorbate, EDTA—strongly interfere. The tolerance limit (*2*) of ions such as copper, cerium, chromium, and palladium can be increased by preliminary extraction of these ions with 2-thenoyltrifluoroacetone (*4*). Interferences due to anions can be eliminated by anion exchange; whereas those due to certain cations can be removed by masking with suitable sequestering agents. The tolerance limits of the ions are listed in Table II.

From 10 runs with 130 μg., of zirconium(IV), using a general procedure, the average recovery was 96.4 ± 1.2% with a standard deviation of 2.0%.

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Modification of Flask Method of Sulfur Determination

Determination of Sulfates with Sulfonazo III

SIR: The flask method (*2*) is the most convenient method for determination of organic sulfur. The modification of this method by Wagner (*3*), who used titration with barium perchlorate and visual indication with thorin, is considered the best. A recent investigation (*1*) of the color reaction of sulfonazo III [2, 7-bis-(*o*-sulfophenylazo)chromotropic acid] with barium ions resulted in excellent sensitivity and selectivity. Sulfonazo III can also be used for visual indication in the barium perchlorate titration of sulfate ions. Compared to the use of thorin, the end point is much sharper and is unaffected by pH changes. The reaction should be carried out in a homogeneous aqeuous-nonaqueous solution, because an aqueous medium permits formation of the sulfonazo III–barium complex. Water and acetone appear to be the best medium. The aprotic solvent acetone decreases the dissociation of sulfonazo III, and in this way the formation of the sulfonazo III–barium complex is hindered. Organic sulfur can also be determined by using the flask method and sulfonazo III indicator.

Table I. Determination of Sulfur in Various Samples

Sample	% S Calcd.	 Found[a]	Std. dev., %
Chromotropic acid (dihydrate)	18.00	17.84	±0.16
1-Cysteine	26.47	26.41	±0.17
Potassium sulfate	18.40	18.40[b]	±0.08
Sulfanilic acid	18.52	18.48	±0.16
Taurine	25.62	25.46	±0.18
Thiosemicarbazide	35.19	35.22	±0.20
Thiourea	42.13	41.97	±0.24

[a] Average value from 5 determinations.
[b] Average value from 10 determinations.

EXPERIMENTAL

For combustion and titration, 250-ml. or 300-ml. Schöniger flasks were used. Barium perchlorate (0.01*M*) was prepared by dissolving 2.37 grams of reagent grade barium perchlorate in distilled water and making up to 1 liter. The solution was standardized by titration with reagent grade potassium sulfate, previously dried at 110° C. Sulfonazo III (0.1%) was prepared by dissolving 0.1 gram of sulfonazo III in 100 ml. of distilled water. This solution is stable for many months. Medical grade oxygen was used directly from the cylinder, and all other chemicals used were reagent grade.

Procedure. A 0.15-ml. sample of 30% hydrogen peroxide and 4 ml. of distilled water are placed in a Schöniger flask. The flask is filled with oxygen, and a 4- to 7-mg. sample is combusted and then absorbed by shaking in the absorption solution for 15 minutes. The flask is opened, 3 ml. of acetone and 3 drops of sulfonazo III solution are added, and the solution is titrated with barium perchlorate solution. The red color of the solution changes sharply to blue at the end point.

A blank solution is unnecessary if Schleicher-Schuel filter paper No. 589[2] is used for the combustion step. For calculations, 1 ml. of barium perchlorate solution is the equivalent of 0.32066 mg. of sulfur. Other salts, such as potassium chloride and sodium perchlorate, interfere when present in excess of 0.1 mmole. Primary potassium phosphate interferes in excess of 0.01 mmole.

RESULTS

Typical results from the determinations are given in Table I. Work in this laboratory indicates that the titration can be used for the determination of inorganic sulfur if a quartz combustion tube and a spiral absorber are used in place of the Schöniger flask.

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Gas Chromatographic Analysis of Aromatic Hydrocarbons with Modified Bentonite Columns

Effect of Bentone 34 Concentration on Performance of Packed Columns

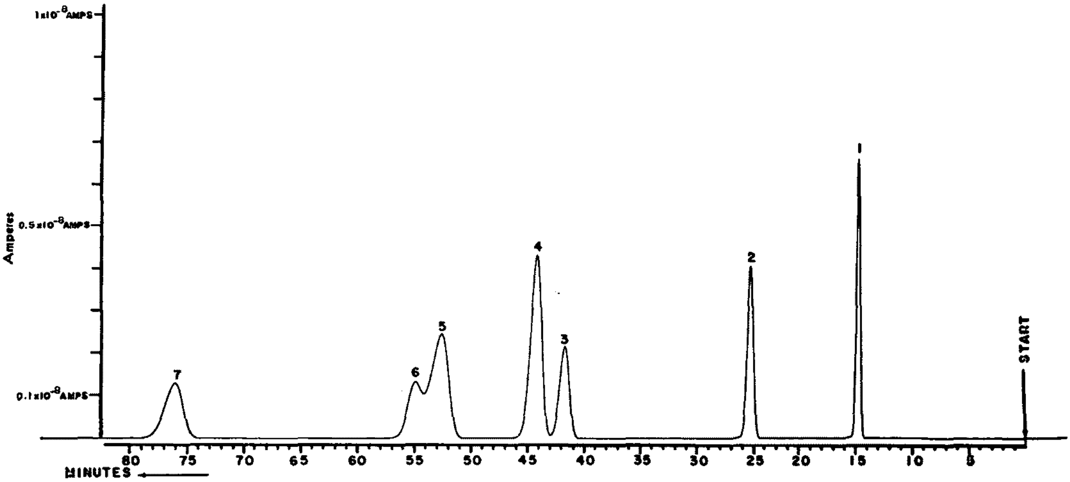

Figure 1. Chromatogram of aromatic hydrocarbons on column made from new batch of Bentone 34

Column packing: 11.54% DC-200/500 and 11.54% Bentone 34. Peaks: 1. benzene, 2. toluene, 3. ethyl benzene, 4. *p*-xylene, 5. *m*-xylene, 6. *o*-xylene, 7. isopropyl benzene

SIR: The use of modified Bentone 34 (dimethyldioctadecylammonium bentonite) packed columns for the separation of the xylene isomers has been the subject of numerous publications (*1*, *2*, *4–6*). Of these five publications, owever, only two (*2*, *6*) have shown the separation of isopropyl benzene and *o*-xylene. Because isopropyl benzene is present in almost all xylene mixtures, this separation is as important as the analysis of the xylene isomers. To maintain the above separations, we have found it necessary to reoptimize the weight per cent of silicone oil and Bentone 34 used in our columns when a new batch of Bentone is used. The activity of each batch of Bentone appears to be different.

EXPERIMENTAL

A Perkin-Elmer Model 800 gas chromatograph equipped with a differential flame ionization detector was used for these studies. The recorder was a Leeds & Northrup Speedomax Model G with a full-scale span of 5 mv. All of the tubing used for fabricating the columns was 15-feet × $^1/_8$-inch o.d. × 0.085-inch i.d. stainless steel. The various packings used for carrying

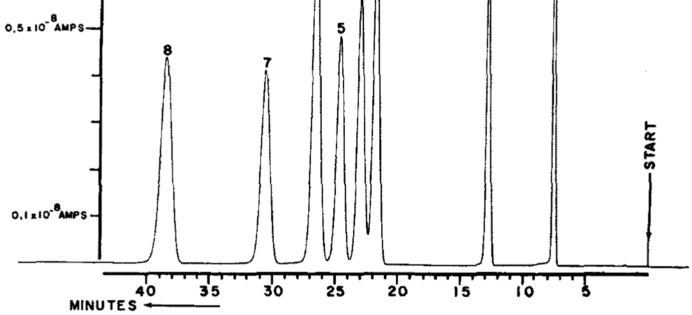

Figure 2. Chromatogram of aromatic hydrocarbons. Bentone 34 same as Figure 1

Column packing: 16.16% DC-200/500 and 3.03% Bentone 34. Peaks: 1. benzene, 2. toluene, 3. ethyl benzene, 4. *p*-xylene, 5. *m*-xylene, 6. *o*-xylene, 7. Isopropyl benzene, 8. *n*-propyl benzene

Table I. Effect of Liquid Phase and Bentone on Column Efficiency

Weight % DC-200/100	Weight % Bentone 34	*n*	HETP (mm.)	*R* *p*-xylene–*m*-xylene	*R* *m*-xylene–*o*-xylene	*R* *o*-xylene–isopropyl benzene
19.42	2.91	6750	0.7	0.96	1.9	5.7
16.16	3.03	7220	0.6	1.53	0.9	3.1
12.63	3.16	7950	0.6	2.12	0.6	2.5
12.25	6.12	9495	0.5	4.14	=0	1.4
11.54	11.54	10390	0.4	3.98	0	0.9

out the analyses contained DC-200/100 methyl silicone oil (Dow Corning Corp., Midland, Mich.), Bentone 34 (National Lead Baroid Division, Houston, Texas) and nonacid washed chromosorb W (Johns-Manville Corp., New York, N. Y.). The various ratios that were used are listed in Table I. The operating temperatures for the column, injector, and detector were 100°, 215°, and 175° C., respectively. A carrier gas flow rate of 12.7 ml. per minute (measured at column outlet) was used in all cases.

The column materials were made using the conventional slurry technique. After packing, the column was coiled and then preconditioned at 140° C. for 30 minutes.

DISCUSSION

Our early work on the modification of Bentone 34 showed that columns made with equal weights of silicone oil and Bentone 34 gave the best results. Later results obtained on a column made in the same manner but with a new batch of Bentone 34 gave the results shown in Figure 1.

To find the correct ratio of silicone oil to Bentone 34, five different column materials were made. Table I shows the weight per cent of the silicone oil and Bentone 34 used in each column. Also shown in this table are the number of theoretical plates and the HETP values obtained for each column calculated for the *n*-propylbenzene peak along with the resolution values calculated for the following peak pairs: *p*-xylene and *m*-xylene; *m*-xylene and *o*-xylene; and *o*-xylene and isopropyl benzene. The equations used for the calculations correspond to the internationally accepted nomenclature (*3*). Using this data it is possible to predict that the best column for the analysis of these materials would be one containing 16.16% silicone oil and 3.03% Bentone 34. Figure 2 shows the chromatogram obtained on this column.

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Preparation of High Purity Acetonitrile

Sir: The favorable dielectric, solvent, and optical properties of acetonitrile (MeCN) have resulted in its wide use in spectrophotometric and electrochemical experiments and in peptide chemistry. Practical grade MeCN generally contains, as impurities, water, unsaturated nitriles, toluene, and various aldehydes and amines. The reagent material has higher chemical purity but may actually have poorer optical qualities and is not suitable for electrochemical use. Similarly, commercially available spectro grade MeCN does not show optimum optical or electrochemical properties.

The generally accepted method for purifying MeCN is that given by Weissberger (*4*). It involves successive refluxing with P_2O_5 and Na_2CO_3, followed by careful distillation through a good rectifying column. MeCN of high purity was prepared with the use of this method by Janz and Danyluk (*3*), who refluxed the MeCN with P_2O_5 six times for 36 hours each time before continuing with the Na_2CO_3 treatment and distillation. MeCN prepared by us with this method has a boiling point of 81.7° C. at 763 mm., contains less than 0.05% water, and is a satisfactory voltammetric solvent. GLC analysis does reveal, however, a substantial amount (ca. 0.5%) of an impurity which apparently forms an azeotrope with MeCN and which is not removed until the greater part of the charge has been distilled over.

Other procedures listed by Weissberger include azeotropic distillation with methylene chloride, benzene, or trichloroethylene. These methods are only intended to remove water and could not produce solvent with generally satisfactory optical or electrochemical properties.

Purification procedures intended to produce solvent for use for reductions at the mercury electrode have been described by Coetzee *et al.* (*1*). Of the several variations described, that recommended for general use involves stirring with calcium hydride for 48 hours followed by fractionation from P_2O_5, with a final fractionation from CaH_2. This procedure is inadequate when the solvent is intended for optical or anodic electrochemical use because no provision is made for removal of small amounts of aromatic hydrocarbons which absorb in the 260- to 280-mμ region and which are oxidized at the platinum electrode.

We suggest the following procedure for purifying MeCN: place 800 ml. of practical grade MeCN in a 1-liter round-bottom flask, add 10 grams of anhydrous Na_2CO_3 and 15 grams of $KMnO_4$. Distill at 5 to 10 ml./min. into a receiver protected from atmospheric moisture. Make the distillate slightly acidic with concentrated sulfuric acid. Decant from precipitated ammonium sulfate and distill through a 30-plate rectifying column at 10 ml/hr. with a reflux ratio of 20:1. A small forecut, typically 40 ml., must be discarded. The resulting MeCN has a boiling point of 82.0° C. at 763 mm. GLC examination of solvent prepared by this procedure revealed two impurities amounting to less than about 0.1% which appear to be unreactive at a platinum anode. The water content was less than 0.01%.

This method appears to offer definite advantages when compared with the procedures decribed above. It produces solvent of generally higher purity, it is rapid, only about one day being required before usable solvent is obtained, and it is much less wasteful of solvent. Solvent prepared by this procedure has been used within the potential range of +2.3 volts, with $NaClO_4$ at a platinum electrode, to −2.7 volts, with tetraethylammonium bromide at a mercury electrode. Potentials are expressed relative to the aqueous S.C.E.

MeCN purified by the $KMnO_4$ pro-

Table I. Comparison of Acetonitrile from Various Sources

Source and grade	n_D^{20}	d^{25}, g./ml.	Transmittance at 200 mμ, %	UV cutoff, mμ[a]	Coulombs[b]	Background, μa.
Matheson Practical	1.34897	0.77728	0	225	...	...
Baker Reagent	1.34515	0.77719	0	226	10.8	480
Eastman Spectro	1.34427	0.77691	0	215	2.3	310
P_2O_5–Na_2CO_3 treated	1.34438	0.77701	0	216	3.3	330
Na_2CO_3–$KMnO_4$ treated	1.34429	0.77686	55	<200	2.0	180
PhCOCl–$KMnO_4$ treated	1.34393	0.77683	85	189	0.5	155
Lit. (*1*)	1.34433	0.77691	0	215	...	...
Lit. (*3*)	1.34388	0.77680	..	...	...	...
Lit. (*4*)	1.34411	0.77683	..	...	...	...

[a] Defined as wavelength at which transmittance of 1 cm. of material reaches 10% when 1 cm. of water used as reference.

[b] Explained in text.

cedure is adequate for voltammetric and coulometric purposes. This procedure is recommended for general electrochemical use, both for oxidations and reductions. However, higher optical purity can be obtained if the MeCN is first treated with benzoyl chloride according to the following procedure: place 800 ml. of practical grade MeCN and 10 ml. of benzoyl chloride in a 1-liter round-bottom flask and reflux for 1 hour. If there is more than 0.2% water present, it must be removed by distillation prior to adding the benzoyl chloride. Distill at 5 to 10 ml./min. into a receiver containing 10 ml. of water (to hydrolyze any benzoyl chloride carried over). Add 20 grams of Na_2CO_3, reflux for 2 hours, and distill into a receiver fitted with a drying tube. Add 10 grams of anhydrous Na_2CO_3, 15 grams of $KMnO_4$, and continue with the $KMnO_4$ procedure described above. Again, a small forecut must be discarded prior to collection. The size of this forecut is dependent upon the amount of water picked up but averages 50 ml.

GLC examination of solvent prepared according to this procedure showed one impurity, just discernable with a flame ionization detector. Water was not detectable by thermal conductivity GLC. By this procedure we have obtained isolated samples with 100% transmittance at 200 mμ, but the 85% listed in Table I is more typical. The boiling point of this solvent was 82.0° C. at 763 mm.

For purposes of comparison we have subjected a sample of commercial spectral grade solvent and a sample of MeCN purified according to the method of Coetzee to the same tests given MeCN prepared by our methods. Eastman spectral grade MeCN contained approximately 0.1% water together with four other impurities, two of which constitute roughly 0.02% each and two of which are too small to measure by flame ionization GLC. Solvent prepared by the calcium hydride–phosphorus pentoxide method showed an absorption maximum in the 260- to 280-mμ region. Conditions for the GLC analyses are indicated in Table II.

A measure of the purity of MeCN is the number of coulombs required to electrolyze it anodically to background. The data given in Table I show the number of coulombs to electrolyze 75 ml. of solvent to a constant background at 2.3 volts *vs.* S.C.E. in a three-compartment cell with a platinum anode, together with the limiting background current reached in each case. All samples were 0.10*M* in $NaClO_4$ which had been recrystallized from water–ethanol, dried under vacuum, and stored over P_2O_5.

According to Herzberg (*2*), the UV spectrum of MeCN vapor has a band extending from about 190 mμ to 160 mμ, centered near 167 mμ. We have examined the UV spectrum of the material with 85% transmittance at 200 mμ in both the liquid and vapor state with a McPherson single beam vacuum spectrometer. The vapor spectrum shows that absorption becomes appreciable at 175 mμ and increases steadily to 165 mμ, the limit of the hydrogen lamp source. In the liquid phase in a 1-cm. cell, absorption becomes appreciable at 195 mμ and cutoff occurs at 189 mμ.

The optical qualities of MeCN deteriorate on standing. One sample of material having 85% transmittance at 200 mμ showed a reduction to 55% after 3 weeks in a stoppered flask. Contact with stopcock grease must be avoided; MeCN will dissolve sufficient Apiezon N to ruin its optical qualities altogether. A most useful criterion of solvent purity is the UV cutoff. We have noted that solvent showing UV cutoff above 200 mμ invariably exhibited undesirably large background currents and detectable impurity peaks on GLC examination.

ACKNOWLEDGMENT

The authors thank Donald Barnes of the Florida State University Chemistry Department for obtaining the vacuum UV spectra.

Table II. Summary of Gas Liquid Chromatography Data

Column	Operating conditions	Compound	Relative retention time
1/8 in. × 8 ft., 20% Dowfax 9N9, 2 1/2% NaOH on Chromosorb-P[a]	Temp., 100° C. Carrier flow, 20 ml./min.	Ethylamine	0.31
		Propionaldehyde	0.49
		Acetonitrile	1.00
		Acrylonitrile	1.35
		Benzene	1.50
		Toluene	3.10
1/8 in. × 8 ft., 20% Duo-Seal Vacuum pump oil, 2 1/2% NaOH on Chromosorb-P[a]	Temp., 70° C. Carrier flow, 20 ml./min.	Acrylonitrile	0.75
		Acetonitrile	1.00
		Benzene	1.98
1/4 in. × 12 ft., 5% GE SX-50 on Fluoro Pak[b]	Temp., 60° C. Carrier flow, 55 ml./min.	Water	0.71
		Acetonitrile	1.00

[a] Used in Aerograph 600-c chromatograph with flame ionization detector.

[b] Used in F & M 500 chromatograph with thermal conductivity detector, 150-ma. filament current.

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Aqueous Sodium Borohydride Chemistry

The Coinage Metals, Copper, Silver, and Gold

SIR: A previous publication describes procedures for the quantitative separation of lead and barium, of cadmium and mercury, of lead and zinc, and the semiquantitative separation of cadmium and zinc (*3*). Since this technique is simple and rapid and does not require elaborate equipment, the investigation was continued to develop procedures for the reduction of the coinage metals.

EXPERIMENTAL

Apparatus and Reagents. The pH of the solutions was determined with a Beckman Zeromatic pH meter.

SODIUM BOROHYDRIDE. Approximately 1% aqueous solution was prepared just before use from 98+% sodium borohydride purchased from Metal Hydrides, Inc. Solution concentrations were approximated on a weight basis—for example, 1% $NaBH_4$ was made by dissolving 1 gram of $NaBH_4$ in 100 ml. of solution.

GOLD(III) CHLORIDE. Stock solutions of gold chloride, approximately $0.06N$, were prepared by dissolving pure metallic gold in chlorine water and diluting to 1 liter.

The $0.1N$ solutions of copper chloride, copper nitrate, copper sulfate, and silver nitrate were standardized using established procedures described in the literature (*2*).

Procedure. Twenty-five-milliliter aliquots of copper chloride, copper nitrate, copper sulfate, and silver nitrate were adjusted to initial pH values of 2, 5, 7, 9, and 11. Fifty milliliters of aqueous sodium borohydride were added dropwise to each. The reduction medium was mixed with a magnetic stirrer and the reductions were carried out in a well ventilated hood. The metallic precipitates which formed were collected on No. 2001 Selas crucibles, washed with distilled water and acetone, vacuum dried, and dissolved in nitric acid. The solutions were boiled to expel dissolved oxides of nitrogen and were transferred to Erlenmeyer flasks. The copper present was determined by the iodine method (*1*). The silver was determined volumetrically with a standard thiocyanate solution using ferric alum as the indicator for one set of samples, and gravimetrically as the chloride for another set. A third set of samples, after the reduction of the silver by sodium borohydride, was collected on crucibles, washed well with distilled water, and finally with acetone, and then dried in a vacuum desiccator.

For the study of the reduction of gold(III) by sodium borohydride, a set of test solutions containing Au(III) ion were made 1.0, 0.5, and $0.1N$ in HCl, 1.0, 0.5, and $0.1N$ in NaOH, $0.1N$ in HNO_3, and $0.1N$ in NH_3. For these experiments the sodium borohydride was dissolved in $0.1N$ NaOH and added dropwise with constant stirring. The reaction mixture was left standing overnight or digested on a hot plate for 1 to 2 hours. The resulting brown spongy precipitate was filtered and washed thoroughly with water. The precipitate was transferred to a porcelain crucible, the filter paper was charred off, and then the residue was brought to a red heat in a Bunsen burner flame. The crucibles were cooled and weighed. The precipitates were washed with water, dissolved in a 1:1 hydrochloric acid solution and 30% hydrogen peroxide, and tested for boron.

RESULTS AND DISCUSSION

Reduction of Copper(II). When sodium borohydride is added to a copper(II) solution there is a marked change from a blue colored solution or a blue colored precipitate to a green then to a brown colored solution or precipitate and finally to a reddish brown solid or to a black finely divided velvety solid depending on conditions used. Both forms contain shiny pieces of, apparently, free copper. These observations and the differences in the solubilities of the products in various solvent systems suggest that possibly copper(II) is reduced to copper(I) then to copper(0) or to a mixture of copper metal and small percentages of some other copper species.

A study was made of the effect of anions present and of the sodium borohydride solvent system. In all instances the copper was completely recovered as determined by quantitative tests on the precipitate and by qualitative tests on the filtrate. The results are given in Table I.

The anion present and the solvent system for the reducing agent affect the nature of the precipitate, and under some conditions a product of varying and undetermined composition is obtained. However, the direct weighing of the product can be made the basis for the quantitative determination of copper in the absence of interfering species if the copper(II) salt is a nitrate, or if it is a sulfate and the reduction is carried out in the presence of ammonia.

Reduction of Silver(I). When sodium borohydride is added to the silver nitrate aliquots, there is a rapid evolution of hydrogen and the solution turns brownish black. With samples adjusted to initial pH 11 with

Table I. Effect of Anion Present and Solvent System for $NaBH_4$ on Reduction of Cu(II) Salts

	Solvent for $NaBH_4$					
	H_2O		$6N$ NH_3		$15N$ NH_3	
Copper species used to prepare Cu(II) solution	Cu in precipitate, %[a]	Rel. std. dev., %	Cu in precipitate, %[a]	Rel. std. dev., %	Cu in precipitate, %[a]	Rel. std. dev., %
$CuCl_2$	96.23	0.2				
$Cu(NO_3)_2$	99.88	0.2				
$CuSO_4$	92.15	0.03				
$Cu(NH_3)_4Cl_2$	100.1	0.7	94.88	0.05	93.18	0.2
$Cu(NH_3)_4(NO_3)_2$	100.5	1.3	99.72	0.5	99.79	0.5
$Cu(NH_3)_4SO_4$	100.9	0.7	100.0	0.6	99.96	0.06

[a] Average of three values.

