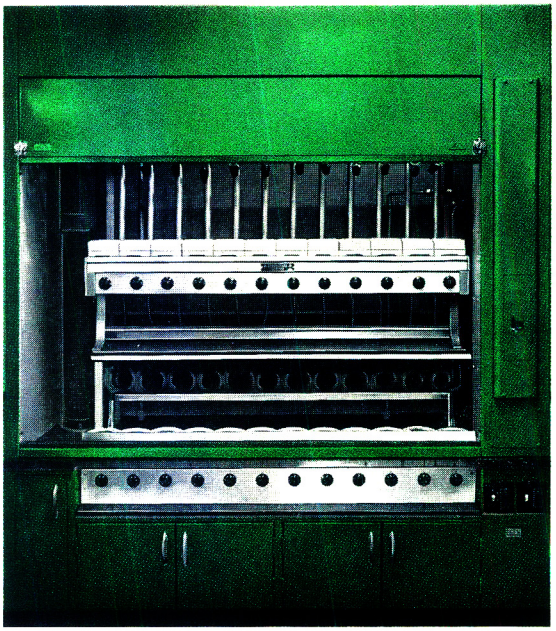
MARCH 1965

ANALYTICAL CHEMISTRY



SCIENCE vs. THE LAW P. 27



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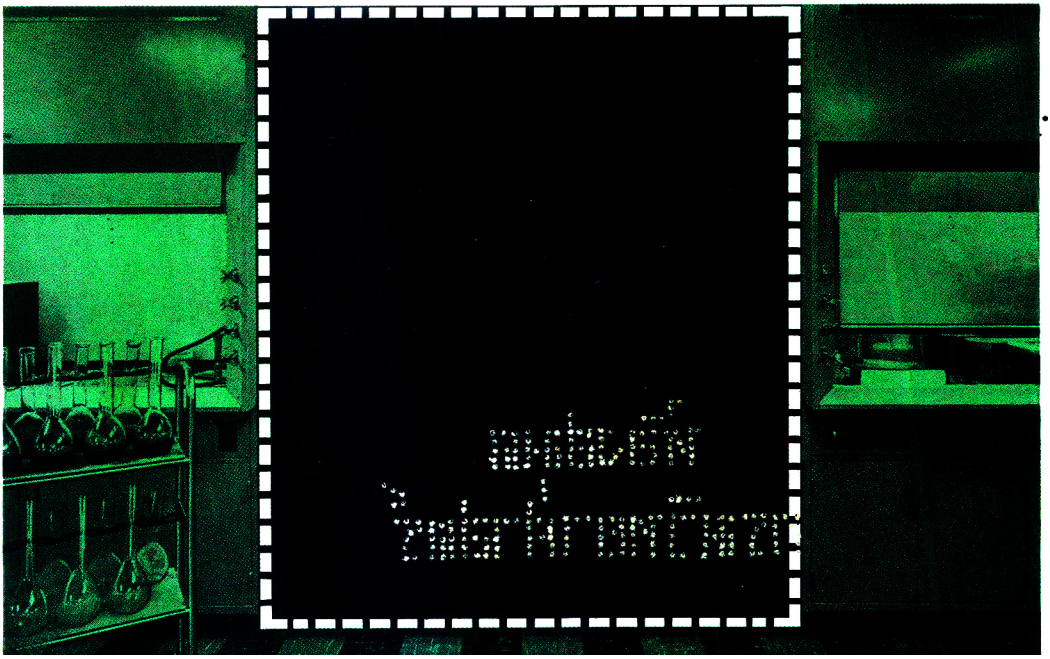

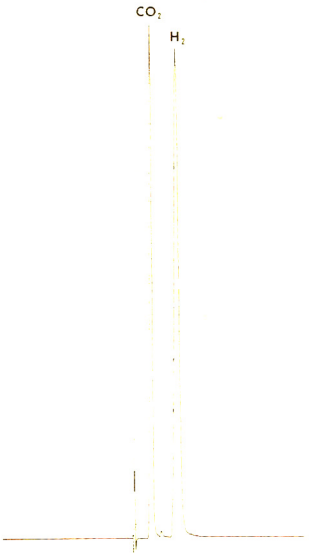

Readout for a typical carbon and hydrogen analysis

Sample: Diallyldiphenylphosphonium Bromide ($C_{18}H_{18}PBr$)
Sample Weight: 0.6657 mg
Oxygen Flow Rate: 40.0 cc/min
Analysis Time: 79 seconds
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Theoretical: 62.26% C, 5.81% H

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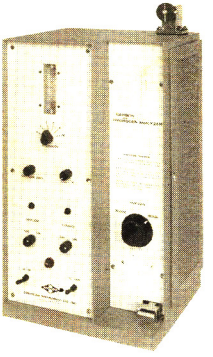

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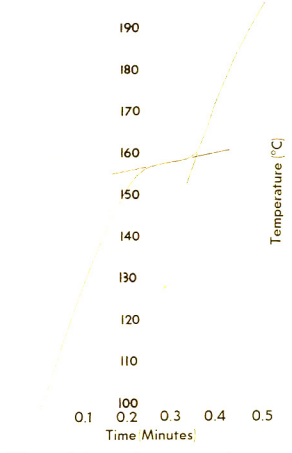

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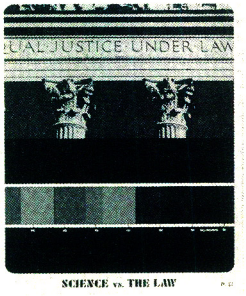

SCIENCE vs. THE LAW

The demarcation between science and the law is presented in an artistic version as this month's cover. For the related feature, Science *vs.* The Law, see page 27 A.

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CONTENTS

REPORT FOR ANALYTICAL CHEMISTS

A discussion of court cases with emphasis on Supreme Court decisions which have been at variance with scientific evidence is given in this month's Report..... **27 A**

NEWS SECTION

The complete program of the Division of Analytical Chemistry to be presented at the 149th National ACS Meeting in Detroit, Mich., April 5 to 9, is given. The LSU Symposium on Modern Methods of Analytical Chemistry is summarized. Various meetings and symposia are scheduled. Universities have planned summer short courses on analytical methods..... **41 A**

EDITOR'S COLUMN

Various reference standards programs which serve the drug industry and biological sciences are discussed..... **89 A**

LABORATORY OF THE MONTH

Instruments and research objectives of the Research and Development Center of the National Steel Corporation are featured **101 A**

INSTRUMENTATION

Dr. Müller discusses research and development and some aspects of creativity in modern-day society..... **117 A**

BOOKS...75 A
BRIEFS...9 A
CALENDAR OF EVENTS...56 A
NEW CHEMICALS...138 A
EDITORIAL...321
FUTURE ARTICLES...156 A
MANUFACTURERS' LITERATURE...141 A
NEW PRODUCTS...127 A
READERS' INFORMATION SERVICE...124 B

Scientific Communications

Gas Analysis by X-Ray Fluorescence Emission Spectrometry. C. R. Hudgens and George Pish. . . 414

Analytical Oxidation of Americium with Sodium Perxenate. H. P. Holcomb 415

Generalized Chronopotentiometric Potential-Time Equations and Their Application to Quasi-Reversible Processes. L. B. Anderson and D. J. Macero 322

An Instrument for Cyclic Voltammetry. C. K. Mann . . . 326

Digital Computer Program for Calculation of Molecular Formulae. D. A. Usher, J. Z. Gougoutas, and R. B. Woodward 330

Continuous Titrations with a Tubular Mercury–EDTA Electrode. W. J. Blaedel and R. H. Laessig. 332

Controlled-Potential Coulometric Titration of Uranium(VI) in Aqueous Solutions of Sodium Fluoride. W. R. Mountcastle, Jr., L. B. Dunlap, and P. F. Thomason. . . 336

Determination of Uranium and Americium-Curium in Urine by Liquid Ion Exchange. F. E. Butler 340

Rapid and Nondestructive Analysis of Sulfur and Calcium by Radioactivation and Photoneutron Counting. Saadia Amiel and J. O. Juliano. 343

Application of Galvanic Cell to Measurement of Oxygen-Consuming Enzyme Systems. Harry Lipner, L. R. Witherspoon, and Anne Wahlborg 347

Decay of Cesium^{137} Determined by Absolute Counting Methods. J. S. Merritt and J. G. V. Taylor 351

Coupled Reaction System for Determination of Transaminase Enzymes. Application to Glutamic Oxaloacetic Transaminase. G. P. Hicks and W. J. Blaedel. . . 354

Preconcentration of Trace Elements by Precipitation Ion Exchange. Fouad Tera, R. R. Ruch, and G. H. Morrison. 358

Solvent Extraction Equilibria of Certain 8-Quinolinols and Their Zinc(II) Chelates. Fa-Chun Chou, Quintus Fernando, and Henry Freiser 361

Determination of Tin in Hydrogen Peroxide Solutions by Atomic Absorption Spectrometry. E. J. Agazzi . . 364

Determination of Azide Ion by Hydrogen Ion Titration after Oxidation with Nitrite. R. G. Clem and E. H. Huffman 366

Wickbold Combustion and Spectrophotometric Analysis Procedure for Trace Amounts of Organic Chlorine in Viscous Polybutene Polymers. R. D. Rowe 368

Spectrophotometric Determination of Pentaborane with Pyridine. Application to Air Analysis. H. G. Offner 370

Study of the Pi Complexes of 2,4,7-Trinitrofluorenone with Phenols, Aromatic Hydrocarbons, and Aromatic Amines. G. H. Schenk, P. W. Vance, Johanna Pietrandrea, and Carolyn Mojzis 372

Isolation and Identification of Alcohols in Cold-Pressed Valencia Orange Oil by Liquid-Liquid Extraction and Gas Chromatography. G. L. K. Hunter and M. G. Moshonas 378

Gas Chromatographic Determination of Free Formic and Acetic Acids in Cigarette Smoke. E. T. Oakley, Ludwig Weissbecker, and F. E. Resnik 380

Quantitative Gas Chromatography of Amino Acids. Preparation of *n*-Butyl *N*-Trifluoroacetyl Esters. W. M. Lamkin and C. W. Gehrke 383

Study of the Photoionization Detector for Gas Chromatography. D. C. Locke and C. E. Meloan 389

Semiquantitative Determination of Impurities in Bisphenol A by Circular Paper Chromatography. N. H. Reinking and A. E. Barnabeo 395

Aromatic Hydrocarbons Produced during Combustion of Simple Aliphatic Fuels. Mitsugi Mukai, J. F. Thomas, and B. D. Tebbens 398

Nuclear Magnetic Resonance Spectra-Structure Correlations for Chlorinated 2,2-Difluoropropanes. H. F. White 403

Refractive Indices of Sucrose-Water Solutions in the Range from 24 to 53% Sucrose. D. F. Charles 405

Condensation Pressure Analyzer and Its Application to Continuous Uranium Hexafluoride Determination. W. S. Pappas and C. W. Weber 407

Determination of Diphenylhydantoin by Ultraviolet Spectrophotometry. Jack Wallace, John Biggs, and E. V. Dahl. 410

Corrections 382, 413

Correspondence

Influence of Electrometer Noise on Limit of Detectability in Atomic Absorption and Atomic Emission Flame Spectrometry. J. D. Winefordner and Claude Veillon 416

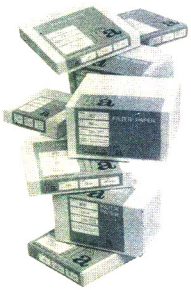
Spectrophotometric Determination of Iron, Nickel, Copper, and Cobalt in Tungsten and Tungsten Alloys. George Norwitz and Herman Gordon 417

Rapid Removal of Transuranium Elements from Aqueous Solutions Prior to the Determination of Total Lanthanide Fission Products. F. L. Moore and W. T. Mullins 419

Voltammetric Determination of the Monomethylether of Hydroquinone with a Carbon–Ceresine Wax Paste Electrode. J. R. Covington and R. J. LaCoste . . 420

Studies of Recovery by Foam Fractionation on 1-Naphthylamine. R. P. Poncha and B. L. Karger . . 422

NEW CATALOG



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CONTRIBUTED ARTICLES

Ultraviolet Spectrophotometric Determination of Trace Quantities of Phosgene in Gases. **W. B. Crummett and J. D. McLean** 424

Use of Highly Acid Supporting Electrolytes in Polarography. Observed Changes in Polarographic Waves of Selenium(IV) upon Standing. **G. D. Christian, E. C. Knoblock, and W. C. Purdy** 425

Modification of Ferrous Ion Reduction Method for Nitroglycerin. **R. S. Lambert and R. J. DuBois** 427

Fluorescence of the Aluminum [1-(2-Pyridylazo)-2-Naphthol] Complex. **J. G. Surak, M. F. Herman, and D. T. Haworth** 428

Switching Circuitry for Fast Chronopotentiometry. **R. A. Osteryoung** 429

An Improved Method for Determination of Selenium in Biological Material. **L. M. Cummins, J. L. Martin, and D. D. Maag** 430

Use of In Situ Reactions for Characterization of Alcohols and Glycols by Nuclear Magnetic Resonance. **V. W. Goodlett** 431

Mass Spectrometric Differential Thermal Analysis. **H. G. Langer, R. S. Gohlke, and D. H. Smith** 433

Determination of Americium-243 by Separation and Counting of Neptunium-239 Daughter. **C. J. Banick** 434

Mass Spectrometer Used as Detector and Analyzer for Effluent Emerging from a Capillary Gas Liquid Chromatography Column. **Ragnar Ryhage, Sten Wikstrom, and G. R. Waller** 435

Molybdenum(V)–Thiocyanate Complex Extracted into Chloroform. **O. W. Kolling** 436

Spectrophotometric Determination of Calcium in Uranium Using Glyoxal Bis-(2-Hydroxyanil). **Alcidio Abrão** 437

Rapid Gas Chromatographic Analysis of Fractional Microgram Concentrations of Lebaycid. **B. J. Gudzinowicz** 439

Aids for the Analytical Chemist

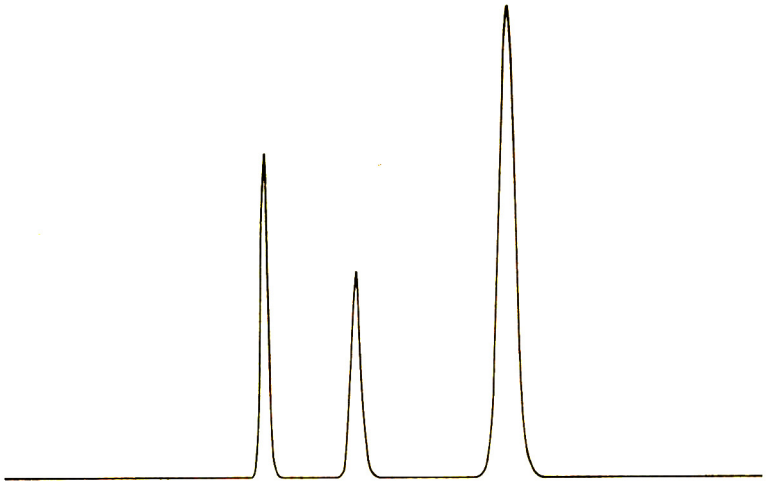
Quartz Window Cuvette Prepared by Sealing Quartz to Borosilicate Glass. **W. T. Roubal** 440

A Scanning Potentiostat. **K. I. Wood** 442

Powdered Sugar Adsorbent for Detection of Chlorophyll Components in Thin Layer Chromatography. **Marvel-Dare Nutting, Martin Voet, and Robert Becker** 445

Variable-Speed, Motorized Buret for Rapid, Semi-automatic Neutralization of Small Volumes. **L. F. Ebell** 446

Simultaneous Dual Column Gas Chromatographic Modification. **B. M. Mitzner and W. V. Jones** 447



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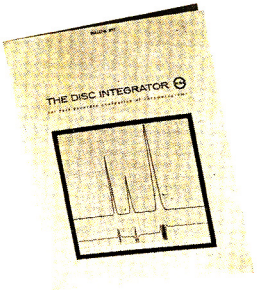

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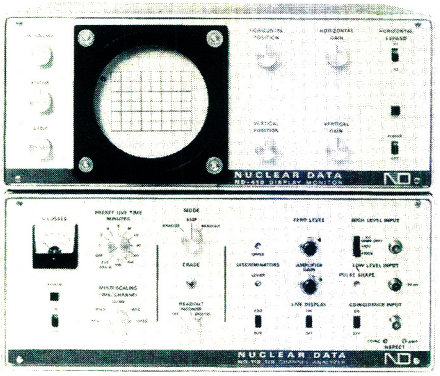

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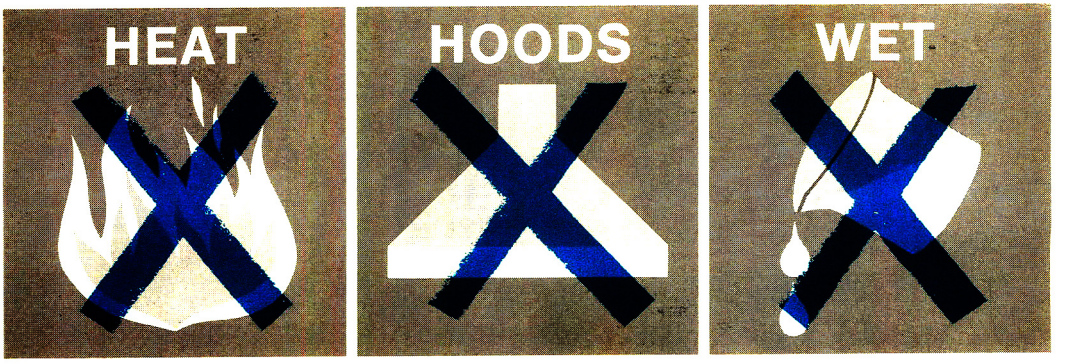

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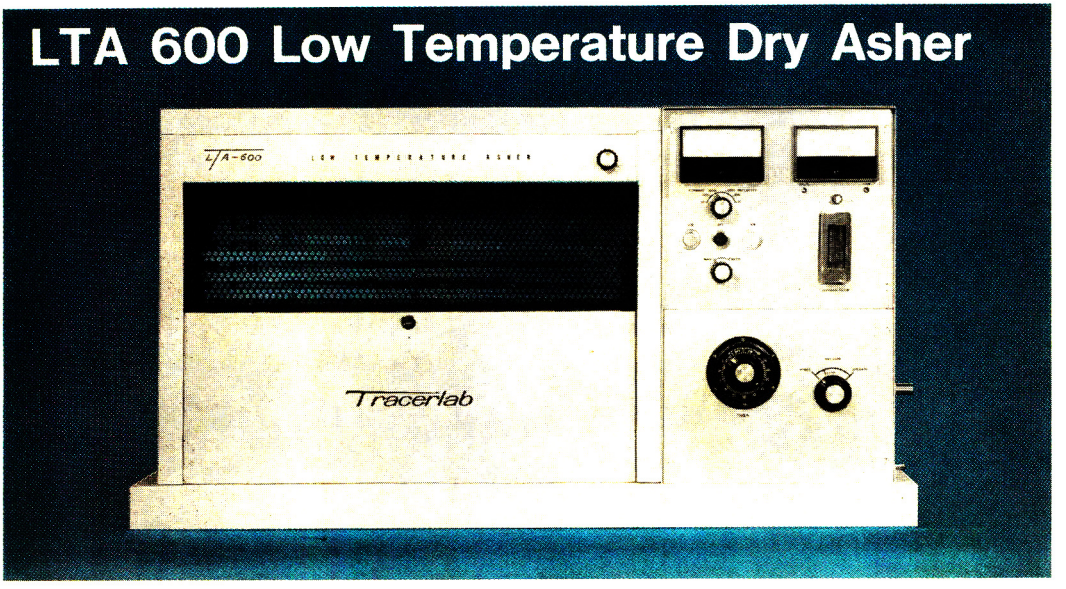

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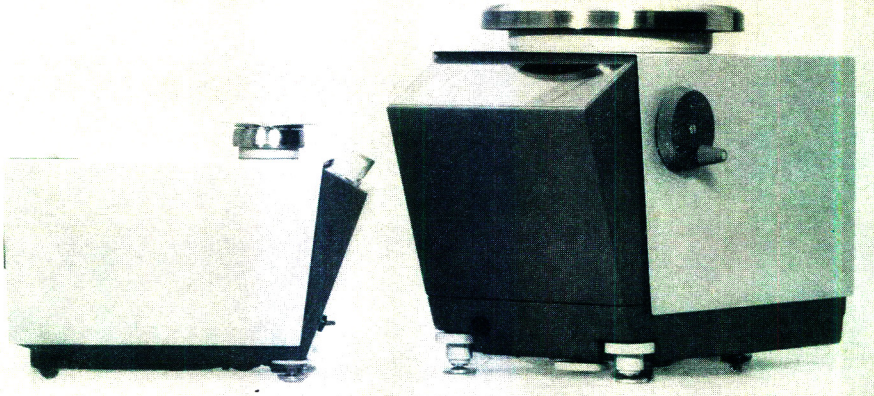

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AC BRIEFS

Highlights of the scientific and technical articles in this issue

Generalized Chronopotentiometric Potential-Time Equations and Their Application to Quasi-Reversible Processes

A general potential-time relationship for quasi-reversible, first order electrode reactions without kinetic complications has been considered. Previously attention has been focused on completely reversible and/or completely irreversible processes.

LARRY B. ANDERSON, and DANIEL J. MACERO, Department of Chemistry, Syracuse University, Syracuse, N. Y.

Anal. Chem. 37, 322 (1965)

An Instrument for Cyclic Voltammetry

This paper describes an instrument which makes use of operational amplifiers, but which incorporates all-electronic D.C. coupled switching to achieve increased versatility in operation. Also, a sampling device is described which permits exclusion of charging current when fast sweeps are used.

CHARLES K. MANN, Department of Chemistry, Florida State University, Tallahassee, Fla. 32306

Anal. Chem. 37, 326 (1965)

Digital Computer Program for Calculation of Molecular Formulae

A digital computer program which is written in FORTRAN for use with the IBM 1620 calculates and prints all molecular formulae that correspond to a given elemental percentage composition.

D. A. USHER, J. ZANOS GOUGOUTAS, and R. B. WOODWARD, The Chemistry Department, Harvard University, Cambridge, Mass.

Anal. Chem. 37, 330 (1965)

Continuous Titrations with a Tubular Mercury–EDTA Electrode

The continuous potentiometric titrator has been adapted to chelometric titrations with EDTA. A mercury coated tubular platinum electrode (MTPE) has been used rather than the mercury drop or pool types that have been used previously.

W. J. BLAEDEL, and R. H. LAESSIG, Department of Chemistry, University of Wisconsin, Madison, Wis. 53706

Anal. Chem. 37, 332 (1965)

Controlled-Potential Coulometric Titration of Uranium(VI) in Aqueous Solutions of Sodium Fluoride

Conditions were established for the quantitative controlled-potential coulometric reduction of U(VI) in aqueous solutions of NaF, and possible interferences were checked. The method was applied to a number of synthetic reactor-fuel dissolver solutions.

W. R. MOUNTCASTLE, Jr., LOUISE B. DUNLAP, and P. F. THOMASON, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Anal. Chem. 37, 336 (1965)

Determination of Uranium and Americium-Curium in Urine by Liquid Ion Exchange

Liquid ion exchange has been used for determination of actinide elements. Di-2-ethylhexyl phosphoric acid (HDEHP) and triisooctylamine (TIOA) were used to develop analytical techniques for the actinides Th through Cm.

F. E. BUTLER, Savannah River Plant, E. I. du Pont de Nemours and Co., Aiken, S. C.

Anal. Chem. 37, 340 (1965)

Rapid and Nondestructive Analysis of Sulfur and Calcium by Radioactivation and Photoneutron Counting

A method based on the counting of photoneutrons in deuterium is applied to the analysis of sulfur and calcium. No chemical processing is required—only a simple and versatile apparatus is used.

SAADIA AMIEL and J. O. JULIANO, Nuclear Chemistry Department, Soreq Research Estabishment, Atomic Energy Commission, Yavne, Israel

Anal. Chem. 37, 343 (1965)

Application of Galvanic Cell to Measurement of Oxygen-Consuming Enzyme Systems

The tyrosinase oxidation of tyrosine to dopachrome was studied with the galvanic cell, the Warburg, and a spectrophotometer, and the data obtained are compared. The limits of accuracy, sensitivity, and reproducibility of the galvanic cell application were studied.

HARRY LIPNER, L. R. WITHERSPOON, and ANNE WAHLBORG, Departments of Biological Science and Chemistry, Florida State University, Tallahassee, Fla.

Anal. Chem. 37, 347 (1965)

Decay of Cesium-137 Determined by Absolute Counting Methods

Since Cs^{137} is an important long-lived fission product and a useful γ-ray standard, there has been a demand for accurate measurements of its radioactivity. A new and more precise value for the 662 k.e.v. γ-ray abundance and a value for the β-branching ratio to the 662 k.e.v. level in Ba^{137} are reported.

JANET S. MERRITT and J. G. V. TAYLOR, Chalk River Nuclear Laboratories, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada

Anal. Chem. 37, 351 (1965)

Coupled Reaction System for Determination of Transaminase Enzymes. Application to Glutamic Oxaloacetic Transaminase

The automation of the determination of glutamic oxaloacetic transaminase (GOT) by a coupled reaction system is described. The method should be applicable to determination of many other transaminase activities.

G. P. HICKS, and W. J. BLAEDEL, Departments of Medicine and Chemistry, University of Wisconsin, Madison, Wis.

Anal. Chem. 37, 354 (1965)

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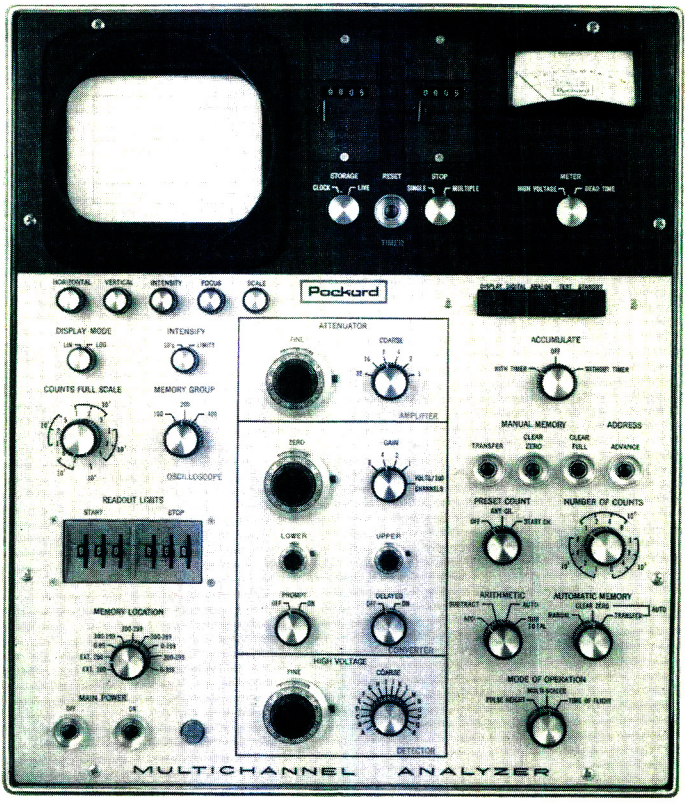

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Preconcentration of Trace Elements by Precipitation Ion Exchange

A new approach minimizes the restrictive selectivity of column ion exchange, yet preserves a number of its advantages. This is accomplished by immobilization of the matrix on the column by precipitation, followed by the nonselective elution of as many of the elements as possible before dissolution of the precipitate.

FOUAD TERA, R. R. RUCH, and G. H. MORRISON, Department of Chemistry, Cornell University, Ithaca, N. Y.

Anal. Chem. 37, 358 (1965)

Solvent Extraction Equilibria of Certain 8-Quinolinols and Their Zinc(II) Chelates

The analytical advantages of the use of 2-methyl-8-quinolinol in the extraction and subsequent determination of zinc(II) are outlined, and equilibrium distribution ratios have been determined for the extraction of zinc(II) with quinolinols into chloroform as a function of pH and concentration.

FA-CHUN CHOU, QUINTUS FERNANDO, and HENRY FREISER, Department of Chemistry, University of Arizona, Tucson, Ariz.

Anal. Chem. 37, 361 (1965)

Determination of Tin in Hydrogen Peroxide Solutions by Atomic Absorption Spectrometry

A sample containing 45% or less of hydrogen peroxide is injected into an oxyhydrogen flame and absorption of the tin 2863-A. line by the tin atoms in the flame is measured. The tin concentration is obtained by reference to a calibration curve.

E. J. AGAZZI, Shell Development Co., Emeryville, Calif.

Anal. Chem. 37, 364 (1965)

Determination of Azide Ion by Hydrogen Ion Titration after Oxidation with Nitrite

The method presented here overcomes previous difficulties in the analysis of azide ion. It is based upon the stoichiometric consumption of two hydrogen ions for each azide ion oxidized by nitrile.

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

Anal. Chem. 37, 366 (1965)

Wickbold Combustion and Spectrophotometric Analysis Procedure for Trace Amounts of Organic Chlorine in Viscous Polybutene Polymers

The Wickbold apparatus is well suited for trace chlorine analysis because of good combustion characteristics, high sample introduction rate, and isolation from atmospheric contaminants. The colorimetric procedure used here depends on the formation of the stable ferric thiocyanate complex.

RICHARD D. ROWE, Cosden Oil & Chemical Co., Box 1311, Big Spring, Texas

Anal. Chem. 37, 368 (1965)

Spectrophotometric Determination of Pentaborane with Pyridine. Application to Air Analysis

Pentaborane and pyridine associate in a hydrocarbon solvent to form a soluble yellow-colored adduct, and the absorbance of this adduct is proportional to the pentaborane concentration.

HARRY G. OFFNER, Rocketdyne, A Division of North American Aviation, Inc., Canoga Park, Calif.

Anal. Chem. 37, 370 (1965)

Study of the Pi Complexes of 2,4,7-Trinitrofluorenone with Phenols, Aromatic Hydrocarbons, and Aromatic Amines

The selectivity of certain π-acids as complexing agents has been investigated. The size and number of rings are important factors that have been discussed.

GEORGE H. SCHENK, PATRICIA W. VANCE, JOHANNA PIETRANDREA, and CAROLYN MOJZIS, Department of Chemistry, Wayne State University, Detroit, Mich. 48202

Anal. Chem. 37, 372 (1965)

Isolation and Identification of Alcohols in Cold-Pressed Valencia Orange Oil By Liquid-Liquid Extraction and Gas Chromatography

This paper describes the isolation of alcohols from cold-pressed orange oil using a nonaqueous extraction procedure followed by separation by gas chromatography and spectrometric identification. The nonalcoholic materials were removed from the alcohol fraction by column chromatography.

G. L. K. HUNTER, and M. G. MOSHONAS, Fruit and Vegetable Products Laboratory, Winter Haven, Fla.

Anal. Chem. 37, 378 (1965)

Gas Chromatographic Determination of Free Formic and Acetic Acids in Cigarette Smoke

Free formic and acetic acids in complex mixtures containing formates and acetates can be determined by adsorption onto a strong base anion exchange resin in the fluoride form, followed by methylation and elution from the resin and subsequent separation and determination by gas chromatography.

E. T. OAKLEY, LUDWIG WEISSBECKER, and F. E. RESNIK, Philip Morris Research Center, Richmond, Va.

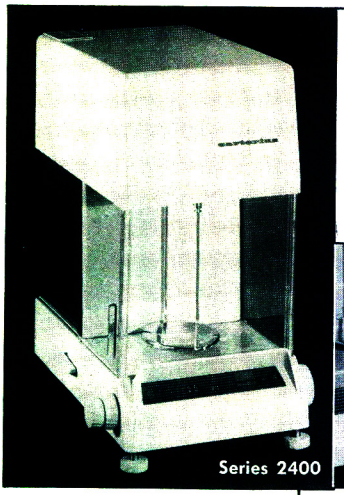
Anal. Chem. 37, 380 (1965)

Quantitative Gas Chromatography of Amino Acids. Preparation of *n*-Butyl *N*-Trifluoroacetyl Esters

This study evaluates the problems involved and the reactions required in the quantitative conversion of amino acids into volatile derivatives suitable for gas liquid chromatographic analysis. Also, a procedure was developed for preparation of *n*-butyl *N*-trifluoroacetyl esters of amino acids for use in chromatographic analysis.

WILLIAM M. LAMKIN and CHARLES W. GEHRKE, Department of Agricultural Chemistry, University of Missouri, Columbia, Mo.

Anal. Chem. 37, 383 (1965)



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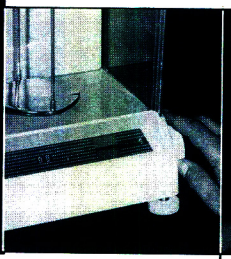

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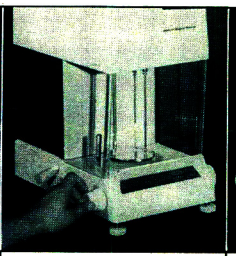

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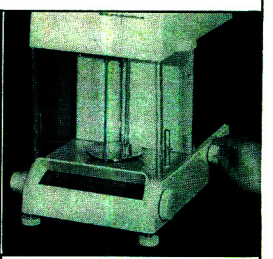

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Manual Tare (Optional)	20g	20g	50g	20g	20g	20g	50g
Optical Range	10g	1g	1g	1g	10g	1g	1g
Optical Tare Range	—	—	—	—	10g	1g	1g
One Optical Scale Division (digital)	100 mg	10 mg	10 mg	10 mg	100 mg	10 mg	10 mg
One Micrometer Division (digital readability)	1 mg	0.1 mg	0.1 mg	(*)	1 mg	0.1 mg	0.1 mg
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The apparent ionization efficiency of the device, which has a noise level of 10^{-12} amp. and a background current of 5×10^{-10} amp., is about 10^{-4}. The linear dynamic range is 10^5. The minimum detectable quantity of propane is 2×10^{-10} gram.

DAVID C. LOCKE and CLIFTON E. MELOAN, Department of Chemistry, Kansas State University, Manhattan, Kan.

Anal. Chem. 37, 389 (1965)

Semiquantitative Determination of Impurities in Bisphenol A by Circular Paper Chromatography

Reversed-phase circular paper chromatography is used to determine the principal impurities in commercial bisphenol A. As little as 0.03% of impurity was detected.

N. H. REINKING and A. E. BARNABEO, Plastics Division, Research and Development Department, Union Carbide Corp., Bound Brook, N. J.

Anal. Chem. 37, 395 (1965)

Aromatic Hydrocarbons Produced during Combustion of Simple Aliphatic Fuels

This is a continuation of previous work concerned with the analysis of products formed during combustion at atmospheric pressure from simple fuels. The current products of interest include benzene and the simple alkyl substituted derivatives.

MITSUGI MUKAI, J. F. THOMAS, and BERNARD D. TEBBENS, University of California, Berkeley, Calif.

Anal. Chem. 37, 398 (1965)

Nuclear Magnetic Resonance Spectra-Structure Correlations for Chlorinated 2,2-Difluoropropanes

The NMR spectra of a series of terminal chlorinated 2,2-difluoropropanes have been studied. Proton-fluorine coupling constants are found to vary with molecular composition and are related to the proton-fluorine dihedral angle.

HORACE F. WHITE, Research and Development, Chemicals Division, Union Carbide Corp., South Charleston, W. Va.

Anal. Chem. 37, 403 (1965)

Refractive Indices of Sucrose-Water Solutions in the Range from 24 to 53% Sucrose

Measurements were made of the refractive index of sucrose-water solutions in the 22 to 59% sucrose range, and new values are given. The calculation of a five-place sucrose refractive index table now appears possible.

D. F. CHARLES, California and Hawaiian Sugar Refining Corp., Crockett, Calif.

Anal. Chem. 37, 405 (1965)

Condensation Pressure Analyzer and Its Application to Continuous Uranium Hexafluoride Determination

An inexpensive analyzer for determining uranium hexafluoride in gas streams is described. The design basis, a development model, and the application to an automatic plant stream analyzer are presented.

W. S. PAPPAS and C. W. WEBER, Technical Division, Oak Ridge Gaseous Diffusion Plant, Union Carbide Corp., Nuclear Division, Oak Ridge, Tenn.

Anal. Chem. 37, 407 (1965)

Determination of Diphenylhydantoin by Ultraviolet Spectrophotometry

Diphenylhydantoin in blood can be analyzed by conversion to a product which has a high molar absorptivity in the ultraviolet region. Diphenylhydantoin can be determined in the presence of other drugs without preliminary separation.

JACK WALLACE, JOHN BIGGS, and ELMER V. DAHL, Forensic Toxicology Branch, USAF Epidemiological Laboratory, Lackland Air Force Base, Texas

Anal. Chem. 37, 410 (1965)

Scientific Communications

Gas Analysis by X-Ray Fluorescence Emission Spectrometry

C. R. HUDGENS and GEORGE PISH, Monsanto Research Corp., Mound Laboratory, Miamisburg, Ohio

Anal. Chem. 37, 414 (1965)

Analytical Oxidation of Americium with Sodium Perxenate

H. PERRY HOLCOMB, Savannah River Laboratory, E. I. du Pont de Nemours and Co., Aiken, S. C.

Anal. Chem. 37, 415 (1965)

Correspondence

Influence of Electrometer Noise on Limit of Detectability in Atomic Absorption and Atomic Emission Flame Spectrometry

J. D. WINEFORDNER and CLAUDE VEILLON, Department of Chemistry, University of Florida, Gainesville, Fla.

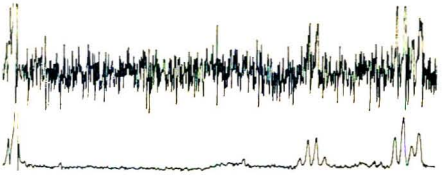
Anal. Chem. 37, 416 (1965)

Spectrophotometric Determination of Iron, Nickel, Copper, and Cobalt in Tungsten and Tungsten Alloys

GEORGE NORWITZ and HERMAN GORDON, Pitman-Dunn Laboratories, Frankford Arsenal, Philadelphia 37, Pa.

Anal. Chem. 37, 417 (1965)

Because becomes



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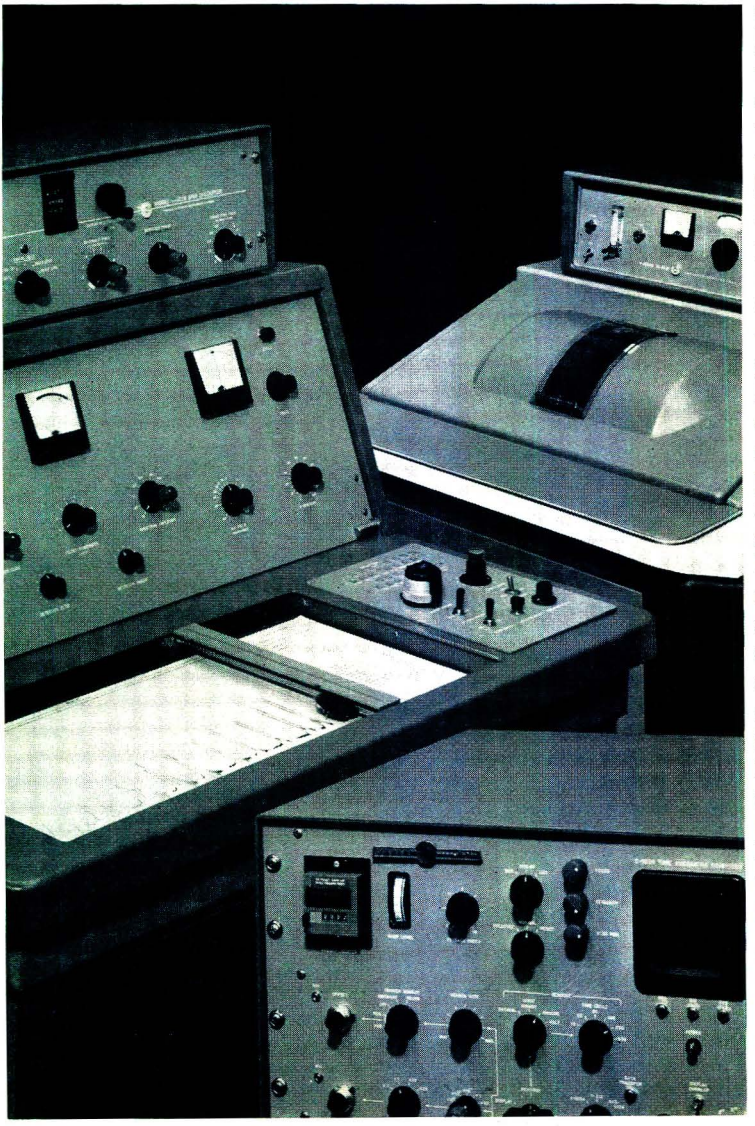

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Rapid Removal of Transuranium Elements from Aqueous Solutions Prior to the Determination of Total Lanthanide Fission Products

FLETCHER L. MOORE and W. THOMAS MULLINS, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Anal. Chem. 37, 419 (1965)

Voltammetric Determination of the Monomethylether of Hydroquinone with a Carbon–Ceresine Wax Paste Electrode

JOHN R. COVINGTON and RENE J. LACOSTE, Rohm & Haas Co., 5000 Richmond St., Philadelphia, Pa.

Anal. Chem. 37, 420 (1965)

Studies of Recovery by Foam Fractionation on 1-Naphthylamine

RUSTOM P. PONCHA and BARRY L. KARGER, Department of Chemistry, Northeastern University, Boston, Mass. 02115

Anal. Chem. 37, 422 (1965)

Ultraviolet Spectrophotometric Determination of Trace Quantities of Phosgene in Gases

W. B. CRUMMETT and J. D. McLEAN, Special Services Laboratory, The Dow Chemical Company, Midland, Mich.

Anal. Chem. 37, 424 (1965)

Use of Highly Acid Supporting Electrolytes in Polarography. Observed Changes in Polarographic Waves of Selenium (IV) upon Standing

GARY D. CHRISTIAN, EDWARD C. KNOBLOCK, and WILLIAM C. PURDY, Division of Biochemistry, Walter Reed Army Institute of Research, Washington, D. C. 20012, and Department of Chemistry, University of Maryland, College Park, Md. 20742

Anal. Chem. 37, 425 (1965)

Modification of Ferrous Ion Reduction Method for Nitroglycerin

R. S. LAMBERT and R. J. DUBOIS, Hercules Powder Co., Bacchus Works, Magna, Utah

Anal. Chem. 37, 427 (1965)

Fluorescence of the Aluminum [1-(2-Pyridylazo)-2-Naphthol] Complex

J. G. SURAK, M. F. HERMAN, and D. T. HAWORTH, Department of Chemistry, Marquette University, Milwaukee, Wis. 53233

Anal. Chem. 37, 428 (1965)

Switching Circuitry for Fast Chronopotentiometry

R. A. OSTERYOUNG, North American Aviation Science Center, 1049 Camino dos Rios, Thousand Oaks, Calif.

Anal Chem. 37, 429 (1965)

An Improved Method for Determination of Selenium in Biological Material

LAURENCE M. CUMMINS, JOHN L. MARTIN, and DALE D. MAAG, Department of Chemistry, Colorado State University, Fort Collins, Colo.

Anal. Chem. 37, 430 (1965)

Use of In Situ Reactions for Characterization of Alcohols and Glycols by Nuclear Magnetic Resonance

V. W. GOODLETT, Research Laboratories, Tennessee Eastman Co., Division of Eastman Kodak Co., Kingsport, Tenn.

Anal. Chem. 37, 431 (1965)

Mass Spectrometric Differential Thermal Analysis

HORST G. LANGER, ROLAND S. GOHLKE, and DENNIS H. SMITH, The Dow Chemical Co., Eastern Research Laboratory, Framingham, Mass.

Anal. Chem. 37, 433 (1965)

Determination of Americium-243 by Separation and Counting of Neptunium-239 Daughter

CYRIL J. BANICK, Savannah River Laboratory, E. I. du Pont de Nemours and Co., Aiken, S. C.

Anal. Chem. 37, 434 (1965)

Mass Spectrometer Used as Detector and Analyzer for Effluent Emerging from Capillary Gas Liquid Chromatography Column

RAGNAR RYHAGE, STEN WIKSTROM, and G. R. WALLER, Laboratory for Mass Spectrometry, Karolinska Institutet, Stockholm 60, Sweden

Anal. Chem. 37, 435 (1965)

Molybdenum(V)—Thiocyanate Complex Extracted into Chloroform

ORLAND W. KOLLING, Department of Chemistry, Southwestern College, Winfield, Kan. 67156

Anal. Chem. 37, 436 (1965)

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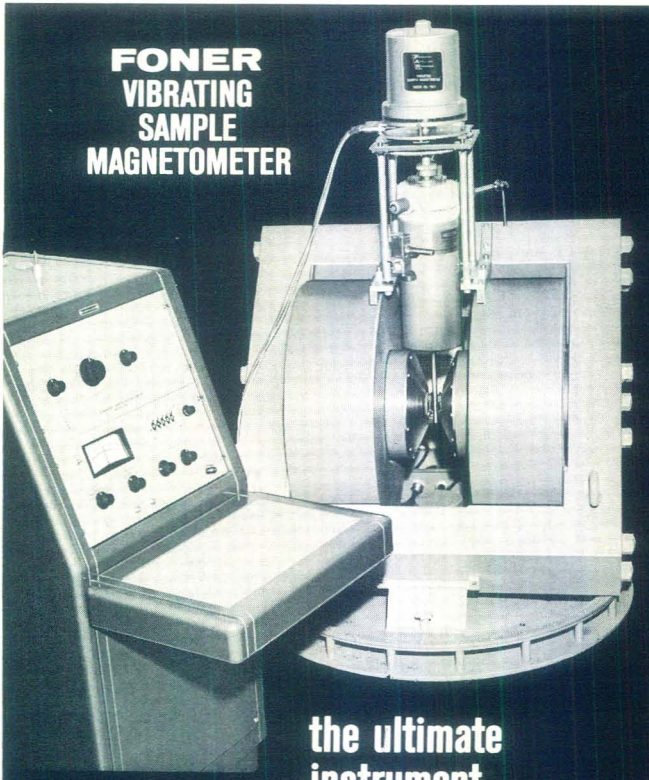
FONER VIBRATING SAMPLE MAGNETOMETER



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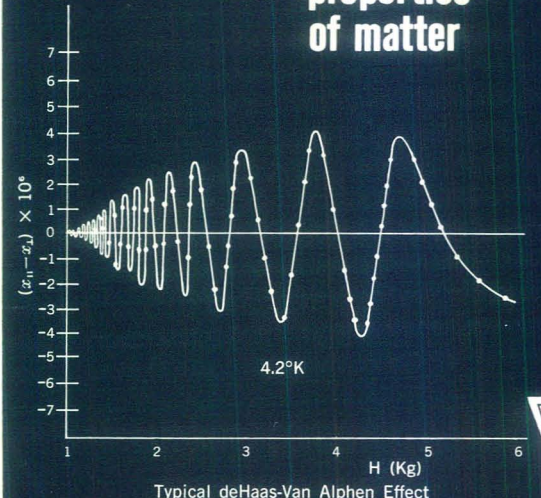

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BRIEFS

Spectrophotometric Determination of Calcium in Uranium Using Glyoxal Bis-(2-Hydroxyanil)

ALCÍDIO ABRÃO, Radiochemistry Division, Instituto de Energia Atomica, Sao Paulo, Brazil

Anal Chem. 37, 437 (1965)

Rapid Gas Chromatographic Analysis of Fractional Microgram Concentrations of Lebaycid

B. J. GUDZINOWICZ, Jarrell-Ash Co., 590 Lincoln Street, Waltham, Mass.

Anal. Chem 37, 439 (1965)

Aids for the Analytical Chemist

Quartz Window Cuvette Prepared by Sealing Quartz to Borosilicate Glass

WM. T. ROUBAL, U. S. Bureau of Commercial Fisheries and The Department of Food Science and Technology, University of California, Davis, Calif.