Table II. Percentage of Silver Recovered after $NaBH_4$ Reduction of Ag(I)

	Determination of Ag					
	Volumetrically with SCN^-		Gravimetrically as AgCl		Directly as Ag	
Initial pH	Ag in precipitate, %[a]	Rel. std. dev., %	Ag in precipitate, %[a]	Rel. std. dev., %	Ag in precipitate, %[a]	Rel. std. dev., %
2	99.89	0.09	99.81	0.11	100.06	0.07
5	99.86	0.08	99.96	0.20	100.00	0.13
7	99.97	0.09	99.82	0.15	100.04	0.07
11	100.04	0.00	99.68	0.15	100.77	0.18

[a] Average of four values.

Table III. Gravimetric Analysis of Reduction Products from Known Amount of Gold(III)

Procedure	Au taken, mg.	Au found, mg.	Av. % Au recovered (95% Confidence Limits)
Oxalic acid reduction	107.1	106.1 ± 0.4[a]	99.10 ± 0.6
Sodium borohydride reductions			
Au(III) in 0.1N HCl	107.1	107.9 ± 0.3	100.8 ± 0.2
Au(III) in 0.1N HNO_3	100.0	100.7 ± 0.2	100.7 ± 0.3
Au(III) in neutral solution	100.0	100.4 ± 0.3	100.4 ± 0.3
Au(III) in neutral solution	107.1	107.4 ± 0.2	100.3 ± 0.3
Au(III) in 0.5N NaOH	107.1	108.1 ± 0.2	100.8 ± 0.2

[a] ±, the standard deviation from the mean for the 95% Confidence Limits.

NaOH, the silver ion is precipitated as the insoluble Ag_2O. The reduction of this species takes place slowly but completely.

The results, summarized in Table II show that under all conditions employed, Ag(I) is converted quantitatively to Ag(0), and that in weakly acidic and neutral solutions, the contamination is at a level so low as to have no significant analytical effect.

A consideration of the data in Table II suggests a gravimetric procedure for the determination of silver in silver salt solutions in the absence of interfering ions. This procedure would consist of the addition of aqueous sodium borohydride to a very weakly acidic or neutral solution. (The statistical "t" test indicates no reason for believing that there is any significant difference between the sets in the determination of silver at pH 2, 5, and 7). The reduced silver would be collected on Selas crucibles, washed with distilled water, then with acetone. That the product from such a procedure can be weighed directly as silver to give analytical results comparable to standard methods is apparent from the data in Table II. By this procedure, sodium borohydride could be used for the preparation of pure silver and simultaneously for the analysis of the amount of silver present.

Reduction of Gold(III). The Au (III) reduction product digests in 1 hour to give spongy brown or black lumps (containing yellow specks), which form is readily filterable. When ignited in a porcelain crucible in a Bunsen flame, the precipitate turns to the dull yellow color of pure gold. The dissolved precipitates give a negative flame test for boron.

The comparative study of the standard oxalic acid method with the sodium borohydride method is given in Table III. The sodium borohydride procedure is much simpler and more rapid than other standard methods for determination of gold and allows wider limits in the acidity of the reaction medium. An important factor of the borohydride procedure is the ease with which the gold precipitate is digested; it requires less than one hour as compared to at least four hours by the oxalic acid procedure. The oxalic acid precipitate is very fine, almost colloidal, and offers difficulty in filtration. One disadvantage of the borohydride reduction is its nonselectiveness, as contrasted to the high selectivity of the oxalic acid as a reducing agent for Au(III).

Sodium borohydride thus offers a new, simple, rapid method for the determination of silver and gold from solutions of Ag(I) and Au(III) ions in the absence of interfering species—namely, the reduction of the element by the reagent in dilute acid or neutral solution and the weighing of the dried reduction products.

The coinage metals cannot be separated from one another using $NaBH_4$ according to our procedure described in the previous publication (*3*) because they are all reduced within the limits of the pH range studied. Also, when our procedures are employed, cobalt, nickel, palladium, platinum, cadmium, mercury, tin, lead, arsenic, antimony, and bismuth when present in solutions of the coinage metals interfere with the purity of the reduction products. However $NaBH_4$ reduction under appropriate conditions leads to near quantitative separation of the coinage metals from the metals listed.

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Addendum. Simultaneous Use of Beta-Particle Transmission and Backscatter Gauges for Determining Hydrogen, Carbon, and Oxygen Percentages in Liquids

SIR: It has come to our attention that in our recent paper (*1*) we failed to acknowledge the prior work of Gray, Clarey, and Beamer (*2*) on a similar topic. Generally, the instruments and techniques (*2*) are capable of higher accuracy than ours, but are more expensive and tedious.

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A Three-Column, Two-Detector Gas Chromatographic Method for the Simultaneous Analysis of a Mixture of Fixed Gases and Hydrocarbons

SIR: In a study of the photochemical decomposition of several azo compounds a novel gas chromatographic technique was devised for the analysis of all the resulting decomposition products. This technique makes use of three columns and two thermal conductivity detectors connected in series. Previous investigators have utilized multicolumn methods which incorporate sample splitting devices (*4*, *6*), backwashing of columns (*1*), valve switching (*3*, *5*, *8*), and series arrangements (*7*). The analytical method described in this note differs from those previously described in that it is possible to display on a single recorder the analysis of a mixture containing C_2–C_6 hydrocarbons plus nitrogen and oxygen and to obtain quantitative analytical results with automatic integration of peak areas. Higher boiling compounds are resolved in short times without drastic temperature changes during the analysis and without sacrificing resolution or analytical accuracy.

The technique uses a commercially available gas chromatograph to which two additional columns and a detector are connected in series. The principle of operation is that the dual column chromatograph performs in its usual manner with a column chosen for its ability to separate the high boiling components within a reasonable time. The unresolved low boiling constituents and fixed gases pass into a second column which will separate the low molecular weight hydrocarbons efficiently at room temperature. The fixed gases are then passed into an adsorption column, maintained at room temperature, in which they are separated and detected by the reference side of the second detector. A block diagram of the apparatus used appears in Figure 1.

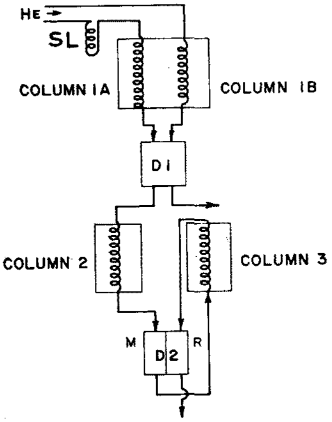

Figure 1. Schematic representation of multicolumn multidetector gas chromatography system

EXPERIMENTAL

A Perkin-Elmer Model 820 gas chromatograph with flow controller was modified by the installation of a sampling valve equipped with a sample loop for the injection of gaseous samples, and a temperature controller for the thermal conductivity detectors. The combination of a precise temperature controller with dual column operation produces a stable base line during temperature programming. Detector 2 was a Burrell K2 katharometer enclosed in an insulated oven, the temperature of the oven being controlled by a rheostat. Power was supplied to the W2 filaments in this detector by a Gow Mac Model 9999 regulated power supply. The output of each detector was brought to a switching network by which the proper detector and polarity could be chosen for observing a given component. Columns 1*A* and 1*B* consisted of 25 feet of 0.19-inch i.d. copper tubing filled with 25% w./w. Apiezon L on 40–60 mesh Chromosorb P. Column 2 consisted of 30 feet of 0.19-inch i.d. copper tubing filled with 30% w./w. squalane on 40–60 mesh Chromosorb P, and column 3 consisted of 15 feet of 0.19-inch i.d. copper tubing filled with 40–60 mesh 5A molecular sieve. Squalane was chosen for the analysis of lower hydrocarbons in preference to other possible substrate materials such as carbitol, hexadecane, dimethyl formamide, or dimethyl sulfolane (*2*) because column bleeding is much more of a problem with the latter materials. Severe bleeding from column 2 would be expected to contaminate the molecular sieve column in a short time and reduce its separation efficiency. Because it has a higher capacity for contaminants, molecular sieve 13X has been recommended for a series column application (*7*). However, in the present study no difficulties were encountered using molecular sieve 5A.

Columns 1*A*, 2, and 3 in series were operated with a flow rate of 42 cc./minute of helium; detector 1 was maintained at 120° C. and detector 2 at 175° C. Columns 2 and 3 were operated at room temperature while column 1 was held initially at room temperature and programed ballistically to 60° C. after the emergence of butane from column 2.

RESULTS AND DISCUSSION

Figure 2 illustrates typical chromatograms obtained with the combined column system and shows the separation achieved by each of the columns. Figure 2*A* was obtained when detector 1 was used to monitor the effluent of the Apiezon "L" column in the combined system. Figures 2*B* and 2*C* illustrate the signal produced by the measuring and reference side of detector 2. Figure 2*D* presents the final chromatogram obtained by switching the recorder from detector 1 to detector 2 and by reversing polarity at the appropriate points. The final chromatogram illustrates the quality of results and demonstrates that it is readily possible to achieve, in a reasonable time, a complete resolution of the components contained in this fairly complex mixture. The analysis may be displayed on a single recorder equipped with a mechanical integrator, which is used to obtain a quantitative analysis of this mixture. Table I illustrates the reproducibility and precision of an analysis achieved with the present system for a mixture containing equal concentrations of C_2–C_6 hydrocarbons.

To ensure that the retention times of each compound are different in the final system, some exact combination of partitioning agent, column length, and temperature must be determined empirically for the analysis in question. Because this arrangement permits separate control of temperature in each column and because there are only modest synergistic effects, it is not as difficult to achieve an optimum configuration as might at first be supposed.

Table I. Reproducibility of Analysis of Synthetic Mixture

Mole Fraction of Compound						
C_2H_4	C_2H_6	C_3H_6	C_3H_8	nC_5H_{12}	nC_4H_{10}	nC_6H_{14}
0.142	0.142	0.142	0.143	0.141	0.144	0.145
0.141	0.142	0.143	0.143	0.144	0.144	N.D.
0.143	0.144	0.144	0.142	0.146	0.142	0.139
0.143	0.141	0.144	0.142	N.D.	0.141	0.144

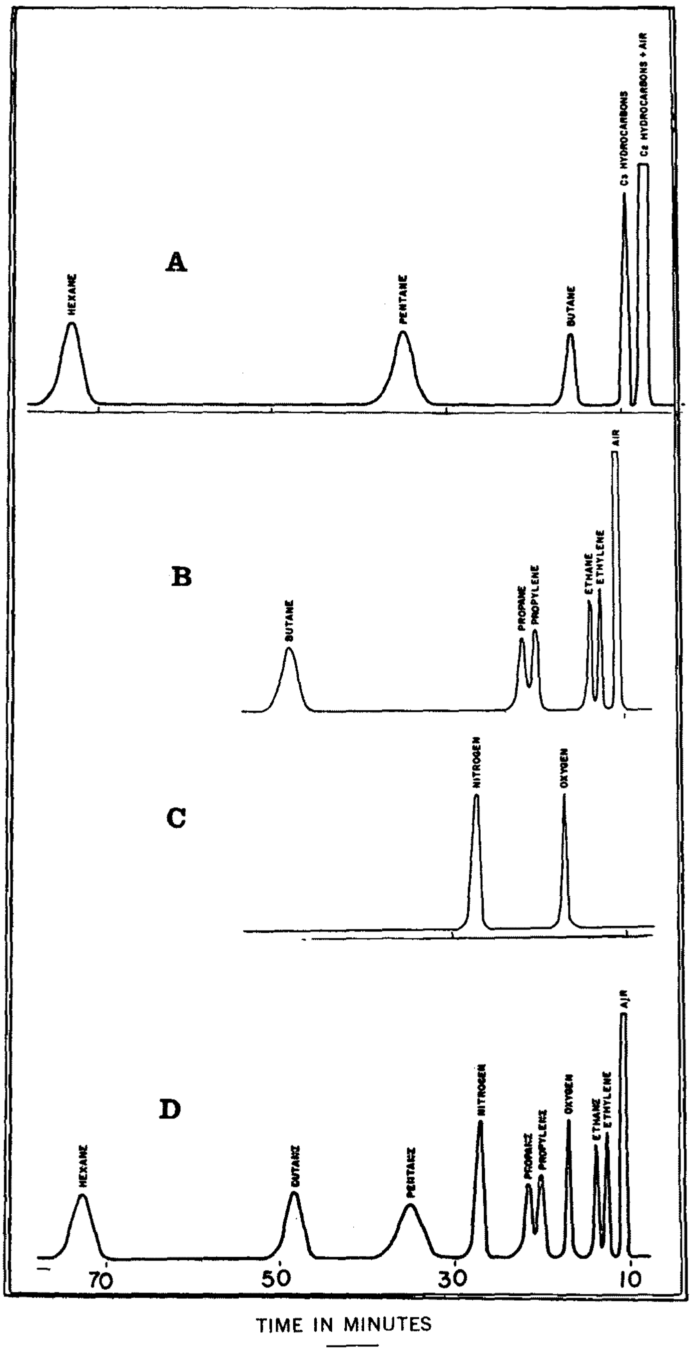

Figure 2. Typical chromatogams obtained wih combined column system

A is produced by monitoring effluent from column 1*A*, detector 1; *B* is effluent from Column 2; and *C* is the signal produced on the reference side of detector 2 by effluent from Column 3. Figure 2*D* is the final chromatogram produced by selection of the proper detector and signal polarity. The temperature of Columns 1*A* and 1*B* is ballistically programmed from room temperature to 60° C. after butane is eluted from Column 2

The system greatly reduces the time required for analysis of a complex mixture and displays the chromatogram of all components on a single strip chart, eliminating the need for repeated injections of representative aliquots of the mixture into various chromatographic columns with the attendant possibility of fractionation or contamination. The method is readily extended to other problems whenever it is necessary to analyze a mixture of high and low boiling components plus fixed gases. The present arrangement of the first column to provide adequate resolution of high boiling components within a reasonable time, of a second column to resolve the low boiling constituents incompletely separated by the first column, and a molecular sieve or other adsorption column for the resolution of fixed gases is thought to be the optimum arrangement for a multicolumn system.

A useful variation of this method which may be suggested is the incorporation of a flow reversal valve following detector 2 so that the direction of helium flow in the system may be reversed overnight. The use of such a flow reversal valve with moderate heating of the molecular sieve column would have the effect of eluting high boiling components from the molecular sieve and squalane columns by backwashing, so that it should not be necessary with such an arrangement to recondition the column. Although we have used the present arrangement for some months without the necessity of reconditioning the columns, it is certain that the simple system which we have used will ultimately require a conditioning treatment.

A variation of this procedure, investigated in the course of developing the technique, was the incorporation of a four-way flow switching valve between column 1*A*, 1*B* and 2. After air and the lower hydrocarbons had entered the second column, this valve was switched to vent the high boiling components after they had passed through the first column. To eliminate base line instability as a result of flow changes, a restriction was placed in the vent line to match empirically the back pressure produced by the other two columns. This modification proved to be quite satisfactory for qualitative analysis. However, the relative calibration factors are quite sensitive to flow rate in the detector at the time that a particular component is emerging, and the intermediate flow switching procedure proved unsatisfactory for quantitative work.

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signed and constructed the temperature control system and power supplies for the detectors used in the analysis, and assisted in the design of the flow system.

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Purification of Hexamethylbenzene by Zone Refining and Determination of Its Melting Point

SIR: For heat capacity and vapor pressure measurements, it has been necessary to prepare as pure a sample of hexamethylbenzene as possible (*1*). We have prepared a sample of hexamethylbenzene with 0.1 mole % impurity by zone melting and have determined its melting point by modern procedures. An apparatus has been developed which allows purity determinations to be made by the melting point method of Mair, Glasgow, and Rossini (*6*) at temperatures above 150° C. with a precision roughly comparable to that obtained at room temperature. With this apparatus the purity of the starting material and the purified sample was determined. We were thus able to estimate the melting point of the ideally pure compound.

Melting points cited elsewhere, along with the method of purification, are: 164° C., fractional crystallization from ethanol (*4*); 165° C., recrystallization from benzene (*8*); 164.8 ± 0.1° C., recrystallization from benzene after recrystallization from chloroform and ethanol three times (*5*); and 165.5° C., fractional crystallization from ethanol (*9*), as compared with our lowest initial freezing point of 165.644° C. for the purified compound. The discrepancies in the values, along with the difficulties in purifying this compound and in determining its melting point, make it desirable to report our results at this time.

The apparatus used for the purification was similar to the one described by Herrington, Handley, and Cook (*2*). Because of an increase in specific volume on melting, as well as at the second-order transition at 110° C., the specific volume of liquid hexamethylbenzene at the melting point is about 23 % greater (*8*) than that of the solid at room temperature. For this reason the usual procedure of zone refining resulted in breakage of the glass tube. The purification was therefore begun with hexamethylbenzene packed tightly in a borosilicate glass tube, rather than in the form of a continuous ingot. The zone purification process was carried out four times in a nitrogen atmosphere with a zone travel rate of 60 mm. per hour. At this rate of travel the contents of the tube separated into well defined regions during the first pass with a gap of about 20 mm. between each, thus allowing room for expansion in the second pass. After the fourth pass these sections had united so that a fifth pass was not attempted.

Because hexamethylbenzene has a vapor pressure of about 50 mm. Hg at the melting point (*5*), the freezing point determinations must be done in a closed system. The upper part of the inner wall of the double-walled borosilicate glass vessel which contained the sample was ground, to provide a means for closing the apparatus with a mating ground joint which formed part of the cap. The cap itself was provided with a ground joint, to provide entry for the thermometer, and a pumping exit. The stirrer shaft entered the apparatus through a stuffing box, containing two Teflon washers, which was soldered on to a Kovar seal whose glass end formed part of the cap. This gastight seal permitted free reciprocal motion of the shaft, with the aid of a constant speed motor and suitable cams. Teflon sleeves over the male half were used instead of grease to seal both ground joints.

The space containing the sample could be evacuated to a dynamic vacuum of about 1 mm. Hg. A positive pressure of about 6 cm. Hg of purified nitrogen was maintained over the sample during all runs.

The whole apparatus was immersed in a stirred thermostat whose temperature could be controlled to ±0.5° C. at any desired temperature below that of the melting range.

Temperatures were measured with a platinum resistance thermometer previously calibrated in this laboratory at the ice, steam, and sulfur points as discussed by Moessen (*7*). The equation of Hoge and Brickwedde (*3*) was used to compensate for deviations of 0.01° and 0.02° C., respectively, in the values of the ice and steam points from those of the original calibration.

The sample for the purity determinations of the purified material, weighed 42.4 grams (about 25% of the total charge) and was a mixture of two sections of the column of "pure" material symmetrically located with respect to the middle, so that it would give a value representative of the entire pure sample. The results (Table I) show that the unpurified hexamethylbenzene contained 0.26 mole % impurity, and that the impurity present in the product was 0.1 mole %. The mole fraction of impurity was calculated as outlined by

Table I. Purity Data for Hexamethylbenzene

Sample (detn. no.)	Initial freezing point, t_1 (°C.)	Mole % impurity[a]	Δt[b]	t_0[c] (°C.)
Unpurified (1)	165.576	0.264 ± 0.020	0.205	165.781 ± 0.016
Purified (1)	165.644	0.120 ± 0.009	0.093	165.757 ± 0.007
Purified (2)	165.693	0.080 ± 0.007	0.062	165.755 ± 0.005
Purified (3)	165.659	0.093 ± 0.030	0.072	165.731 ± 0.023
				Av. 165.75 ± 0.02

[a] Average of 6 values calculated from fraction frozen. R.m.s. error given for each.
[b] Lowering of initial freezing point due to calculated amount of impurity.
[c] Freezing point of absolutely pure compound, given by $t_1 + \Delta t$. R.m.s. error given for each, and for average.

Mair, Glasgow, and Rossini (*6*) using 4930 cal./mole for the heat of fusion. These results, along with the initial freezing points, give the melting point of pure hexamethylbenzene as 165.75 ± 0.02° C.

The uncertainty arises mainly from discrepancies in the initial freezing points (column 2, Table I) and to some extent from the uncertainty in the total time required for complete crystallization, from which the fraction frozen at any time was calculated.

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Factors Affecting the Selection of a Cobalt Analysis Line for Atomic Absorption Spectrometry

SIR: Information available in the literature concerning cobalt investigations by atomic absorption spectrometry has been generally limited to the evaluation of detection limits and analytical methods. Allan (*1*, *2*), Gatehouse and Willis (*5*), and McPherson, *et al.* (*6*) indicate the 2407.2 A. line as the most sensitive analysis line. Fuwa and Vallee (*4*) established very low detection limits for cobalt using the 2424.9 A. line. Robinson (*9*) listed detection limits for three relatively low absorbing lines, the strongest of which was 3529.0 A. in an oxycyanogen flame. Menzies (*8*) found the 3533.4 A. line best suited to his apparatus.

A study of several cobalt absorption lines indicates the proper choice of analysis line to be influenced by experimental parameters. The factors controlling such selection are discussed with respect to atomic absorption variables.

EXPERIMENTAL

Reagents. The cobalt stock solution was prepared from reagent grade $CoCl_2 \cdot 6H_2O$ dissolved in distilled water. Working concentrations (0–100 p.p.m.) were obtained by appropriate dilutions.

Apparatus. The atomic absorption unit was a D.C., single beam system assembled from a Hitachi-Perkin-Elmer Model 139 spectrophotometer and an optical bench containing the atomizer-burner, hollow cathode source, and associated equipment. The Westinghouse WL 22814 cobalt hollow cathode tube was powered by a Kepco Model ABC 425M 0.05% regulated D.C. power supply (Kepco, Inc., Flushing, N. Y.), operated in the constant current configuration (Kepco Instruction Manual, Model ABC 425M). A small beam, constricted by adjustable slits on each side of the burner, was collimated prior to passage through the flame and then focused on the monochromator entrance slit with bi-convex quartz lenses. A 10-cm. slot atomizer-burner (Perkin-Elmer Corp., Norwalk, Conn.) assembly was operated at the following conditions: 2.2 liters/minute acetylene, 7.1 liters/minute atomizer air, and 10.9 liters/minute auxiliary air. The sample uptake rate was 7.0 ml./minute. A D.C. solenoid shutter system mounted on the adjustable slit in front of the tube allowed the hollow cathode radiation to be cut off. An HTV R106 photomultiplier tube was used as the detector in the Model 139 photomultiplier attachment. The readout device was the direct reading meter on the spectrophotometer. A Heath EUW-20A potentiometric recorder was also used as a readout for some measurements.

RESULTS AND DISCUSSION

Cobalt exhibits a line rich spectrum in both emission and absorption. Table I shows the relative absorption of both ground state and non-ground-state transition lines of cobalt (*7*) for a 50-p.p.m. solution. There are eight lines which show an absorption greater than 25% and could prove reasonably useful in atomic absorption cobalt determinations in the range of 0–100 p.p.m. The 2424.9 A., 2521.4 A., 2411.6 A., and 2407.2 A. lines would be suitable for analyses at the low p.p.m. range. The complexity of the cobalt hollow cathode emission spectrum necessitates the use of narrow slits to avoid the inclusion of radiation other than the analysis line. The absorption values shown were determined under conditions which do not represent maximum sensitivity and could be improved if necessary for specific determinations.

Working curves were prepared for several cobalt absorption lines to determine their linearity over a particular concentration range. Figure 1 shows working curves run at a hollow cathode tube current of 25 ma. Most of the lines show a pronounced curvature

Table I. Absorption of Selected Cobalt Lines

Wavelength A.	% Absorption	Wavelength A.	% Absorption	Wavelength A.	% Absorption
		A. Ground state transitions			
4234.0	ND	3082.6	ND	2424.9	75.2
4190.7	ND	3044.0	17.5	2407.2	58.1
3909.9	ND	3013.6	ND	2384.9	ND
3526.8	9.5	2989.6	5.2	2365.1	ND
3474.0	4.2	2987.2	3.4	2309.0	4.5
3465.8	7.0	2928.8	ND	2295.2	4.0
3412.6	10.3	2521.4	68.6	2274.5	2.2
3121.4	ND	2435.8	27.3	2174.6	ND
		B. Non-ground state transitions			
3575.4	3.8	3453.5	10.0	2439.0	12.6
3533.4	ND	3442.9	3.6	2432.2	42.2
3529.0	3.0	3431.6	4.2	2419.1	1.5
3513.5	5.2	3405.1	6.0	2415.3	28.8
3506.3	4.2	2536.0	16.0	2411.6	59.6
3502.3	3.5	2529.0	26.4		

Cobalt solution = 50 p.p.m.
ND = not detectable
Slit width = 0.10 mm.
HCT current = 18 ma.