Anal. Chem. 37, 440 (1965)

A Scanning Potentiostat

K. I. WOOD, Division of Protein Chemistry, C.S.I.R.O., Wool Research Laboratories, Parkville N2, Melbourne, Victoria, Australia

Anal. Chem. 37, 442 (1965)

Powdered Sugar Adsorbent for Detection of Chlorophyll Components in Thin Layer Chromatography

MARVEL-DARE NUTTING, MARTIN VOET, and ROBERT BECKER, Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Albany, Calif. 94710

Anal. Chem. 37, 445 (1965)

Variable-Speed, Motorized Buret for Rapid, Semiautomatic Neutralization of Small Volumes

LORNE F. EBELL, Department of Forestry of Canada, Victoria, British Columbia

Anal. Chem. 37, 446 (1965)

Simultaneous Dual Column Gas Chromatographic Modification

BERNARD M. MITZNER and WALTER V. JONES, International Flavors & Fragrances, 521 West 57th St., New York, N. Y. 10019

Anal. Chem. 37, 447 (1965)

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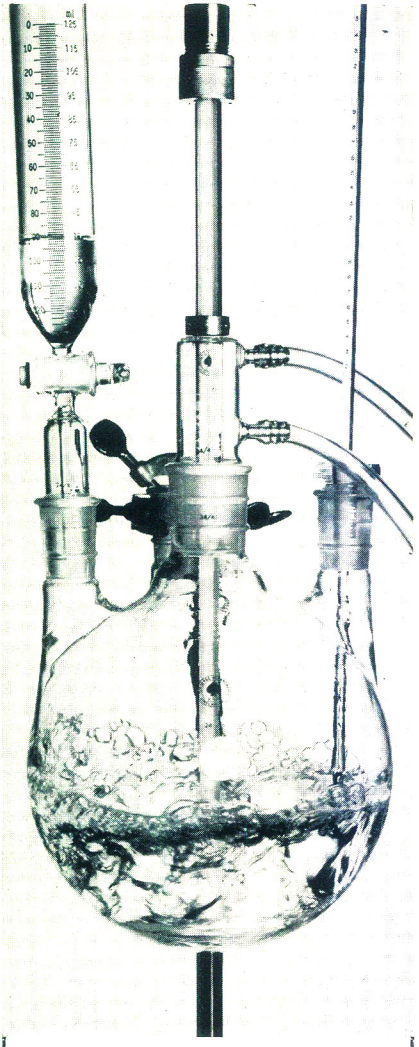

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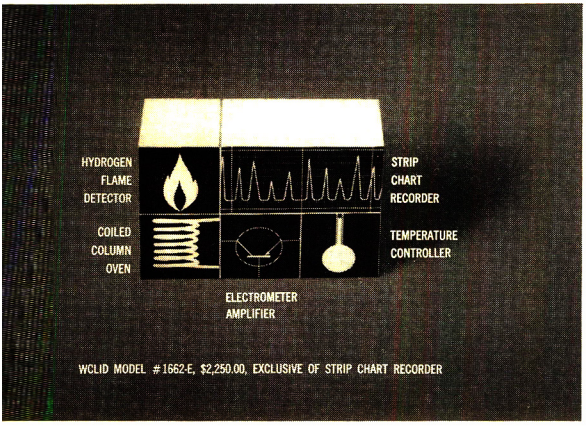

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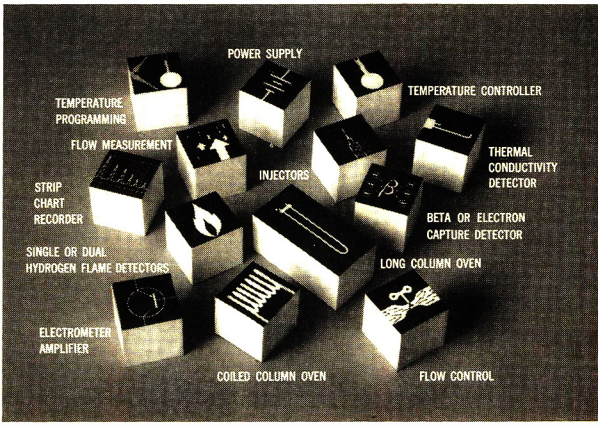

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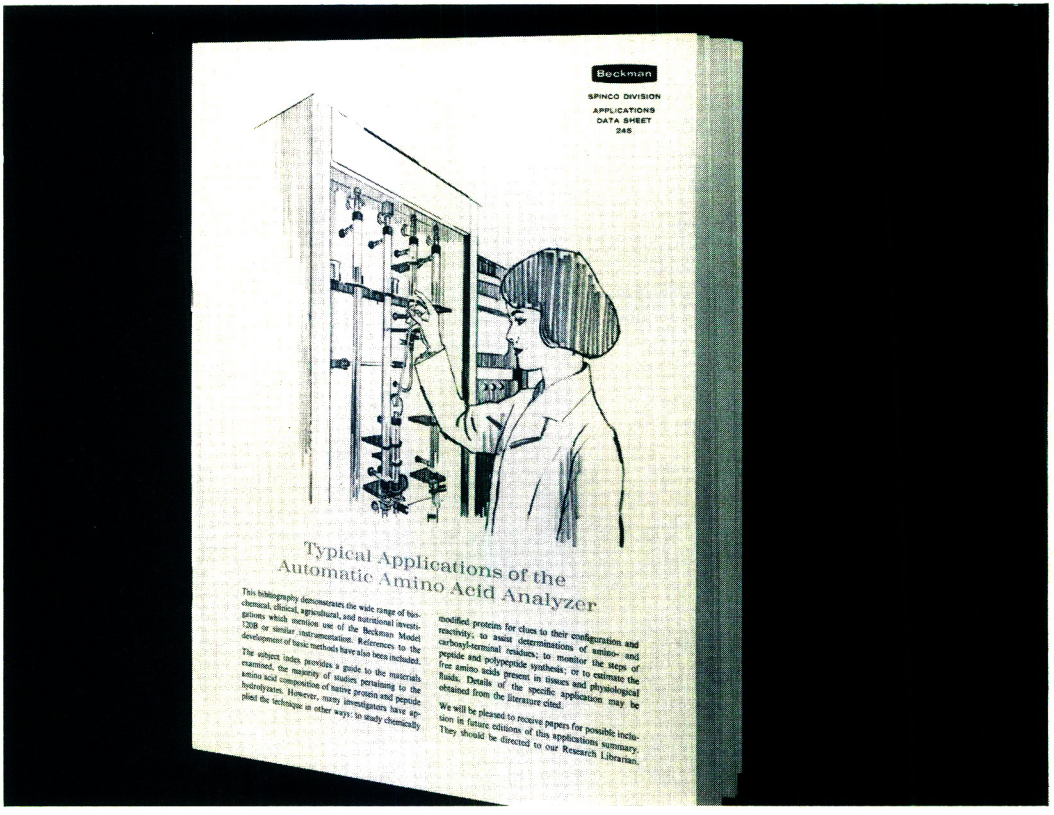

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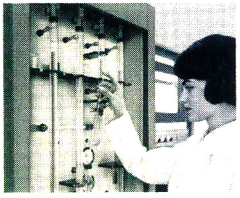

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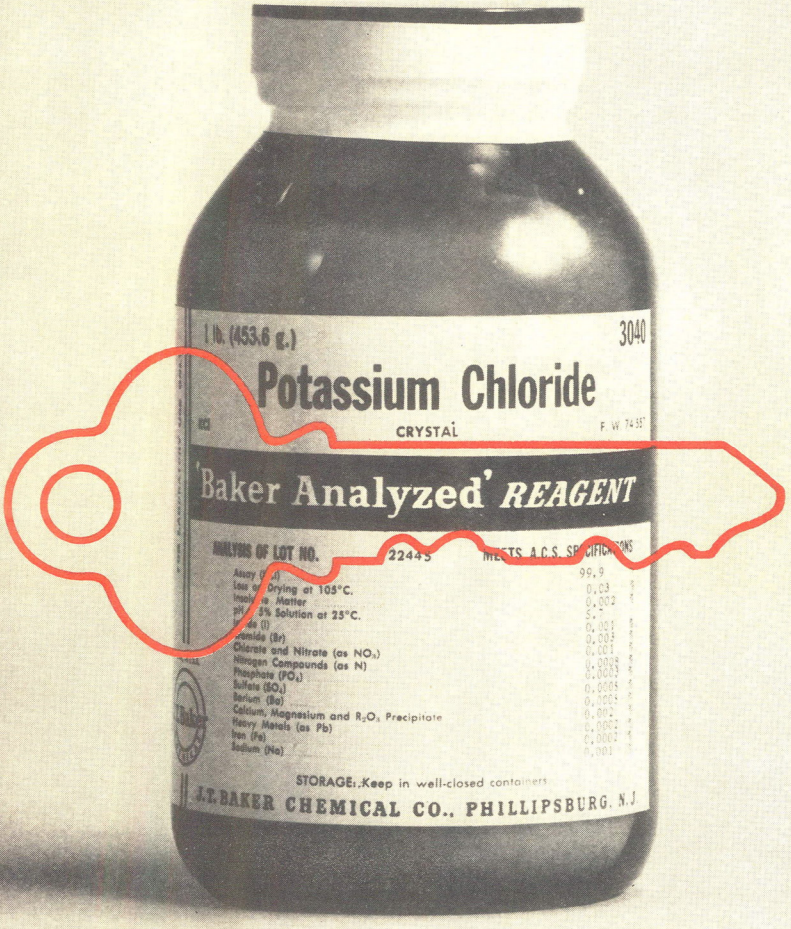

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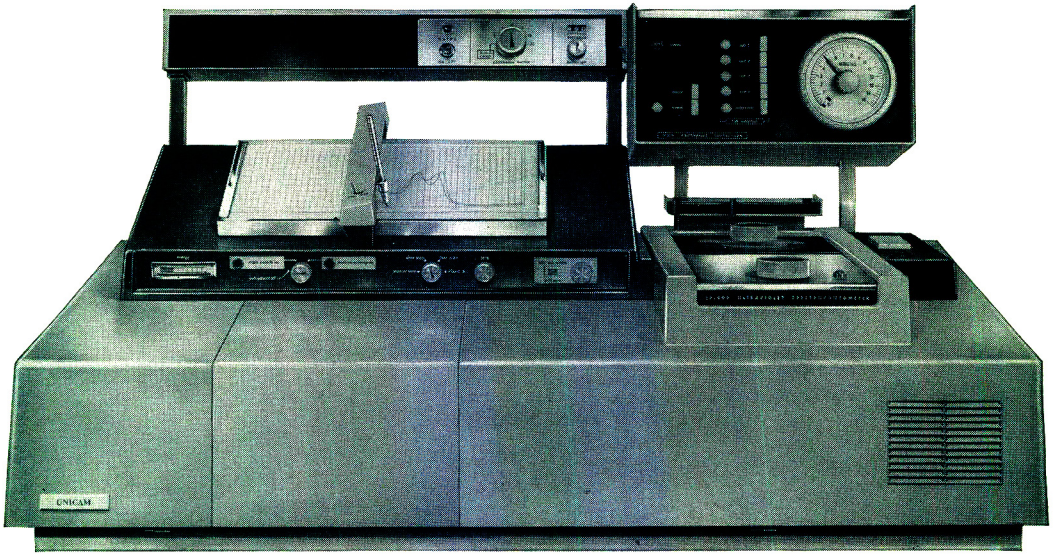

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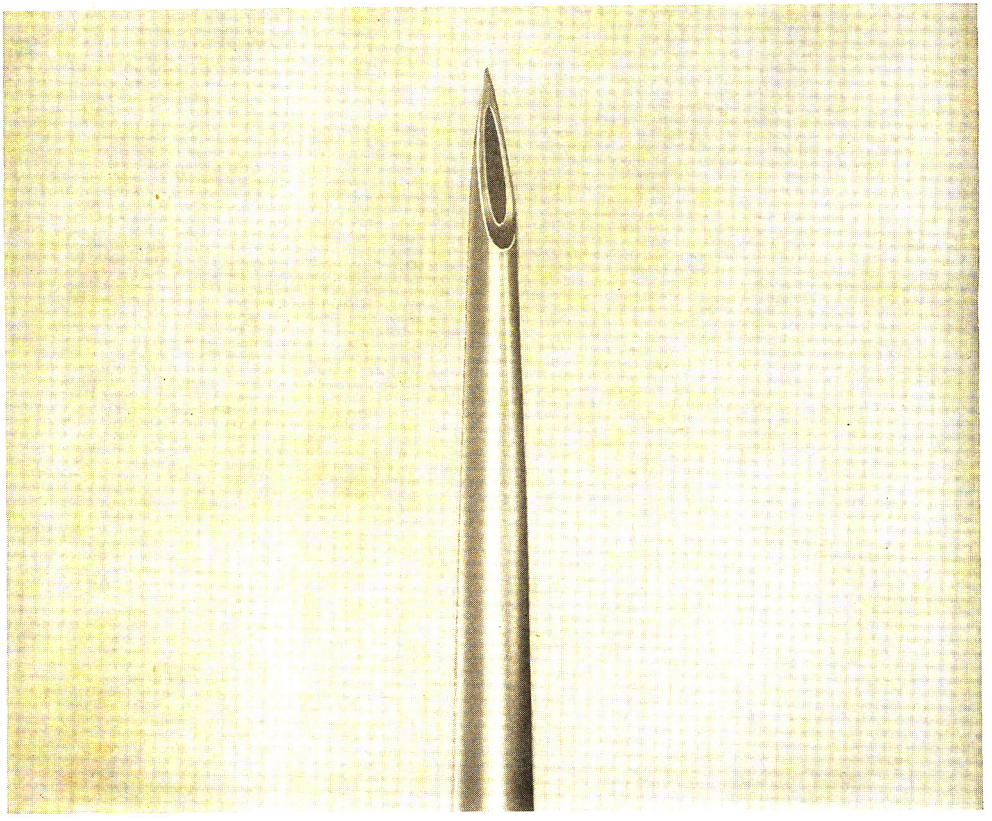

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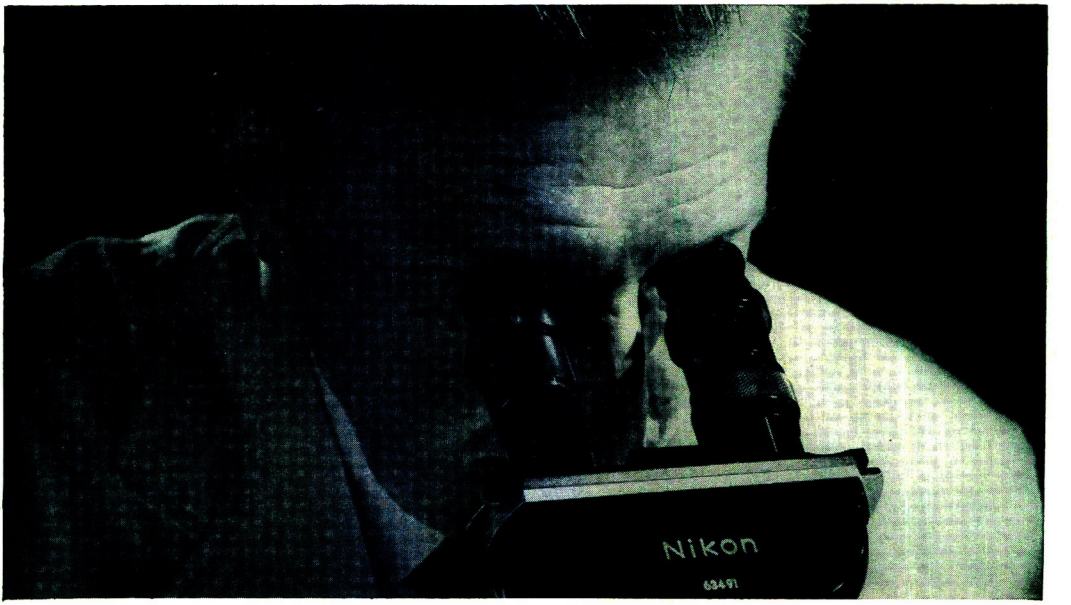

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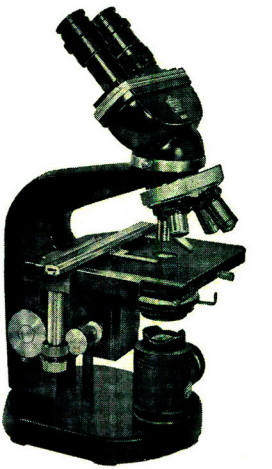

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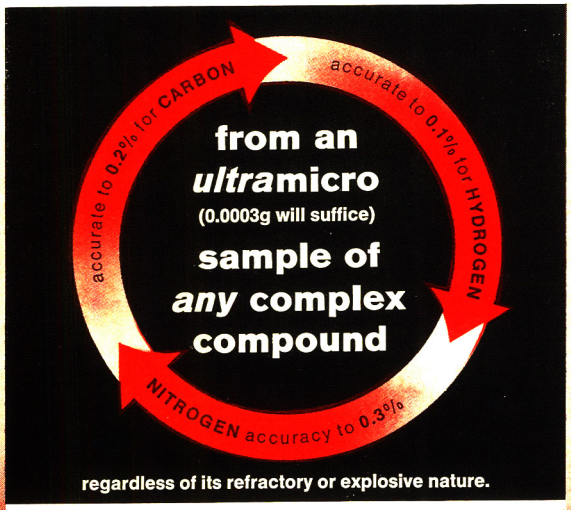

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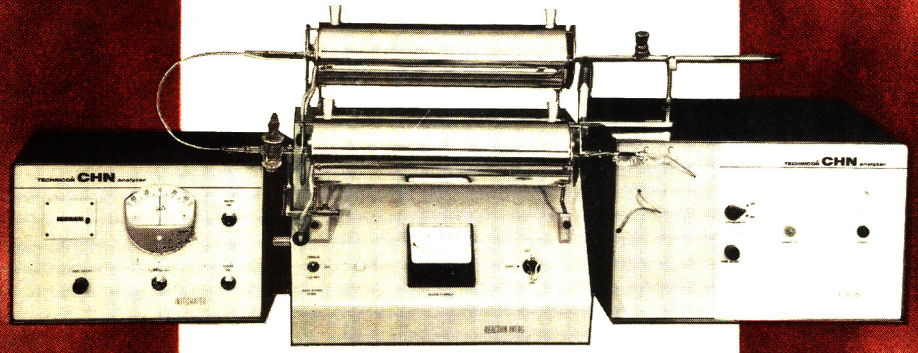

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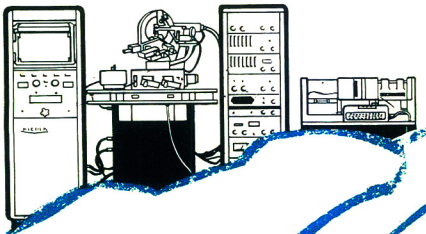

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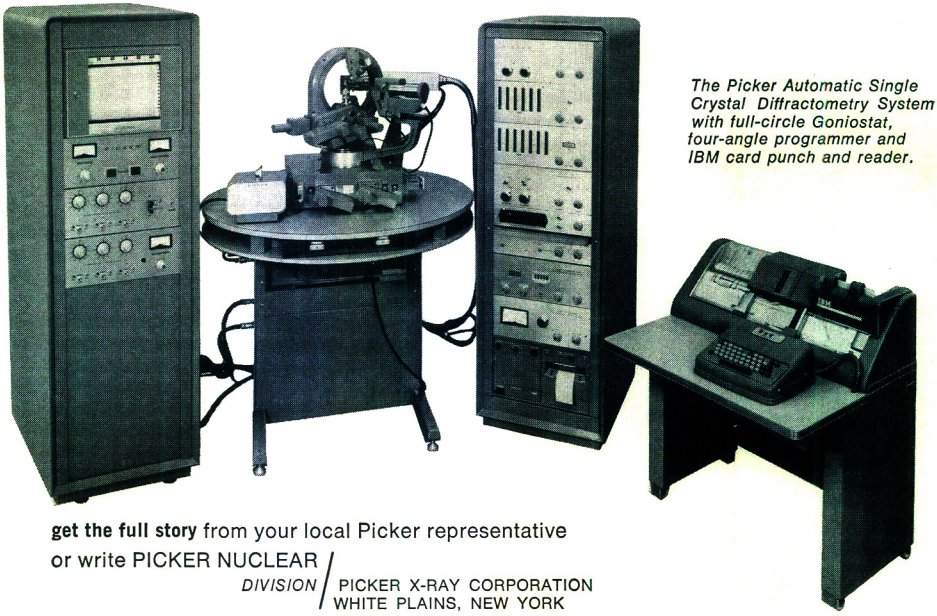

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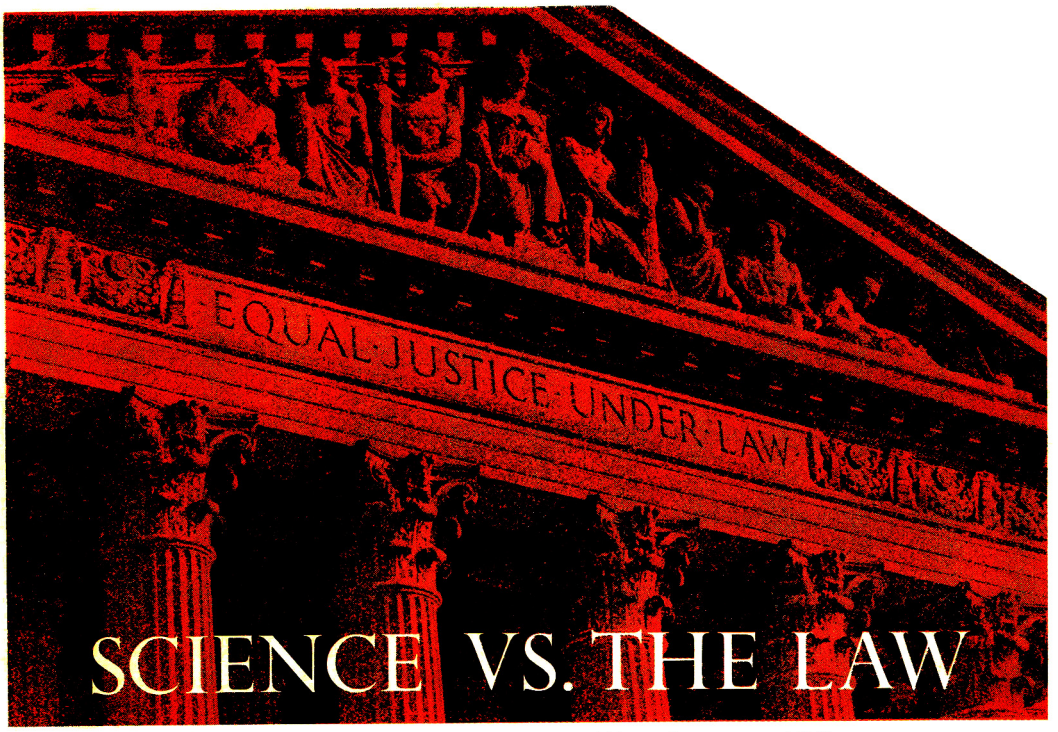

SCIENCE VS. THE LAW

by **Daniel T. Dragel,** *Director of the Crime Laboratory, Chicago Department of Police*

OVER THE YEARS THE METHODS OF LAW ENFORCEMENT and crime detection have undergone a gradual awakening to the benefits of scientific methods. A new branch of science has emerged—Dr. Paul Kirk of the University of California, who has been a leading figure in its development, has called it "criminalistics." It has been defined as "that profession and scientific discipline directed to the recognition, identification, individualization, and interpretation of physical evidence through application of the natural sciences and science matters."

Although criminalistics is not analytical chemistry, these sciences are closely allied by virtue of the sameness of instruments and methods. New methods have accelerated and heightened the importance of the scientific evidence presented before courts of law: neutron activation analysis, pyrolysis coupled with gas chromatography, and zone electrophoresis are examples. Thus, over a period of time chemists have been drawn more closely into the drama of courtroom life.

In the investigation of crime a decade or two ago, a confession was of utmost importance in the establishment of guilt. This was based, of course, on the premise that a person in full possession of his faculties would not confess to a crime which he did not commit, and thus sacrifice his life, his liberty, or his property. However, in the present day the use of confessional evidence is being seriously challenged because of the expressions of the Supreme Court of the United States. The Court has abandoned the old test of voluntariness and trustworthiness and has moved toward the arbitrary exclusion of confessions on purely technical grounds. Law enforcement, therefore, has found it necessary to adjust its methods by substituting scientific physical evidence for confessional evidence when possible.

Does the chemist actually enter the legal aspects of a criminal case in the establishment of the corpus delicti? This is not infrequent. Does the chemist in effect interpret the law in a variety of areas? Of necessity he does in relation to fireworks statutes, degrees of intoxication, arson, and narcotics cases. Is it the sole duty of the chemist to testify for the prosecution and the people? The chemist has a moral obligation to bring out any matters mitigating in favor of a defendant. When this happens, there is no hesitancy in testifying for the defense.

The courtroom chemist is an unusual breed of expert, since he must be a paragon of courtesy and knowledge. However, his scientific endeavors are critically reviewed by laymen lawyers and judges who have, at the most, only a very rudimentary knowledge of chemistry. Prominent practicing lawyers have made uncomplimentary references in pursuit of this class of experts, such as: "Experts are like radishes—you can buy them by the bunch."

But through ordeal and battle the general chemist and the forensic chemist have gained the recognition of the bench and bar, and their testimony falls within that branch of the law of evidence dealwith expert opinion testimony.

The courts have promulgated certain tests in order to qualify an expert. The test of admissibility of expert testimony is whether the witness' peculiar skill and knowledge, not common to men in general, enable him to draw an inference where men of common experience with all the facts proved would be left in doubt (*New England Glass vs. Lovell, 7 Cush. Mass. 319*).

Occasionally the chemical expert is confronted by a chemical lawyer who has gained some knowledge by enlisting the aid of a consultant. The lawyer may ask that the structural formula for a compound such as methadon hydrochloride be placed on the board. Further, he may ask that the empirical formula be recited from the witness stand. Instead of repeating the statutory definition, 4-4-Diphenyl-6-Dimethylamino-Heptanone-3 Hydrochloride, the witness might recite 4-4-Diphenyl-2-Dimethylamino Heptanone-5 Hydrochloride. On appeal, the court, being unversed in chemical nomenclature, would probably hold that the state failed to identify the narcotic drug as defined in the statute.

Whether or not the proffered expert possesses the necessary qualifications is a decision resting within the discretion of the trial court. Where there has been a futile attempt by the cross-examiner to show a lack of qualifications, the examiner is afforded the opportunity to impugn the witness by showing a motivating interest, error in the observed or assumed facts, error in conclusions or opinions, and specific impeachment by contradictory or inconsistent statements or writings.

To reveal more fully the gross inconsistencies in court decisions that give rise to the conflict between science and the law, a series of cases which were decided by higher courts and which involve various aspects of expert testimony will now be discussed.

Spectroscopy is employed daily in most industrial and research laboratories for the purpose, among others, of control or identification. In the police laboratory, spectroscopy compares and identifies, and helps steer the investigation of crime by illuminating the course of the investigator. But, in the actual trial of the case, if spectroscopy findings are encased in doubt and conjecture, it is not a true scientific tool, and its admission in evidence in a criminal case would not be justified.

A search of the law reveals that spectroscopy entered a murder trial as early as 1886 in a New England case, *Rex vs. Cole*. Some question arose in relation to a stain on a blunt instrument. A chemist testified that the stains on the object were blood stains, and that his determination was based on experiments conducted with a spectroscope. These findings were received in evidence without objection, and no appeal was taken.



Daniel T. Dragel is a Captain of Police with the Chicago Police Department. He has been director of the Scientific Crime Detection Laboratory for the past 5 years, and has been associated with the Department since 1935. He is a graduate of the University of Illinois with a Ph.C. degree in 1932, and of DePaul University, with a LL.B. degree in 1940. He has served on important committees dealing with criminal law for the Illinois Bar Association and the National Safety Council, and has contributed numerous articles on scientific crime detection to leading police and law journals. Mr. Dragel is a member of the American Chemical Society, the American Academy of Forensic Sciences, the F.B.I. National Academy, and the Illinois Bar Association, and is a registered pharmacist in the State of Illinois

It would appear that the ease of admissibility of spectroscopy evidence in this case set a precedent, thus opening the door to all future spectroscopy evidence. However, the progressive path of spectroscopy leading to the courtroom encountered resistance thereafter and its admission in evidence in a criminal proceeding was fought in a lower court, followed by a proceeding in the highest tribunal in the land, the Supreme Court of the United States.

In *Medley vs. U. S. 155 Fed. (2) 857* in 1946, the defendant Medley was indicted for the murder of one Nancy Boyer. The prosecution sought to prove that the bullets taken from the body of Nancy were fired by the defendant. Bullets found in the possession of the defendant had been filed in a fashion similar to those that caused the victim's death. A fingernail file was found on the defendant, which contained particles of metal, and these particles were compared by spectroscopy with the bullets removed from the body. The defendant was convicted on the evidence and he appealed, assigning as error the improper admission of expert testimony.

In support of his argument the defendant contended that the branch of science designated as spectroscopy is so little known that it lacks the degree of certainty to justify its use in a criminal case. The defendant further contended that the case was on equal footing with a polygraph case, *Frye vs. U. S., 293 Fed. 1013*. In that case it was decided that courts will go a long way in admitting expert testimony deduced from a well-recognized scientific principle. However, lie detection has not gained the requisite scientific recognition among authorities to justify its use in court. The Supreme Court affirmed the conviction of Medley and, in so doing, gave recognition to the science of spectroscopy.

In *Hand vs. State, 26 Ala. App. 317*, a murder conviction was set aside by the upper court, thus averting another travesty of justice. A knife was the death instrument

in the case, and testimony by the expert in the trial court was as follows: "There was something on the knife that looked red—I couldn't say that it was blood—I did the best I could—but I could not tell." Obviously the testimony for the state lacked evidential value and would carry no weight with the testimony rendered by the expert. But, additional testimony induced by the prosecuting attorney was as follows: ". . . but a knife similar to this, with a blade a half inch wide and two inches long would have made that wound." The implication of this testimony and its effect upon the jury resulted in a finding of guilty. The expert in his subsequent testimony stated in effect that the red spots which he could not identify as blood in his prior testimony, are now identified as blood because the knife caused the wound. If the defense counsel in the case failed to see the significance of the testimony, the trial court on its own motion should have interrogated the witness in the interest of fair play and justice.

In the case of *State vs. Dunn, 116 La. 532,* the Supreme Court solved some blood problems which, ostensibly, chemists heretofore were unable to solve. The question arose, will fire preclude the identification of human blood? The Court stated that fire will not preclude identification.

It appears that blood or bloodstains were found on a sewing machine in a house destroyed by fire. The State's chemist on the witness stand chemically identified the blood stains, and stated that they were human in origin. The defendant objected to the admission of the testimony and stated that blood on a sewing machine in a house destroyed by fire could not be identified as blood and, further, if the expert could identify the specimen as blood, then his testimony was inadmissible because the tests performed on the exhibits were not made under similar conditions, i.e., in a burning building. According to the defense counsel in this case we must assume that it was incumbent upon the state to place an expendable chemist in a burning house to conduct tests on blood during the conflagration!

A recent narcotic case, *People vs. Lott, 181 N.E. (2) 112,* decided by the Supreme Court of Illinois, casts some doubt on the ability of the courts to interpret scientific testimony in relation to the morphology of marihuana.

A trial court found the defendant Lott guilty of the sale of marihuana cigarettes. Lott was sentenced to a term of not less than ten years and not more than ten years and a day, and he brought a writ of error contending that the articles sold were not composed of a narcotic drug under the statute.

The Supreme Court of Illinois reversed the decision of the trial court, holding that the defendant was not guilty of unlawful sale of narcotics where contents of the cigarettes allegedly sold were mature portions of the cannabis plant. The statute relied upon by the court, Ill. Rev. Stat. 1959, Chap. 38, par. 192.28-2.17 reads: "Cannabis includes all parts of the plant Cannabis Sativa L., commonly known as marihuana, . . . , but shall not include the mature stalks of such plant . . ."

It is readily apparent from a reading of the applicable statute that mature stalks are excluded from the operation of the Act, or that mature stalks of marihuana are not marihuana within the meaning of the Act.

The People's chemist testified on direct examination that microscopic and chemical tests were performed on the exhibits. On cross examination the chemist testified that the exhibits were mature portions of the marihuana plant. Mature portions of the marihuana plant may well consist of fragments of mature stalks, but, for the most part, mature portions of the marihuana plant consist of leaves, flowering tops, and fruits (seeds) which are not excluded from the operation of the Act.

Thus the question arises, did the Supreme Court of Illinois, in the interpretation of expert testimony as applied to the law of the case, intend the natural meaning conveyed by its decision? If the court did so intend, then in criticism one is prone to state that the court was somewhat confused, its decision

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arbitrary and without legal precedent, and contrary to scientific finding.

In order to place a landmark case in proper perspective, it might be well to lay the groundwork by using as a base a narcotic case decided by the Supreme Court of the United States in *Rochin vs. California, 342 U. S. 165, 1952.* Law enforcement officers entered a room in Los Angeles County and observed two capsules on a nightstand beside a bed. The defendant Rochin seized the capsules and swallowed them. The officers, after a futile attempt to retrieve the capsules, took the defendant to a hospital and requested a doctor to attach a stomach pump. The two capsules were recovered, analyzed, and found to contain morphine. This was the chief evidence against the defendant, and he was convicted. The upper court in the State of California affirmed the conviction.

The Supreme Court of the United States reversed the conviction on the ground that the evidence was obtained by brute force, was offensive to even hardened sensibilities, and thus was a denial of due process of law under the 14th Amendment to the Federal Constitution. The Court added, in part, that in each case due process of law requires an evaluation based on a disinterested inquiry pursued in the spirit of science. . . . .

It appears almost as if the Court wandered aimlessly through the Constitution and finally found an amendment upon which to base its reversal. The Court did not say that the recovery of the capsules was an unreasonable search and seizure under the 4th Amendment, nor did the majority of the Court indicate that the case falls within the self-incrimination clause of the 5th Amendment. However, one justice in a concurring but separate opinion stated that the self-incrimination clause applies not only to oral utterances, but to incriminating real evidence as well.

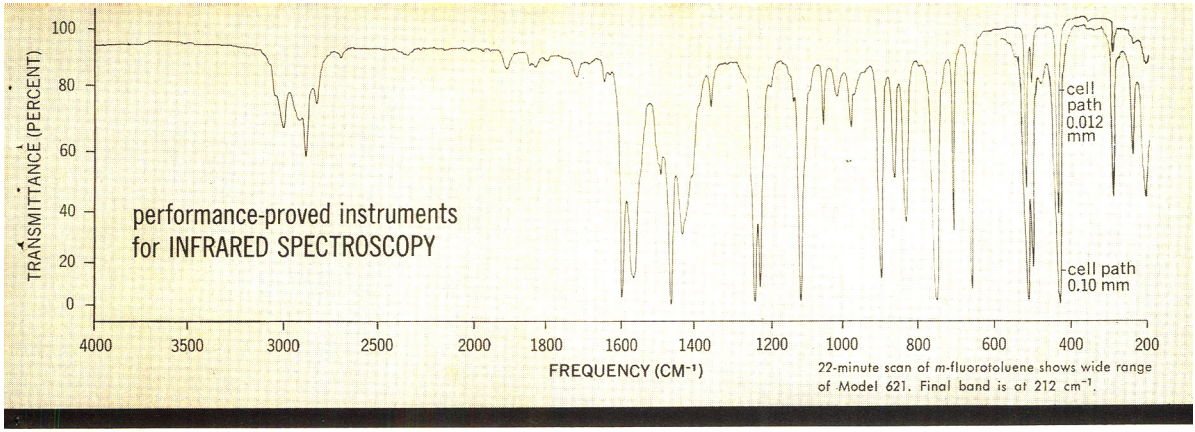
In an endeavor to stay abreast of the high tribunal, let us peruse another Supreme Court case, *Breithaupt vs. Abram, 352 U. S., 432, 1957.* The case went up to the Supreme Court of New Mexico on a writ of habeas corpus and it was dismissed.

Following an accident, the defendant Breithaupt was removed to a hospital and, while unconscious, a blood sample was taken from him by the resident doctor. The alcohol content of his blood was determined by an expert chemist, and the evidence accumulated led to his conviction. The defendant alleged that he was deprived of his constitutional rights by the admission of expert testimony with reference to the analysis of the blood specimen. The defendant further alleged that he was required to give evidence against himself, that the evidence was obtained by unlawful search and seizure, and that he was denied due process of law as outlined in the 14th Amendment. In his brief to the Supreme Court of the United States, the defendant cited the Rochin case. However, in a 6 to 3 decision the Supreme Court *affirmed the conviction of the defendant.*

Chief Justice Warren, a dissenter in the case, stated that invasion of the body, conscious or unconscious, is a denial of due process. Justice Douglas, in a separate dissent, stated that evidence involuntarily obtained should not be admitted; further, that it was repulsive to him for the police to insert needles into unconscious persons (which was not actually done).

It is difficult to reconcile the decision of the Breithaupt case with the decision of the Rochin case. If the principle enunciated in the Rochin case is intended to apply to certain types of cases in which official misconduct offends personal interest and shocks the conscience, then the Breithaupt case properly falls within that category. What could be more shocking than a trespass of one's body in the removal of blood while unconscious?

The decision in the Breithaupt case was handed down some five years after the decision in the Rochin case. May we infer, then, that the Court has renounced its reasoning in the Rochin case and has positioned itself to admit into evidence any incriminating real evidence illegally obtained by state officers? This interpretation is not



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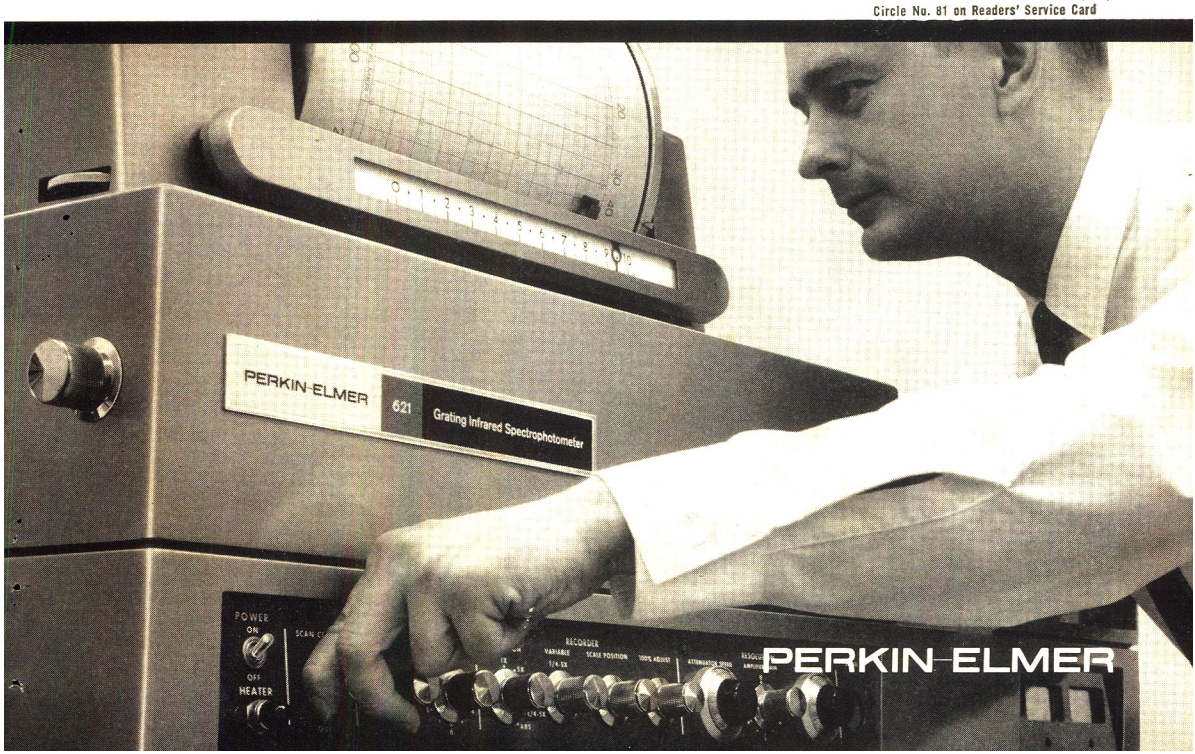

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unreasonable in view of the stain of illegality in the Breithaupt case resulting from an assault and battery upon the body in the form of a venous puncture while unconscious.

In a number of cases thereafter the Court shied away from its holding in the Breithaupt case. Finally, in *Mapp vs. Ohio, 81 Sup. Ct. 1684, 1961,* the Court in clear and crisp language clarified its views with the adoption of the exclusionary rule, a rule applicable to the inadmissibility of illegally obtained evidence and binding upon all state officers: "The exclusionary rule in search and seizure cases holds that the states are now required, by reason of the due process clause, to exclude from state criminal trials evidence seized in violation of the constitutional rights of the accused by state officers."

Would the decision of the Mapp case have retroactive effect and thus bring about a reversal in the Briethaupt case? This question was answered by the majority of the Court in *United States ex rel Linkletter vs. Walker, 323 Fed (2) 11, 1963,* wherein they held against retroactivity. The opinion of the dissenting justice is interesting. He stated that the exclusionary rule is required by the Constitution, and that the Court does not pronounce a new law, but maintains and expounds the old one.

While the rule in Mapp is an unequivocal policy declaration of the Supreme Court of the United States intended to guide and control local law enforcement, law enforcement would probably have been better off without it. This is not to say that law enforcement condones the use of illegally obtained evidence. As a matter of fact it is frowned upon according to the rules of leading police administrators regulating the conduct of police in the administration of criminal justice.

But we should be ever mindful that criminal justice must find its counterpart in justice for the public and the offended. It follows that our courts should be more voluble and proclaim more frequently that due process of law inures to the benefit of all citizenry as well as the individual wrongdoer. END

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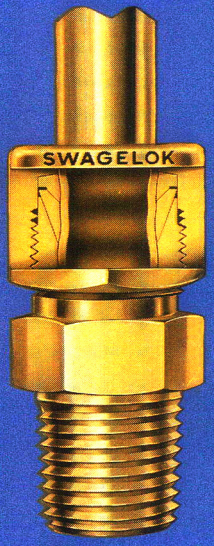

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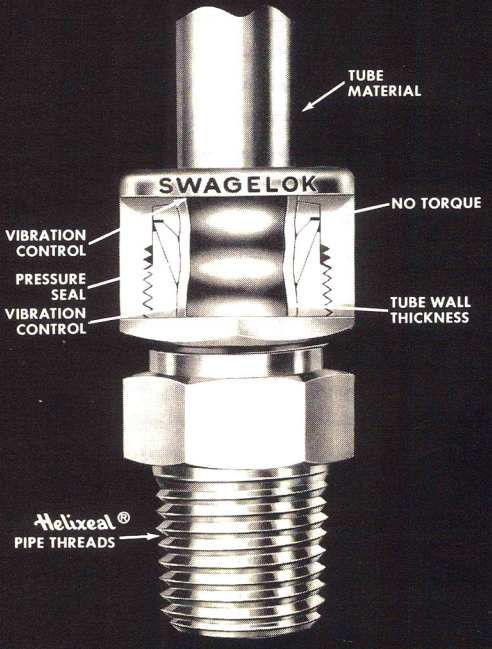

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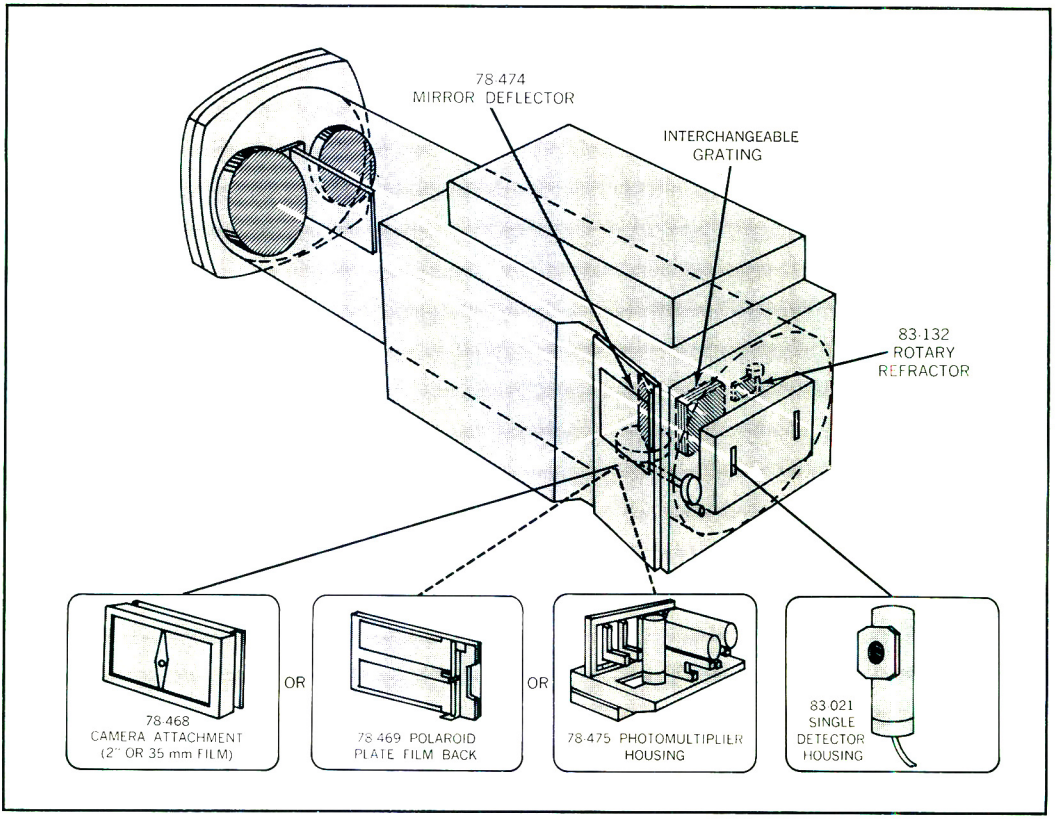

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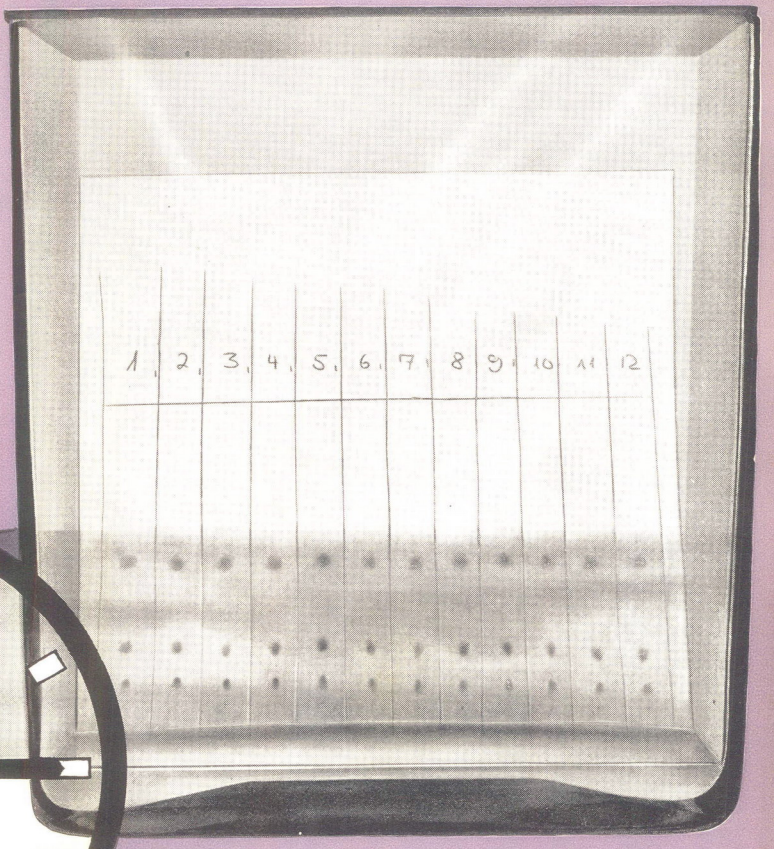

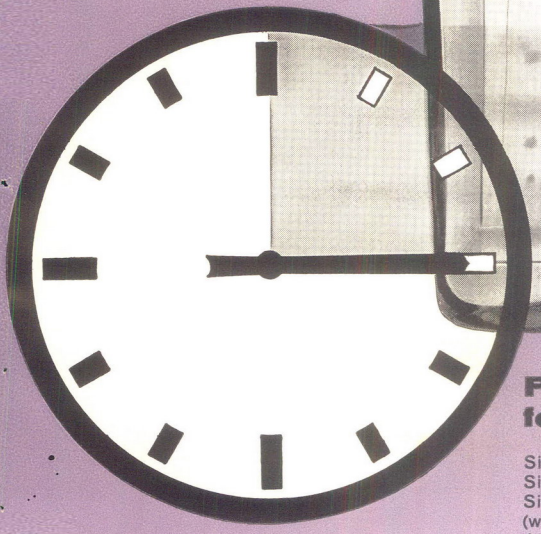

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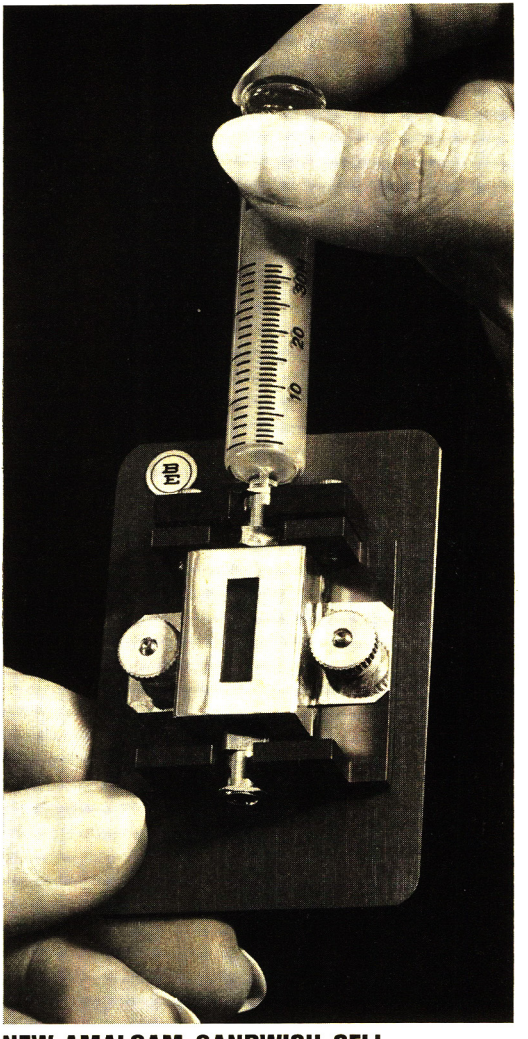

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For Micro Samples

Now in use in hundreds of laboratories, the automated Coleman Model 29 Nitrogen Analyzer is providing rapid, exact results for an almost unlimited range of materials.

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

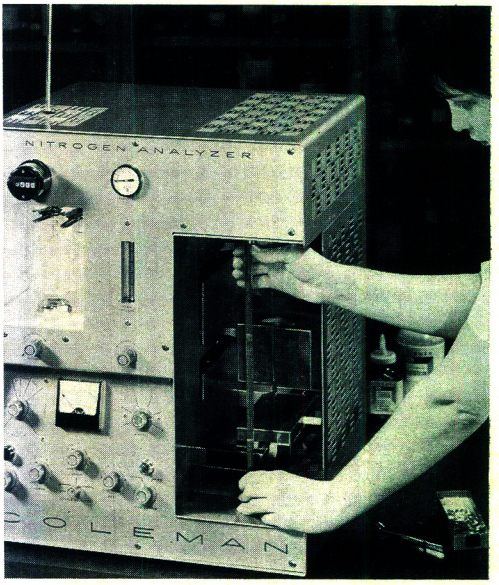
A special extraction technique, announced in a recent issue of ANALYTICAL CHEMISTRY, permits the instrument to be used for trace analysis with materials containing as little as 20 ppm nitrogen.

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

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

Condensed Specifications:
Sample . . . any material that pyrolyzes at temperatures up to 1000° C.
Sample size . . . from 5 to 50 milligrams, generally.
Operating cycle . . . 8 minutes.
Accuracy . . . results correspond to theory ±0.2% nitrogen.
Readout . . . digital counter in microliters.