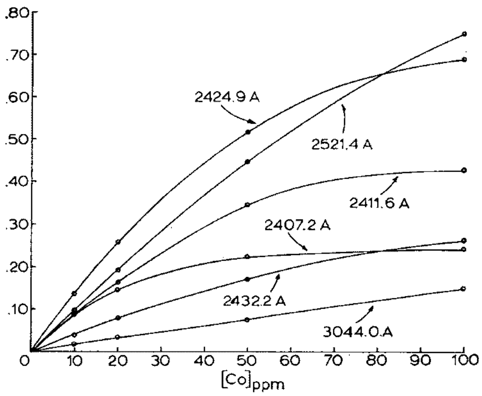

Figure 1. Cobalt working curves

Hollow cathode tube current = 25 ma.

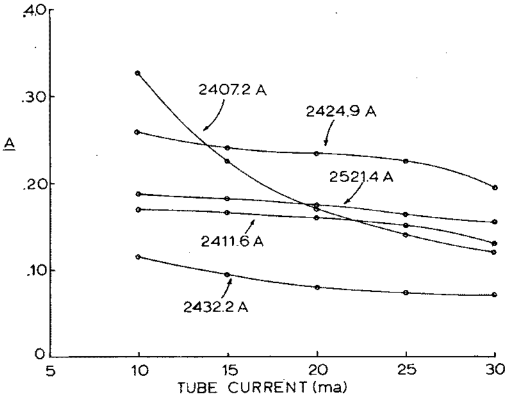

Figure 2. Effect of tube current on absorbance

20 p.p.m. cobalt

past 50 p.p.m. In the case of the 2407.2 A. line, the severe deviation from linearity arises from the presence of an adjacent interfering line which is too close to allow resolution with the monochromator employed in this study. David (*3*) also mentions interference from this line. Reduction of the slit width to 0.022 mm., which corresponds to a spectral band pass of approximately 0.5 A., fails to provide sufficient resolution to correct the nonlinearity of the working curve. The 2424.9 A. and the 2521.4 A. lines are of comparable sensitivity, but the latter shows somewhat greater linearity. The 3044.0 A. line, though of low absorption strength, produces a nearly linear working curve which might be suitable for those cobalt determinations in which high sensitivity is not a major requirement.

Figure 2 shows the change in absorbance produced by varying the hollow cathode tube current from 10 to 30 ma. Four of these lines show a relatively small increase in absorbance as the tube current is decreased and the emission line width becomes more narrow. The sensitivity of the 2407.2 A. line, however, is considerably altered, particularly in the region from 10 to 20 ma. This is possibly due to an increase in I_{AL}/I_{IL} with a decrease in current, where I_{AL} is the intensity of the 2407.2 A. analysis line and I_{IL} is the intensity of the unresolved interference line, possibly the 2407.7 A. cobalt line. Absorption measurements taken with a 500-p.p.m. cobalt solution, a concentration sufficient to absorb essentially all of the 2407.2 A. radiation, show 55% of the incident radiation unabsorbed at 30 ma., while only 19% remains unabsorbed at 10 ma.

The most sensitive analysis would suggest the use of the 2407.2 A. line at a very low current, narrow slit width, and an analysis concentration of less than 50 p.p.m. However, since cobalt does not show particularly strong hollow cathode emission at such low currents and slit width, the line emission intensity from the hollow cathode tube may be so low as to make stable and reproducible measurements difficult to obtain. It may be advantageous to increase the tube current to a point where the signal-to-noise ratio is more favorable, if maximum sensitivity is not required. At these higher currents (above 15 ma.) the sensitivity of the 2407.2 A. line is less than that of certain other lines (Figure 2). Furthermore, since the sensitivities of these lines are not as dependent on tube current, the emission intensity from the hollow cathode tube may be increased with the sacrifice of only a small amount of absorption. The greater linearity of the 2521.4 A. and 3044.0 A. lines may be of considerable importance if the concentration of the cobalt analysis solutions may vary over a range such as 10–100 p.p.m. The sharp curvature of the working curves of several of the analysis lines would make determinations in the range above 50 p.p.m. quite difficult. The 3044.0 A. line appears to be very suitable for analyses where high sensitivity is not required. However, this emission line is rather weak from the hollow cathode tube. There is also more flame background around this line which would require compensation in D.C. systems and which might introduce photomultiplier noise even in modulated instruments.

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Potentiometric Quantitative Determination of Sodium Aminoethylthiosulfates and Aminoethylthiosulfuric Acids

SIR: The protective utility of β-aminoethylthiosulfuric acid against ionizing radiation has been established (*3*). The physiological investigation of this radio-protective effect of the acid and its derivatives requires analytical methods for assaying these compounds.

Heretofore, no simple analytical methods have been applied to aminoethylthiosulfuric acid or sodium aminoethylthiosulfate determinations. Saville (*6*) devised an analytical method which involves oxidation with bromine water to the corresponding sulfonyl bromide, followed by reaction with cyanide, giving cyanogen bromide which is estimated colorimetrically. Thiols, disulfides, thiocyanates, and related compounds interfere. Displacement of sulfite from thiosulfuric acid by cyanide or thiol has been studied as a possible method for quantitative estimation of the thiosulfate group, but yields of sulfur dioxide greater than 80% could not be obtained (*4*). No references to aminoethylthiosulfate analyses were found.

The feasibility of titrating these compounds in nonaqueous solvents (*2*) has been investigated and new, accurate analytical methods for the quantitative determination of these compounds have been perfected. The thiosulfuric acid group is too weakly acidic for aqueous titration but the proton can be titrated effectively in pyridine solvent. The anion of sodium aminoethylthiosulfates is too weakly basic for aqueous titration, but the anion can be titrated effectively in ethylene glycol solvent. The titrations are standard procedures for weak acids (*1*) and acid salts (*5*) but have not been heretofore applied to aminoethylthiosulfuric acid derivatives.

EXPERIMENTAL

Modified Reference Electrode. A Beckman sleeve-type calomel electrode containing methanol saturated with KCl was used.

Preparation and Standardization of 0.1*N* Tetrabutylammonium Hydroxide. Prepare the titrant precisely as directed in reference (*1*). Standardize the titrant by potentiometric titration of benzoic acid.

Preparation and Standardization of 0.1*N* $HClO_4$. Dissolve 7.2 ml. of perchloric acid (72%) in ethylene glycol and dilute to 1 liter. Standardize the titrant by potentiometric titration of a 10-ml. aliquot of standard 0.1*N* NaOH.

Analytical Procedure for Aminoethylthiosulfuric Acids. Accurately weigh a sample which will require a titration of 2 to 10 ml. into a 250-ml. beaker. Add a few drops of water to dissolve the sample. Add pyridine solvent (50 ml.) and titrate potentiometrically with standard 0.1*N* tetrabutylammonium hydroxide. Pyridine contains acidic impurities and a blank titration is necessary.

Analytical Procedure for Aminoethylthiosulfates. Accurately weigh a sample which will require a titration of 2 to 10 ml. into a 250-ml. beaker. Add a few drops of water to dissolve the sample. Add ethylene glycol (50 ml.) and titrate potentiometrically with 0.1*N* $HClO_4$ in ethylene glycol, as in the above procedure. Blank corrections are unnecessary.

Table I. Analysis for Aminothiosulfuric Acid Derivatives

	Microanalysis		Potentiometric titration		
Compound	S calcd., %	S found, %	Grams added	Grams found	Purity, %
1. $NH_2CH_2CH_2S_2O_3H$	...	...	0.2652 0.2712	0.2660 0.2709	100.3 99.9
2. $HOCH_2CH_2OCH(OH)CH_2NHCH_2CH_2$-$S_2O_3H$	23.3	23.5	0.1648 0.0793	0.1650 0.0783	100.1 98.7
3. $HOCH_2CH(OH)CH_2NHCH_2CH_2S_2O_3H$	27.7	27.9	0.0934 0.1090	0.0924 0.1087	98.9 99.7
4. $CH_3CH(OH)CH_2NHCH_2CH_2S_2O_3H$	29.8	30.0	0.0916 0.1018	0.0922 0.1016	100.6 99.8
5. $(HOCH_2)_2C(OH)CH_2NHCH_2CH_2S_2O_3H$	24.5	24.8	0.0639 0.0554	0.0645 0.0555	100.9 100.2
6. $HOCH_2CH_2CH_2NHCH_2CH_2S_2O_3H$	29.8	29.9	0.0670 0.0696	0.0679 0.0701	101.3 100.7
7. $HOCH_2CH_2NHCH_2CH_2S_2O_3H$	31.9	32.0	0.0408 0.0535	0.0416 0.0549	102.0 102.6
8. $HOCH_2CH(OH)CH(OH)CH_2NHCH_2CH_2$-$S_2O_3H$	24.5	23.7	0.0141 0.0172	0.0156 0.0189	110.6 109.9
9. $HOCH_2CH_2OCH_2CH_2NHCH_2CH_2S_2O_3H$	26.1	26.1	0.0337 0.0529	0.0335 0.0531	99.4 100.0
10. $HOCH_2CH_2OCH_2CH_2NHCH_2CH_2NHCH_2$-$CH_2S_2O_3H \cdot C_4H_4O_4$	15.9	14.9	0.0237 0.0210	0.0258 0.0231	108.9 110.0
11. $HOCH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2$-$S_2O_3H \cdot C_4H_6O_6$	15.7	15.8	0.0770 0.0546	0.0753 0.0529	97.8 96.7
12. $NH_2CH_2CH_2S_2O_3Na$	...	...	0.1031 0.1573 0.1235	0.1030 0.1580 0.1241	99.9 100.4 100.5

RESULTS AND DISCUSSION

These procedures were applied to several compounds and the data are given in Table I. Compounds 1 through 10 were titrated with the standard base. Compounds 11 and 12 were titrated with the standard acid. The purity factors indicate that these two potentiometric titration techniques are adequate for assay of aminoethylthiosulfuric acid derivatives. The poorer results with compounds 8 and 10 are expected from the sulfur microanalyses; although the carbon, hydrogen, and nitrogen microanalyses of compounds 8 and 10 checked, the sulfur analyses indicated that contamination was present.

Acidic impurities, neutralized at potentials similar to thiosulfuric acid, interfere and must be removed. The most likely contaminants in this procedure are mercaptans from thiosulfate reduction, and these do not interfere. The difference in equivalence potential between mercaptans and thiosulfuric acids was 200 mv., the mercaptan being a weaker acid. The simultaneous determination of mercaptans and thiosulfuric acids is readily possible by this titrimetric procedure.

Thymol blue has the same equivalence point as thiosulfuric acid, and the titrimetric procedure is simplified by using two drops of 0.3% thymol blue in isopropyl alcohol as a visual end point indicator. The visual end point, however, is less precise than the potentiometric end point (±0.05 ml. *vs.* ±0.01 ml.).

There is one class of aminoethylthiosulfates which cannot be acid-titrated in ethylene glycol. The *N*-acetyl and *N*-formyl derivatives of aminoethylthiosulfates were neutral salts in ethylene glycol, and hence could not be assayed by titration.

These titrations are now performed on a routine basis in this laboratory to assay research quantities of these compounds.

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Derivatives of β-aminoethylthiosulfuric acid used in this investigation were synthesized by M. H. Gollis, J. E. Harris, and J. C. James.

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Amperometric Titration of Primary Amides

Sir: In an earlier paper (*2*) a method was described for the spectrophotometric titration of primary aliphatic amides with hypobromite in basic solution. Although this procedure is satisfactory for aliphatic amides, it cannot be used for the analysis of aromatic amides because of the instability of the primary reaction product, the corresponding aromatic *N*-bromamide, in basic solution. The decomposition products of the *N*-bromamide are rapidly oxidized by hypobromite, and no suitable end point can be found.

This communication deals with a new titrimetric procedure for amides which can be utilized for the analysis of both aliphatic and aromatic amides. The sample of amide is dissolved in a dioxane–water mixture which is 1*M* in hydrochloric acid, and titrated with a standard solution of calcium hypochlorite using an amperometric end point.

EXPERIMENTAL

Reagents and Apparatus. An approximately 0.5*N* solution of calcium hypochlorite was prepared by dissolving reagent grade calcium hypochlorite in water, followed by filtration to remove solid calcium carbonate. The solution was standardized iodometrically. No change in titer was evident over a 1-month period, in contrast to that evident with the more dilute solution used previously (*2*).

The amides used were of the highest purity obtainable from commercial sources and were used without further purification.

The amperometric titration apparatus consisted of a dry cell potential source, a divider, an RCA Model WV-84B microammeter, a Leeds and Northrup pH meter, a rotating platinum electrode, and a saturated calomel electrode.

Procedure. A 25-ml. aliquot containing 0.5 mmole of amide in dioxane was diluted to exactly 150 ml. with aqueous HCl so that the final solution was ~1*M* in HCl and 20% dioxane. The applied potential was set to +0.4 volt *vs.* S.C.E., and the calcium hypochlorite titrant was added in 0.5-ml. increments. The resulting current readings were taken after the addition of each increment of titrant, corrected for dilution, and plotted against volume of titrant. The best straight lines were drawn through the experimental points, and the intersection of these two straight lines was taken as the end point.

RESULTS AND DISCUSSION

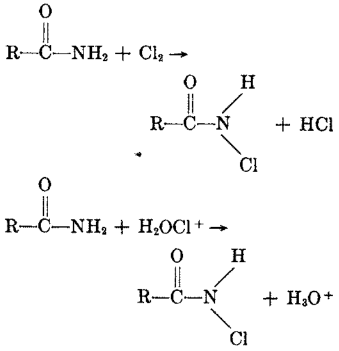
The results of the titration of a number of primary amides are given in Table I. Although these results were obtained with a 0.5-mmole sample of amide, as small a sample as 0.05 mmole was titrated with 0.05*N* calcium hypochlorite with only a slight decrease in accuracy and precision. The time required to complete a titration was about 10 minutes.

The reaction utilized in this procedure is the *N*-chlorination of the primary amide in 1*M* hydrochloric acid with a chlorinating agent produced by the addition of calcium hypochlorite. The exact nature of the chlorinating agent, however, is not known, and it is probable that both chlorine and protonated hypochlorous acid may be involved The sequence of reactions suggested is:

$$OCl^- + H^+ \rightarrow HOCl$$

$$HOCl + H^+ \rightarrow H_2OCl^+$$

$$HOCl + HCl \rightarrow Cl_2 + H_2O$$



$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Cl_2 \rightarrow R-\overset{O}{\overset{\|}{C}}-N\begin{matrix}H\\Cl\end{matrix} + HCl$$

$$R-\overset{O}{\overset{\|}{C}}-NH_2 + H_2OCl^+ \rightarrow R-\overset{O}{\overset{\|}{C}}-N\begin{matrix}H\\Cl\end{matrix} + H_3O^+$$

Table I. Amperometric Titration of Primary Amides

Amide	No. of trials	Av. apparent purity, %	Std. dev., %
Benzamide	8	99.6	0.6
o-Toluamide	9	100.6	0.9
p-Toluamide	5	97.0	0.6
Acetamide	6	99.6	1.3
Propionamide	3	100.0	0.7
n-Butyramide	3	100.4	0.5

Undoubtedly chlorine is the predominant chlorinating species when hydrochloric acid is used, because the reaction between hypochlorous acid and hydrochloric acid is rapid (*1*). However, similar titrations were performed using 1*N* sulfuric and 1*N* perchloric acids instead of hydrochloric, and identical titration results were obtained, even though the rate of chlorination was markedly slower than when hydrochloric acid was used. Because the calcium hypochlorite titrant contained an appreciable amount of free chloride, chlorine is probably still the major chlorinating agent, but the protonated hypochlorous acid may be involved also.

The excess chlorinating agent slowly decomposes after the end point of the titration has been passed. The rate of decomposition of 1*M* hydrochloric acid is approximately 1% per minute. A number of methods were attempted to stabilize the chlorinating agent, but none was successful. For example, if the solution being titrated is made 12*M* in chloride ion, the decomposition rate is diminished to 0.3% per minute, but almost no chlorination of benzamide was noticed after 30 minutes. Bromine was also substituted for chlorine, but no *N*-bromination was noticed in a reasonable time period.

The following technique was then developed to eliminate errors due to the slight instability of the chlorinating agent. A direct titration was carried out, but the first experimental point after the end point was taken with only a slight excess (usually about 25%) of hypochlorite. The remaining points, which determined the second segment of the titration curve, were then assumed to be constant if the current decreased less than 1 μa. per minute.

This procedure can be used successfully for primary aliphatic amides and for aromatic amides which are not substituted or which are substituted only with alkyl groups. The presence of other functional groups substituted on the aromatic ring in general causes interference in the determination of the amide group. Electron-withdrawing groups such as nitro and carboxyl reduce the rate of *N*-chlorination, and also adversely affect the equilibrium constant. Electron-donating groups activate the ring so that chlorination of the ring takes place readily, and the exact stoichiometry of the titration reaction becomes uncertain. In addition, substituted groups such as amino, carbonyl, and hydroxy are easily oxidized by hypochlorous acid in the titration medium.

Preliminary experiments indicate that a possible solution to this problem of interference by ring substituents is exhaustive bromination in acid solution. If the unknown sample is treated with bromine, most of the ring sites which would ordinarily be chlorinated during the titration are brominated. Also, easily oxidizable groups are oxidized by the bromine, and the excess bromine can then be driven off by heating. Under these conditions bromination on the amide nitrogen does not take place.

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Determination of Adsorbed Ethylene and Propylene Oxides by Distillation and Titration

SIR: A modified method for determining adsorbed volatile epoxides that is both simple and rapid has been developed. Such epoxides are not directly titrateable, due to very slow elution into the titrating medium and obscure end points. Mechanical preparation of the sample such as grinding or shredding does not materially improve this condition; it provides error through loss of the adsorbed volatiles during preparation and does not eliminate the obscure end points. Since hydrogen bromide reacts virtually instantaneously and the elution is of a physical rather than a chemical nature, other reactants—as in the method of Jay (*3*)—likewise do not make direct titration feasible. Methods using excess reactant with back-titration as in the procedures by Schecter, Wynstra, and Kurkjy (*4*) and Durbetaki (*2*) are also inadequate because of the prolonged elution and hence reaction time, and the varied interferences found with the different adsorbing materials. Current methods generally elute the epoxide by aeration and bubbling through a reacting solution; such techniques are time consuming and awkward to handle.

In this method, adsorbed epoxides are released from the adsorbing material by distillation in monochlorobenzene, collected in a receiving medium, and titrated with a standard hydrogen bromide solution, using crystal violet as an indicator, as in the method by Durbetaki (*1*).

Because ethylene and propylene oxides are known to be quite reactive, it was anticipated that a reaction between these epoxides and the adsorbents would take place during the distillation. Recovery studies were made by exposing the materials to pure ethylene and propylene oxides, weighing the amount adsorbed, and subsequently determining the epoxides by this procedure. Consistently low values were obtained, and the amount of unrecovered epoxide from each adsorbent followed the expected pattern in terms of individual adsorbent reactivity; in all cases, the value was minimal. Blank distillations and titrations were conducted on unexposed samples of the same size to determine the reagent and indicator values and to compensate for any volatile reactant originally in the material. All such values thus obtained were found to be consistent and minimal for each adsorbent studied.

EXPERIMENTAL

Apparatus. The apparatus used were as follows: a 250-ml. round-bottom flask with 24/40 ground joint; a 300-mm. West condenser with 24/40 ground joints; a 75° connecting tube with 24/40 joints; a 105° adapter tube with 24/40 joint; a 75-ml. collecting flask; and a 250-ml. heating mantel with voltage regulator.

Procedure. Place an accurately weighed 2-gram sample of the adsorbent in the distilling flask with 2–3 glass beads and add 100 ml. of monochlorobenzene; apply apiezon "Q" wax to the glass joints. Add 15 ml. of glacial acetic acid to the receiving flask, and connect the apparatus with the tip of the condenser adapter tube covered by the glacial acetic acid in the receiving flask. Set the voltage regulator at 75 volts and distill until one half of the monochlorobenzene has

Table I. Epoxide Recovery

Adsorbed (mg./gram)	Unrecovered (mg./gram)	Recovered, %
Propylene oxide in gum rubber; 2-gram samples		
1.8	0.0	100.0
5.0	0.2	96.1
9.6	0.2	97.8
12.8	0.2	98.6
19.9	0.7	96.7
22.1	0.8	96.1
26.6	1.2	95.5
31.5	0.9	97.9
54.5	1.5	97.2
68.7	2.2	96.6
Ethylene oxide in gum rubber; 2-gram samples		
0.7	0.1	87.5
1.2	0.1	88.0
4.8	0.4	92.1
5.2	0.6	89.4
16.1	1.4	91.2
18.6	2.0	89.0
26.4	2.2	91.7
58.6	3.6	94.2
69.7	4.6	93.4
(18.5)[a]	2.1	88.9
(11.8)	1.3	88.9
Propylene oxide in tygon; 2-gram samples		
1.4	...	100.0
12.9	...	102.7
14.5	0.1	99.4
17.0	...	100.4
24.8	0.2	99.4
39.3	0.4	99.0
52.3	...	101.5
63.4	...	100.4
Propylene oxide in polyethylene; 2-gram samples		
1.0	0.0	100.0
1.1	0.0	100.0
3.5	0.0	100.0
3.8	0.0	100.0

[a] 5-gram samples.

distilled over. Smooth, semirapid, and consistent distillation (approximately 20 minutes) is essential.

Rinse the adapter tube with 10 ml. of monochlorobenzene and titrate the distillate with the 0.1*N* hydrogen bromide in glacial acetic acid, using 0.1% crystal violet indicator in glacial acetic acid.

Calculations: Milligrams of epoxide recovered per gram of sample material =

$$\frac{\text{ml. HBr} \times \text{N} \times \text{E.W.}}{\text{wt. of sample}} - \frac{\text{ml. HBr} \times \text{N} \times \text{E.W.}}{\text{wt. of blank sample}}$$

Refer to calibration graph for total absorbed epoxide.

Notes. The condenser is air cooled.

Glassware must be scrupulously clean and dry; do not use other glass joint lubricants.

Glacial acetic acid is used in the receiving flask to prevent obscure endpoints caused by traces of moisture in the sample. Small amounts of moisture do not otherwise interfere except for increased blank titers.

For each different material that is tested for epoxide, it is necessary to determine blank values.

Calibration. Several 2-gram samples of the adsorbent in question are exposed to the pure epoxide in a disiccator, for different lengths of time, to adsorb varying quantities of gas and are weighed to determine the amount of gas adsorbed in each. A minimum of three samples, and preferably five or six, should be run, covering the complete range of the expected epoxide concentration. The amount of epoxide recovered (a blank determination is run on several unexposed samples, and this average value subtracted from the value found on exposed samples is the amount recovered) from each sample by distillation and titration is then plotted against the amount adsorbed as determined by weight. In subsequent determinations then, the total adsorbed epoxide is found by referring the amount recovered to this calibration graph.

RESULTS AND DISCUSSION

The unrecovered epoxide is presumed to be due to a reaction between the adsorbed epoxide and the adsorbent during distillation; the reaction product thus formed (unrecovered epoxide in milligram per gram of sample) increases with the epoxide concentration and is dependent on the nature of a given adsorbent. With controlled distillation for a specific period of time, recovery from the different adsorbents was consistent over a wide range of concentration, and with the construction of a calibration graph, is considered to be complete. Relative standard deviations for the determinations of ethylene and propylene oxides in gum rubber are 2.2% and 1.3%, respectively. Deviation in less reactive adsorbents is smaller. The detection limits of ethylene and propylene oxides are 0.04 mg. and 0.06 mg., respectively. Data are presented in Table I.

Table II gives the values obtained on conducting blank distillations and titrations.

Table II. Blank Determinations (calcd. as ethylene oxide)

	mg./gram found; 2-gram samples
Polyethylene	0.2
	0.2
	0.2
	0.2
Rubber	0.4
	0.3
	0.5
	(0.9)[a]
	(0.9)
Vinyl	0.1
	0.2

[a] 5-gram samples.