Ask for Bulletin AB-291



For Larger Samples

Specially designed to meet requirements of materials that require extensive sample preparation before a representative sample can be obtained, the Coleman Model 29A accepts samples up to 500 milligrams. Even larger samples of inorganic materials are analyzed without difficulty.

The instrument is finding wide application in laboratories working with such diverse materials as foods, feeds, grains, soils, fertilizers, milk products, and biological materials.

To accept the larger samples, the instrument incorporates an expanded combustion system, extended combustion cycle, and a larger, modified nitrometer for measurement of the greater volumes of nitrogen. The measurement operation is speeded by a reversible electric motor in the precision syringe-and-micrometer screw adjustment.

The Model 29A minimizes the work formerly required in preparing samples of non-homogeneous materials for microanalysis.

Condensed Specifications:
Sample . . . any material that pyrolyzes at temperatures up to 1000° C.
Sample size . . . 50 up to 500 milligrams; up to one gram or more for inorganic materials.
Operating cycle . . . 12 minutes.
Accuracy . . . results correspond to theory ±0.2% nitrogen.
Readout . . . motor-driven digital counter.

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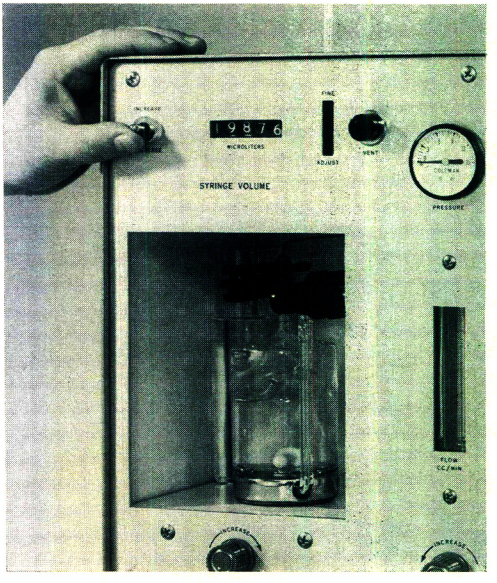

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AUTOMATED ELEMENTAL ANALYZERS for direct oxygen; for carbon-hydrogen

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The Coleman Model 36 Oxygen Analyzer is an automated combustion instrument for the direct determination of oxygen content in liquid and solid materials. Direct determination provides results which are independent of the errors associated with determination by difference.

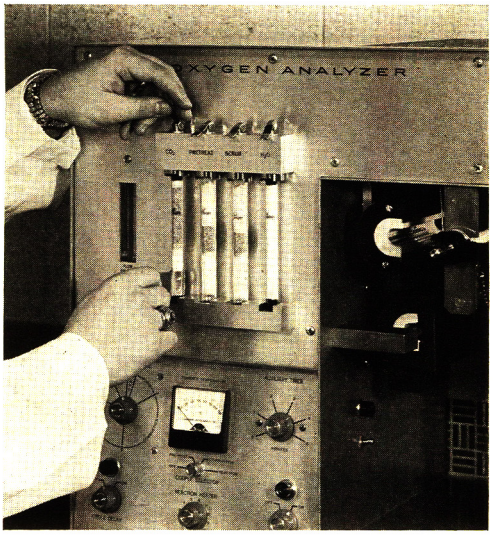
The instrument automatically performs a modified version of the Unterzaucher method for direct oxygen. The use of a special platinized carbon catalyst permits conducting the procedure at 180° C. below the conventional procedure; this improves reproducibility and lengthens component life.

Automatic operation—performing repetitive operations in exactly the same manner, delivers data faster, easier and with considerably more precision than manual methods.

The instrument is ideal for applications in pharmaceutical, rubber, plastics, organics and petroleum research and control laboratories as well as in academic research.

Condensed Specifications:
Sample . . . any material that pyrolyzes at temperatures up to 900° C.
Sample size . . . from 2 to 30 milligrams.
Operating cycle . . . 21 minutes.
Accuracy . . . results correspond to theory ± 0.3% oxygen.
Readout . . . gravimetric.

Ask for Bulletin AB-292



For Carbon-Hydrogen Analysis

An instrument for the laboratory determination of carbon and hydrogen, the Coleman Model 33 automatically performs the accepted Pregl method. It provides great advances in speed, precision, and convenience over the manual method by exactly reproducing the essential conditions of the analysis.

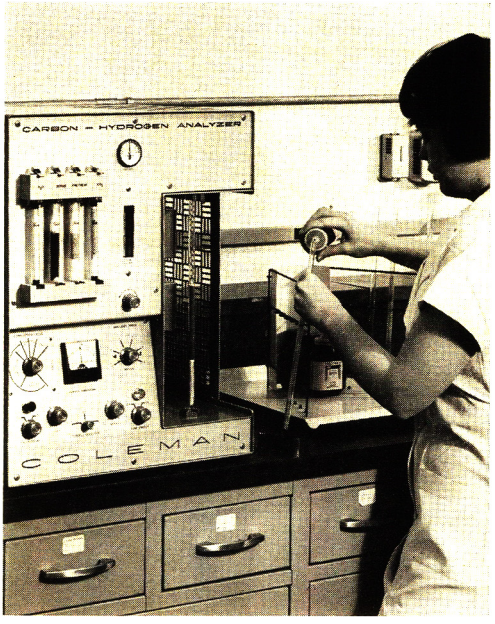
In operation, the instrument burns a micro sample in an atmosphere of high-purity oxygen, separating the sample into its elemental constituents. Hydrogen is converted to water; carbon is converted to carbon dioxide. These compounds are absorbed in separate absorption tubes and the values easily calculated after differential weighing of the absorption tubes.

The instrument makes complete determinations of carbon and hydrogen within an 8-minute operating cycle. Routine analyses can be completed at the rate of 4 to 5 per hour.

The Coleman Model 33 is valuable in research and product control laboratories is working with a wide variety of materials including pharmaceuticals, petroleum, heavy chemicals, plastics and organics.

Condensed Specifications:
Sample . . . any material that pyrolyzes at temperatures up to 1000° C.
Sample size . . . 2 to 50 milligrams.
Operating cycle . . . 8 minutes.
Accuracy . . . results correspond to theory ±0.2% carbon, ±0.2% hydrogen.
Readout . . . gravimetric.

Ask for Bulletin AB-273



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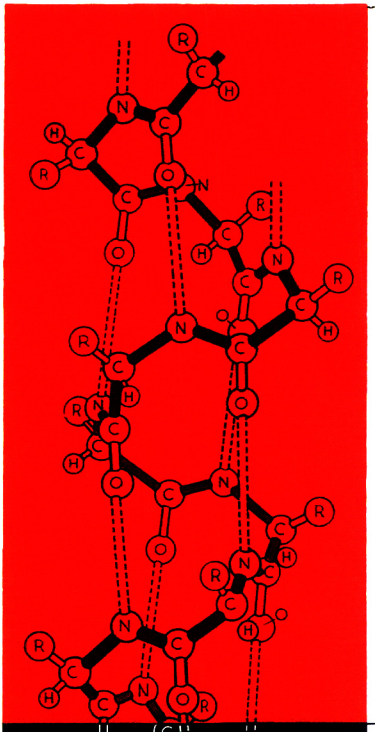

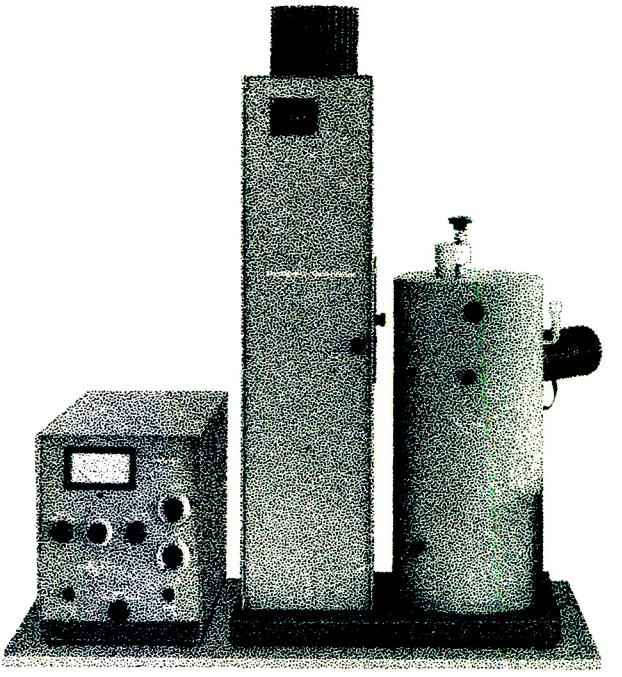

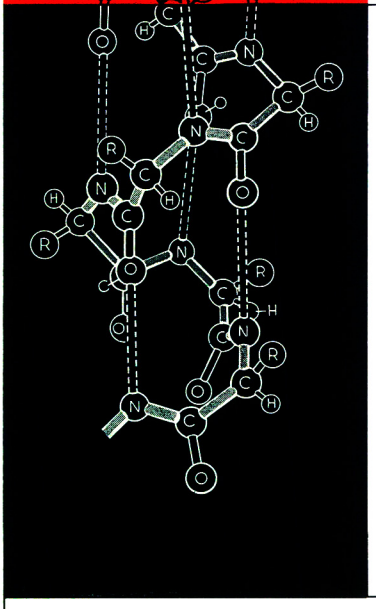

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Analytical Division Program in Detroit Honors Three ACS Award Winners

THE COMPLETE PROGRAM for the 149th National ACS Meeting to be held in Detroit, Mich., April 4 to 9, appears in *Chemical and Engineering News*, February 22 issue.

The Division of Analytical Chemistry will hold its sessions at Cobo Hall. In addition to the presentation of general papers and the special award symposia, meetings will cover the following topics: electrochemistry in nonaqueous solvents, titrimetry and equilibrium in nonaqueous solvents, and quantitative determination of functional groups. Over 75 scientific papers will be presented.

James Schoolery, Varian Associates, E. H. Sargent Instrumentation Award Winner, will discuss "Evolution of High Resolution NMR Spectroscopy" on Monday afternoon. The Lab-Line Award Winner, Stephen Dal Nogare, E. I. du Pont de Nemours & Co., will describe "New Developments in Gas Chromatography" at a symposium on Tuesday morning. Finally, the Fisher Award Symposium consisting of two sessions, Wednesday morning and afternoon, will honor Charles N. Reilley of the University of North Carolina. Dr. Reilley will present an address at 4:00 on Wednesday afternoon.

The Analytical Chemistry Division will meet for dinner at 6:30 Tuesday evening, and will hold a business meeting Wednesday morning.

An innovation at this National Meeting is the opportunity for registrants to enroll in ACS sponsored short courses. Each course will be given in the chemistry department of Wayne State University. F. W. McLafferty is in charge of a course on mass spectrometry (Apr. 3 and 4; $35); H. E. Zimmerman will lead a course on photochemistry (Apr. 3 and 4, $35); and G. R. Choppin is chairman of a course on radiochemistry (Apr. 8 to 10, $50). Detailed information on these courses is available by consulting *Chem. Eng. News* 43, No. 6 (1965) or writing to: American Chemical Society, ACS Educational Secretary, 1155 Sixteenth St., N. W., Washington, D. C. 20036.

In addition to the technical programs of the various divisions of the ACS, the 1965 Midwest Chemical Exposition at Cobo Hall will feature from 150–200 exhibits.

ANALYTICAL DIVISION PROGRAM

Donald H. Wilkins, Chairman — John K. Taylor, Secretary

Monday Morning, April 5

GENERAL PAPERS

A. L. Underwood, Presiding

10:05 Numerical Solution of Nonlinear Integral Equations. R. S. Nicholson, Michigan State University, East Lansing, Mich.

10:30 Use of the Difference between the Forward and Reverse Quarter Wave Potentials as a Measure of Electrochemical Reversibility. Raymond Levine, Rohm and Haas Research Laboratories, Springhouse, Pa., D. J. Macero, Syracuse University, Syracuse, N. Y.

10:50 Stereochemical Specificity in the Electrochemical Reduction of Diphosphopyridine Nucleotide. J. N. Burnett, Leon Mandell, A. L. Underwood, Emory University, Atlanta, Ga. 30322.

11:15 Polarographic Determination of Cysteine Using the Catalytic Tin(IV) Reaction. S. L. Phillips, R. A. Toomey, International Business Machines Corp., Data Systems Division, Box 390, Dept. C27, Bldg. 702, Poughkeepsie, N. Y.

11:35 Electrochemistry of Iron Porphyrin Compounds. D. G. Davis, R. F. Martin, D. J. Orgeron, Louisiana State University in New Orleans, New Orleans, La. 70122.

Monday Afternoon, April 5

E. H. Sargent Instrumentation Award Address

L. B. Rogers, Presiding

2:05 Introduction of James Schoolery. R. W. Mattoon, Abbott Laboratories, North Chicago, Ill. 60064.

2:15 Sargent Award Address: Evolution of High Resolution NMR Spectroscopy. James Schoolery, Varian Associates, 611 Hansen Way, Palo Alto, Calif.

GENERAL

L. B. Rogers, Presiding

3:25 Reversible Deposition of Metals on Solid Electrodes by Voltammetry with Linearly Varying Potential. G. Mamantov, University of Tennessee, Knoxville, Tenn., ORNL, Oak Ridge, Tenn., D. L. Manning, J. M. Dale, ORNL, Oak Ridge, Tenn.

3:40 Adsorption of Metal Complexes at Mercury Electrodes. R. W. Murray, D. J. Gross, University of North Carolina, Chapel Hill, N. C.

4:00 Millicoulometric Determination of n-Values in the Polarographic Reduction of Cadmium and Iodate Ions. A. M. Wilson, Emory University, Atlanta, Ga. 30322.

4:20 Amperometric Titration of Perchlorate with Tetraphenylstibonium Sulfate. M. D. Morris, Pennsylvania State University, University Park, Pa. 16802.

4:40 Polarographic Reduction of Metals in Tri-n-Butyl Phosphate. James Katekaru, L. A. Knecht, University of Cincinnati, Cincinnati, Ohio. 45221.

Tuesday Morning, April 6

Lab-Line Award Symposium

R. S. Juvet and J. Mitchell, Jr., Presiding

9:05 Progress in High Inlet Pressure Gas Chromatography. J. C. Giddings, M. N. Myers, P. D. Schettler, University of Utah, Salt Lake City 12, Utah.

9:30 Porous Thin Layer Modified Glass Bead Supports for Gas Chromatography. J. J. Kirkland, E. I. du Pont de Nemours & Co., Wilmington, Del.

9:55 A New Process Stream Gas Chromatograph. R. Kieselbach, E. I. du Pont de Nemours & Co., Wilmington, Del.

10:05 A New Sensitive Selective Detector for Gas Chromatography. Arthur McCormack, Stephen Tong, W. D. Cooke, Cornell University, Ithaca, N. Y.

10:30 Hexaminecobalt(III) Tricarbonatocobaltate(III). A

New Analytical Reagent. C. E. Bricker, J. A. Baur, University of Kansas, Lawrence, Kan.

10:55 Study of Organic Structure via Mercury (6 $^3P_1$)-Sensitized Photolysis and Gas Chromatography. R. S. Juvet, L. P. Turner, University of Illinois, Urbana, Ill.

11:20 Introduction of Stephen Dal Nogare. John Mitchell, Jr., Dupont Experimental Station, Wilmington, Del.

11:30 Lab-Line Award Address: New Developments in Gas Chromatography. Stephen Dal Nogare, E. I. du Pont de Nemours & Co., Wilmington, Del.

Tuesday Afternoon, April 6

Section A

SYMPOSIUM ON ELECTROCHEMISTRY IN NONAQUEOUS SOLVENTS

David H. Geske, Presiding

2:05 Electrochemically Generated Chemiluminescence. R. C. Lansbury, David Roe, D. M. Hercules, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

2:30 Comparison of Electrode Potentials in Different Solvents. J. F. Coetzee, University of Pittsburgh, Pittsburgh, Pa. 15213.

3:30 The Reduction of Oxygen to Superoxide Anion in Aprotic Solvents. D. L. Maricle, W. G. Hodgson, American Cyanamid Co., 1937 West Main St., Stamford, Conn.

4:00 Comparisons of Electrode Reactions in Aqueous and Nonaqueous Media. J. Fritsch, P. Malachesky, R. N. Adams, University of Kansas, Lawrence, Kansas.

4:30 Anodic Reactions of Aliphatic Amines in Acetonitrile. C. K. Mann, Karen Barnes, J. F. O'Donnell, P. J. Smith, Florida State University, Tallahassee, Fla. 32306.

Tuesday Afternoon, April 6

Section B

GENERAL

B. L. Karger, Presiding

2:05 Separation of Aromatic Amines by Reversed Phase Chromatography. C. E. Hedrick, University of Pennsylvania, Philadelphia, Pa. 19104.

2:25 Normal Hydrocarbon Determination Using 5A Molecular Sieves. W. S. Ferguson, Marathon Oil Co., P. O. Box 269, Littleton, Colo.

2:45 Anomalous Gas Chromatographic Retention Time Characteristics of Cholesteryl Esters Near Mesophase Transition Temperatures. E. M. Barrall II, R. S. Porter, J. F. Johnson, California Research Corp., P. O. Box 1627, Richmond, Calif.

3:15 Studies of Recovery and Selective Separation by Foam Fractionation. B. L. Karger, Northeastern University, Boston, Mass.

3:40 Structure Determination of Fatty Acids and Their Esters—New Catalyst for Carbon Skeleton Chromatography. Morton Beroza, U. S. Dept. of Agriculture, Agricultural Research Center, Beltsville, Md.

4:05 Rapid Determination of Individual Mercaptans in Sour Gasoline Boiling Range Stocks. V. Brand, D. A. Keyworth, Universal Oil Products Co., 30 Algonquin Rd., Des Plaines, Ill. 60016.

Wednesday Morning, April 7

Section A

Fisher Award Symposium

W. D. Cooke, Presiding

9:05 Solvent Extraction of Metal Ions with Trifluoroacetylacetone-Isobutylamine. W. G. Scribner, Monsanto Research Corp., Dayton, Ohio. 45407.

9:20 Determination of Diethylene Glycol Content of Polyethylene Terphthalate. J. R. Kirby, A. J. Baldwin, R. H. Heidner, Chemstrand Research Center, Inc., Box 731, Durham, N. C.

9:35 New Specific, Sensitive Methods for Determining Amine and Carboxyl End Groups in Nylon. R. G. Garmon, M. E. Gibson, Chemstrand Research Center, Inc., P. O. Box 731, Durham, N. C.

9:50 Colorimetric Method for Chlorine in Dilute Aqueous Solution. J. D. Johnson, D. A. Okun, Rahnar Overby, School of Public Health, University of North Carolina, Chapel Hill, N. C.

10:10 Application of Quantitative Electrodeposition of Thin Metal Films on Pyrolytic Graphite as Reactor Flux Monitors. H. B. Mark, Jr., F. J. Berlandi, Basil Vassos, University of Michigan, Ann Arbor, Mich.

10:30 Development of a Versatile Electrode System for Thin Layer Electrochemical Studies and Its Characterization by Chronopotentiometry and Chronoamperometry. D. M. Oglesby, S. H. Omang, C. N. Reilley, University of North Carolina, Chapel Hill, N. C.

10:50 Electrochemistry in a Thin Layer of Solution between Twin Working Electrodes with Independent Potential-Current Control. L. B. Anderson, C. N. Reilley, University of North Carolina, Chapel Hill, N. C.

11:10 An Operational Amplifier A.C. Polarograph with Admittance Recording. J. W. Hayes, C. N. Reilley, University of North Carolina, Chapel Hill, N. C.

11:30 Divisional Business Meeting.

Wednesday Morning, April 7

Section B

GENERAL

R. G. Bates, Presiding

9:05 Kinetics and Mechanism of Pyridine Catalyzed Bromination of Phenols in Glacial Acetic Acid. R. J. Cohen, C. O. Huber, University of Wisconsin-Milwaukee, Milwaukee, Wis. 53211.

9:25 Oxidation-Reduction Reactions in Nonaqueous Media. Effect of Picrate on Cerium(IV). Byron Kratochvil, Marie Tipler, University of Wisconsin, Madison, Wis. 53706.

9:45 Chronopotentiometric Reduction of Oxygen in Sulfuric Acid Media. D. G. Peters, R. A. Mitchell, Indiana University, Bloomington, Ind.

10:25 Behavior of Weak Bases in Methanol–Water Solvents. R. G. Bates, M. Paabo, M. Woodhead, R. A. Robinson, National Bureau of Standards, Washington, D. C.

10:50 Spectrophotometric Titration of Copper by Chelometry in Nonaqueous Solvents. R. A. Bournique, Marquette University, Milwaukee, Wis. 53233, J. Cempura, B. Maciejewski, M. A. Peters, D. Redovich.

Wednesday Afternoon, April 7

Section A

Fisher Award Symposium

W. D. Cooke, Presiding

2:00 De-Tailing and Sharpening of Response Peaks in Gas Chromatography. J. W. Ashley, Jr., C. N. Reilley, University of North Carolina, Chapel Hill, N. C.

2:20 Exchange Kinetics of 1-1,2-(Propylenedinitrilo)tetraacetic Acid and (Ethylenedinitrilo)tetraacetic Acid with Cu(II) and Pb(II) Chelates. C. J. Cruz, "Dacron" Research Lab, Kinston, N. C., C. N. Reilley, University of North Carolina, Chapel Hill, N. C.

2:40 Nuclear Magnetic Studies of Metal Aminopolycarboxylate Complexes. R. J. Day, C. N. Reilley, University of North Carolina, Chapel Hill, N. C.

3:00 NMR Studies of the Rate of Exchange of Cadmium-EDTA with EDTA. Rate of Formation of Mixed-Ligand Precursors. J. L. Sudmeier, C. N. Reilley, University of North Carolina, Chapel Hill, N. C.

3:20 N,N-Dimethylbenzylamine (A) as a Reagent for the Determination of the Deuterium Content of D_2O–H_2O) Mixtures by NMR. D. E. Leyden, C. N. Reilley, University of North Carolina, Chapel Hill, N. C.

3:40 Introduction of C. N. Reilley. N. Howell Furman, Princeton University.

4:00 Fisher Award Address. Charles N. Reilley. University of North Carolina, Chapel Hill, N. C.

Thursday Morning, April 8

Section A

SYMPOSIUM ON TITRIMETRY AND EQUILIBRIUM IN NONAQUEOUS SOLVENTS

Stanley Bruckenstein, Presiding

9:05 Acid-Base Equilibria and Titrations in Inert Solvents. I. M. Kolthoff, University of Minnesota, Minneapolis, Minn. 55455.

10:00 Titrimetric and Equilibrium Studies Using Indicators Related to Nile Blue A. Marion Davis, National Bureau of Standards, Washington, D. C. 20234.

11:00 Behavior of Glass Electrodes in Nonaqueous Solvents. W. Simon, Swiss Federal Institute of Technology, Universitatstr. 6, 8006, Zurich, Switzerland.

Thursday Morning, April 8

Section B

GENERAL

Henry Freiser, Presiding

9:05 EDTA Titrations Using a Continuous Titrator with Direct Readout. W. J. Blaedel, R. H. Laessig, University of Wisconsin, Madison, Wis. 53706.

9:25 Complexes of Pyridine-2-Amidoxime. G. A. Pearse, Jr., Le Moyne College, Syracuse, N. Y. 13214.

9:45 Solvent Extraction Equilibrium of Certain 8-Quinolinols and Their Zinc(II) Chelates. Fa-Chun Chow, Quintus Fernando, Henry Freiser, University of Arizona, Tucson, Ariz.

10:30 Aqueous Solution Equilibria of Molybdenum(VI)-Aminocarboxylic Acid Chelates. R. J. Kula, University of Wisconsin, Madison, Wis.

10:50 Purity Checks in the Preparation of Trisodium Pentacyano-Aminoferrates. D. J. Kenney, G. G. Clinkemaillie, Brother Cyril Leo Michiels, F.S.C., University of Detroit, Detroit, Mich. 48221.

Thursday Afternoon, April 8

Section A

SYMPOSIUM ON TITRIMETRY AND EQUILIBRIUM IN NONAQUEOUS SOLVENTS

Stanley Bruckenstein, Presiding

2:00 Acid-Base Equilibria in Tert-Butyl Alcohol. L. W. Marple, Iowa State University, Ames, Iowa. 50010.

3:00 Acid-Base Indicator Ranges in Pyridine. J. S. Fritz, F. E. Gainer, Iowa State University, Ames, Iowa. 50010.

3:30 Salt Enhancement of Acidity in Nonaqueous Solvents and Its Application to Determining Weak Acids in the Presence of Anhydrides. H. W. Wharton, Procter & Gamble Co., Miami Valley Laboratories, P. O. Box 39175, Cincinnati, Ohio. 45239.

4:00 Fused Salt Spectrophotometry. D. M. Gruen, Argonne National Laboratory, 9700 South Cass Ave., Argonne, Ill. 60440.

Thursday Afternoon, April 8

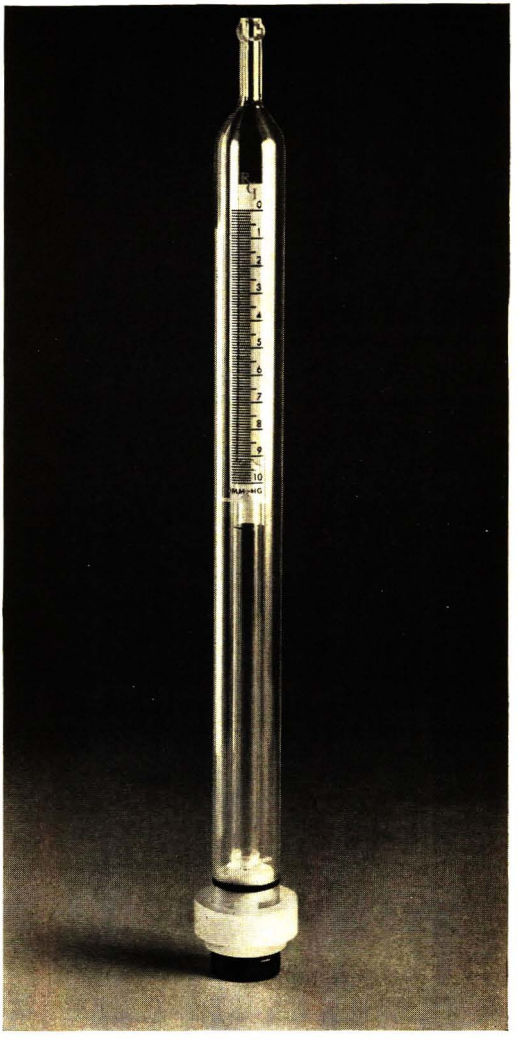
Section B

GENERAL

George G. Guilbault, Presiding

2:05 Photomicrographic and Microradiographic Method for Qualitative Analysis of Solid Propellants. Tin Boo Yee, Propulsion Laboratory, U. S. Army Missile Command, Redstone Arsenal, Ala. 35808.

2:20 Direct Determination of Oxygen in Organophosphorus Compounds by Graphite-Pipe Reduction. B. D. Holt, Argonne National Laboratory, 9700 South Cass Ave., Argonne, Ill. 60440.



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2:40 Fluorometric Substrates for Cholinesterase. G. G. Guilbault, D. N. Kramer, Detection Research Division, Edgewood Arsenal, Md.

3:00 Modified Butyl Bromide Method for Determination of Oxygen in Cesium. V. A. Stenger, W. R. Kramer, H. H. Gill, R. J. Moolenaar, Dow Chemical Co., Midland, Mich.

3:20 Galvanic-Coulometric Monitoring of Sulfur Dioxide in Air. P. Hersch, R. Deuringer, Beckman Instrument Co., Fullerton, Calif.

Friday Morning, April 9

Section A

SYMPOSIUM ON ORGANIC FUNCTIONAL GROUP ANALYSIS

C. A. Reynolds, Presiding

9:05 A Classical Organic Analysis Problem: Estimation of Tertiary Alcohols by Acetylation. G. H. Schenk, Johanna Pietrandrea, William Wilson, Carolyn Mojzis, Patricia Vance, Wayne State University, Detroit, Mich. 48202.

9:50 Solvent Effects on Bromination Analysis. J. G. Hanna, Sidney Siggia, Olin Mathieson Chemical Corp., New Haven 4, Conn.

10:30 Some Observations on the Use of a Modified Van Slyke Method for Determination of Amino Nitrogen in Organic Compounds. L. M. Brancone, A. N. Prezioso, Lederle Laboratories, Pearl River, N. Y.

11:05 Physical Chemistry of Acid-Dye Extraction Technique for Basic Nitrogenous Compounds. Takeru Higuchi, Eugene Roubal, University of Wisconsin, Madison, Wis. 53706.

Friday Morning, April 9

Section B

GENERAL

G. H. Morrison, Presiding

9:05 Dialkylphosphates as Calcium Carriers for the Liquid Scintillation Assay of Ca^{45}. S. M. Bosma, W. H. Fuller, R. J. Hannapel, J. E. Hardcastle, University of Arizona, Tucson, Ariz.

9:25 Spectrum Scanning in Direct Reading Spectrochemical Analysis. H. D. Du Bois, J. C. Guffy, California Research Corp., P. O. Box 1627, Richmond, Calif. 94802.

9:50 Quantitative Sensitivity in Atomic Absorption Spectroscopy. Juan Ramirez-Muñoz, Norman Shifrin, August Hell, Beckman Instruments, Inc., 2500 Harbor Blvd., Fullerton, Calif.

10:30 Preconcentration of Trace Elements by Precipitation Ion Exchange. Fouad Tera, R. R. Ruch, G. H. Morrison, Cornell University, Ithaca, N. Y.

10:50 Infrared Studies in the Bending Region of Petroleum Asphaltics: Nature of Alkyl Groups. Teh Fu Yen, J. G. Erdman, Mellon Institute, 4400 Fifth Ave., Pittsburgh 13, Pa.

Friday Afternoon, April 9

SYMPOSIUM ON ORGANIC FUNCTIONAL GROUP ANALYSIS

C. A. Reynolds, Presiding

2:00 Applications of Direct Injection Enthalpimetry. Joseph Jordan, P. T-S. Pei, R. C. Buchta, Jr., Pennsylvania State University, 212 Whitmore Laboratory, University Park, Pa. 16802.

2:45 Differentiation of Fatty Alkanolamides by Adsorption Chromatography and Differential Reaction Rate Saponification. F. H. Lohman, Procter and Gamble Co., P. O. Box 39175, Cincinnati, Ohio. 45239.



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Speakers review new developments in conventional and unusual analytical techniques

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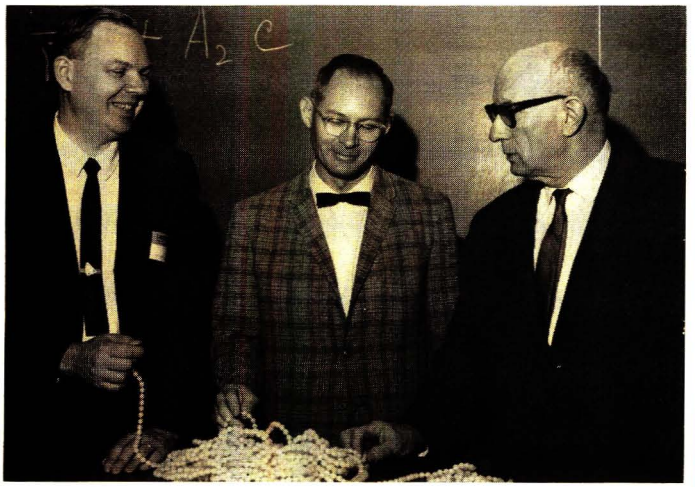
Between 15 and 20 laboratory supply houses and instrument manufacturers exhibited new and improved analytical equipment and services to about 250 registrants for the symposium.

Mössbauer Effect. Dr. G. K. Wertheim of Bell Telephone Laboratories described a number of diverse uses of the Mössbauer effect in analysis. For example, the Mössbauer effect can be used to measure the mean square vibrational amplitude (Debye–Waller factor) and mean square velocities (thermal red shift) of atoms in solids. It also can be used to measure the *s*-electron density at the nucleus (isomer shift), which is related to chemical bonding, and to study electric and magnetic hyperfine interactions.

The Mössbauer effect has proved especially useful in studying magnetically ordered materials and some paramagnetic solids. These studies involve determining the hyperfine structure of materials. Nondestructive analysis is possible, for example, of iron in beryllium and iron compounds in minerals and meteorites.

Activation Analysis. Recent developments in nuclear activation analysis cover the field, involving technology, equipment, and uses, according to Dr. E. L. Steele of General Atomic Division/General Dynamics Corp. Techniques such as variable-energy neutron and charged-particle activation analysis have significantly increased the degree of selectivity during irradiation. Particles with energies above the thresholds of desired reactions, but below the thresholds of interfering reactions, are used to re-



Fred W. Billmeyer, Jr., Rensselaer Polytechnic Institute (left) and Marcel J. E. Golay, Perkin-Elmer, speakers at the Louisiana State University Symposium on Modern Methods of Analytical Chemistry, discuss Dr. Billmeyer's model of a polymer chain with Dr. Eugene W. Berg, LSU, general arrangements chairman for the symposium

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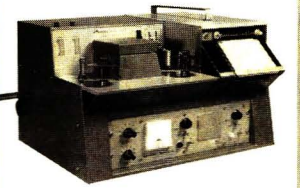

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duce need for involved radiochemistry with the techniques.

Equipment developments include small, relatively inexpensive laboratory sources which have a neutron yield of 2.5×10^{11} neutrons per second. Automated sample handlers are available which select samples, send them to a core position for preset time, return them to a detector system, collect the spectra, and transfer the data to a computer.

As sensitivity, precision, and speed of nuclear activation analysis increase, its uses increase. These uses include criminalistics, surface analysis for corrosion and catalyst studies, pesticide uptake, trace elements in biological systems, inert tracer studies with stable isotopes, and quality control. Oxygen determinations with activation analysis, for example, can give data equal to, or better than, longer established methods.

Tritium Labeling. The increased availability of tritium and simplicity of some labeling techniques make tritiated organic compounds popular tracer materials, said Dr. J. K. Lee of the University of Kansas. Some of the important labeling methods include exposure to tritium gas (Wilzbach method), use of lithium-6 or helium-3 as a source of tritium to react with organic compounds to be labeled, and catalyzed exchange with tritiated mineral acids such as $THSO_4$ or TH_2PO_4. Reaction products of labeling reactions usually are complex mixtures of tritiated compounds. The separation can successfully be achieved by recycling chromatographic techniques.

Dr. Lee emphasized flow counting of effluent from gas chromatographs in the radioassay of tritium in organic compounds. Tritiated compounds emerging from the columns can be burned and then counted at room temperature. Such a technique frequently is used in studies of kinetics and mechanisms of gas reactions.

Chromatography. More and more, chromatography is being used with other techniques in analysis. Dr. Harry V. Drushel of Esso Research Laboratories covered several combinations of gas chromatography and spectral techniques such as infrared and mass spectrometry.

Methods of trapping from the gas chromatograph vary with the equipment and nature of the problem, but trapping techniques usually are secondary to proper selection and interpretation of spectral data. For example, phosphorescence spectra is especially valuable in identifying nitro-

gen compounds isolated from petroleum and in studies of mechanisms of catalytic denitrogenation.

Looking to the future, a supersensitive, rapid-scan infrared spectrometer is needed to study the small quantities of material separated by capillary gas chromatography. Such a spectrometer and a time-of-flight mass spectrometer would make a powerful team.

Pollution Analysis. Column, paper, and thin layer chromatography as used with spectral methods for analysis of air pollutants were reviewed by Dr. Eugene Sawicki of the Robert A. Taft Sanitary Engineering Center. These techniques are used to determine amounts of carcinogens, cocarcinogens, and anticarcinogens in air. The spectral techniques are used as needed for groups of compounds found in air. For example, after functional groups are changed to chromophores of fluorophores through redox or organic synthetic methods, absorptimetric, fluorometric, phosphorimetric, quenchofluorometric and quenchophosphorimetric methods are used. Other aids discussed were the fluorescene excimer bands of aromatic compounds and phosphorimetry to analyze polar organic compounds.

Water Pollutants. Dr. Andrew W. Breidenbach of the Division of Water Supply & Pollution Control of the U. S. Public Health Service covered various analytical techniques required for determination of trace quantities of organic chemicals, particularly pesticides, in water.

Usually, carbon adsorption is used first to concentrate chemicals from large samples of water. Then thin layer chromatography is used for cleanup and initial separation of carbon chloroform extracts before gas chromatography.

Chromatography. Dr. Marcel J. E. Golay of Perkin-Elmer, who replaced Dr. A. I. M. Keulemans of Eindhoven, The Netherlands, indicated that columns of the tubular type have a marked advantage over packed columns for gas chromatographic work. However, preparative columns must be of the packed type because of the large size required. Both types of columns can have their efficiency increased significantly by recirculation of materials to be separated. The price paid for increased resolution so achieved is a restriction on the number of components which can be separated.

Dr. Golay also covered the apparent paradoxical conflict with the second law of thermodynamics to



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which the concept of ideal gas chromatography can lead. Under certain circumstances, a decrease in entropy can be calculated for gas chromatographic separation.

Thus, in chromatography also, one of "Maxwell's demon's" cousins has appeared and its exorcism possibly can be accomplished by an anology to certain effects which occur in shock waves. For example, a shock wave advancing from a high temperature to a low temperature region of a medium causes an increase in entropy. Here, this is the price paid for maintaining the sharpness of the wave. A wave front traveling in the opposite direction from a low to a high temperature region cannot be a shock wave for a decrease in entropy could be associated with such a wave.

Similarly, Dr. Golay believes that under some conditions, the sharp bands permitted by the concept of ideal gas chromatography can not be approached physically even with columns having a very large number of theoretical plates. He suggests that experimental work is required to substantiate the analogy.

Polymer Analysis. Molecular weight distributions in polymers are found by a variety of experimental methods, each influenced by factors such as range of applicability, precisions, accuracy, convenience, and cost, according to Dr. Fred W. Billmeyer, Jr., of Rensselaer Polytechnic Institute. Thermodynamic methods of cryoscopy, ebulliometry, and osmometry have proven absolute accuracy for measuring number-average molecular weight. Other thermodynamic methods, light scattering, equilibrium ultracentrifugation, and approach-to-equilibrium ultracentrifugation, give weight-average molecular weight. Transport properties, such as sedimentation constant, diffusion constant, intrinsic viscosity, or the Newtonian melt viscosity, can be empirically correlated with molecular weight. Although in principle, pairs of these properties can be combined to yield molecular weights, use of such results requires caution, particularly with random coil polymers.

Thermochemical Titration. Use of heats of reaction as a methodological tool in modern analytical chemistry has not been fully exploited, said Dr. Joseph Jordan of Pennsylvania State University. Thermochemical titrations can be successful in situations in which all free energy methods (potentiometric titrations or color indicators) fail. This is because most conventional methods rely solely on equilibrium constants where thermochemical, or "enthalpy," titrations include an entropy term. As a result, enthalpy titrations can be applied to all broad categories of analytically important reactions, including proton transfer (acid–base), electron transfer (oxidation–reduction), chelation, and precipitation.

Direct injection enthalpimetry (DIE) is a technique which with thermometric enthalpy titrations could have a spectacular development—parallel to electroanalytical chemistry during the past 25 years. In DIE, the heat evolved during a reaction serves as a measure of the concentration of an unknown. An excess of an unstandardized reagent is injected into an unknown solution and the corresponding heat pulse is monitored within 0.01 second.

Recent work by Dr. Jordan and coworkers at Penn State include analytical uses of rare spontaneous, but endothermic, reactions. For example, chelations of divalent and trivalent cations with EDTA (all of which possess highly negative free energies) range from exothermic processes with heats as large as −13 kcal. per mole to endothermic heats of +13 kcal. per mole. Thus nonseparative analysis of mixtures may be possible by successive exothermic and endothermic chelation steps.

In other examples, organic functional analysis has been done by adding an excess of nitrous acid to sulfonamides and measuring the heat of diazotation. The technique also has been used to determine limiting exchange capacities of synthetic resin particles in dilute aqueous suspensions and quantitative analysis of anionic and cationic surfactants by measuring the heat of ion-pair formation between oppositely charged micelle-ions.

Mass Spectrometry. Dr. F. W. McLafferty of Purdue University reviewed the field of mass spectrometry in general and then covered specifics of some analytical applications. For example, ion empirical formulas can now be directly determined on submicrogram samples by parts-per-million accuracy mass analysis with recording speeds such that direct monitoring of gas chromatographic eluants is possible.

Another unique application is studies of unstable species from high energy reactions. Direct sampling from the reaction region of a flame, a glow discharge, flash photolysis, or a shock tube permits identification and study of radicals, ions, and metastable molecules before secondary reactions can occur.

Society for Applied Spectroscopy National Meeting

The 4th National Meeting of the Society for Applied Spectroscopy will be held at the Denver Hilton Hotel, Denver, Colo., from August 30 to September 3. Major areas for sessions include: atomic absorption, microwave, infrared, Raman, ultraviolet-visible arc-spark, flame and x-ray emission-absorption spectroscopy; laser and electron probes; gamma-ray and nuclear particle spectrometry; gas chromatography; radiochemistry; differential thermal analysis; thermogravimetric analysis; and electrochemistry. Symposia are also planned on: geologic applications of mass spectroscopy, aplications of spectroscopy to semiconductor materials, water analyses, high resolution spectroscopy, and nuclear materials and reactor components. Original papers are being solicited and those interested should forward a short description of the proposed contents before April 1 to Merlyn L. Salmon, Fluo-X-Spec Laboratory, 718 Sherman St., Denver, Colo. 80203.

Chemical Instrumentation Course

A course designed to give research chemists a working knowledge of electronic circuits and their application to instrumentation, "Introduction to Chemical Instrumentation," will be given at Purdue University, July 11 to 30. Each participant works individually at a Malmstadt-Enke Instrumentation Laboratory by Heath. Additional information is available from Prof. H. L. Pardue, Chemistry Department, Purdue University, Lafayette, Ind. 49907.

X-Ray Conference

The X-Ray Analysis Group of The Institute of Physics and The Physical Society will hold its Spring Conference on April 8 and 9 at the University of Edinburgh, Scotland. The training of a crystallographer will be the subject April 8 and current work in structure analysis will be the topic on April 9. The closing date for applications for attendance will be about March 6. Further details and application forms are available by writing to The Institute of Physics and The Physical Society, 47 Belgrave Square, London, S. W. 1, England.



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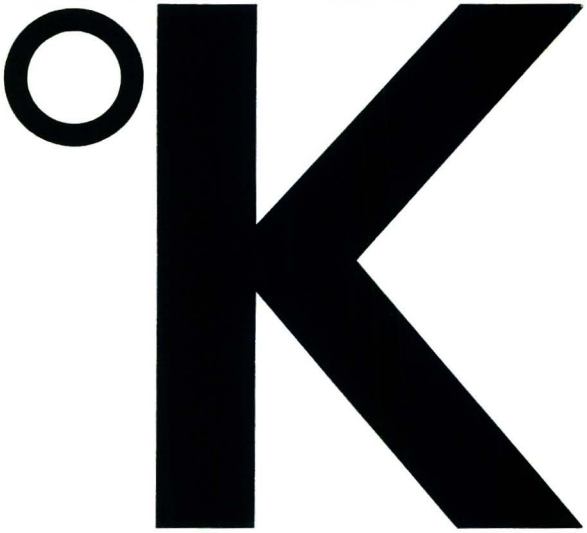

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NMR Spectroscopy Institute

The Fourth Annual Nuclear Magnetic Resonance Spectroscopy Institute will be held June 21 to 25 at Canisius College. The lectures and laboratory sessions will be presented by N. F. Chamberlain, Humble Oil and Refining Co., and L. R. Johnson, Varian Associates. Elementary theory will be given the first day. The following four days, for the intermediate student, will deal with the interpretation of spectra and applications. The fee for this program is $100. Those interested should write to Dr. Herman Szymanski, Canisius College, 2001 Main St., Buffalo, N. Y. 14208.

Advanced Seminar on Activation Analysis

An advanced seminar on activation analysis will be held at General Atomic, San Diego, Calif., April 26 until noon on April 28. This meeting follows the Texas A & M Conference on Modern Trends in Activation Analysis which will be held April 19 to 22. Invited speakers, both foreign and U. S., will present papers at an advanced level at the California seminar. All techniques and areas of application will be included. The activation analysis facilities at General Atomic will be toured and some equipment will be demonstrated. Further information on this meeting is available from V. P. Guinn, General Atomic, P. O. Box 608, San Diego, Calif. 92112.

Industrial Analysis

"Industrial Organic Analysis" is the theme of a meeting to be held at the Drawbridge Inn, Sarnia, Ontario, October 4–6. Sponsored by the Analytical Chemistry Division, The Chemical Institute of Canada, sessions are being planned on such topics as: trends in industrial analysis, classical analytical methods, advances in analytical spectroscopy, and characterization of polymers.

There will be three additional general sessions, one of which will be devoted to gas chromatography. Papers are invited for these general sessions with particular interest centered on instrumental methods. Titles and short abstracts are requested by April 1, and should be sent to: R. M. Small, Research Department, Polymer Corp. Limited, Sarnia, Ont., Canada.

Mass Spectrometry Course

An intensive course on molecular structure determination by mass spectrometry will be given April 21 to 23 at Purdue University, Lafayette, Ind. The course is designed to acquaint professional-level chemists with the potentialities of the method through lectures, demonstrations, and actual practice. Emphasis will be placed on how to obtain the spectrum, reduce it to useful data, and relate these to the molecular structure of the compound. Five different instruments will be used in demonstrations. Chairman of the course is F. W. McLafferty. Inquiries should be sent to the conference coordinator, M. E. Ocker, Division of Conferences and Continuation Service Center, Purdue University, Lafayette, Ind. 47907.

Thermometric Titrimetry Symposium

A joint one-day symposium on thermometric titrimetry is being organized by the Midlands Section and the Special Techniques Group of the Society for Analytical Chemistry, The Birmingham and Midlands Section of the Royal Institute of Chemistry and the Birmingham and Midlands Section of Chemical Industry at Birmingham University on Wednesday, September 15. Anyone interested in submitting papers or demonstrating thermometric titrimetry apparatus should write to M. L. Richardson, A.R.I.C., A.C.T. (Birm), John & E. Sturge Ltd., Lifford Chemical Works, Lifford Lane, Kings Norton, Birmingham, 30, England.

Activation Analysis Courses

The following one-week courses on activation analysis will be held at General Atomic's San Diego Laboratory: "Activation Analysis Applications in the Petroleum and Chemical Industries," March 15–19; "General Activation Analysis Course Covering Both Reactor and Accelerator Neutron Sources," June 14–18; "Activation Analysis Applications in Biology and Medicine," Sept. 20–24; and "Activation Analysis with Small Accelerators for Research and Quality Control," Nov. 1–5. No prior knowledge of radiochemistry is required, but a background in analytical chemistry is helpful. Tuition for each course is $400. Additional details on these programs are available from R. M. Watkins, P. O. Box 608, San Diego, Calif. 92112.

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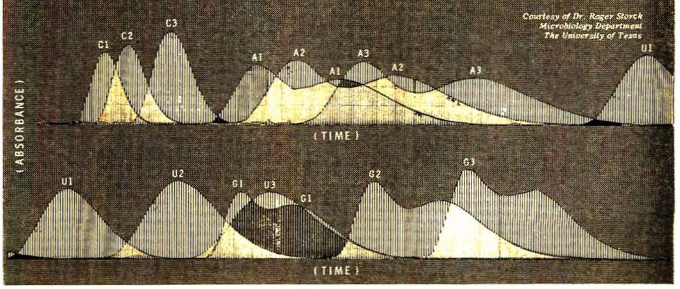

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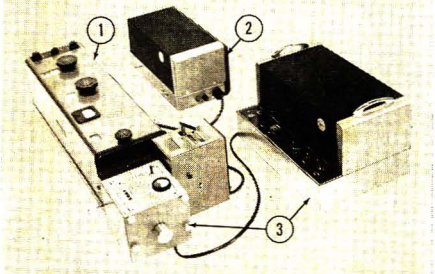

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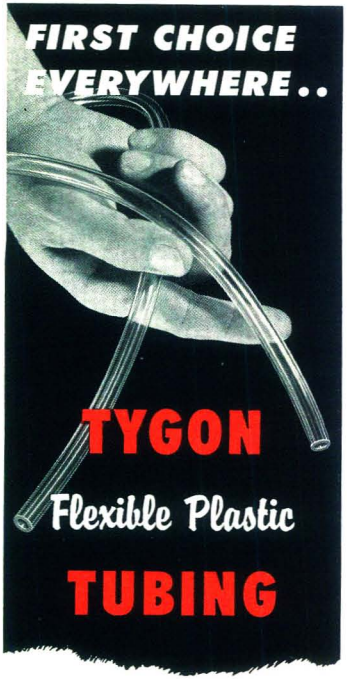

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Infrared Spectroscopy

Two courses in infrared spectroscopy will be given by the University of Minnesota. The first course, "Techniques of Infrared Spectroscopy," will be given July 20 through July 24; the second course, "Chemical Interpretation of Infrared Spectra," will be given July 26 through July 30. The courses are related but operate independently and participants may register for either or both. The lecture courses begin with the fundamentals and carry through to include recent developments; discussion seminars provide opportunity for treatment of advanced topics. Participants should have basic training in chemistry and physics, but not necessarily in spectroscopy. The techniques course includes basic optics and instrument theory, instrument design, and sample preparation. Laboratory work will acquaint participants with both grating and prism instruments. The interpretation course will provide systematic coverage of the group frequencies useful in chemical diagnosis and structure determination. Enrollment for each course is limited. Those interested should write to the Director, Center for Continuous Study, University of Minnesota, Minneapolis, Minn. 55455 or to Prof. Bryce Crawford, Jr.

Radioactivity Conference

The Institute of Physics and The Physical Society is arranging a conference on Low Level Radioactivity Measurements—Limitations and Techniques to be held July 5 and 6 at The Imperial College of Science and Technology, London, England.

It is hoped that the conference will be of value both to workers in the field and to those not already engaged in low level measurement; appropriate introductory survey papers are being arranged. Main session headings will be: introduction–historical review; radiation detection–recent developments; separation and analysis–recent advances; accuracy; special topics. Further information on this meeting and applications for attendance are available from the Administration Assistant, The Institute of Physics and The Physical Society, 47 Belgrave Square, London, S. W. 1, England.