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AIDS FOR THE ANALYTICAL CHEMIST

New Method for Determination of Hydrocarbon-in-Water Solubilities

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In connection with a study of the bubble column slurry reactor (*2*), data on solubility of cyclohexene in water at room conditions became necessary. No results were found in the literature. Published experimental methods applicable to hydrocarbon-water systems either required complex, expensive equipment or were suitable only for compounds much more soluble than cyclohexene. Against this background, a new method was developed as part of the reactor work. This technique requires only commonly available, inexpensive apparatus and yet is suitable for determination of extremely minute solubilities of hydrocarbons in water.

During preparation of this report, the literature was thoroughly rechecked for solubility methods applicable to gas-liquid and water-hydrocarbon systems. Among the additional references obtained were disclosures (*8, 9*) of two methods of sample preparation similar to the one described. However, to the best of the author's knowledge, the new method as an entity has in no sense been anticipated in the literature.

Apparatus. The apparatus used in the reactor study and in the solubility work consisted of a vertical borosilicate glass tube (height, 4 ft.; diameter, 1 inch) with a fritted glass disk sealed in at the bottom. This apparatus, jacketed for temperature control, was filled with water (or other solvent of interest). A carrier gas was supplied continuously to a bubbler filled with cyclohexene (or other solute). The resulting gas-vapor mixture was dispersed into the reactor through the fritted disk. After a suitable period, the flow was diverted from the reactor. When all bubbles had risen through the column, a sample bulb was connected to a side line (see Figure 1).

This means of preparation of a saturated solution also served to quantitatively remove dissolved air and/or other foreign gases. In a number of other published solubility methods, there is always a question as to whether this removal has been completed.

During the operation, valve *a* (Figure 1) had been closed and remained so. Valve *b* was opened and the space between valves *a* and *c* was evacuated. Valve *c* was then closed and valve *a* opened; a sample of volume v_r was then drawn from the reactor. Valves *a* and *b* were closed. The bulb was disconnected and alternatively shaken and placed in the same water bath from which the jacket of the reactor was supplied. After several repetitions to ensure equilibrium, and while still in the bath, the bulb was connected to an inclined closed-end mercury manometer.

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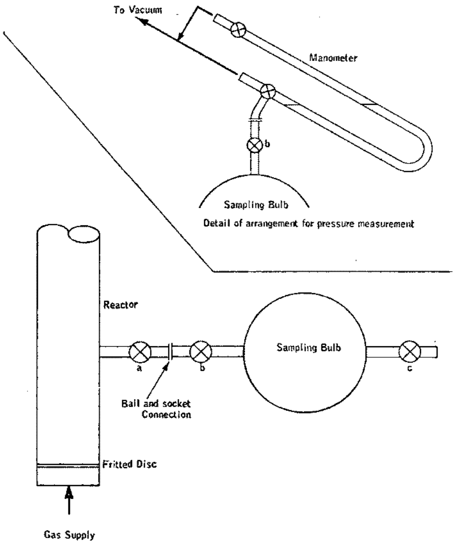

Figure 1. Schematic diagram of apparatus for determination of solubility of vapors and gases in liquids

The space between valve *b* and the top of the mercury column was evacuated. Valve *b* was then opened to the manometer. The total pressure p_n in the bulb before opening was obtained from the manometer reading and a calibration of the volume of the connection between valve *b* and the top of the mercury column as a function of the manometer reading.

In addition to the bulb pressure, it was necessary to know the vapor pressure p_3° of the solute at the bubbler temperature, the bubbler total pressure P_B, the volume v_l of liquid in the bulb, the volume v_g of gas-vapor mixture in the bulb, the solubility of the carrier gas in the solvent at the reactor temperature T, and the vapor pressure p_1° of the solvent at T. From this information it was possible to calculate the solubility of cyclohexene in water. A development of the relationships employed follows.

THEORY

The reactor was operated at approximately atmospheric pressure. For this mild condition, it was assumed that the hydrocarbon vapor would follow a Henry's law solubility expression

$$c_i = p_i/M_i \qquad (1)$$

Here the vapor is taken to be component i, and c_i is the concentration of component i in a liquid phase at equilibrium with a vapor phase in which the partial pressure of component i is p_i. The Henry's law constant is M_i. Of course this expression would hold only for the region

$$p_i < p^\circ_i \qquad (2)$$

where p_i° is the vapor pressure of the hydrocarbon at the temperature under consideration. Equation 1 was also assumed to apply to the carrier gas.

From the values of p_3°, P_B, and p_1° it was possible to calculate the partial pressure p_{ir} of each component i ($i = 1$ for solvent, $i = 2$ for carrier, $i = 3$ for solute) in the gas-vapor mixture leaving the reactor during the saturation process. According to Equation 1, the amount of carrier or of solute in the sample was $p_{ir}v_r/M_i$. After the new equilibration in the sample bulb, each material was distributed between the vapor and liquid phases present. If the partial pressure of component i in the volume v_g was p_{is}, then the amounts in the two phases were, respectively, $p_{is}v_g/R_gT$ and $p_{is}v_l/M_i$, where R_g is the gas constant. Then by material balance

$$p_{ir}v_r/M_i = p_{is}v_g/R_gT + p_{is}v_l/M_i \qquad (3)$$
$$i = 2,3$$

Neglecting the other components, at the new equilibrium the ratio of the amount of H_2O in the vapor space to the amount in the liquid is much less than unity. As an example consider the typical conditions 77° F. and $v_g/v_l = 1$. The saturation specific volumes of vapor and liquid H_2O at 77° F. are (*3*) 694.9 and 0.01607 cu. ft./lb., respectively. Under these conditions the above-mentioned ratio is 0.01607/694.9 = 0.0000231 lb. H_2O as vapor per lb. H_2O as liquid. Therefore, the amount of solvent vaporized during the sampling process was completely negligible and $v_r \approx v_l$. Thus Equation 3 may be rearranged to read

$$M_i = (R_gTv_l/v_gp_{is})\,(p_{ir} - p_{is}) \qquad (4)$$

Each component contributes to the total pressure observed in the vapor space in the bulb:

$$p_n = \Sigma p_{is} = p_{1s} + p_{2s} + p_{3s} = p_1^\circ + p_{2s} + p_{3s} \qquad (5)$$

The value of p_{2s} was obtained from Equation 4, using the known value of M_2. Equation 5 yielded p_{3s} by difference. Substitution of the latter value into Equation 4 effected a determination of M_3, the desired result.

DISCUSSION

Several precautions were necessary in order to apply this method successfully. To avoid a small difference between two nearly equal quantities, the cyclohexene partial pressure in the bulb must be as large as possible relative to the total pressure. This condition was achieved by selecting as insoluble a carrier gas as possible, by employing a reactor feed mixture as rich in cyclohexene vapor as possible, and by operating at as low temperatures as possible in order to keep the vapor pressure of water low. Nitrogen, the most insoluble of the common gases, was used as the carrier. The bubbler was operated just under room temperature. The situation was quite manageable with respect to the water vapor pressure up to about 125° F. and reproducible results were obtained from this temperature down to 77° F.

Other fine points must be considered. The connection between bulb and reactor was originally evacuated along with the bulb. The volume of this connecting line was less than 3% of the bulb volume, and furthermore, after sampling, but before the bulb was disconnected, this space was filled with a vapor-liquid mixture of roughly the same proportions as those obtaining in the bulb itself. It can be seen from Equation 4 that only the ratio v_l/v_g enters into the calculation of M_i and therefore essentially no correction was required.

Extensive trials indicated that for organic solvents the sampling bulb must be equipped with Teflon (Du Pont) plug stopcocks, lubricated with a small amount of glycerin. For aqueous solvents, the sampling bulb can be equipped with conventional borosilicate glass plug stopcocks lubricated with silicone or other grease insoluble in the liquid. These procedures made it possible to avoid leaks completely. The smallest leakage into the bulb could be detected conveniently because of the presence of the liquid.

When the bulb temperature is higher than that of the manometer, material may distill over during the pressure

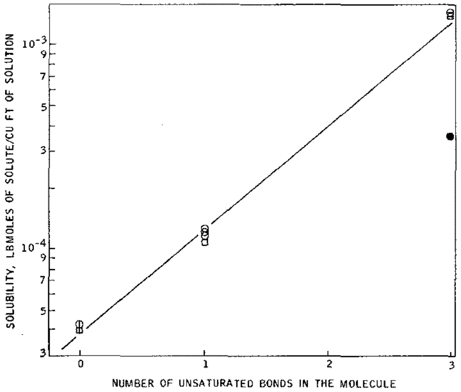

Figure 2. Solubility of organic compounds in water at 77° F.

Solute	Number of unsat. bonds in molecule	Symbol	Source of data
Cyclohexane	0	⦶	Extrapolation of data of Kudchadker and McKetta (5)
		◫	McAuliffe (7)
Cyclohexene	1	○	This work
		□	Duque-Estrada *et al.* (1)
Benzene	3	⊖	Klevens (4)
		⊟	McAuliffe (7)
		●	Extrapolation of data of Kudchadker and McKetta (6)

The indicated values are those which would occur in an aqueous phase when the partial pressure of the solute over the solution is equal to the vapor pressure of the solute at 77°F, and when the total pressure is 1 atm. abs.

measurement. This phenomenon may be avoided by placing the manometer as well as the bulb in the water bath. Since this step was not taken in the present work, only the results obtained at 77° F. (room temperature) will be reported.

The possibility of flashing of solutes upon opening the bulb to the manometer was neglected. The pressure reduction was slight as the connection was very compact and no bubbles were seen to form in the liquid.

RESULTS

As an adjunct to this work, the solubility of cyclohexene in water was also measured by Duque-Estrada, Bayne, and Manalan (*1*), employing the gas-chromatographic method of McAuliffe (*7*).

The results of three determinations of M_3 by the method described in the present report were converted by use of Equation 1 into concentrations that would exist in equilibrium with an organic liquid phase. The result of Duque-Estrada *et al.* (the average of two determinations) was already in this form. These cyclohexene data and literature results for cyclohexane (*5, 7*) and benzene (*4, 6, 7*) are compared in Figure 2 and Table I. The correlation obtained appears to indicate that hydrogen bonding between unsaturated bonds and water molecules is a primary determinant of solubility. The format used in the figure was developed independently although the bonding phenomenon has been noted previously, e.g., (*6*).

CONCLUSIONS

The agreement between the cyclohexene solubility results obtained from two very different methods supports the validity of the new method described herein. The consistency with data for other compounds provides further support. Whenever more sophisticated apparatus is not available, the new method should be a convenient means of measuring very small solubilities.

Table I. Solubility of Organic Compounds in Water at 77° F.[a]

Solute	Solubility × 10^4 lb. mole solute/cu. ft. solution	Source of data
Cyclohexane	0.425	Extrapolation[b] of data of Kudchadker and McKetta (*5*)
Cyclohexane	0.405	McAuliffe (*7*)
Cyclohexene	1.14 1.21 1.28	This work
Cyclohexene	1.07	Duque-Estrada *et al.* (*1*)
Benzene	14.9	Klevens (*4*)
Benzene	14.2	McAuliffe (*7*)
Benzene	3.63	Extrapolation of data of Kudchadker and McKetta (*6*)

[a] The indicated values apply to the situation in which the partial pressure of the solute over the solution equals the vapor pressure of the solute at 77° F., and in which the total pressure is 1 atm. abs.

[b] Extrapolation was carried out on the basis of the assumption that the solubility obeys an Arrhenius expression.

ACKNOWLEDGMENT

T. K. Sherwood provided valuable guidance for the research and was especially encouraging in the development of the solubility method.

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The method described in this report was developed while the author was a National Science Foundation Graduate Fellow. Equipment purchases were from funds established at MIT by Sun Oil Co. and Eastman Kodak Co., and library facilities were extended by Esso Research and Engineering Co.

Preparation and Use of Lead-212 Tracer

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During an investigation on the separation of lead-210 from ores and mill products by dithizone, a convenient radioactive tracer was sought to facilitate the work. The radioactive isotopes of lead most suitable for general use as tracers are those of masses 203, 210, and 212. All other isotopes have half lives too short for other than special purposes. Lead-203 is produced by nuclear bombardment reactions and is quite expensive and not readily available. Its half life of 52 hours would not permit shipment to locations very far from its point of preparation economically, and the tracer would require frequent replacement to permit continuous experimentation over any significant period of time.

Lead-210 is very difficult to measure directly because of the low energy of both the beta particles and gamma radiation resulting from its decay. Its bismuth-210 daughter has an energetic beta emission but its half life of 5 days would require an 18-hour delay in counting to obtain even 10% of the lead-210 activity taken. Particularly, bismuth-210 is a pure beta emitter and has to be obtained essentially free of absorbing solids and liquids before counting can be accomplished. In contrast, lead-212 has a 0.239-Mev. gamma ray of 45% abundance which permits direct counting of aqueous solutions in a scintillation well counter. Its half life of 10.6 hours is long enough to present no problems due to decay and short enough that the tracer will be regenerated to about 75% of its maximum equilibrium value on standing overnight. Since this nuclide is present in appreciable activities in natural thorium compounds, it is readily available at very low cost. Both the lead-212 and its bismuth daughter can be removed quantitatively from dilute acid solution by the well-known dithiocarbamate extraction (*1*). Thus, a continuing and virtually inexhaustible supply of inexpensive gamma-emitting tracer is easily available at all times.

The disadvantage of having to prepare the tracer for each days work is essentially nullified by the simplicity and speed of the procedure described in the present work, only about 45 minutes being required after the initial preparation. Other methods of preparing lead-212 tracer have been summarized in a recent excellent review of the radiochemistry of lead (*1*) but are generally not as rapid, efficient, or easily adaptable to large-scale preparation as the present procedure. The only significant disadvantage associated with use of lead-212 as a tracer is the necessity of waiting for 8 hours to obtain more than 99.5% ingrowth of the 60.6-minute bismuth-212 and 3.1-minute thallium-208 daughters in the lead fraction and decay from the bismuth fraction before results can be obtained by gross gamma counting when tracing reactions in which lead and bismuth are separated from each other.

EXPERIMENTAL

Preparation of Tracer. Place 200 grams of reagent grade $Th(NO_3)_4 \cdot 4H_2O$ and 110 ml. of 72% perchloric acid into a 600-ml. beaker. Heat the mixture on a high-temperature hot plate until all solid salts have dissolved and the evolution of nitric acid changes to heavy white fumes of perchloric acid. Continue the evaporation of excess perchloric acid until the froth at the surface of the solution tends to crust over while still on the hot plate. Cool the solution and add 20 ml. of 72% perchloric acid and 400 ml. of water. Boil the solution gently for a few minutes to dissolve the cake and to volatilize decomposition products of perchloric acid and cool. The solution will be about $0.7M$ in perchloric acid and 450 ml. in volume.

Transfer the thorium perchlorate solution into a 500-ml. separatory funnel and shake vigorously for 1 minute with 20 ml. of a 1% solution of diethylammonium diethyldithiocarbamate (DDTC) in chloroform. Draw off the extract into a 250-ml. separatory funnel containing 100 ml. of water and 10 ml. of 72% perchloric acid. Repeat the extraction with another 10-ml. aliquot of the 1% DDTC solution and add the extract to the separatory funnel containing the first one. Shake the 250-ml. funnel vigorously for 1 minute to wash the combined extracts and draw off the organic layer into a 250-ml. Erlenmeyer flask. Add 2 ml. of 50% sodium hydrogen sulfate ($NaHSO_4$) and 2 ml. of concentrated nitric acid to the flask containing the combined extracts and heat carefully on the hot plate until the chloroform has evaporated.

Place the flask on a high-temperature hot plate covered with a thin piece of asbestos cloth and heat strongly until nitric acid has been expelled and a black cake of charred organic matter is obtained. As soon as the charred mass is completely dry and immobile and no further charring is evident, remove the flask from the hot plate to prevent small losses of lead by volatilization.

Cool the flask and add 3 ml. of a 1 to 1 mixture of concentrated nitric and 72% perchloric acids and boil until the black suspension becomes colorless and excess perchloric acid has evaporated. Do not attempt to evaporate the DDTC extract to dryness with perchloric acid before the thermal charring or the organic matter will ignite in a sudden burst of white-hot fire and over 75% of the tracer will be volatilized. Add 10 ml. of water and 1 ml. of concentrated hydrochloric acid and boil the solution for 1 minute, cool and dilute to 10 ml. Each 1-ml. aliquot will contain approximately 8.5×10^5 c.p.m. under the conditions used.

Extract the thorium perchlorate solution in the 500-ml. separatory funnel with 20 ml. of straight chloroform for 1 minute to clean up traces of diethyldithiocarbamate and decomposition products. Discard the chloroform extract and store the aqueous solution until more tracer is needed. It is advisable to discard the first batch of tracer obtained from a new sample of natural thorium to remove all extractable impurities including natural lead that might be present. After standing overnight, the freshly-ingrown tracer will be carrier free.

Counting Procedure. The lead-212 is determined by gross gamma counting in a 3-inch thallium-activated sodium iodide well crystal in aqueous solutions of up to 75-ml. volume contained in 100-ml. polystyrene bottles. Each sample should be compared to a standard within a few minutes under the same counting conditions to ensure constant counting efficiency and to eliminate decay corrections. The standard should contain approximately the same salt content as those samples containing a significant fraction of the total activity. Particular care should be taken to adjust the level of each sample solution by dropwise addition of water until the height is within about 0.1 mm. of that of the standard for maximum precision, especially on high-counting samples. This height adjustment should be made immediately before counting to eliminate any effect of differences in temperature between sample and standard on their volumes.

Since lead-212 decays initially at a rate of 0.1% per minute, sufficient activity should be used so that the desired statistical precision can be obtained on 1-minute counts to maximize the number of samples that can be counted before the standard must be recounted. If all low-counting samples are counted first and the standard is then counted midway through the remaining group of high-counting samples, more samples can be counted with less error due to decay. At least 2×10^5 c.p.m. should be present at time of counting to keep the statistical error on 1-minute counts less than 0.5% at the 95% confidence level but more than

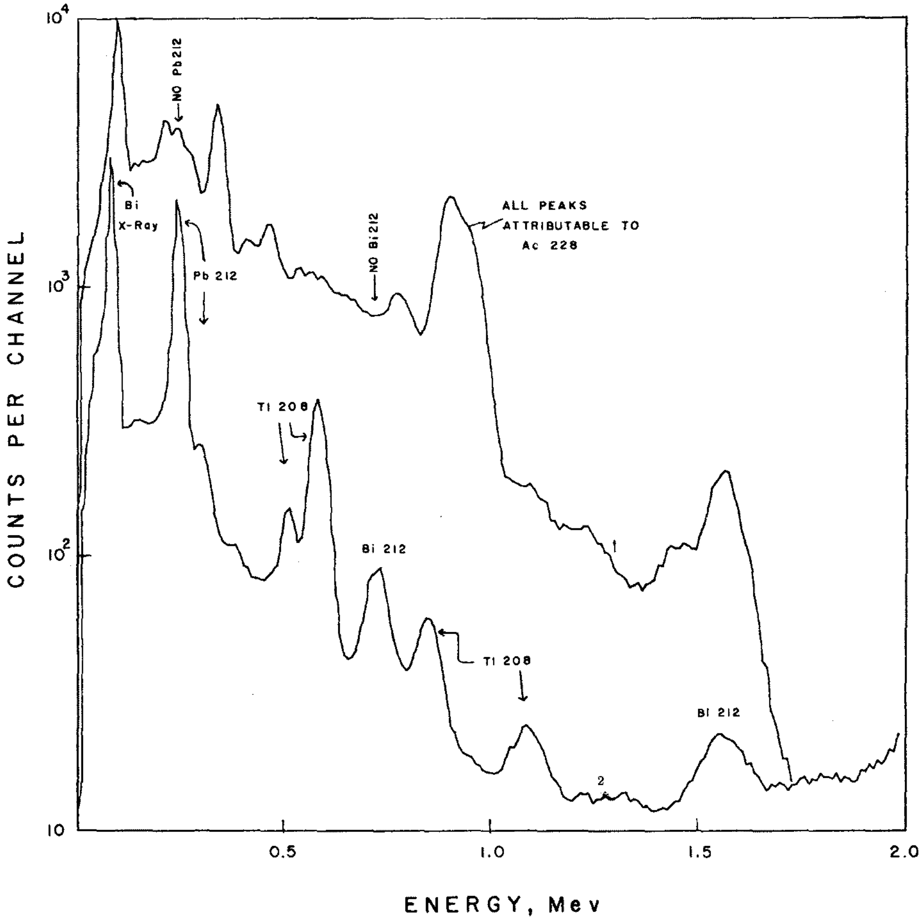

Figure 1. Separation of lead-212 from thorium nitrate

Curve 1. Aqueous solution after extraction
Curve 2. Diethyldithiocarbamate extract

about 5 × 10^5 c.p.m. should not be present because of increasing coincidence losses. Since the samples will generally have to stand overnight to allow reestablishment of equilibrium with the bismuth-212 and thallium-208 daughters, approximately four times as much activity should be taken initially for both standards and samples as is desired to have present at time of counting to compensate for the decay occurring on standing.

DISCUSSION

Two hundred grams of 13-year-old thorium nitrate gives approximately 8.5 × 10^6 c.p.m. of lead-212 tracer under the conditions described, 75% of which will be regenerated in 21 hours. Even starting with as much as 10^6 c.p.m. per run, at least 5 experiments and 1 standard can be made each day and maintained indefinitely on this quantity of thorium. Many more samples can be maintained if slightly lower precision is acceptable or if the samples can be counted after 8 hours instead of having to wait until the following morning. Larger quantities of activity can be obtained by direct scaleup of the conditions used in the present work. Even freshly-manufactured natural thorium compounds will give virtually maximum activity due to the retention of the 1.9-year thorium-228 during manufacture at the equilibrium concentration present in the original ore.

The efficiency of the present separation is demonstrated graphically by the gamma ray spectra shown in Figure 1. The upper curve was obtained from the aqueous thorium solution immediately after extraction and consists entirely of actinium-228 with no trace of lead-212, bismuth-212 or thallium-208 being detectable. The lower curve is a spectrum of the DDTC extract and shows the same equilibrium distribution of all three nuclides that existed in the original sample of thorium nitrate. Other tests using tracer under similar conditions showed that recovery of both lead-212 and bismuth-212 was greater than 99%. Thallium-208 is not removed quantitatively under the conditions employed but grows back to equilibrium very quickly because of its short half life. No trace of actinium-228 could be detected in the extract. Furthermore, the activity of the entire extract was followed by gross gamma counting through several half lives of lead-212 without finding any evidence of contamination from thorium or radium precursors which would prevent complete decay of the tracer with the half life of lead-212.

Table I. Distribution of Lead-212 Tracer

	Recovery, %		
Fraction	Run A	Run B	Run C
1	1.0	0.1	0.3
2	0.7	0.0	1.0
3	0.3	1.1	0.2
4	0.0	0.0	0.0
5	0.0	0.0	97.8
6	97.8	0.0	0.4
7	0.1	0.0	0.0
8	0.3	0.2	0.0
9		1.5	0.1
10		0.2	0.0
11		92.8	
12		4.1	
13		0.1	
Material balance	100.2	100.1	99.8

Some of the data obtained in connection with other work are shown in Table I to demonstrate the effectiveness of lead-212 as a tracer. Dithizone was being used to separate lead and bismuth both from the samples and from each other. Every fraction obtained through the entire analytical procedure was counted separately so that the distribution of lead could be studied. About 1.5×10^6 c.p.m. of tracer was taken initially for both the experiment and standard. All solutions were counted the following day at which time the standard counted approximately 4×10^5 c.p.m. The data shown are not specially selected but represent the first three experiments performed using the lead-212 tracer. The material balances obtained show the excellent precision with which the tracer could be accounted for even over the large number of fractions obtained. All subsequent work has further confirmed the effectiveness and convenience of this tracer. By using gamma spectrometry, information on the distribution of bismuth can be obtained simultaneously. Use of a gamma-emitting tracer has proved particularly useful in demonstrating the losses of lead produced by volatilization, ion exchange to glass surfaces and silica, and reduction and consequent alloying during fusions in platinum dishes. The relatively short-lived lead-212 can also be used to determine the yield in the radiochemical determination of lead-210.