Spectroscopy Courses

Arizona State University will again offer two different and distinct courses in spectroscopy during the summer of 1965. The fifth annual program in Infrared and Ultraviolet Absorption Spectroscopy, August 2–6, and the tenth annual program in Modern Industrial Spectroscopy, August 16–27, are particularly designed for chemists and others from industrial laboratories which make use of spectrophotometric and spectrographic equipment, respectively. These intensive courses of lectures and practical laboratory work serve to train personnel to staff these installations. Each program includes basic theoretical considerations and practical instrumental training with the first course devoted principally to infrared techniques and the second to optical emission techniques.

Enrollment in each course is limited to ensure each student adequate time for personal operation of the instruments. At least ten infrared spectrophotometers and five spectrographs, together with the necessary auxiliary equipment, are available for the two courses, respectively. The cost for the infrared program is $125 and the cost for the emission program is $200. For complete information please write to Dr. Jacob Fuchs, Director, Modern Industrial Spectroscopy, Arizona State University, Tempe, Ariz.

Laser Publication

Laser Focus is a new semi-monthly publication devoted to laser technology. Current developments and articles covering the broad scope of laser activity from applications of lasers to more technical discussion on developments in laser types, techniques, systems, materials, and peripheral equipment are presented. Editorial material is prepared by Teknics, Inc., a Lathrup Village, Mich., firm specializing in reporting and interpreting developments in advanced technologies. All editorial material should be sent to: William E. Bushor, Editor, *Laser Focus*, Teknics, P. O. Box 14, Lathrup Village, Mich. 48037. Issues will be in the hands of subscribers on the 1st and 15th of each month. Subscription costs are six months, $19; one year, $36; two years, $70. For information on subscriptions, Contact: S. Leroy Sykes, International Data Corp., 355 Walnut St., Newtonville, Mass. 02160.

Infrared Spectroscopy Seminar

Xavier University and the Cincinnati Section of the Society for Applied Spectroscopy are cosponsoring an infrared spectroscopy seminar. Persons interested in attending the seminar are requested to write to Dr. Richard

O'Neil, Department of Chemistry, Xavier University, Cincinnati, Ohio. The following topics will be presented on the dates indicated: Molecular Spectroscopy, Ellis Lippincott, University of Maryland, March 17; Infrared Spectroscopy (Rocksalt Region), Robert Gore, Perkin-Elmer Corp., March 24; Infrared Spectroscopy (Far Infrared), Freeman Bentley, Wright-Patterson Air Force Base, March 31; Infrared Instrumentation, Jonathan Amy, Purdue University, April 7; and Inorganic Infrared Spectroscopy, John Ferraro, Argonne National Laboratory, April 14.

X-Ray Analysis Conference

The 14th Annual Conference on Applications of X-Ray Analysis will be held August 25 to 27 at the Albany Hotel, Denver, Colo. The following sessions on x-ray are planned: diffraction, emission spectrography, microprobe analysis; absorption and microscopy, instrumentation, topography, and small angle scattering. Special sessions will cover soft x-rays and effects of chemical combination on x-ray spectra. Papers for this meeting are invited; titles and abstracts are due April 16; manuscripts (two copies) are due July 16. Further information is available from William M. Mueller, Denver Research Institute, University of Denver, Denver Colo. 80210.

EUCHEM Meetings

Three informal chemical conferences have been planned for this year in Europe. The EUCHEM Conferences are being patterned after the Gordon Research Conferences held in the United States. The first conference on electron spin resonance will meet March 28 to April 2 at the Royal Agricultural College at Cirencester, Gloucestershire. Information on this meeting is available from Dr. D. H. Whiffen, Basic Physics Div., National Physical Laboratory, Teddington, Middlesex, England. A conference on high temperature chemistry will be held April 26 to 30 at Schloss Elmau in Bavaria. Informaton on this meeting may be obtained from Prof. Schafer, Institute of Inorganic Chemistry, University of Munster, Germany. Finally, from September 9 to 12 at Sarlat (a small village in France), a conference on mass spectrometry will be held. Prof. M. Fetizon, École Polytechnique, 17 Rue Descartes, Paris 5, France can supply information on this meeting. Details on the planning of the EUCHEM conferences are contained in *Chem. Eng. News* **45**, No. 3, 57 (1965).

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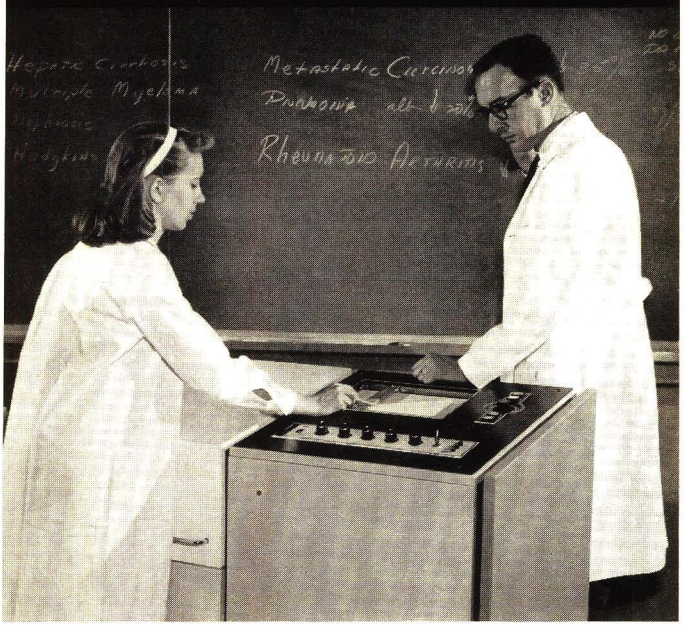

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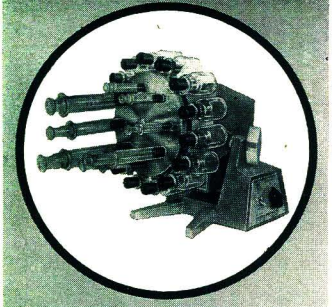

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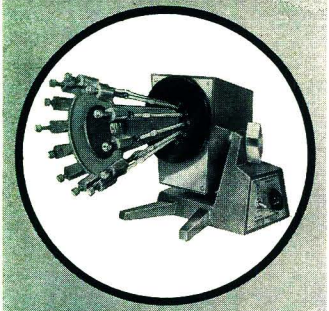

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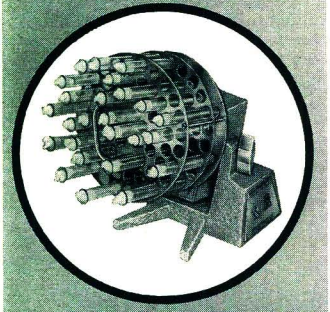

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Electron Microanalyzer Course

The Department of Metallurgy at the Massachusetts Institute of Technology will offer a two-week program on "The Electron Microanalyzer and Its Applications" from June 21 through July 2. The program is designed to provide an understanding of the principles involved in the operation of the electron microanalyzer, with special emphasis on its application to metallurgical problems. The first week will deal with instrumentation, and the second week will be devoted to analytical procedures, applications, and microdiffraction techniques. Tuition is $350. Further information may be obtained by writing to the Director of the Summer Session, Room E19-356, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

International Symposium on Thermal Analysis

An International Symposium on Thermal Analysis, sponsored by the Northern Polytechnic Department of Chemistry will be held in London, England, April 13 and 14. In addition to five invited lectures, there will be contributed papers on all aspects of the technique and application of thermal analysis. An exhibition will display a wide range of commercially available thermal analysis equipment. The main lectures are: Derivatography, L. Erdey, Technical University of Budapest, Hungary; Atmosphere Effects in Differential Thermal and Thermogravimetric Analysis, P. D. Garn, University of Akron, U. S. A.; Kinetic Studies by Thermogravimetry, G. Guiochon, École Polytechnique, France; Causes of Error in Thermogravimetry, M. Harmelin, Laboratoire de Recherches Micro-Analytiques, France; and A Survey of Miscellaneous Thermal Methods, W. W. Wendlandt, Texas Technological College, U. S. A.

Further information on this meeting is available from Drs. M. J. Frazer and B. R. Currell, Department of Chemistry, Northern Polytechnic, Holloway Rd., London, N. 7, England.

International Chromatography Meeting

The Greek Chemists Association in cooperation with the Association for the Development of Spectographic Methods (G.A.M.S.-France), is organizing the 3rd International Meeting under the title: Journées Internationales de la Séparation Immédiate et

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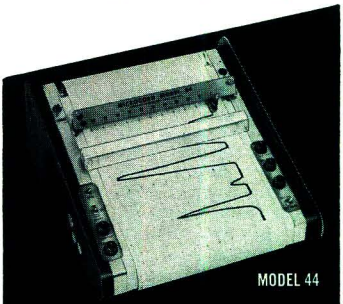

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de la Chromatographie. The meeting will be held in Athens, Greece, on September 25. For further information write to Dr. G. Patissakis, Professor of the Technical University of Athens, G.A.M.S., 1 rue Gason Boissier, Paris 15e, France.

First ACS Middle Atlantic Regional Meeting

The First Middle Atlantic Regional Meeting will be held on Thursday and Friday, February 3 and 4, 1966, at the Sheraton Hotel in Philadelphia. This Meeting will be the first of an annual series, replacing the former Delaware Valley and Metropolitan Regional Meetings. Dr. Walter Clavan, Pennsalt Chemicals Corp., is General Chairman for this first meeting.

The cosponsoring ACS local sections (and respective meeting cochairmen) are: Delaware (Dr. E. J. Vandenberg, Hercules Research Center), Lehigh Valley (Dr. A. J. Diefenderfer, Lehigh University), Monmouth County (Dr. W. Pfefferle, Engelhard Industries, Inc.), New York (Dr. P. Regna, The Squibb Institute for Medical Research), North Jersey (Dr. W. L. Hawkins, Bell Telephone Laboratories, Inc.), Philadelphia (Dr. W. Clavan), Princeton (Dr. G. J. Kent, Rider College and Dr. A. Lutz, American Cyanamid Co.), Southeastern Pennsylvania (Dr. L. H. Dunlap, Armstrong Research and Development Center), South Jersey (Dr. D. M. Nace, Socony Mobil Oil Co.) and Trenton (Dr. E. H. House, Trenton Junior College).

There will be nine scientific divisions for the presentation of papers. These (with their respective chairmen) are: Analytical Chemistry (Mr. O. I. Milner, Socony Mobile Oil Co.), Chemical Education (Dr. A. Breyer, Beaver College), Industrial and Engineering Chemistry (Mr. M. Sittenfield, Marcus Sittenfield and Associates), Inorganic Chemistry (Dr. A. G. MacDiarmid, University of Pennsylvania), Medicinal and Biochemistry (Dr. J. L. Rabinowitz, Veterans Administration Hospital), Organic Chemistry (Dr. C. W. Jefford, Temple University), Petroleum Chemistry (Dr. H. Shalit, Atlantic Refining Co.), Physical Chemistry (Dr. J. Varimbi, Bryn Mawr College) and Polymer Chemistry (Mr. J. Brodnyan, Rohm and Haas Co.).

Further information may be obtained from Dr. Walter Clavan, Pennsalt Chemicals Corp., Technological Center, King of Prussia, Pa. 19406.

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J802	**2,4-Dimethylhexane**, 'Baker' $CH_3CH_2CH(CH_3)CH_2CH(CH_3)_2$ FW 114.23 B.P. 109-110°C.	10 g. 25 g.	14.00 30.00
J930	**2,8-Dimethyl-5-nonanone**, 'Baker' $(CH_3)_2CHCH_2CH_2COCH_2CH_2CH(CH_3)_2$ FW 170.30 B.P. 212-216°C.	25 g. 100 g.	13.00 25.00
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P657	**Mesoxalic Acid Monohydrate**, 'Baker' $HOCOC(OH)_2COOH$ FW 136.06 M.P. 118-120°C.	1 g. 10 g.	4.00 35.00
Q472	N,N'-**Methylenebisformamide**, 'Baker' $HCONHCH_2NHCHO$ FW 102.09 M.P. 139-141°C.	25 g. 100 g.	13.00 40.00
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◆ Fe-59	5	3×10^5	36.00
Pb-210	5	1×10^5	32.00
◆ P-32**	3	3×10^5	30.00
◆ Pm-147	3	3×10^5	36.00
◆ K-42**	3	3×10^5	36.00
◆ Na-22	3	3×10^5	36.00
◆ Na-24**	3	3×10^5	36.00
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CALENDAR OF EVENTS

Mar. 1 to 5 — **Sixteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.** Penn-Sheraton Hotel, Pittsburgh, Pa. *Contact:* Dr. W. G. Fateley, Mellon Institute, 4400 Fifth Ave., Pittsburgh, Pa. 15213. Page 52 A, Feb.

Mar. 15 to 19 — **Conference on Modern Analytical Methods in Food and Biological Chemistry.** Heidelberg, Germany. Sponsors: German Chemical Society Sections of Analytical Chemistry and Food Chemistry; Society of Physiological Chemists; and German Society of Clinical Chemists. Contact: GDCh-Geschäftsstelle, 6 Frankfurt (Main), Postfach 9075, Germany.

Mar. 17 to 19 — **15th National Instrument Society of America Conference for the Iron & Steel Industry.** Pick-Roosevelt Hotel, Pittsburgh, Pa. *Contact:* H. M. Gravatt, Allegheny Ludlum Steel Corp., Research Center, Alabama Ave., Brackenridge, Pa.

Mar. 18 — **American Microchemical Society Meeting.** Hotel Abbey, New York City. Speaker: Dr. Joseph Jordan. Subject: Thermal Titrations. *Contact:* R. A. Hofstader, Esso Research and Engineering Co., P. O. Box 121, Linden, N. J.

Mar. 19 to 20 — **Biennial Symposium of New York Microscopical Society.** Statler-Hilton Hotel, New York. *Contact:* T. G. Rochow, American Cyanamid Co., Room 467A, Stamford, Conn. Page 89 A, Feb.

Mar. 23 — **Twenty-First Annual Conference of the Rochester Society for Quality Control.** University of Rochester, Rochester, N. Y. *Contact:* John C. Holahan, Xerox Corp., Marine Midland Bldg., Webster, N. Y.

Mar. 25 to 26 — **Tenth Symposium on Advances in Tracer Methodology.** Das Zurcher Kunsthaus, Zurich, Switzerland. *Contact:* New England Nuclear Corp., 575 Albany St., Boston, Mass. Page 50 A, Jan.

Mar. 28 to Apr. 2 — **EUCHEM Conference on Electron Spin Resonance** Royal Agricultural College at Cirencester, Gloucestershire, England. *Contact:* Dr. D. H. Whiffen, Basic Physics Div., National Physical Laboratory, Teddington, Middlesex, England. Page 53 A, Mar.

Mar. 29 to Apr. 2 — **Laboratory Apparatus & Materials Exhibition.** Earls Court, London, England. *Contact:* Janet Wheaton, U. T. P. Exhibitions, Ltd., 3 Racquet Court, Fleet St., London E. C. 4, England. Page 51 A, Jan.

Mar. 31 to Apr. 2 — **Conference on Nonconventional Electron Microscopy.** University of Cambridge, England. *Contact:* Administration Assistant, the Institute of Physics and The Physical Society, 47 Belgrave Square, London, S. W. 1, England. Page 90 A, Feb.

Coming Events

Apr. 2 to 3—**Chemistry Education Conferences.** Henry Ford Community College, Dearborn, Mich. *Contact:* William T. Mooney, Jr., El Camino College, Via Torrance, Calif. 90506. Page 93 A, Feb.

Apr. 4 to 9—**149th ACS National Meeting.** Detroit, Mich. Includes Analytical Division sessions. *Contact:* Dr. John K. Taylor, National Bureau of Standards, Washington, D. C. 20234. Page 41 A, Mar.

Apr. 7 to 9—**Anniversary Meeting of the Chemical Society.** Glasgow, Scotland. Symposia on Physical Methods of Structure Determination and Non-Aqueous Solvents and Melts will be included. *Contact:* General Secretary, The Chemical Society, Burlington House, London W. 1, England.

Apr. 8 to 9—**Spring Conference of X-Ray Analysis Group of The Institute of Physics and The Physical Society.** University of Edinburgh. *Contact:* The Institute of Physics and The Physical Society, 47 Belgrave Square, London, S. W. 1, England. Page 49 A, Mar.

Apr. 9—**Spring Meeting of Gulf Coast Spectroscopic Group.** Fontainebleau Hotel, New Orleans, La. *Contact:* Raymond J. Carroll, Cities Service Co., P. O. Box 1562, Lake Charles, La. Page 58 A, Mar.

Apr. 13 to 14—**International Symposium on Thermal Analysis.** London, England. *Contact:* Drs. M. J. Frazer and B. R. Currell, Department of Chemistry, Northern Polytechnic, Halloway Rd., London, N. 7, England. Page 54 A, Mar.

Apr. 19 to 22—**International Conference on Modern Trends in Activation Analysis.** Texas A&M University, College Station, Texas. *Contact:* Dr. R. E. Wainerdi, Texas A&M University, College Station, Texas. Page 50 A, Oct.

Apr. 25 to 28—**Annual Meeting of the Scientific Apparatus Makers Association.** The Greenbrier, White Sulphur Springs, W. Va. *Contact:* Scientific Apparatus Makers Association, 20 North Wacker Drive, Chicago, Ill. 60606.

Apr. 26 to 28—**Advanced Seminar on Activation Analysis.** San Diego, Calif. *Contact:* V. P. Guinn, General Atomic, P. O. Box 608, San Diego, Calif. 92112. Page 50 A, Mar.

May 4 to 7—**Spring Meeting of Division of Rubber Chemistry, ACS.** Fontainebleau Hotel, Miami Beach, Fla. Includes symposium on physical and chemical testing. *Contact:* John M. Bolt, International Latex Corp., P. O. Box 30152, Memphis, Tenn. Page 50 A, Jan.

May 5 to 8—Sixth International ISA Pulp and Paper Instrumentation Symposium. Hotel Northland, Green Bay, Wis. *Contact:* Instrument Society of America, 530 William Penn Place, Pittsburgh, Pa.

May 6 to 8—Conference on Purification of Materials. Waldorf Astoria Hotel, New York City. *Contact:* Marvin S. Brooks, Air Force Cambridge Research Laboratories, Hanscom Field, Bedford, Mass. Page 89 A, Feb.

May 11 to 14—V Symposium on Gas Chromatography. Berlin, Germany. Sponsor: Subcommission for gas chromatography, German Academy of Science's Chemical Section. *Contact:* Unterkommission für Gas Chromatographie, Liepzig O 5, Permoserstr. 15, Germany. Page 76 A, Sept.

May 12 to 13—ASTM National Forum on the Control of Water Quality. ASTM Headquarters, Philadelphia, Pa. *Contact:* American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa.

May 16 to 21—13th Annual Conference on Mass Spectrometry and Allied Topics. Sheraton-Jefferson Hotel, St. Louis, Mo. *Contact:* Dr. H. M. Rosenstock, National Bureau of Standards, Washington, D. C. 20234. Page 42 A, Dec.

May 31 to June 2—Fifth Australian Spectroscopy Conference. Perth, Western Australia. Sponsor: Australian Academy of Sciences. *Contact:* Dr. A. J. Parker, Dept. of Chemistry, University of Western Australia, Nedlands, Western Australia.

June 7 to 11—International Carbon-14 and Tritium Dating Conference. Washington State University, Pullman, Wash. *Contact:* Dr. R. M. Chatters, Radioisotopes and Radiations Laboratory, Washington State University, Pullman, Wash. 99163. Page 93 A, Feb.

June 9 to 11—Analytical Chemistry Summer Symposium. University of Wisconsin, Madison, Wis. Sponsors: ACS Division of Analytical Chemistry and ANALYTICAL CHEMISTRY. Subject: Bioanalytical Techniques. *Contact:* William B. Mason, University of Rochester, School of Medicine and Dentistry, 260 Crittenden Blvd., Rochester 20, N. Y.

June 13 to 18—ASTM 68th Annual Meeting. Purdue University, Lafayette, Ind. *Contact:* American Society for Testing and Materials, 1916 Race St., Philadelphia 3, Pa.

June 14 to 17—Sixteenth Mid-America Symposium on Spectroscopy. Sheraton-Chicago Hotel, Chicago, Ill. *Contact:* Louis R. Pearson, American Can Co., Research Center, Barrington, Ill. Page 50 A, Jan.

June 14 to 18—Symposium on Molecular Structure and Spectroscopy. Ohio State University. *Contact:* Professor K. Narahari Rao, Department of Physics, Ohio State University, 174 West 18th Ave., Columbus, Ohio. 43210. Page 49 A, Jan.

June 24 to 26—Conference on Small-Angle X-Ray Scattering. Syracuse University. *Contact:* H. Brumberger, Department of Chemistry, Syracuse University, Syracuse N. Y. 13210. Page 50 A, Jan.

June 28 to 30—Physical Chemistry Division of ACS Summer Symposium. State University of New York, Buffalo. Subject: Relaxation kinetics of organic, inorganic, and biochemical processes in solution. *Contact:* Dr. Gordon M. Harris, State University of New York at Buffalo, Acheson Hall-Chemistry Road, Buffalo, N. Y. 14214. Page 47 A, Jan.

July 1 to 2—10th Annual Symposium on the Art of Glassblowing. Jack Tar Hotel, San Francisco, Calif. Sponsor: American Scientific Glassblowers Society. *Contact:* Alfred Walrod, Varian Associates, 611 Hansen Way, Palo Alto, Calif.

July 5 to 6—Conference on Low-Level Radioactivity Measurements—Limitations and Techniques. Imperial College of Science and Technology, London, England. *Contact:* Administration Assistant, The Institute of Physics and The Physical Society, 47 Belgrave Square, London, S.W.1., England. Page 52 A, Mar.

July 12 to 17—XII International Spectroscopy Colloquium. University of Exeter, England. *Contact:* Mrs. C. E. Arregger, F.Inst.P., 1, Lowther Gardens, Prince Consort Rd., London, S. W. 7, England. Page 58 A, June.

July 12 to 18—XX International Congress on Pure and Applied Chemistry. Moscow, Russia. *Contact:* Secretary General, Executive Committee of the XX International Congress on Pure and Applied Chemistry, Institute of Chemical Physics, U.S.S.R. Academy of Sciences, Vorobyevskoye chaussée 2-b, Moscow V-334, U.S.S.R. Page 43 A, Dec.

July 19 to 23—SAC Conference Nottingham, England. Sponsor: Society for Analytical Chemists. *Contact:* Mr. A. S. Beidas, Standards Department, Boots Pure Drug Co., Ltd., Station St., Nottingham, England.

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, Demark. *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 46 A, Aug.

Aug. 24 to 28—23rd Annual Meeting Electron Microscopy Society of America. New York City. *Contact:* Dr. Leonard Ross, Department of Anatomy, Cornell University Medical College, 1300 York Ave., New York City, N. Y.

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. 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.

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Standardized Solutions of Toluene-C^{14} and Toluene-H^3. For internal calibration in liquid scintillation counting. Supplied in flame-sealed glass ampoules. Stated activities are within ±2% of true values. Individual certification supplied with each standard.

Model 188270 Toluene-C^{14} (5 ml, 3×10^6 dpm nominal).....$20.00
Model 188280 Toluene-H^3 (5 ml, 5×10^6 dpm nominal).....$20.00

Detailed specifications are available on request, as are current schedules containing complete radiochemical listings and information. Please write, or call 312 827-4456 collect.

NUC:G-4-271

NUCLEAR-CHICAGO
A DIVISION OF NUCLEAR-CHICAGO CORPORATION
351 Howard Avenue, Des Plaines, Illinois 60018
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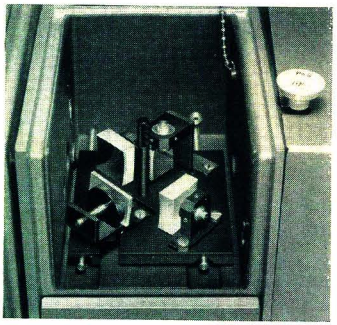
ACCESSORIES INCREASE CAPABILITIES OF THE MODEL 450



Highly versatile as a basic analytical instrument, the Perkin-Elmer Model 450 Ultraviolet Spectrophotometer has even more impressive capabilities with accessories to perform extra functions. Here are some of the auxiliaries that are available:

Specular Reflectance Accessory (illustrated)—versatile analytical tool for pursuing mirror reflectance and coating material absorption studies, including glass coatings on tanks, food can coatings, protective metal coatings. Also may be used to determine thickness of thin films.

Diffuse Reflectance Attachment — records the diffuse reflectance of a variety of solid samples; also the transmittance of turbid or otherwise highly scattering materials.

Spectral Fluorescence Attachment—converts the instrument into a recording spectrophotofluorimeter for charting absorption spectra and fluorescence emission data.

Microsampling Beam Condenser—obtains excellent spectra of liquid samples as small as 0.04 ml. Particularly useful in low concentration biomedical applications and to obtain spectra of very small solid samples.

Temperature-controlled Cell Mount — for Perkin-Elmer Cylindrical Sample Cells, maintains any specified temperature from 0°C to 100°C within 0.5°C. Helps determine the kinetics of reactions at various temperatures.