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Zone Refiner with Temperature Control

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In ZONE REFINING, the heat is usually applied by radiation (*1*, *3*). The temperature of the sample is not directly controlled. For many samples, however, elevated temperature endangers purity because of rearrangement, decomposition, or reaction with atmosphere. Therefore, it is often desirable to control the maximum temperature to which any part of the sample is subjected, or at least to know it accurately.

When the zone refining process is in smooth operation it may be possible to estimate the temperatures to which the sample is being exposed. When the process is starting up, on the other hand, the temperature in any given region of the sample may be highly unpredictable. If the container is initially filled with granular material, or even melted material with voids, the isolated portions of the sample may often reach significantly higher temperatures than does any portion during the ideal steady-state process. After all voids have been eliminated the subsequent passes may or may not remove impurities resulting from the overheating. With some samples the complete elimination of voids may be difficult or impossible.

The fundamental problem is that the temperature is determined by the accidental value of thermal resistance, together with a fixed heat flow from a source of very high temperature. To control the temperature properly the heat should flow to the sample, from a source whose controlled temperature is close to that of the sample, through a comparatively low thermal resistance. The maximum sample temperature is then limited to the source temperature required for the steady state of the process. .

This objective has been attained by arranging to circulate a fluid of controlled temperature over a narrow band around the sample tube. The constant-temperature band is made capable of motion along the tube by the use of shaft seals.

DESCRIPTION OF APPARATUS

The construction of the fluid carrier is shown in Figure 1. The assembly consists of alternating partitions, *P*, (bearing shaft seals that closely fit the sample tube) and collars, *C*, (each with two tubes for fluid circulation), with a window section, *W*, for each chamber. These parts are separated by gaskets, *G*. The assembly is aligned by the internal shoulders on the collars and by three symmetrically disposed bolts, *B*, and is clamped together by nuts, *N*, bearing on two end plates, *E*. Outside diameter of the end plates is 2.5 inches (63 mm.). A series of three annular compartments is formed by four of the partitions. Each of the compartments has two connecting tubes for fluid circulation and a glass wall for viewing the sample inside.

The shaft seals were automotive-type oil seals (Garlock "Klozure" or equivalent), but O-ring seals or other types might possibly have been used. Interchangeability of units designed for different-sized shafts is desirable. A suitable tolerance to the sample tube's deviations from perfect centering and roundness is necessary.

The fluid carrier was made by assembling a set of parts, all clamped together with gaskets, to permit variations in the number and lengths of the compartments. Any future units having just three compartments can be constructed of fewer pieces and require no more than three gaskets. The compartments may be as short as 1-2 cm. each.

The present unit was slipped over the sample tube while loosely assembled, and then given the final tightening, to ensure correct alignment of the seals. The fluid carrier was attached to the translation mechanism of a Fisher zone refiner. The upper end of the sample tube, protected by a short length of elastomer tubing, was clamped in a three-jaw drill chuck of 0.5-inch capacity, which projected downward from the 10:1 worm gear reducer of a $^1/_{15}$-h.p. variable-speed motor mounted on top of the zone refiner cabinet. The sample tube was in contact only with the driving chuck and the elastic seals in the fluid carrier.

Temperature-controlled heating fluid was circulated through the center compartment and coolant through the top and bottom compartments. The fluids were supplied, through silicone tubing, from two small baths by immersion-type centrifugal circulating pumps. The fluid pressure was slight, flow rates being less than 0.1 liter/minute.

The hot bath was filled with Dow-Corning 510 silicone fluid. The cooling

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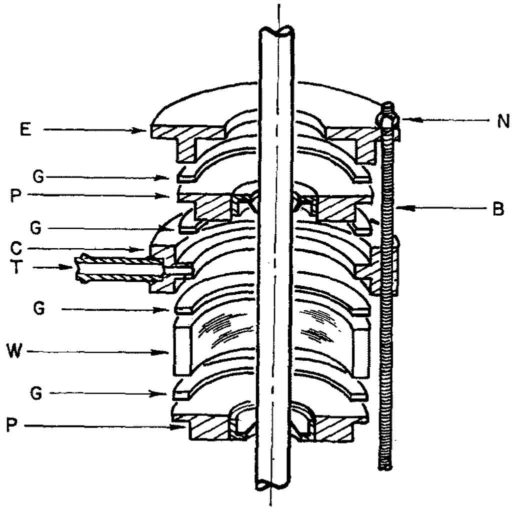

Figure 1. Fluid carrier for temperature control in zone refining

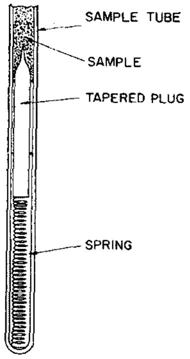

Figure 2. Sample tube arrangement to prevent breakage by expansion of sample in melting

fluid was water containing a colorless emulsifiable oil ordinarily used with machine tools. Tap water, used directly as a coolant, corrodes the metal shells of the shaft seals. Therefore, the tap water was instead run through a copper coil in the emulsified oil bath. The connecting tubes, gaskets, and seals did not deteriorate seriously in contact with the silicone and emulsified oil, although the hot bath was used at temperatures above 160° C. for a number of months. The hot bath was maintained at constant temperature within less than 0.5° C. by a proportioning controller with thermocouple sensor. The sample tubes were made from stock lengths of ordinary borosilicate glass tubing, usually 8 mm. in diameter. In normal operation the tube was rotated at 10–30 r.p.m. The rotation made the molten zone quite symmetrical and possibly reduced the sliding friction of the seals along the tube. The tube was so well lubricated by the circulating fluids that friction was not a strain on the translation mechanism even without rotation. Periodic stopping or reversing of the rotation would improve mixing in the molten zone and thus might improve purification by reducing the concentration of rejected impurity at the advancing solid-liquid interface.

PERFORMANCE

The apparatus was capable of several months' operation with a total fluid leakage of only a few milliliters when used with glass tubing selected to fit the seals. In a single lot of stock tubing, about 80–90% appeared usable for this purpose. The end of the tubing inserted in the shaft seals was always sealed off, or at least fire-polished.

Breakage of the sample tube did occur at times, with deleterious outpouring of the circulating fluids. The inconvenience of such events was reduced by placing the entire zone refiner in a large tray. It is believed that this danger could be minimized, and leakage in routine operation eliminated, by a change in the circulating system. Suction pumps should be used, so that a fluid leak stops the flow and all fluid is automatically removed, and the baths should both be filled with the same fluid and interconnected with a siphon, so that any flow of fluids between adjacent compartments is automatically compensated. Using a single fluid would eliminate the tendency toward foaming in the present baths when leakage occurs from one compartment into another.

The present apparatus has been used for zone refining at speeds from the zone refiner's maximum, about 60 mm./hour, to 1 mm./hour or less (obtained by connecting an auxiliary interrupter in the motor circuit). It has been run continuously for 1–3 weeks with samples of naphthalene and for periods of several months with the straight-chain hydrocarbons $C_{32}H_{66}$ (melting point 89.5° C.) and $C_{94}H_{190}$ (melting point 113.9° C.).

The naphthalene samples eventually formed single crystals while the hydrocarbons apparently remained polycrystalline. Passage of the molten zone upward through the sample appeared to eliminate voids more dependably than downward passage, and the upward motion was therefore used throughout. There appeared to be no hindrance to the use of the apparatus at any temperature for which a suitable heating fluid is available. Special shaft seals can be obtained for considerably higher temperatures, and the temperature of the seals in any event can be held well below the melting point of the sample. For work at considerably higher temperatures with a circulating fluid, the elastomer tubing can be substituted by metal sylphon tubing. Alternatively, an arrangement of telescoping delivery and receiving tubes can be used, with gravity flow through the fluid carrier, to eliminate the flexible connecting tubes entirely.

The stability of the size of the molten zone depended as much on constancy of flow as on temperature control. The bath temperature for zone refining of naphthalene, for example, was 118° C., about 38° higher than the melting point. Connecting tubes without the restricted bore of the present design would be desirable to reduce this differential and thus the sensitivity to variations in pump performance. The length of the molten zone was kept between about 2 and 10 mm., and did not fluctuate rapidly enough to produce a motion of the advancing solid-liquid interface comparable with the slowest translation rates used.

SAMPLE TUBES

The major cause of breakage was not a fault of the apparatus, but a property of the sample itself—its tendency to create pressure on melting by expansion against a column of solid adhering to the sample tube. When experiments were made with naphthalene, it was early observed that sample tubes broke near the bottom, where the new molten zone was formed. In fact, the sealed end of the glass tubing was frequently pushed off and a length of the solid sample extruded. Clearly the 10–30 cm. of crystalline material above adhered to the sample tube so well that the expansion during the melting of the new zone produced high pressures. The problem did not occur with the straight-chain hydrocarbons, and may or may not be serious in a given case depending on the substance and the dimensions of the sample tube. Joncich and Bailey (*2*) have solved this problem by using polytetrafluoroethylene sample tubes. Such tubes would be unsuitable for the present apparatus because rigidity is required for proper rotation, dependable functioning of the shaft seals, and protection of the final crystal from deformation.

The problem was eliminated by the arrangement shown in Figure 2. A tapered glass plug, sliding loosely and supported by a spring, forms the end of the sample space. The molten zone initially extends down to the point where the annular space between the tube and the plug attains its minimum width, but not far beyond. If the sample requires added space for each new zone, the plug moves downward gradually and the spring is compressed. The initiation of crystal growth in the narrow annular space may encourage formation of a single crystal, as does the pointed tip frequently used on sample containers in the Bridgman method.

To avoid excessive pressures no rapid change in length of the molten zone, such as that which occurs on restarting the apparatus after a power failure, should be permitted except at the end of the traverse.

If the solid adhers to the sample tube, the multiple-zone oscillating-heater technique of Sloan and McGowan (*4*) could in principle be used with a fluid carrier of many compartments. Such an arrangement would present mechanical problems because of the large total frictional torque of all the shaft seals. If the solid does not adhere well, the body of solid between two liquid zones might tend to rise or sink and disrupt the continuity of the process. In this case a multiplicity of zones would be undesirable.

ACKNOWLEDGMENT

The author thanks Harold Johnson for his loyal assistance throughout the development and testing of this apparatus and C. P. Saylor for helpful discussion.

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High Precision Conductivity Bridge

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IN THE DEVELOPMENT of methods for the measurement of solubilities of pesticides in water, a conductivity bridge of very high precision for measuring small differences in conductivity was required. Commercially available instruments could not meet all of the required specifications. Therefore, the bridge which is described below was designed and built in our laboratory.

A schematic diagram of the bridge circuit is given in Figure 1. The ratio arms of the bridge are formed by a variable tap autotransformer (ESI Model DT72A or Gersch 1000 Series Inductive Divider). A standard card-wound resistor of low capacitance and inductance, and a Jones conductivity cell make up the comparison arms of the bridge circuit. The two leads from the oscillator are connected directly to the comparison arms of the bridge. The resistances of the leads to the inductive divider are, therefore, effectively eliminated from the comparison arms of the bridge and are incorporated into the ratio arms of the bridge, where the resistance of the leads is negligible compared with the input impedance of the divider (approximately 1,000,000 ohms at 1000 cycles/second). An appreciable error is eliminated by this type circuit, for it was found that errors of the order of 50–100 p.p.m. in ratio measurements resulted from having the oscillator connections at binding posts of the divider. A complete discussion of four terminal resistance measurements is given by Thomas (*2*). The quadrature correction is made with two adjustable air capacitors connected across the over-windings of the autotransformer.

This conductivity bridge offers the following advantages over the Jones Bridge (*1*) which has been used almost universally up to this time for high precision conductivity measurements: the measurements are made using a four-terminal resistance measuring circuit

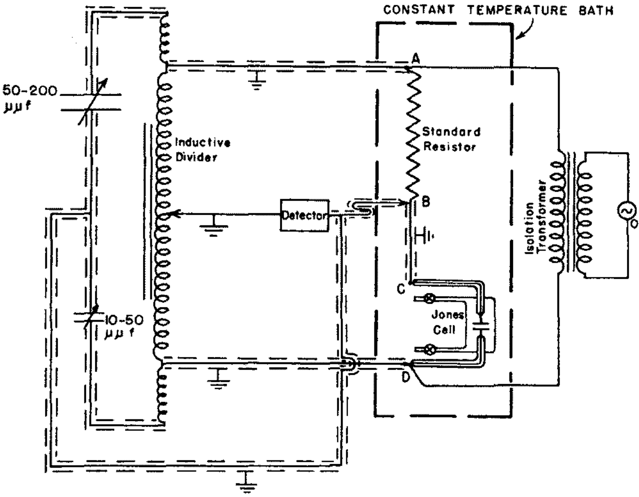

Figure 1. Circuit diagram of conductivity bridge

rather than a two-terminal one as used in the Jones Bridge, therefore, minimizing lead resistance errors; the two comparison arms of the bridge are immersed in a constant temperature bath to eliminate heating and temperature errors; this bridge is capable of greater precision than the Jones Bridge because of the high resolution (0.00002%) of the inductive divider used in it; the circuit may be readily modified to make high precision capacitance and inductance measurements; and it is considerably less expensive than a Jones Bridge.

EXPERIMENTAL

In operation, a resistor of similar value to the resistance of the cell is placed in the circuit between points *A* and *B* (Figure 1) and the cell is connected between points *C* and *D*. Leads from the oscillator and leads from the divider are connected directly to the points *A* and *D*. A balance is obtained by adjusting the divider and the capacitors for minimum response of the null detector. In most of our studies the oscillator frequency was 1000 cycles/second; however, any frequency from 50 cycles/second to 10,000 cycles/second may be used.

For measurements of the highest precision, the resistance of the lead between *B* and *C* must be known. This lead resistance may be evaluated by replacing the conductivity cell with a resistor of known value; the circuit is balanced with the detector connected to the point *B*; the detector lead is then moved to the point *C* and the bridge is balanced again. The difference in the two ratio measurements multiplied by the total resistance between *A* and *D* gives the resistance of the link between *B* and *C*.

To verify the accuracy of this bridge, a calibrated resistor was substituted for the conductivity cell. Agreement between values of the resistor ratios measured at the National Bureau of Standards Laboratory and those measured in our laboratory was ±0.2 p.p.m.

ACKNOWLEDGMENT

The authors acknowledge the cooperation and guidance of Thomas L. Zapf and Patrick H. Lowrie, Jr., of the National Bureau of Standards, and Claude R. Daum and Garth Ghering of the U. S. Geological Survey.

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A Time Base Generator with Digital Readout of Nuclear Magnetic Resonance Line Positions

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THE USE OF an X-Y recorder as a readout device with Varian HR-60 high resolution nuclear magnetic resonance (NMR) spectrometers is well established. In this application the X-axis is driven by an external time base. Spectral calibration is normally accomplished by the sideband technique (*1*, *2*). Line positions are measured by first obtaining a scale factor between the frequency scale and linear distance. The linear distance is measured from each NMR line to the reference line. The value of the linear distance multiplied by the scale factor yields the line position in terms of frequency (cycles per second).

Several disadvantages are inherent in this method of measuring NMR line positions, not the least of which is the amount of time involved. The chief characteristic which affects the accuracy of the NMR line positions is the linearity of the external time base and/or of the recorder. Commercial recorders generally possess linearity of the order of 0.1 to 0.2% of full scale. If the linearity of the external time base is greater than the recorder linearity (considering only the readout device), the accuracy of the line positions is limited only by the linearity of the recorder. The inherent nonlinearity of the slidewire accounts at least in part for the nonlinearity of the recorder. The device described herein provides a more accurate and convenient method for measuring NMR line positions through the use of an operational amplifier in two modes of operation.

The accuracy of NMR line position measurements can be increased in two ways: improving time base linearity and avoiding slidewire nonlinearity. Consider first time base linearity which may be defined as constancy in the time rate of change of a ramp voltage. An excellent method for the production of a linear ramp voltage is the integration of a constant voltage. Assuming in principle that this method will yield a precisely linear ramp voltage, one can see that in practice the linearity of the time base depends upon the specifications of the electronic devices used. We have designed a time base generator of improved linearity using a solid state voltage source with a low temperature coefficient and a high gain, chopper-stabilized operational amplifier.

Consider now the inherent nonlinearity of recorder slidewires. Nonlinearity is the result of the fact that the resistance of the wire per unit distance is not constant. Therefore, when one attempts to correlate voltage with linear distance, using another scale which possesses a linearity different from that of the slidewire, the result is a certain unavoidable error. This error can be avoided by driving the pen through the same distance along the same portion of slidewire by means of an accurate voltage source and then correlating that voltage with distance. The necessity of measuring distance on the chart paper is thereby eliminated, since for a given recorder range the voltage necessary to reach a given point on the slidewire is now known. This voltage can be correlated with the quantity plotted along the abscissa. However, to achieve the greatest possible accuracy in measuring line positions the measurement should be made before the chart has been removed from the recorder. By employing this principle we have devised a method which provides a fast digital readout of NMR line positions in terms of frequency.

EXPERIMENTAL

The device consists of a combination of two modes of operation of an operational amplifier (Dymec Model DY-2460A-M1 with Model DY-2461A-M5 blank plug-in; 2-p.p.m. d.c. gain accuracy including linearity)—i.e., integration of a constant voltage and +1 gain amplification. A schematic representation is given in Figure 1. A photographic view of the time base generator constructed in this laboratory is given in Figure 2. For the integration mode the time constant is 100 seconds. Since stability of the time constant is important, a 10-megohm metal film resistor and a 10-μf. polystyrene capacitor were used. Proper connections for the Dymec 2460A operational amplifier can be found in the Dymec instruction manual.

Ramp voltage linearity depends upon the voltage source stability. To pro-

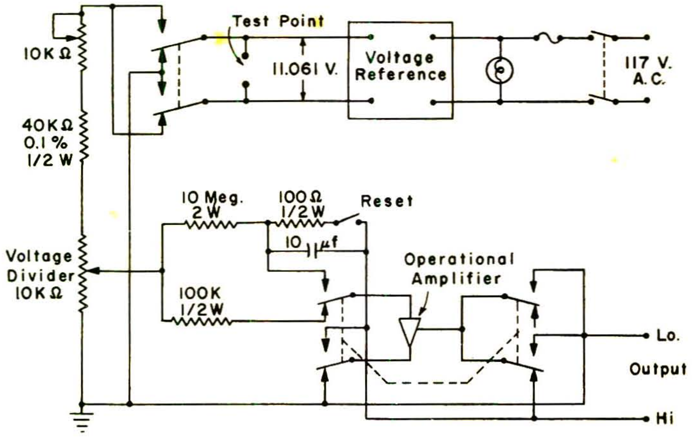

Figure 1. Circuit diagram for time base generator with digital readout of NMR line positions

vide the greatest stability a solid state voltage reference source (CircuitDyne Corp. Model PRIB-115-11.0 G) with a temperature coefficient of ±0.001% was chosen. The 11.061-volt output of the voltage source is reduced by means of a 40K ohm resistor and a 10K Trimpot in series with a 10K ohm, four-decade voltage divider (General Resistance Co. Dial-A-Vider Model DV-4004; linearity at one watt is ±40 p.p.m.). Adjustment of the voltage across the decade divider to 2.0000 volts is accomplished by the Trimpot. The output of the voltage divider is variable in decade fashion from 0.0000 to ±2.0000 volts. With the selection of this voltage a variation of pen speeds from a maximum of 5 seconds per inch to a minimum of 2.7 days per inch can be achieved. Immediately following the voltage source a DPDT (ON-OFF-ON) switch is employed as a polarity reversing switch so that the recorder pen may be driven in either direction or may be stopped in any position. The right to left direction, which is not included on commercial recorders, is more convenient for the recording of NMR spectra. Convenience results because the recording of the spectrum can commence at the reference line (usually tetramethylsilane) at the right-hand side of the chart. The spectrum is displayed according to the usual convention, except that the ringing will be on the low field side of the various lines.

The conversion from one mode of operation to the other is accomplished by means of a four-pole, double-throw (ON-ON) switch. One advantage of this type of time base over one produced by a motor driven potentiometer is that the former permits rapid return of the pen to zero position. This is accomplished by a normally-open push button switch which short circuits the capacitor. A banana jack is connected across the output of the voltage reference supply and is mounted on the front panel as a convenient reference voltage source for other purposes, such as calibrating other instruments.

DISCUSSION

For the time base mode (with the four pole, double throw (ON-ON) switch in the proper position) the pen speed is determined by the settings of the voltage divider and the recorder X-axis range. The direction of pen travel is determined by the position of the DPDT (ON-OFF-ON) switch. Control of whether the pen touches the paper is retained in the recorder so that, if desired, the pen may be driven along the X-axis without touching the paper.

NMR line position measurements are made in the following manner: The chart paper with the spectrum is placed on the recorder platen, using the vacuum hold-down. With the pen up, the decade divider set at 0.0000 and the DPDT (ON-OFF-ON) switch in either ON position the point of the pen is visually aligned with the center of the reference peak. Then the side band frequency is dialed on the decade divider—e.g., 624.8 c.p.s., the decimal point occurring between the third and fourth decades. The pen is then visually aligned with the center of the side-band peak by adjusting the recorder X-axis range control and vernier. Finally, the decade divider is dialed until each NMR line in turn is visually aligned with the pen point. The reading on the divider is the line position in terms of frequency (c.p.s.).

The time base output has a linearity of 0.02% of full scale or better. As the voltage accumulated at a given voltage divider setting time measurements were made at increments of 1 volt. Two time-voltage pairs were used to determine the equation of a straight line. Voltages corresponding to the remaining time measurements were calculated and compared with the observed values. The reproducibility is 0.03% of full scale or better. For a given setting of the voltage divider, the accumulated output ramp voltage both negative and positive at 1000 seconds was measured to the nearest 0.1 mv. The reproducibility figure was calculated by dividing twice the standard deviation of the voltage measurements by the mean value of the output ramp voltage.

The line position (+1 gain) output has a linearity of 0.0075% or better. The voltage corresponding to each digit of the first decade of the voltage divider was measured. Two divider setting-voltage pairs were used to determine a straight line. Voltages corresponding to the remaining divider settings were calculated and compared with the observed values.

A comparison of the conventional and the electronic (described above) methods of measuring NMR line positions is shown in Table I, which gives two average values of the line position in terms of c.p.s. from tetramethylsilane

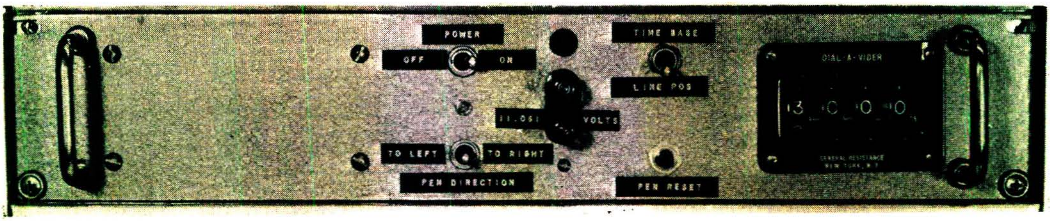

Figure 2. Photographic view of front panel

and the corresponding standard deviations for each line. Ten recordings of each spectrum were obtained at room temperature, using a Varian DP-60 spectrometer. To avoid signal saturation the radio field amplitude was set 60 db, below one-half watt. The external magnetic field was swept at the rate of 0.5 to 1.0 c.p.s./second. Spinning 5-mm. o.d. sample tubes were used to achieve maximum field homogeneity. Calibration of the spectra was accomplished by the usual side-band technique, using a Hewlett-Packard 200 CD wide band oscillator and a 522B counter. Tetramethylsilane (K & K Laboratories Inc., Jamaica, N. Y.) was used as an internal reference.

Table I. Comparison of Two Methods of Measuring NMR Line Positions

	Conventional method		Electronic method	
	Line[a] position	Std. dev.[b]	Line[a] position	Std. dev.[b]
1,1,2-Trichloroethylene	387.4	0.32	387.3	0.21
Chloroform	434.5	1.44	434.8	0.30
Methylene of ester group of ethylcyanoacetate	243.3	1.25	243.4	0.50
	250.3	1.20	250.6	0.64
	257.7	1.17	257.8	0.60
	264.8	1.14	264.9	0.57
Methanol	197.8	0.73	197.8	0.70
	202.8	0.76	202.9	0.75
	252.9	0.78	252.7	0.77
	258.0	0.89	258.0	0.70
	263.0	0.89	263.2	0.75
	268.3	0.88	268.2	0.75
Methoxy group of methyl butyrate	216.8	1.32	216.2	0.70

[a] c.p.s. from tetramethylsilane, solvent–CCl_4
[b] Two sigma values.

Several advantages attend the use of the time base generator described above. In addition to improved linearity and reproducibility, the time base generator affords greater convenience in the recording of NMR spectra, since the pen may be driven in the right-to-left direction. By convention NMR spectra are displayed with magnetic field strength increasing from left to right. Using tetramethylsilane as an internal reference, the reference signal normally occurs further upfield than all other spectral lines. Therefore, one can begin at the beginning with only an irrelevant change in the appearance of the spectrum.

The possibility of error due to the nonlinearity of the recorder slidewire has been eliminated. Consequently, line position measurements are more precise. Convenience also is achieved by correlating voltage with linear distance along the recorder slidewire. Linear distance on the chart paper need not be measured. Also, line positions are rapidly measured in digital form in terms of frequency.

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Combining Gas Chromatography with Nuclear Magnetic Resonance Spectrometry

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GAS CHROMATOGRAPHY has been combined previously with nuclear magnetic resonance spectrometry (NMR) for the identification of effluent fractions from C_8 aldehydes (*4*), isoprenoid hydrocarbons (*2*), isomers of triisobutylene and tetraisobutylene (*3*), and C_7 olefins (*1*). In each of these cases conventional trapping procedures were used. They consist of trapping samples into one vessel and transferring them into another vessel for the NMR examination. These procedures require a relatively large amount of starting material and generally can take a long time (hours or more) to collect a sufficient amount of pure sample for identification. In the present investigation, a new procedure which eliminated the use of a second vessel was developed. Thus, the same vessel into which the sample was trapped could also be used for the NMR examination. As a result of this procedure less sample was required to obtain NMR spectra.

The new procedure of combining gas chromatography with NMR was developed with the use of glass microtubes (NMR Specialties, Inc., New Kensington, Pa.) that became commercially available only last year for NMR studies. These tubes are made of borosilicate glass and contain a bubble at about 15 mm. from the bottom of the tube to coincide with the position of the receiver coil in the spectrometer. The exact position can be determined by filling the bubble with chloroform and by noting the position that corresponds to the maximum signal for the proton resonance. A 1-mm. i.d. capillary leads from the top of the tube to the bubble whose volume is about 35 μl. After several attempts were made to trap effluents directly from a gas chromatograph into these tubes using a 22-gauge syringe needle that was eight inches long, it was found that this fine gauge needle caused a very large pressure drop at the exit of the gas chromatograph. Inefficient operation of the gas chromatograph resulted. To circumvent this difficulty, a pair of microtubes that had a 2-mm. i.d. capillary leading to the bubble were obtained on special request. With the larger capillary, a larger diameter syringe needle (17-gauge) could be used for trapping samples. Thus, less restriction to the helium flow and greater efficiency in trapping was made possible.

A picture of the microtube and equipment used for trapping samples directly from a gas chromatograph is shown in Figure 1. The 17-gauge needle that is eight inches long is seen inside the glass microtube. The tip of the needle is located inside the bubble near the bottom of the tube. The top of the needle is connected to a Luer lock which is silver soldered to a $^1/_4$-inch tubing T. By using a Luer lock connection, the needle can either be attached or removed very quickly and easily from the tubing T. The right side of the T is equipped to connect it to the exit port of a gas chromatograph. The left side is shown uncapped. Whenever a species to be trapped emerges from the exit port, the nut to the immediate left of the T is screwed on the T and tightened to force the carrier gas to pass through the needle in the

---

[1] Present address, Elastomer Chemicals Department, E. I. du Pont de Nemours & Company, Wilmington, Del., 19898.

tube. A "Triclene" and dry ice bath can be used conveniently for trapping the species in the bubble. As soon as the gas chromatograph indicates that the species being trapped is no longer exiting from the chromatograph, the nut is removed first to bypass the gas flow, and the needle is disconnected from the Luer lock.

The next step in the procedure is to add sufficient solvent to the microtube to fill the bubble for the NMR examination. A 50-μl. syringe without needle attached is filled to about the 35-μl. mark with the solvent to be used. Then, the syringe is connected to the 17-gauge needle, and the microtube which still contains the needle is removed from the dry ice–Triclene bath. The solvent is injected into the needle and the tube containing needle is returned to the cold bath. This technique has the effect of washing the inside of the needle with solvent and of dissolving the trapped species in one operation. If more solvent is needed to fill the bubble, the microtube is removed from the cold bath, a few more microliters of solvent are added, and the microtube is returned to the bath to wash the solvent into the bubble.

After the bubble is filled to volume, the needle is removed from the microtube and the trapped species is examined by NMR. Samples that range in boiling points from less than 100° C. to nearly 300° C. have been examined successfully with this procedure. The high boilers require external heating of the tubing T to get them into the needle and to be dissolved by the appropriate solvent.

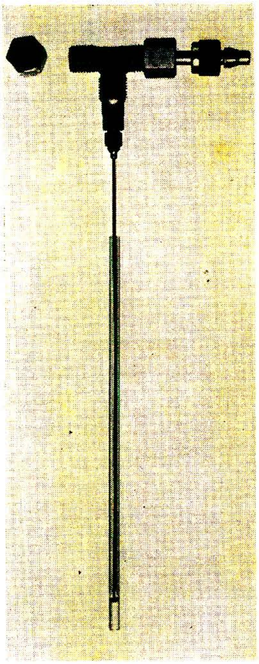

Figure 1. NMR microtube with 17-gauge syringe needle and $^1/_4$-inch tubing T

Results obtained from the use of this direct trapping procedure indicate that a minimum of about 100 to 400 μg. of sample are required to obtain a good NMR spectrum from an A-60 spectrometer. If computer averaging techniques are used or if one of the newer spectrometers such as an HA-100 instrument is used to enhance the signal, proportionately less sample is required to obtain a good spectrum. Thus, the order of several micrograms of sample can readily be obtained as a minimum level of concentration through the use of this trapping procedure to combine gas chromatography directly with NMR.

ACKNOWLEDGMENT

The author thanks W. J. Loomis for his assistance in the development of this technique.

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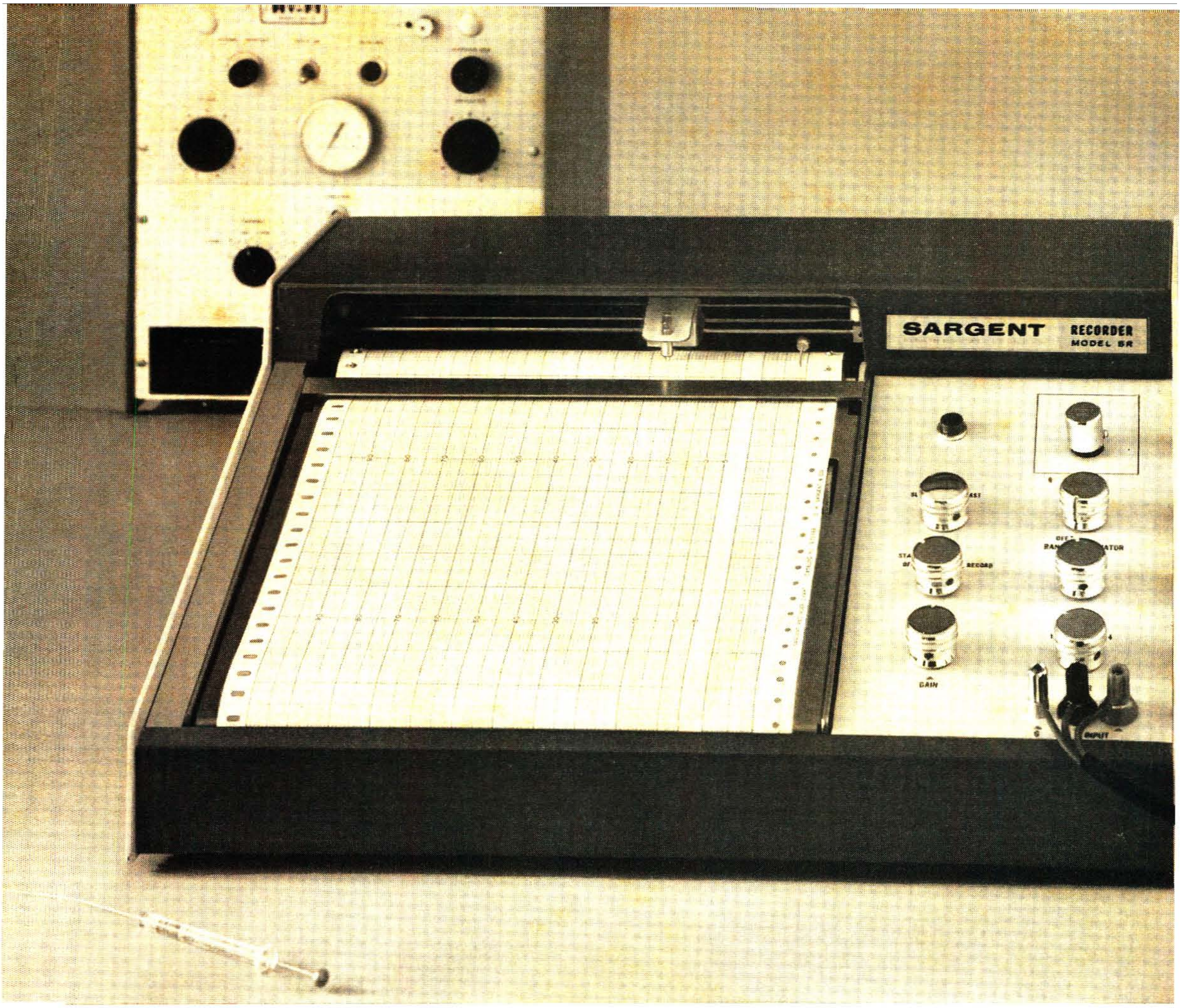

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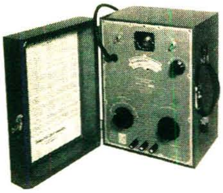

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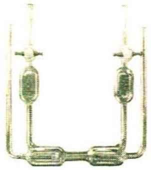

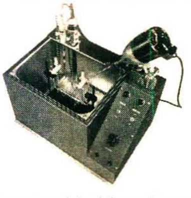

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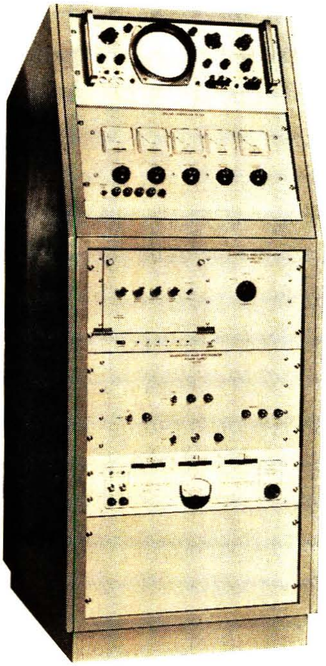

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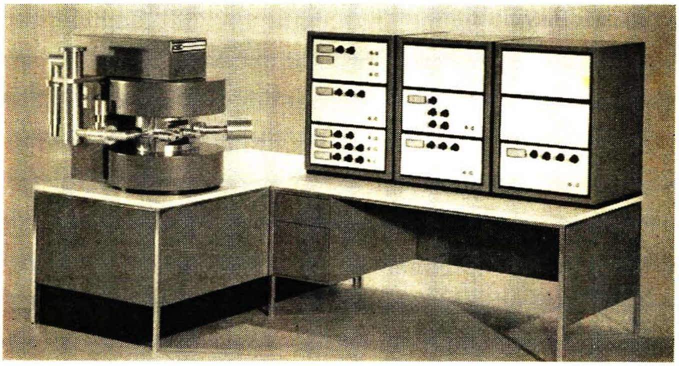

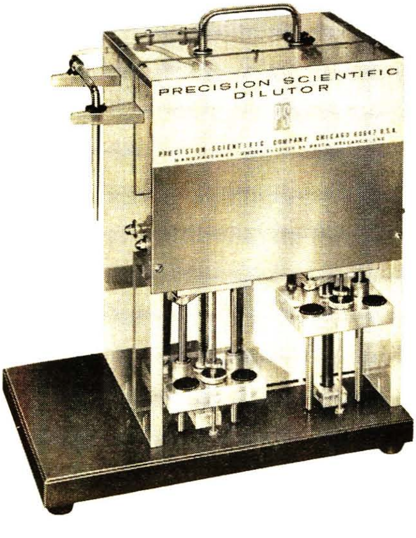

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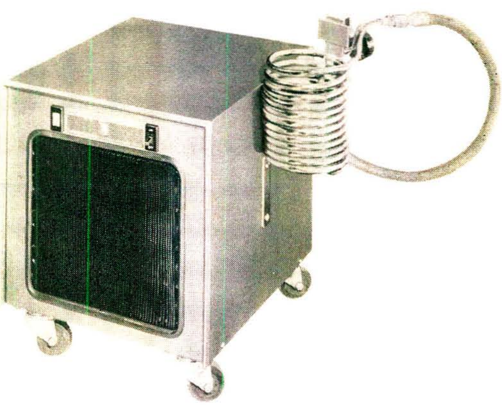

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A few months ago a rapid procedure was published (*J. of Gas Chromatography*, Feb. '65, p. 67) for completely resolving fatty amines by GLC of their N-n-alkyltrifluoroacetamide derivatives. By "completely," the authors meant not just sorting out by the number of carbon atoms but being able to tell the saturates from the unsaturates and the monounsaturates from the polyunsaturates without going through the lengthy business of acetylating the amines to acetamides. The trifluoroacetamides are nothing at all to prepare with *Trifluoroacetic Anhydride*, Eastman 7386. In this case referring to the reagent as Eastman 7386 is more than a convenience. We stopped in to chat at the company where the procedure was devised and learned from one of the authors that the resolution is notably sharper with Eastman 7386 than with other trifluoroacetic anhydrides. Apparently there are cases where a trademark can be as important to the buyer as to the seller. Must be a lot of such cases.

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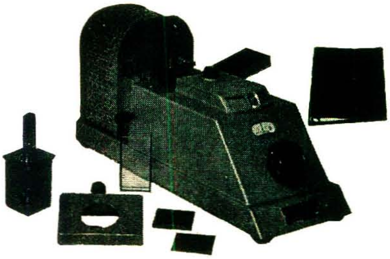

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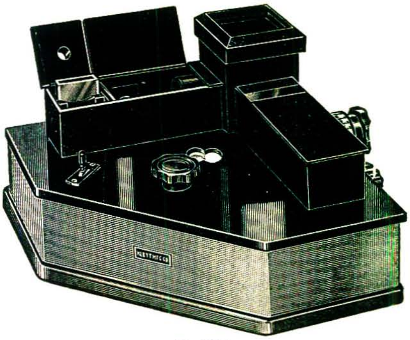

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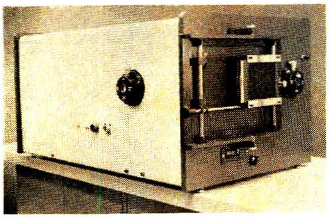

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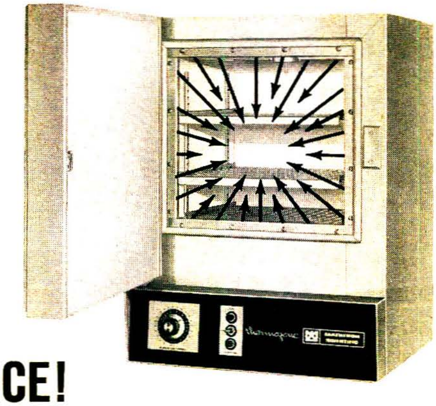

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GRAVITY CONVECTION OVENS	Inside Dimensions	Watts	Price
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52755-20	17" h. x 18" w. x 15½" d.	1250	440.00

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	Inside Dimensions	Price
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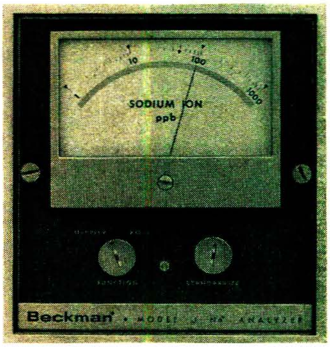
NEW PRODUCTS

Electronic Galvanometers

Several new models of electronic galvanometers are available. Model A has a power sensitivity of 8 × 10^{-16} watt per division. Input resistance is 180 ohms on three ranges of ±30 na., ±300 na., and ±3 na. "B" models differ in these respects: sensitivity, 5 × 10^{-9} ampere/scale div.; 4.5 × 10^{-16} watt/-scale division power sensitivity; input resistance 18 ohms; ±100 na., ±1 μa., and ±10 μa. current ranges. Fluke Mfg. Co., Box 7428, Seattle, Wash. 98133. **410**



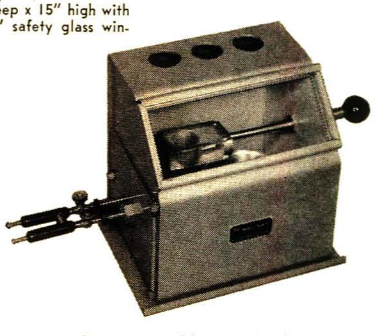
Sodium ion analyzer continuously and automatically determines sodium content in the p.p.b.-range. Basic components of the system include the panel-mountable amplifier unit, consisting of the amplifier with meter; the electrode flow chamber housing the sodium sensitive and reference electrodes; the pH adjusting system; and the necessary tubing and valving. Two standard ranges 1 to 1000 p.p.b. and 1 to 1000 p.p.m. are available; other ranges can be ordered. Beckman Instruments, Inc., 2500 Harbor Blvd., Fullerton, Calif. **411**

Portable Refrigeration Unit

The Porta-Cool is a new portable self-contained refrigeration system for cooling baths in the laboratory. The rapid cooling rate will reduce the temperature of a five-gallon uninsulated tank of water from 25° to 0° C. in less than two hours. The unit is ideal to use with the company's Porta-Temp, compact constant temperature bath heater, controller, stirrer. Used together they make any container a low cost wide range constant temperature bath and circulating system—will maintain a temperature from 5° to 90° C. at a uniformity of ±0.25° C. or better. Precision Scientific Co., 3737 West Cortland St., Chicago, Ill. **412**

PARR *Safety Shield*
For Sodium Peroxide Bombs

Constructed of 3/16" steel plate, 12" wide x 10" deep x 15" high with a 3/4" safety glass window.



This new enclosure provides steel plate protection against accidental explosions when firing any Parr sodium peroxide bomb. It is recommended especially for flame ignition procedures in which the bomb must be heated to a high temperature to force a reaction to completion. It should also be used whenever there is reason to suspect that a sample might react violently during the combustion process.

Ask for Specification 2150

PARR INSTRUMENT COMPANY
211 Fifty-Third St., Moline, Illinois

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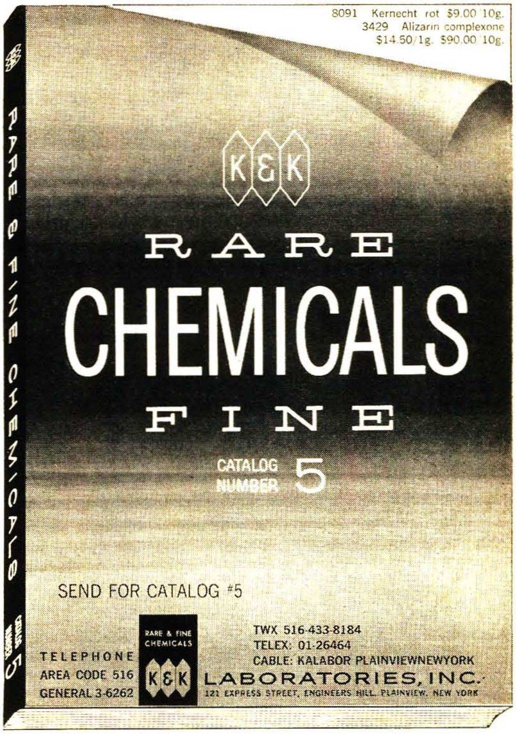

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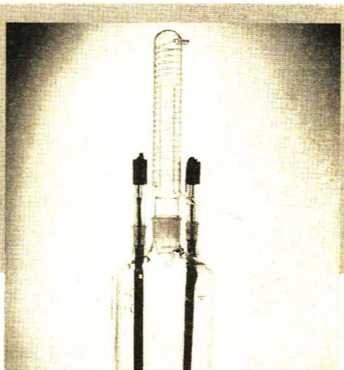

No. 7170, 3 liters per hour

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Condenser design is unique in that it incorporates two independent trapping systems—permits only the hottest, therefore, the purest steam to condense over. If the steam is not hot enough to get through the traps, it refluxes back into the boiling pot. A constant level device and overflow keeps water in the boiling pot at the proper level.

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190

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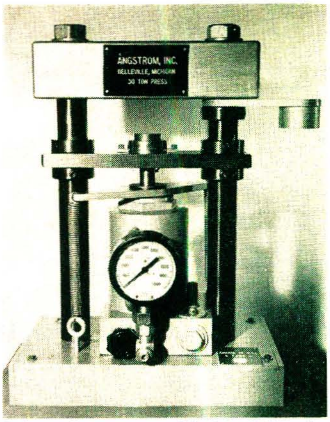
Strip Chart Digitizer

Data from strip chart recorders can be translated semi-automatically onto punch cards for digital computation and programming with the Model 1020 strip chart digitizer. The unit drives a standard keypunch such as the IBM 024, 026, or 526. It is an off-line system and does not require the use of a computer for digitizing. Both X and Y coordinate resolution is 0.01 inch. Drive speed and punching rate are variable. Technical Enterprises Corp., 2217 Calumet Drive, Houston, Texas 77004. **413**

Thin Layer Chromatography Supplies

Glass plates (1″ × 3″ and 8″ × 8″) and 8″ × 8″ Mylar sheets for use in thin layer chromatography are available. Absorbents offered are silica, cellulose, and alumina. A newly developed method of application ensures uniform coverage of absorbent. Ladd Corp., 1215 Washington St., Wilmette, Ill. **414**

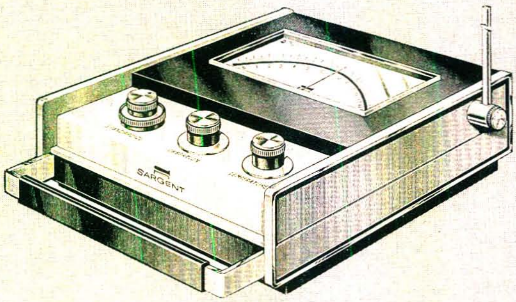


Briquetting press, Model 4500 for routine preparation of x-ray, optical emission, and infrared samples, is a 30-ton press with a two-stage pump for rapid operation. A swing-away anvil allows easy die access. Briquets are formed in one simple operation and there is no need to remove the die to eject the specimen. Standard molds from ¼″ to 1¾″ in diameter are used. Angstrom, Inc., 2454 West 38th St., Chicago 2, Ill. **415**

pH Electrodes

Eleven new electrodes of six basic types—silver billet, platinum, semimicro combination, miniature pH, miniature reference, and mercury internal pH—are now available. They are supplied with varying lead lengths and connectors, and the miniature pH types offer choice of silver–silver chloride or mercury internal elements. There are now 23 electrodes available from the company. Corning Glass Works, Corning, N. Y. **416**

Spectrokem spectrophotometer has a range from 400 to 750 mμ and a bandwidth of 15 mμ. Sensitivity and stability are provided through the use of constant voltage circuitry to both exciter lamp and photoconductive cell. A flow-cell and pump system are available optionally. Golden Instruments, Inc., 2519 N. Elston Ave., Chicago, Ill. 60647. **417**



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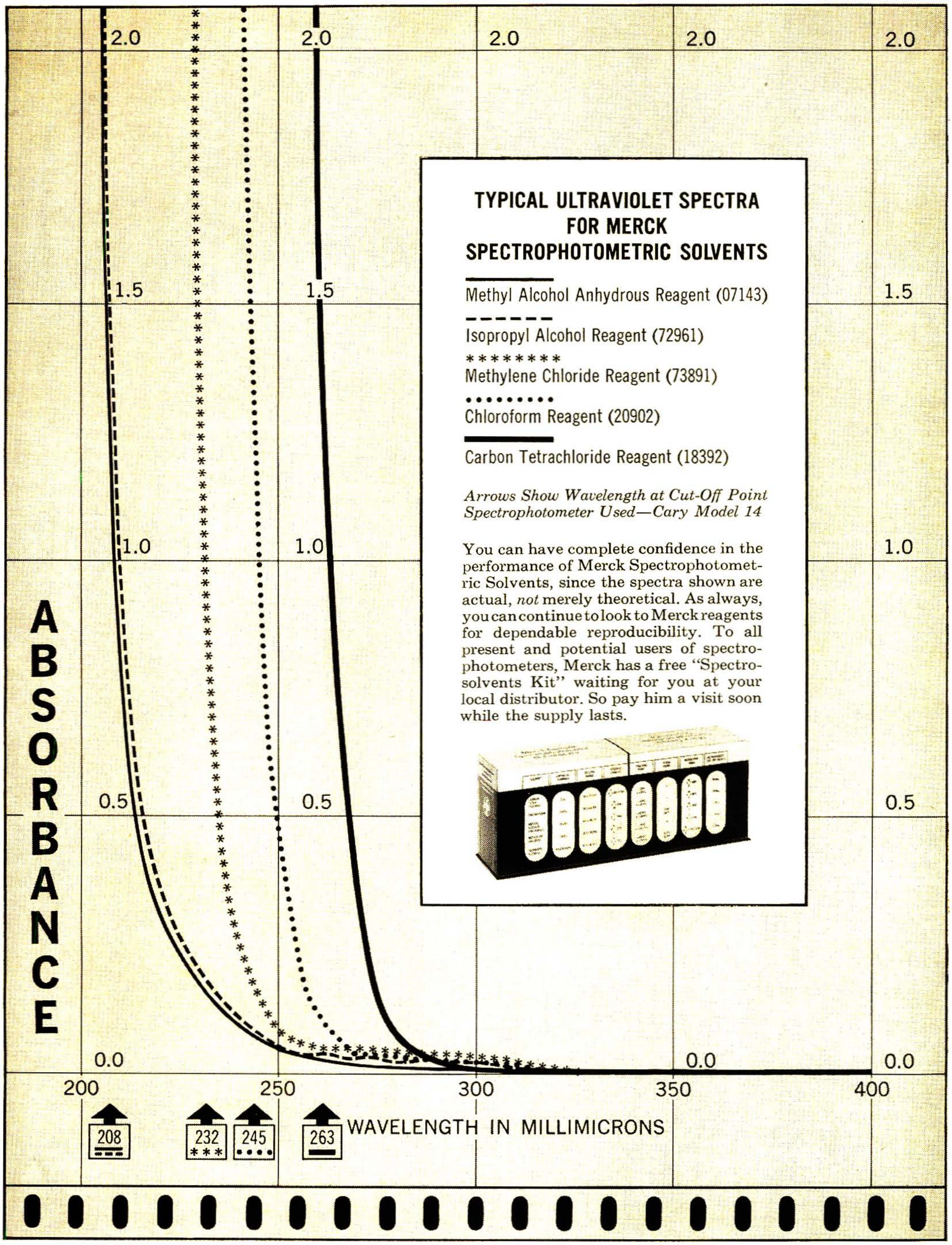

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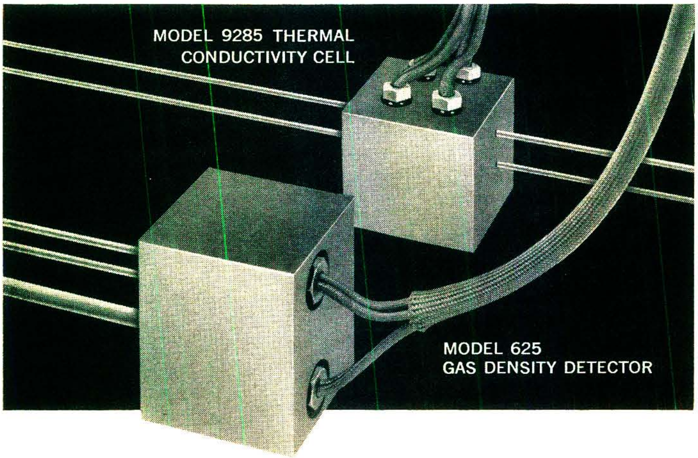

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GAS ANALYSIS INSTRUMENTS SINCE 1935

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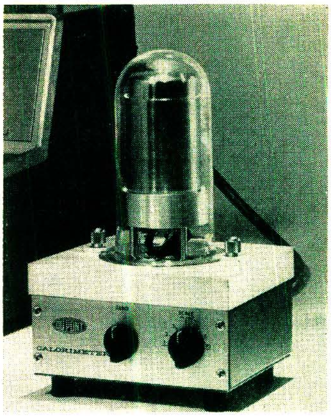

Calorimeter cell shown is the latest plug-in accessory for the Model 900 differential thermal analyzer. The cell measures specific heat and determines heats of transition and reaction in the range from −100° to 700° C. Thermal data obtained with the cell supplements information provided by the basic Model 900 DTA unit. E. I. du Pont de Nemours & Co., Wilmington, Del. **418**

Simulated distillation apparatus produces data comparable to that obtained from a 100-plate analytical distillation unit, but in 1% of the time. Model 900 is applicable for products ranging from C_1 to C_{42} (b/p. 1000° F.) and above. The separation column can be automatically cooled to −60° C. and programmed at linear rates to 300° C. The integrated signal is accumulated and printed out every 10 seconds. Wilkens Instrument & Research, Inc., 2700 Mitchell Dr., Walnut Creek, Calif. 94597. **419**

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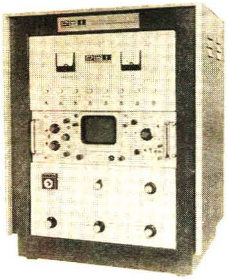
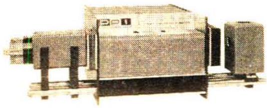
leave off.





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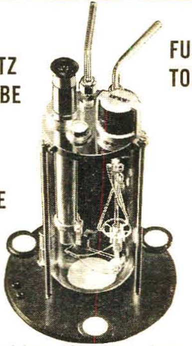

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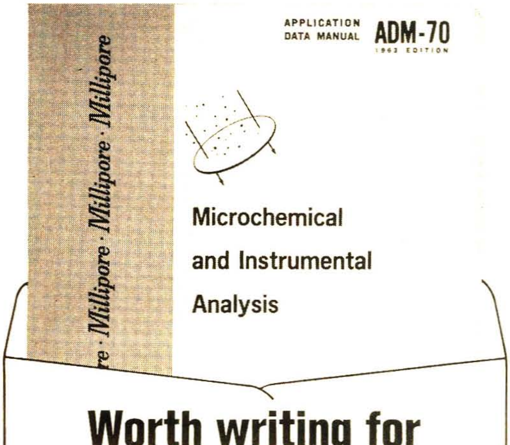

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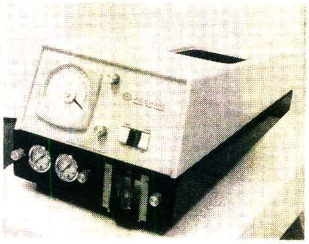

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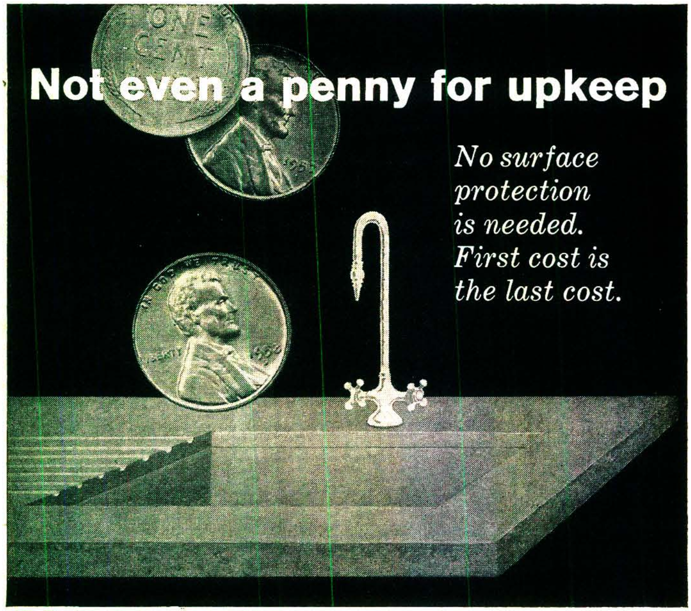

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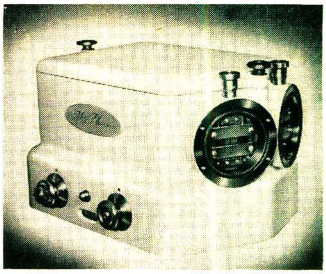

Model 218, 0.3 meter plane grating scanning monochromator, operates in the range 1050 A. to 16 microns. First order resolution is better than 0.25 A. The instrument features special aspheric optical surfaces and snap-in type gratings. Conversion from atmospheric to vacuum operation and flexibility of positioning are offered. McPherson Instrument Corp., 530 Main St., Acton, Mass. 01720. **420**

Acoustic spectrometer Model VII with frequency counter and X-Y recorder can be used to measure Young's modulus, shear modulus, Poisson's ratio, and internal fraction or acoustic absorption. Determination of acoustic absorption bands as a function of frequency and temperature aids in the study of micro- and macro-structure. Samples, solids of any size or shape or liquids, may be in the temperature range of –300° to 1000° C. Frequency range is from 20 to 40,000 cycles; frequency scanning ranges are selectable from 15 to 430 cycles; scanning rates are from 1 to 50 minutes. Resonance amplitudes are recorded as a function of frequency and also linearly or logarithmically with time to permit study of annealing, fatique, gelation, and polymerization. Nametre Co., 1246 Highway 27, Highland Park, N. J. **421**

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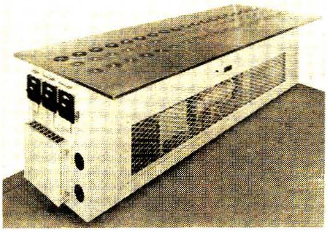

Model V-40-54HC is equipped with three individual temperature baths under a stainless steel table top. Immersion wells are color coded according to bath temperature: red for 160° F.; green for 75° F.; and blue for –40° F. An indicating controller for each liquid area is mounted at the end of the cabinet. The high temperature baths have immersion heaters with safety thermostats to prevent temperature override and liquid agitators to ensure close temperature control. Dimensions are 114″ long × 44″ wide × 34″ high. Cincinnati, Sub-Zero Products, Cincinnati, Ohio 45206. **423**

Flying Spot Particle Analyzer

Pesticide spray droplet size and droplet distribution patterns may now be studied by analyzing droplet photographs. The electronic flying spot particle analyzer makes measurements by scanning 35-mm. film negatives with a 1000-line raster generated by a high resolution cathode-ray tube. The scanned field of the film is about 18 × 18 mm. A high resolution lens images the flying spot on this field. The scanner can resolve and measure images as small as 20 microns. From a series of rapid measurements, size distribution of the droplets, their medium diameter, and the distribution of spaces between them may be studied. Airborne Instruments Laboratory, Deer Park, New York 11729. **424**

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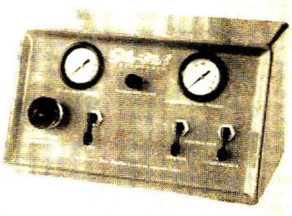

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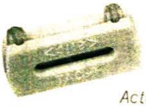

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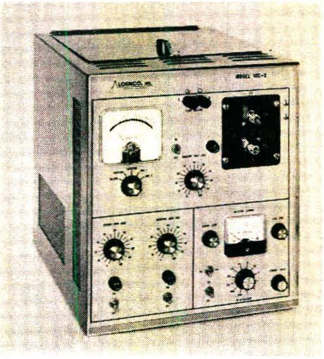
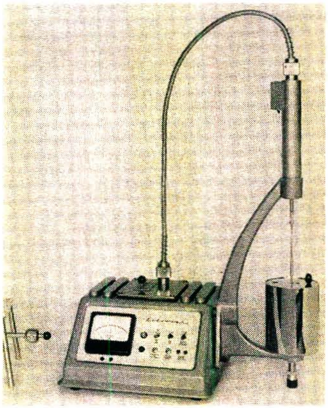


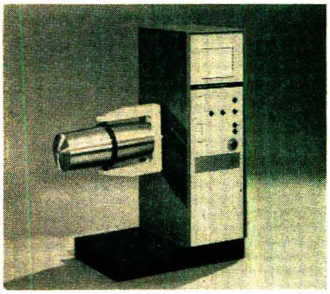
Model 15C Series, designed for both modular and integrated construction concepts, provides the choice of over 2000 feature combinations for gas chromatography. The instrument can be single or dual column, isothermal or temperature programmed. Multiple column switching systems and a choice of all types of detector systems plus two different oven arrangements are possible. Loenco, Inc., 2092 N. Lincoln Ave., Altadena, Calif. **425**



Haake Rotovisco, rotating viscometer offers new accessories for high- and low-temperature investigations in the range from −60° to 400° C. Measuring systems according to the Couette (cup and bob) and plate-cone principles are available. Shown above is the control unit with flexible cable and dual 50/500 gr. cm. measuring head and special high–low temperature Couette tempering vessel. Other new accessories include a pressure/vacuum attachment, and electrical heating with or without a program controller. Brinkmann Instruments, Cantiague Rd., Westbury, N. Y. 11590. **426**

Multiple Target Assembly for Neutron Generators

Model 9525 multiple target assembly contains five targets for fast target changes in neutron generators and other types of positive-ion accelerators. Changes can be made without interrupting the vacuum. The device permits alternate use of standard (1.25 inch diameter) deuterium or tritium targets. It also allows the operator to tune up the accelerator on a depleted target after shut-down periods, and then switch over to a new target for full output operation. Nuclear-Chicago Corp., 359 E. Howard Ave., Des Plaines, Ill. **427**



Model 190B microcalorimeter measures thermodynamic changes—free energy, entropy, enthalpy. Heat changes as small as 5 millicalories are recorded with an accuracy of ±3%. The four-module instrument includes a basic calorimeter unit containing well-insulated twin thermopiles which hold reference and reaction vessels. Electrical connections are such that heat generated by the mixing process is automatically subtracted from the total heat of reaction. Operating temperature of the calorimeter can be held to within ±0.2° C. by the environmental temperature enclosure module which has a range of 4°–70° C. The programmer module provides presetting of up to 7 mixing sequences. Heat measurements are recorded by the recorder-amplifier module which has an attachment for integrating the data. Spinco Division, Beckman Instruments, Inc., 1117 California Ave., Palo Alto, Calif. 94304. **428**

Gas Sample Counting System

A new gas sample counting system combines high efficiency and low background for the detection, measurement, analysis of radioactive gases by the internal gas counting method. The system can measure any beta or alpha emitting sample which can be prepared in the form of a proportional or other suitable counting gas. Special features include guaranteed low background (less than 10 c.p.m. for the 1000-ml. detector); a choice of four detector sizes (100, 250, 500, and 1000 ml.); and seven counting modes with two-detector operation. Carbon dioxide, methane, and other hydrocarbons or gas mixtures can be analyzed if they provide a good proportional plateau below 10 kv. Beckman, Scientific and Process Instruments Division, 2500 Harbor Blvd., Fullerton, Calif. **429**

The Hall effect is applied in this magnetic reaction analyzer. Making use of a constant amplitude magnetizing field and a sensitive field detecting device with flux response independent of frequency, the MRA permits non-contact measurement of the magnetic and electrical properties of metallic materials over a wide thickness range—typically from a fraction of a mil to ½ inch. It is capable of operation at frequencies varying from 20 c.p.s. to 100 kc. to provide optimum operation conditions for each combination of material properties and geometrics. It permits precise vector analysis of magnetic field and eddy currency induction within the test materials. F. W. Bell, Inc., Columbus, Ohio. **430**

Color Sorting System

Automatic measurement and classification of color shades is now possible through the combined use of an automatic colorimeter and a computer. The Colorede instrument compares samples to a standard thirty times per second and performs a logarithmic measurement. Material is classified into shade groups of a preset tolerance. The instrument is programmed with the widely accepted MacAdam system for linearizing color space with respect to the sensitivity of the human eye. The basic system sorts in 27 shade groupings; however, a larger number can be provided. Bulletin HB554 provides a complete description and specifications. Instrument Development Labs., 67 Mechanic St., Attleboro, Mass. **431**

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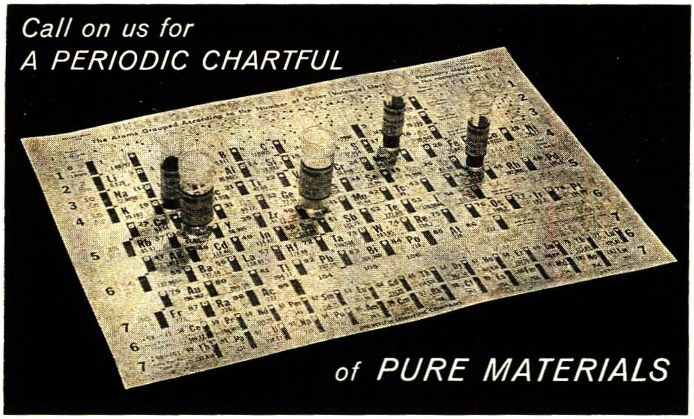

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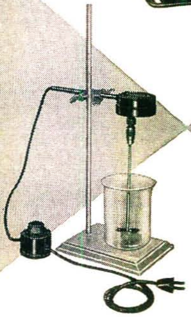

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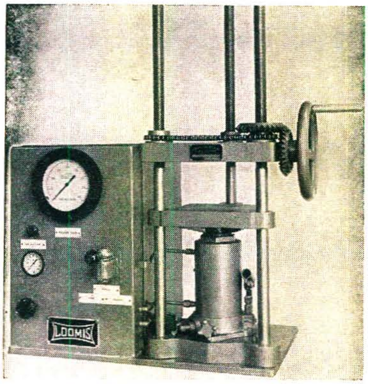

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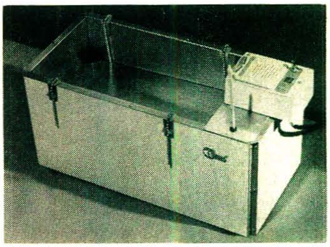


TECAM thermostatic water bath shown is lined with stainless steel and provided with an automatic temperature controller, stirrer, and circulator. Temperature is controlled to ±0.2° C. both within the bath itself or in separate apparatus through which the liquid can be circulated by the attachment of a tube to the pump outlet of the control unit. Temperature control extends from ambient to 95° C. The control unit has a pumping capacity of 53.3 gallons per hour at zero head and is available with either 500- or 1000-watt heater. Four models of baths have capacities of 4.8 to 2.0 gallons. Techne (Princeton), Ltd., 661 Brunswick Pike, Princeton, N. J. **432**

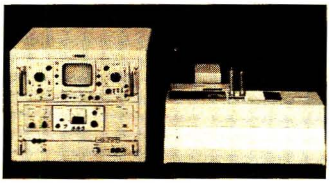
Continuum Radiation Source

A continuum radiation source, consisting of a head and electronic console, has an intensity that approximates that of a black-body at 48,000° K. in the visible and near ultraviolet spectral regions. Continuum extends from 900 to 6000 A., with line emissions to 95 A. The instrument is suited for vacuum–UV absorption spectroscopy, photoluminescence, and radiation damage studies. Pulses of about 2 microseconds duration can be obtained, with risetimes of about 0.4 microsecond to peak. Reproducibility of intensity is within ±5%. This source is a vacuum instrument and requires no gas-purge-fill cycle. When used in absorption spectroscopy studies, the spectrograph pump is adequate for the vacuum needed. TRW Space Technology Laboratories, 139 Illinois St., El Segundo, Calif. **433**

Micropellet Die and Holder for Infrared

Model 316 micropellet die, designed for use with Perkin-Elmer infrared spectrophotometers, allows the formation of a pellet from 10–15 mg. of KBr directly in the pellet holder, which fits into the microcell adapter of the instrument. No beam condenser is needed; reference attenuation of about

55% T is necessary. The sensitivity is slightly more than 7 times that of a $^{1}/_{2}$-inch conventional pellet, and usable spectra have been obtained from as little as $12 \mu g$. of sample. The pellet formed by pressure for 15 seconds at 2000 pounds force is 10–20 microns in thickness. Adaptors for the Perkin-Elmer Infracord, Model 137, and the Beckman IR-5 are also available. W. R. Hewitt, 7257 Richmond Place, St. Louis, Mo. 63143. **434**



The stopped-flow spectrophotometer shown provides a fast and accurate way to mix two liquid components and measure their absorbance as a function of time. Solutions are mixed to 99½ % completion in as little as two milliseconds. Immediate stopping of flow allows absorbance measurements to be made free of interference from turbulence. Minimum sample per measurement for each component is 0.1 ml. The optical system consists basically of a tungsten-iodide lamp with a quartz envelope, and a 215-mm. focal length grating monochromator. Fixed slits are provided for bandwidths of 1, 2, 3, 6 and 12 $m\mu$. Absorbance may be read over the range of 3500 to 8000 A.; an accessory can extend the lower limit to about 2500 A. Durrum Instrument Corp., 925 East Meadow Dr., Palo Alto, Calif. 94303. **435**

Surface-Area Measurements

The Sor-BET performs rapid, accurate BET determinations by the classic procedure of measuring the residual pressure after adsorption of nitrogen by a sample. The instrument differs from conventional units in that nitrogen is selectively adsorbed from a binary gas mixture consisting of helium and nitrogen. Samples measuring from 0.1 to 1500 $m.^2/g$. can be handled with sample sizes ranging from 0.1 gram to 20 grams or higher. If three-point determinations are made, six or more samples may be run in a day. Accessories available include a vapor pressure manometer, calibration volume kit, special sample holders, and vacuum grease. American Instrument Co., 8030 Georgia Ave., Silver Spring, Md. 20910. **436**

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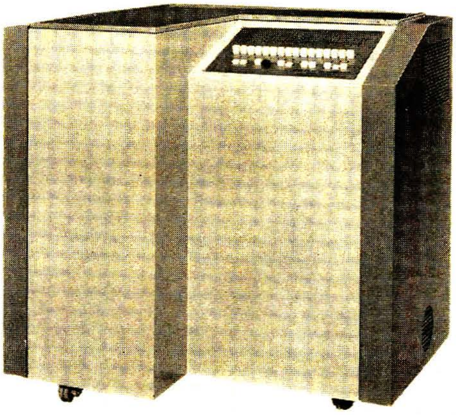

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*See DISSYMMETRIES, Anal. Chem. **36**, 42A (1964); **36**, 66A (1964); Science **143**, 617 (1964) and **144**, 449 (1964)

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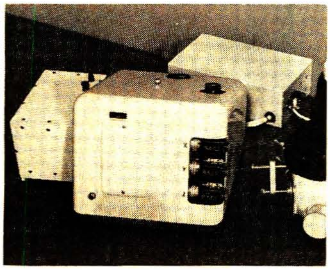


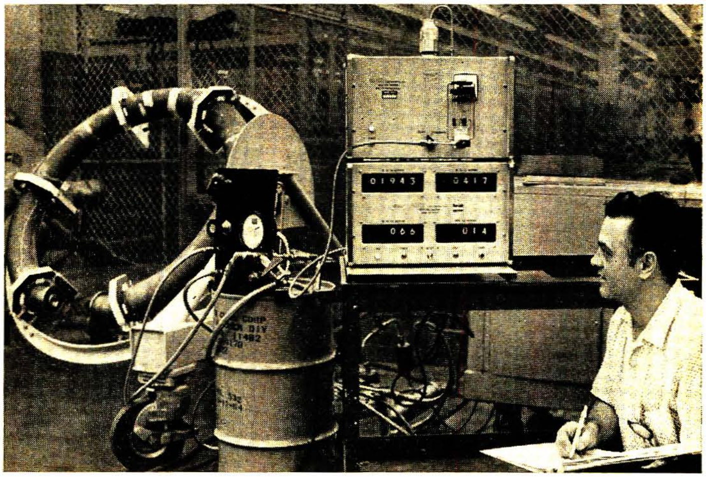
Digital readout tristimulus integrator shown is used with the Spectronic 505 for measuring, specifying, and controlling color. The integrator is self-checking in that five test positions are incorporated in the circuitry to confirm proper functioning. Either a daylight or tungsten lamp can be furnished depending on the application. Bausch & Lomb, Rochester, N. Y. 14602. **438**

Chromatogram Scanner

A new paper and thin layer chromatogram scanner for chemical separation and analysis is available. The scanner permits accurate location and assay of low energy beta emitting radioisotopes by the use of dual, integral rotating collimator and twin, high efficiency detectors. Designated the SC525B, the unit features electronic count rate and recycling integrate modes using a single pen recorder thus avoiding the costly dual pen system. The system has printed board circuits for the ratemeter and power supply and a 10-speed recorder precisely synchronized with the paper feed. Tracerlab, 1601 Trapelo Rd., Waltham, Mass. 02154. **439**

Light-Scattering Particle Counting—Special Report

New Liquid Test Instrument Counts Contaminant Particles Automatically in 1 Minute!



The cleanliness of liquid products can now be verified quickly, easily and accurately at the processing line. A new portable test instrument automatically displays an accurate sample count of the number of particles by size range in any selected sample size. As used by Lockheed Missiles & Space Co., California, in the manufacture of storage diaphragms for the Polaris flight direction control system, the automatic particle counter takes periodic samplings of liquid freon flush from the initial rough cleaning of the storage diaphragms to the final fill. In 1 minute, it registers the particle count of 100 cc of liquid freon in 4 size ranges simultaneously: 15-24 microns; 25-49 microns; 50-100 microns; over 100 microns. The sampling procedure is as follows:

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3. The tank goes to a clean room for further flushing. 100 milliliter samples are tested on the particle counter. Then, 2 gallons of virgin freon are run through the bladder with samples checked on the particle counter. Finally, the tank is filled to capacity with additional virgin freon and a sample is checked on the particle counter. The accurate particle counts provided by the counter assure a minimum of laboratory analyses and eliminate delays of up to 4 hours in manufacturing time for testing a single sample.

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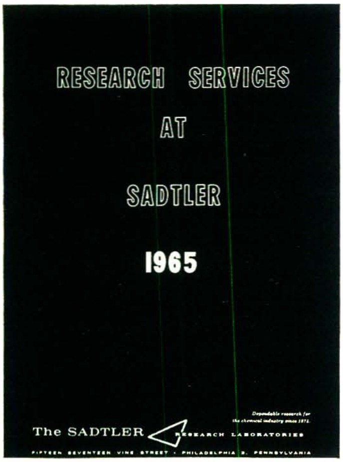
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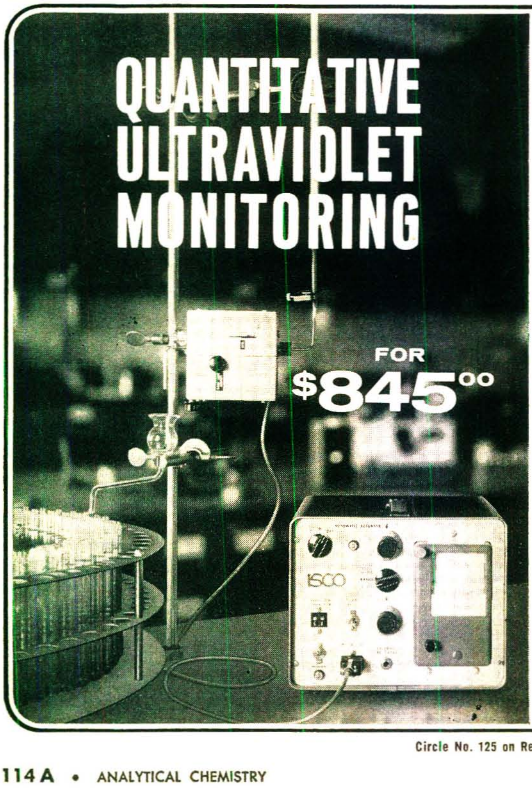

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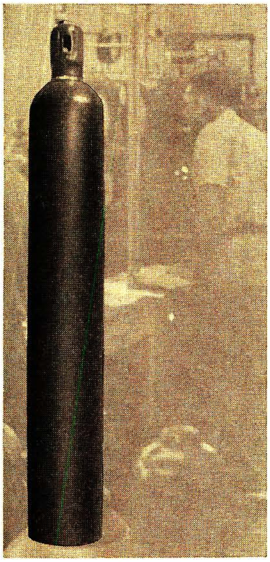

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High Temperature Silicone Oil

A new low-priced extreme high temperature silicone fluid has a number of uses as a heat transfer medium in the laboratory. Identified as SF-1093, the material will withstand service up to 700 hours in air at 550° F. It is ideal for high-temperature baths. General Electric, Silicone Products Dept., Waterford, N. Y. **502**

Adsorbents for Thin Layer Chromatography

Several new adsorbents for thin layer chromatography are available: silica gel PF 254 and silica gel PF 254 + 366 for preparative TLC, both with fluorescent indicators; aluminum oxide PF 254 and aluminum oxide PF 254 + 366 for preparative TLC, both with fluorescent indicators; a micro crystalline cellulose powder; a polyamide powder with fluorescent indicator; and an acetylated polyamide powder. Brinkmann Instruments, Inc., Cantiague Rd., Westbury, N. Y. 11590. **503**

Zinc Selenide

Zinc selenide made by a new process is said to have better transmittancy to infrared than other commercial grades available. It is sold as a relatively stable yellow powder, especially low in sulfur and oxygen. The experimentally determined transmittance of infrared radiation as a function of wavelength corresponds to the values expected theoretically for absolutely pure zinc selenide. Merck & Co., Inc., Rahway, N. J. **504**

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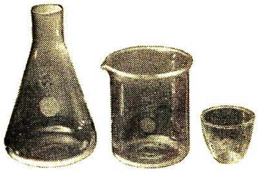

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MANUFACTURERS' LITERATURE

Gas Chromatography Bibliography. Bulletin No. 8A, 5 pages, includes 500 references on the analysis of compounds of biochemical interest. Applied Science Laboratories, Inc., State College, Pa. **601**

Computer Analysis of Aluminum Alloys. A reprint of this article by T. J. Hudson and W. L. Lee is available from Applied Research Laboratories, Inc., P. O. Box 1710, Glendale, Calif. 91209. **602**

High Volume Microfiltration. A 32-page bulletin, HV-1, describes systems for filtering particles, 8 microns to 10 millimicrons, at flow rates of 500 gallons per minute and higher. Prices on various size filter systems are included. Millipore Filter Corp., Bedford, Mass. **603**

Frequency Converter. A 1-page bulletin contains illustrations and specifications of Models 4300 and 4700. Brooks Instrument Division, Emerson Electric Co., Hatfield, Pa. **604**

Plastic Laboratory Ware. A 6-page supplement (No. 565) to the 1964 catalog "Plastics for Science and Industry" contains illustrations, descriptions, and prices of 26 new items. Bel-Art Products, Pequannock, N. J. **605**

Automated Chromatography. Bulletin 34210, 4 pages, describes the Type 34-210 Chromad which integrates, digitizes, and prints out peak areas and peak retention times. CEC, 360 Sierra Madre Villa, Pasadena, Calif. **606**

Recording Accessories. Bulletin Y1904A, 8 pages, describes charts, inks, pens, recording speeds and other features. The Bristol Co., Waterbury, Conn. 06720. **607**

Modular Recording Systems. A 20-page, illustrated brochure (No. 1707) describes the Brush Mark 200, Series 1707 modular recording systems. Brush Instruments Division, Clevite Corp., Cleveland, Ohio. **608**

Vacuum Pumps. Two-stage pump and related equipment are described in an illustrated brochure. Central Scientific Co., 1700 Irving Park Road, Chicago, Ill. **609**

Heavy Liquids. A 20-page booklet contains descriptions of various heavy liquids and suggestions on their application for sink-float density determinations, mineral separations, and quality control. Engineered Materials, P. O. Box 363, New York, N. Y. 10008. **610**

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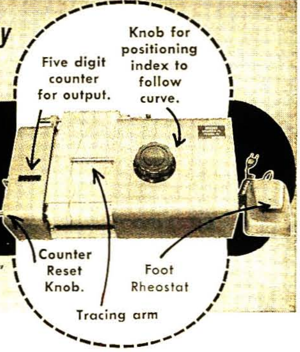

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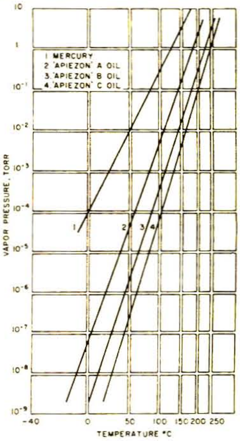

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MANUFACTURERS' LITERATURE

Polarography. Bulletin 13-770, 4 pages, contains illustrations, specifications, and applications of the Elecdropode, Model 65. Fisher Scientific Co., 717 Forbes Ave., Pittsburgh, Pa. **611**

Automatic Preparative Gas Chromatograph. The principal features and specifications of the Model 775 Prep-Master are described in a 4-page bulletin. F & M Scientific Corp., Avondale, Pa. **612**

Research Chemicals. Catalog 5, 51 pages, lists organic and inorganic chemicals with chemical structure, prices, and melting point or boiling point. Gallard-Schlesinger Chemical Mfg. Corp., 580 Mineola Ave., Carle Place, L. I., N. Y. 11514. **613**

Electrophoresis. A 32-page manual contains information for separation of serum proteins, hemoglobins, and LDH isoenzymes on cellulose polyacetate support strips. Gelman Instrument Co., P. O. Box 1448, Ann Arbor, Mich. **614**

Constant Voltage Unit. Bulletin S 900-5c, 2 pages, illustrates and gives specifications of the Honeywell Constant Voltage Unit which provides a stable d-c voltage from ordinary line voltage. Honeywell Inc., M389, Wayne and Windrim Aves., Philadelphia, Pa. 19144. **615**

Laboratory Equipment. A 32-page catalog lists spectrophotometer cells, constant temperature baths, tensionmeters, weather instruments, and other items. Lux Scientific Corp., P. O. Box 272, Canal Street Station, New York, N. Y. **616**

Centrifuge Literature. Model A-2, and Models 30 and 30-R are described in catalogs 70 and 71. Illustrations and specifications are included. Lourdes Instrument Corp., 656 Montauk Ave., Brooklyn, N. Y. 11208. **617**

Fluorometer, Flame Photometer, and Infrared Spectrophotometer. Bulletins 7009-B, 7069, and 7073 contain illustrations, specifications, and applications of these instruments. Beckman Scientific and Process Instruments Division, 2500 Harbor Boulevard, Fullerton, Calif. 92634. **618**

Thermal Analysis. A 16-page brochure, DSC-1, contains illustrations and specifications for differential scanning calorimetry. Perkin-Elmer Corp., Main Ave., Norwalk, Conn. **619**

Sampling Oscilloscope Recorder. Technical bulletin SR100, 2 pages, provides applications, description of operation, specifications, and prices. Nesco Instruments, Division of Datapulse Inc., 509 Hindry Ave., Inglewood, Calif. **620**

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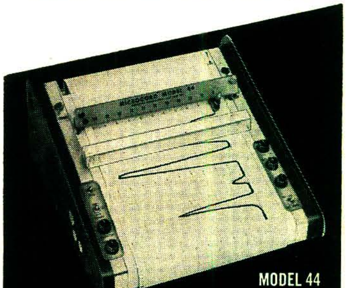

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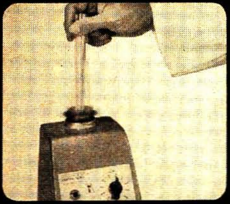

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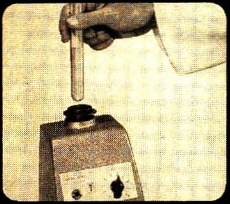

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MANUFACTURERS' LITERATURE

Pulse and Digital Instrumentation. 1965 Condensed Catalog, 4 pages, provides major specifications, and prices for 25 standard pulse generators. Datapulse, 509 Hindry Ave., Inglewood, Calif. 90306. **621**

Scientific Glass Apparatus. The 1965 catalog is available from Eck & Krebs Inc., 29-09 49th Ave., Long Island City 1, N. Y. **622**

Transistorized Nuclear Modules. Specifications and descriptions of scalers, ratemeters, amplifiers, pulse height analyzers, coincidence-anticoincidence and power supplies are included in a catalog from Nuclear Supplies, Inc., P. O. Box 312, Encino, Calif. **623**

Operational Amplifiers. "Generalized Instrumentation for Research and Teaching—A Primer in the Art of Using Operational Amplifiers in General Utility Instrumentation" by C. F. Morrison, Jr., 104 pages, describes the techniques of electronic circuits, feedback, and analog computers. Philbrick Researches, Inc., Allied Dr. at Rte. 128, Dedham, Mass. 02026. **624**

Pyrex Brand Drainline. A 20-page illustrated catalog BP-400, describes fittings, traps, and accessories for acid-waste drainline pipe. Corning Glass Works, Corning, N. Y. **625**

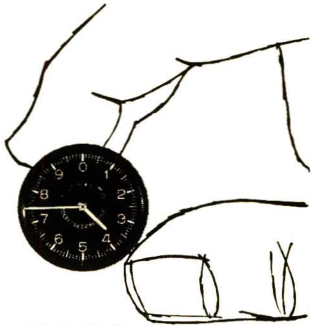
Spectroscopy Equipment. A 24-page catalog contains detailed information and prices on electrodes, plates, chemicals, sieves, and other items. Spex Industries, Inc., Metuchen, N. J. **626**

Automatic Voltage Regulators. Bulletin SVR365, 24 pages, contains applications, diagrams, rating, and specifications of several series of regulators and accessories. The Superior Electric Co., Bristol, Conn. 06012. **627**

Modular Vacuum Systems. An 8-page brochure with accompanying component assembly design kit enables the recipient to design his own high vacuum system. Twenty-four of several hundred systems are illustrated. Ultek Corp., Box 10920, Palo Alto, Calif. **628**

Metallograph. A 12-page catalog contains information on Series N with flatfield objectives and widefield eyepieces. Detailed descriptions and prices are included. Unitron Instrument Co., 66 Needham St., Newton Highlands, Mass. 02161. **629**

Gas Chromatography Accessory Catalog. Photographs, drawings, specifications, and prices are included for stationary phases, solid supports, detectors, syringes, and other items. Wilkens Instrument & Research, Inc., P. O. Box 313, Walnut Creek, Calif. 94597. **630**



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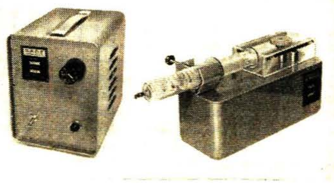

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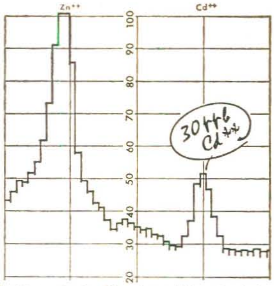

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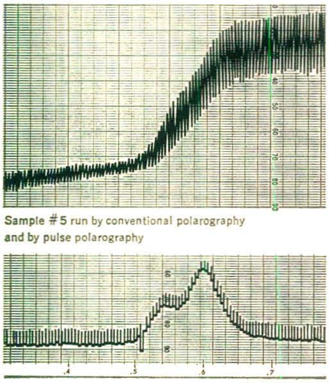
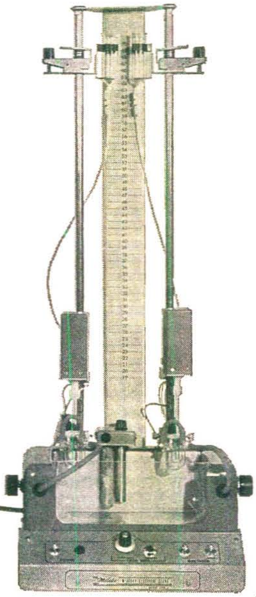
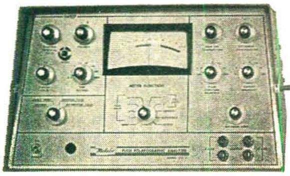


Sample #5 run by conventional polarography and by pulse polarography





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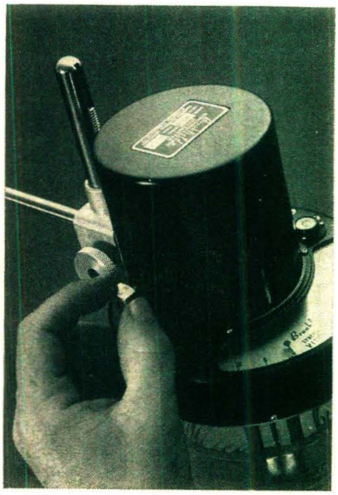

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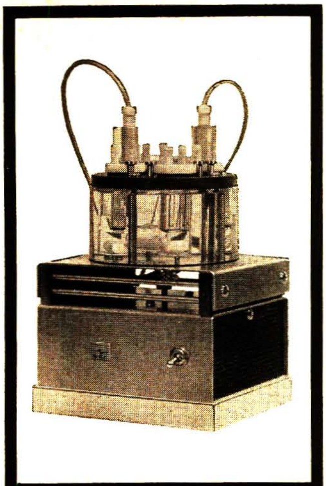

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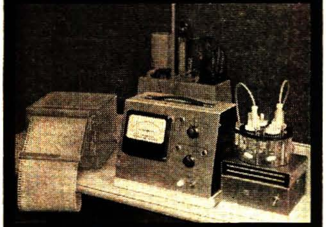

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MANUFACTURERS' LITERATURE

Viscometers and Controlled-Temperature Baths. Bulletin 50, 4 pages, contains illustrations, specifications, and prices of major products available from Cannon Instrument Co., P. O. Box 812, State College, Pa. 16801. **631**

Radiation Dosimetry. A brochure containing information on LiF TLD dosimeters is available. Controls for Radiation, Inc., 130 Alewife Brook Parkway, Cambridge, Mass. **632**

Gas Chromatography References. A bibliography covering air pollution, amino acids, fatty acids, pesticides, steroids, and other subjects is available. Wilkens Instrument & Research, Inc., P. O. Box 313, Walnut Creek, Calif. **633**

LabLog No. 2-65. A 12-page catalog lists a wide variety of laboratory equipment: spectrophotometers, balances, infusion pumps. Will Scientific, Inc., Box 1050, Rochester, N. Y. 14603. **634**

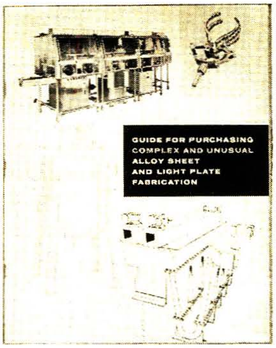
Multi-Point Recorder. Bulletin P1298-A describes the 24-point Dynamaster potentiometer. Operating characteristics discussed include accuracy, slidewire resolution, minimum span, and printing interval. The Bristol Co., Waterbury, Conn. 06720. **635**

Methionyl Peptides. A 2-page pamphlet contains physical and chemical specifications as well as the actual analysis of each product. Prices are also included. Mann Research Laboratories, Inc., Dept. W, 136 Liberty St., New York, N. Y. **636**

Specialty Chemicals for Life Sciences and Polymer Research. Over 350 products are listed in this catalog pertaining to monomers, polymers, catalysts, epoxides, biochemical specialties, and other categories. Polysciences, Inc., P. O. Box 4, Rydal, Pa. 19046. **637**

Precision Magnetic Shields. A 12-page manual, No. 176, contains listings of 114 types of photomultiplier tubes made by 13 manufacturers, and the recommended shield for each tube type. Magnetic Shield Division, Perfection Mica Co., 1322 No. Elston Ave., Chicago, Ill. 60622. **638**

Portable Vacuum Systems. Catalog sheet C-20 describes a line of portable vacuum systems for applications in the low 10^{-6} Torr range. Operating and design features, pumpdown performance figures, and specifications are given for the Model VE-10 and others. Mikros/Division of Varian Assoc., 7634 S. W. Capital Highway, Portland, Ore. 97219. **639**



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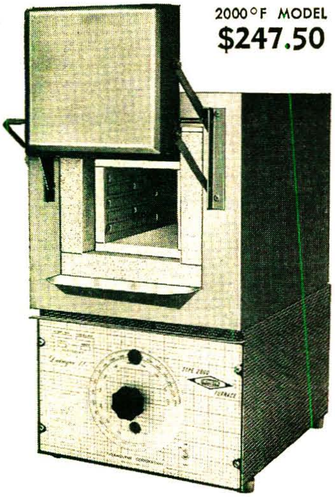

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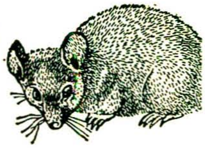

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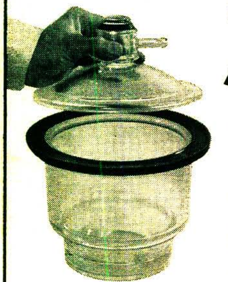

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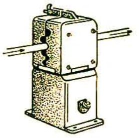

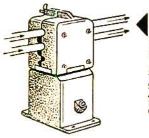

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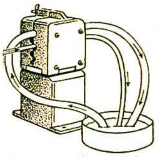

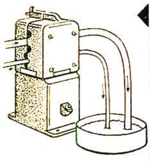

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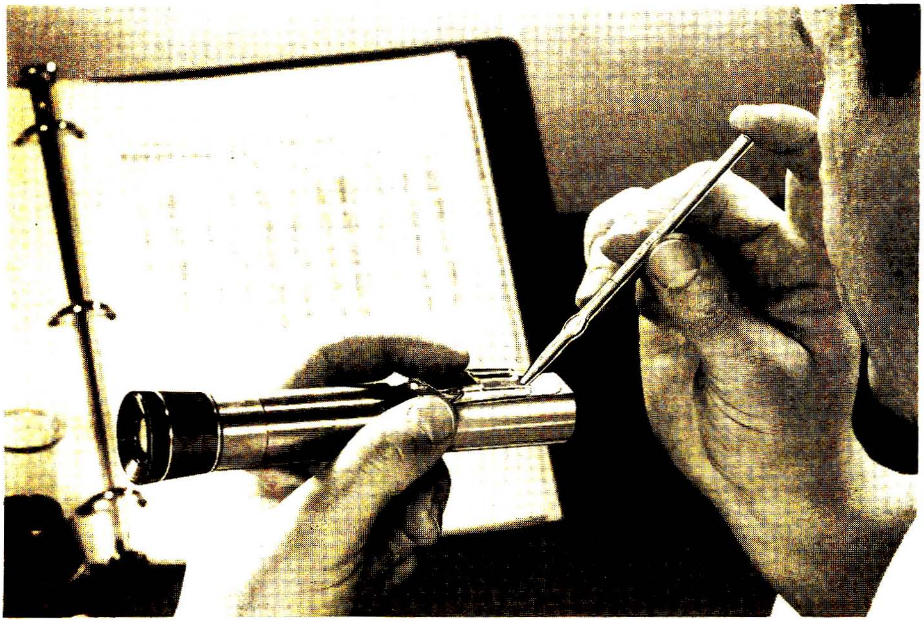

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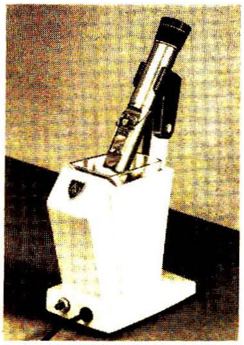

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