Other accessories include Short-Path Liquid Cell; Flame Attachment; Variable-Path Liquid Cell; Reference Screen Kit; Linear Wavelength Converter Accessory; Optical Rotatory Dispersion Accessory. For complete details on Model 450 accessories, write to Instrument Division, Perkin-Elmer Corporation, 702 Main Avenue, Norwalk, Connecticut.

PERKIN-ELMER

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Gulf Coast Spectroscopic Group Meeting

The spring meeting of the Gulf Coast Spectroscopic Group will be held on April 9 in New Orleans, La., at the Fontainebleau Hotel. Host for this meeting is D. R. Ingram of Shell Oil Co. As in the past, there is no limitation of attendance or participation except active interest in the activities of the group. More information on this meeting is available from Raymond J. Carroll, Cities Service Co., P. O. Box 1562, Lake Charles, La.

Northwest Regional Meeting

The Pacific Northwest sections of the American Chemical Society will hold their 20th annual Northwest Regional Meeting on June 14 and 15 at the campus of Oregon State University, Corvallis, Ore. Sessions are planned in analytical chemistry as well as in the other major fields of chemistry. Those wishing to contribute papers in analytical chemistry should submit a brief abstract (150 words) on the standard ACS form to: M. H. Campbell, 222-S Bldg., 200 West Area, CPD-General Electric Co., Richland, Wash. 99352. Final date for receipt of abstracts is April 1.

Industry Items

American Hospital Supply Corp. and **W. H. Curtin & Co.**, have adopted a merger agreement which must be approved by Curtin's stockholders. Curtin, a specialized distributor of technical supplies and equipment used in industrial and research laboratories, will operate as a separate unit. American Hospital Supply is a highly diversified manufacturer and distributor in the fields of health care and science.

J. T. Baker Chemical Co., a subsidiary of **Richardson-Merrell Inc.**, has acquired **Productos Quimicos Berkman, S. A.**, a Mexican manufacturer of reagent chemicals. The Mexican company's name has been changed to **J. T. Baker, S. A.** J. T. Baker has headquarters in Phillipsburg, N. J.; the Mexican company is located in the outskirts of Mexico City.

Corning Glass Works, Corning, N. Y., will consolidate manufacture of high temperature process instruments and controls with laboratory instruments and controls at a newly constructed leased facility in Medfield, Mass. Sales of products for the process control field, will continue to be handled by Corning's Electronic Devices Dept. to be headquartered at Bradford, Pa. Sales of laboratory instruments and controls will be handled by the company's Laboratory Glassware Dept., with headquarters in Corning.

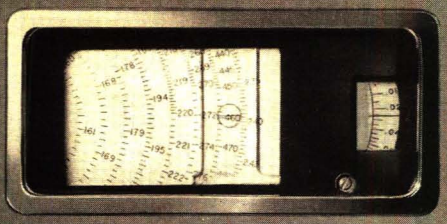
A Commercial Analytical Services Group established by **F & M Scientific Corp.**, Avondale, Pa., will provide consulting and analytical services on a fee basis. Among the services offered will be qualitative, semiquantitative and quantitative gas chromatographic analyses; pyrolysis gas chromatography, clinical GC, quantitative elemental analysis, preparative GC, collection and identification of analytical fractions, pesticide residue analysis, and methods development. An analytical services catalog, giving details and prices, may be obtained by writing the company.

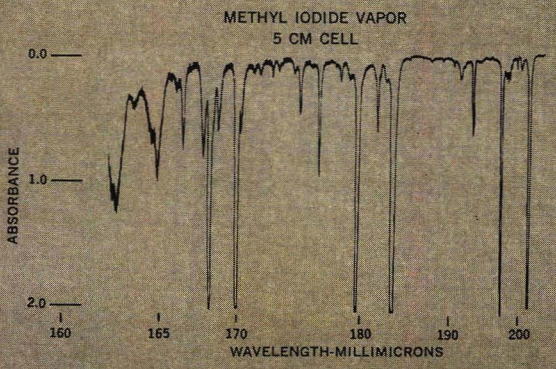
Matheson Co., Inc., is reorganizing its wholly owned subsidiary, **Matheson Scientific**, a distributor of laboratory equipment and chemicals. Matheson Scientific will consist of two divisions, Eastern and Western. The Eastern division with headquarters in Cleveland will include operations in Cleveland, Cincinnati, and Philadelphia. The Western division will have headquarters in Chicago, Ill.

As a result of an agreement with the English firm of **Scientifica**, the Instrument Division of **Barnes Engineering Co.**, 30 Commerce Rd., Stamford, Conn. 06902, has become the exclusive United States distributor for a number of teaching kits and laboratory aids. Among these are magnets, probels, amplifiers, and various NMR and ESR accessories.

Foster D. Snell, Inc., 29 West 15th St., New York City, an independent firm of chemists, engineers, and biologists, has been acquired by **Booz, Allen Applied Research Inc.**, nationwide research, development, and engineering firm. Snell will continue to operate under its present name and to provide professional services including testing and analysis in chemistry.

Varian Associates, Palo Alto, Calif., has entered into negotiations to acquire **Mikros, Inc.**, a Portland, Ore., firm specializing in the vacuum and electron microscope fields. The Mikros product line is complementary to that of Varian's Vacuum Products Division, to which Mikros will report.





performance-proved instruments
for ULTRAVIOLET SPECTROSCOPY

NOW...THE WIDEST RANGE HIGH PERFORMANCE UV INSTRUMENT AVAILABLE

A highly versatile analytical instrument, the Model 450 Spectrophotometer has a new extended range—from 165 to 2700 millimicrons. Its uniquely high energy system allows workable analyses in the far UV with comparatively little purging and no vacuum requirements—while offering the lowest stray light (.0002% at 210 mμ) over the widest range. Model 450—because of its double monochromator—*presents no problems due to stray* even in energy-limited spectral regions.

From the far ultraviolet spectrum to the near infrared, the Model 450 offers superb resolution—separates bands less than 0.3 Angstrom apart at 175 mμ. The *integral* ordinate scale expansion feature lets any weak or recessive band—on any portion of the ordinate—no matter how dense or dilute, to be expanded by factors of 5, 10, 20 or 50 X, with the turn of a dial. A wide choice of accessories broadens the Model 450's applications. With these attachments you can perform, for example, kinetic studies—fluorescence analyses—diffuse reflectance and colorimetric work—temperature sensitive determinations—flame spectra studies of most elements—analyses of micro-samples—optical rotatory dispersion—and many more.

For a fully illustrated brochure and specifications on the Model 450, including sample spectra, write to Instrument Division, Perkin-Elmer Corporation, 702 Main Avenue, Norwalk, Conn.

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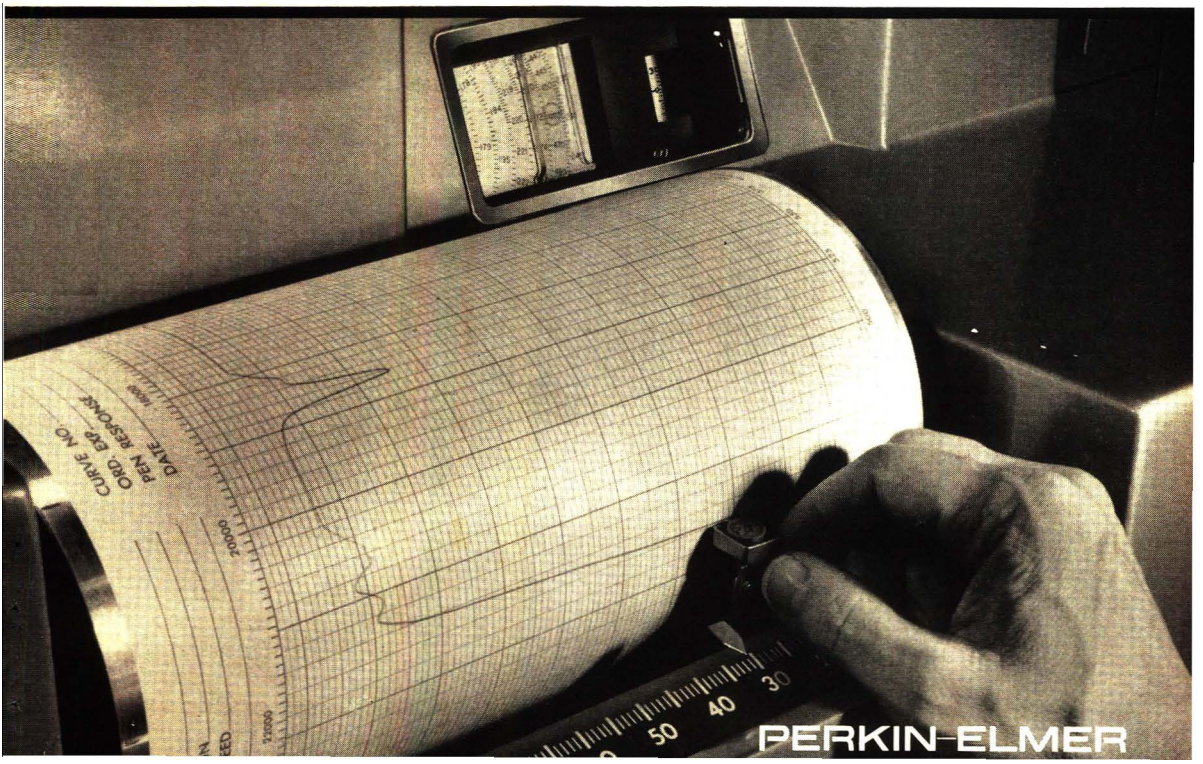
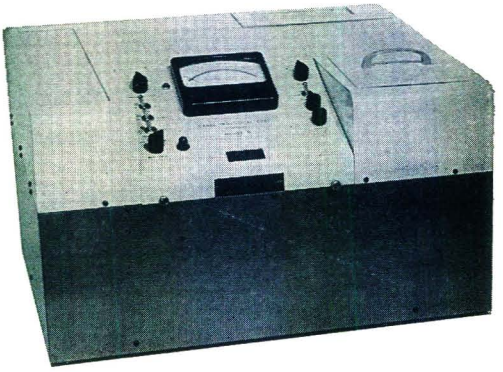
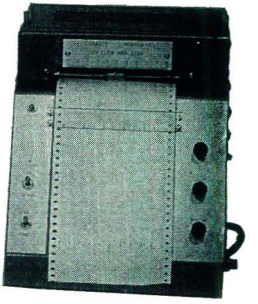


FOR COLUMN CHROMATOGRAPHY AND OTHER FLOW SYSTEMS

FULLY AUTOMATED





UV-VISIBLE

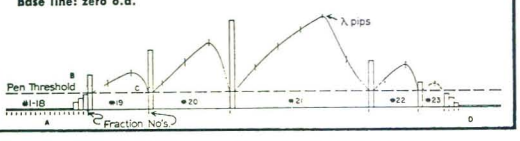
SPECTRAL CURVE ANALYSIS

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

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

A TYPICAL CHART PRESENTATION

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



For full interpretation, request UVA Bulletin

Write for complete details:

CANALCO

Canal Industrial Corporation
4935 Cordell Avenue, Dept. A-3
Bethesda, Maryland

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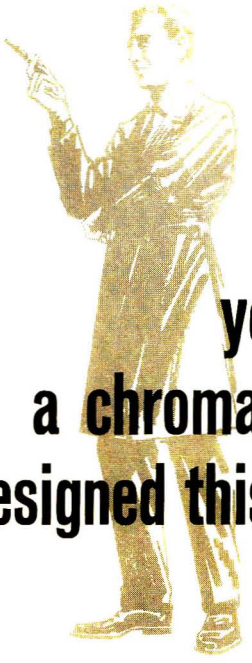

you'd think a chromatographer designed this recorder

TI consulted many gas chromatographers in designing new **servo/riter® II.** The result is everything a chromatographer could ask for — performance, convenience and dependable trouble-free operation.

Take performance — no detectable deadband in **servo/riter II** recorders. The new slidewire has infinite resolution and allows the recorder to detect signals as small as 0.1% of full-scale. Over-all accuracy is better than 0.25% at 1 millivolt full-scale and at pen speeds as fast as 0.4 second.

Convenience is unexcelled. Chart carriage drops forward for easy paper changing; chart can hang free or be taken up; optional tilt-out writing platen permits notation of events. Styled and packaged for the laboratory — with all major controls up-front; range change by plug-in card; chassis is slide-mounted; rear door swings down for simple connection of **any** chromatograph. And, **servo/riter II** is available for table-top operation or rack-mounting.

Trouble-free operation is assured by transistorized electronics, photoconductive chopper, plug-in assemblies and rugged die-castings. For your next chromatogram, try a **servo/riter II** recorder, available with 1 to 6 pens plus optional integrator — wide chart, single pen model from $820.

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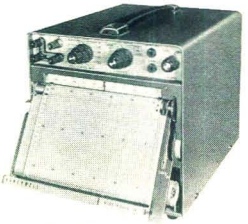
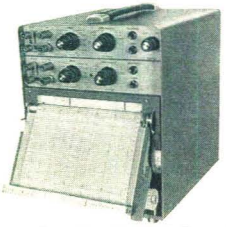
NOW...TWO Compact Portable Lab Recorders from HONEYWELL!



ElectroniK 19 Single-Pen Lab Recorder



ElectroniK 19 Two-Pen Lab Recorder

Honeywell's *ElectroniK 19* Lab Recorder is now available in one-pen or two-pen models. The two-pen model simultaneously and continuously records two independent variables on the same chart. Each variable has separate adjustment knobs, measuring circuit and servo systems. Dimensions are: Single-pen recorder, 8¾" high, 8¾" wide, 11-5/16" deep. Two-pen, 10½" high, 8¾" wide, 11-5/16" deep.

The wide measuring range and variety of features of these recorders give them the versatility needed in many applications. Full-scale spans from 100 microvolts to 100 volts are available in 19 manually selectable calibrated ranges. Zero is continuously adjustable to ±100% of span. Response time is less than 0.5 second full-scale with frequency response of five cycles per second at 10% of span peak-to-peak.

Check the specifications — convincing proof the *ElectroniK 19* recorder is the answer to your lab instrumentation needs.

See these and other Honeywell instruments at the 49th Annual Meeting, Federation of American Societies for Experimental Biology, Atlantic City, N.J., April 10-14, Booths T10, T11, T12.

	The following general specifications apply to single-pen and two-pen models except when noted otherwise.
Input	D-C voltages or D-C currents (with external dropping resistor).
Accuracy	±0.25% of span or 1 microvolt whichever is greater.
Dead Band	0.15% of span.
Pen Speed	Less than 0.5 second span step response time.
Frequency Response	5 cps 10% full span peak to peak sine wave down less than 1% full scale.
D-C Voltage Spans	19 discrete calibrated full scale steps of 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, and 100 millivolts and 0.2, 0.5, 1, 2, 5, 10, 20, 50, and 100 volts.
Zero Adjustment	Continuously adjustable from −100% to +100% of full scale span, with accurate calibration of zero value.
Voltage Reference	Double Zener diode bridge.
Input Impedance	Potentiometric on millivolt range: Infinite at balance, minimum off balance impedance of 25,000 ohms (a.c. or d.c.) per millivolt of span. Voltage spans have constant 4 megohms regardless of balance position.
Source Impedance	Maximum source impedance for specified performance: Millivolt spans—25,000 ohms per millivolt of full scale span; Voltage spans—10,000 ohms for 0.25% loading error regardless of span.
Interference Rejection	"Transverse" (60 cps loop stray): 55 d.b. (565:1). "Longitudinal" (60 cps common mode stray): 170 d.b. (340,000,000:1). Maximum common mode voltage: 120 volts 60 cps; 500 volts d.c. Input circuit isolated and guarded.
Damping	Adjustable to prevent overshoot on full scale or partial scale step functions.
Chart and Scale	6" calibrated width. Evenly graduated in percent from −2 to +102 reading from right to left. Paper continuously ruled with time lines in tenths of an inch; 122 feet per roll. Paper can be continuously rerolled on take-up reel or driven out bottom of chart platen behind lower guide bar. Adjustable sloping chart platen, removable chart transport for replacing charts.
Pen and Ink	Jewel tipped pen using disposable ink cartridge mounted on pen carriage. Mechanical pen lifter. Single-Pen: Purple record. Two-Pen: Purple and red records.
Chart Speeds	10 fixed speeds of 10, 5, 2, 1 minutes per inch and 40, 20, 10, 5, 2, 1 seconds per inch at 60 cps plus "Stand By"
Power Requirements	110 to 130 V a.c.; 50 or 60 cycles. Also available for 200 to 240/220 to 260 V. a.c. at $5.00 additional.
Case	Bench type with carrying handle and 7-foot, 3-conductor, cord and plug. Textured dark beige finish.
Input Connections	Input signal, shield and ground connected to 5-way binding posts on front panel.
Environmental Conditions	Ambient temperature: 60°F to 95°F (35°F to 120°F without damage). Humidity: 5% to 95% RH.
Weight	Single-Pen: Less than 20 pounds. Two-Pen: Less than 29 pounds.
Accessories	Chart roll, ink, lubricating oil, pen cleaner, power cord adapter and instructions.

TO ORDER, SPECIFY: Model 19301-01-01 single-pen portable lab recorder, $1100.
Model 19302-11-01 two-pen portable lab recorder, $1995.

Note: Prices net F.O.B., U.S. factory. All prices and specifications subject to change without notice.

Honeywell
INDUSTRIAL PRODUCTS GROUP
PHILADELPHIA, PA. 19144

HONEYWELL INTERNATIONAL Sales and service offices in principal cities of the world.

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The acceptance of the original Gammascope in a wide variety of applications has prompted the development of an even more versatile system — the Gammascope II. The basic concept of a low cost, self-contained 100-channel Pulse Height Analyzer has been retained. New circuitry, housed in a more compact cabinet, now adds inputs for multiscaling and Mössbauer effect studies. New output circuits permit readout on virtually every type of analog and digital equipment. The Gammascope II truly offers the physicist, chemist or biologist an instrument equally useful for class room demonstrations or exacting experiments. (Gammascope 101 is still available for applications where its features are especially useful.)

4 Switch Selected Operating Modes

100-channel analysis — this provides a high resolution spectrum analysis of charged particles. Scale expansion provides resolution equivalent to 800 channels for storage of a selectable portion of the spectrum. In this capacity the Gammascope will effectively replace the single-channel spectrometer in nuclear medicine, radio-chemistry, and nuclear physics research.

Single-channel analysis — window controls on the Gammascope permit selection of an energy range of interest intensified on the multi-channel spectrum display. With controls set for the range of interest, the instrument provides pulses in that range for counting on an external scaler. Pulses selected by the window can also be used for counting in the multi-scaler mode, or for sampling of the velocity signal in Mössbauer studies.

Multiscaling — the Gammascope provides 100 channels of multiscaling with 8 selectable dwell times from 0.1 to 1000 milliseconds. The single-channel window selects pulses of the desired energy range, which are then automatically stored in successive channels corresponding to a preset time interval. Multiscaling is particularly useful in half-life studies of short-lived isotopes and for investigation of Mössbauer effects.

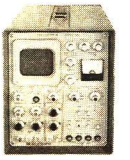
Mössbauer Analysis — The Gammascope is equipped with an input for an analog signal. In addition, in the Mössbauer mode pulses from the detector can be fed to the single-channel analyzer. The output is used to sample the velocity signal by the analog to digital conversion circuitry, thus providing a count in the channel corresponding to the instantaneous amplitude of the velocity. This mode of operation eliminates the necessity for precise timing by the counting channels and the Mössbauer drive, thus greatly simplifying demonstration of Mössbauer effects.

Specifications

Inputs: high level — 0-10 volts (0-100 volts optional); low-level — up to 50 mv. at max gain, polarity negative
Output: compatible with x-y plotter, digital printers, typewriter, paper tape punch, external visual displays, and IBM compatible magnetic tape system.
Memory capacity: 10^5–1 counts per channel
Mössbauer Input: ± 2 volts
Displays: Live: during data accumulation. Static: stored data
Preset Time: live times from 0.1 to 400 minutes and infinity

For full details on the GAMMASCOPE II, contact your nearest TMC office or write Technical Measurement Corp., 441 Washington Avenue, North Haven, Connecticut.

TECHNICAL MEASUREMENT CORPORATION
441 Washington Avenue, North Haven, Conn.

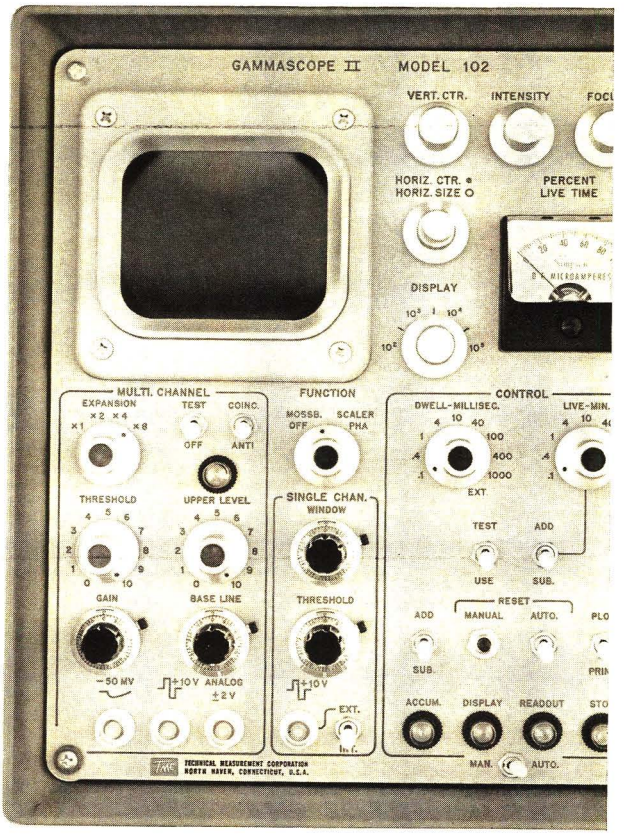


NOW

Gammascope II®

WITH 4 OPERATING MODES

- 100 channel pulse height analysis
- Simultaneous single-channel pulse height analysis
- Multiscaling
- Mossbauer analysis



"See us at the 16th Pittsburgh Conference on Analytical Chemistry at the Penn-Sheraton, Pittsburgh, March 1 5."
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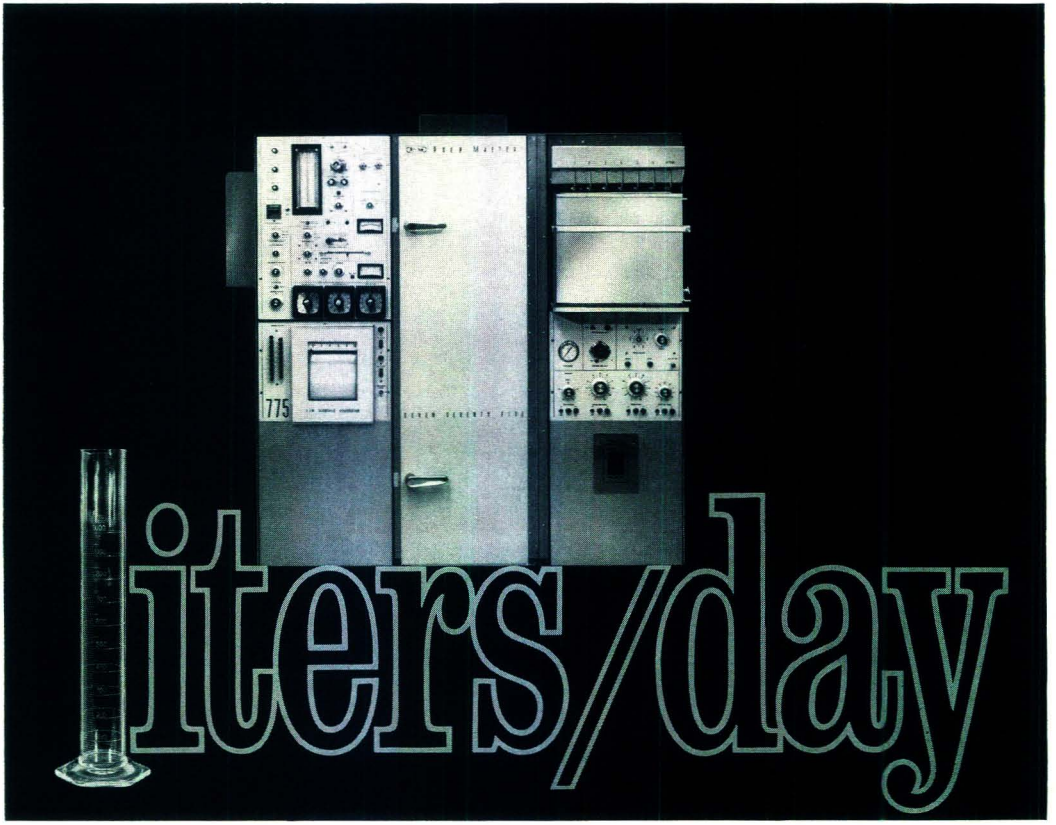

PrepMaster···first true prep scale GC

You measure its throughput not in microliters or milliliters but in liters per day. You measure injection capacity in volumes of more than 100 milliliters per injection. You measure component collection capacity up to one liter per fraction. In automatic operation, you preset the desired number of injections on a built-in counter and let the PrepMaster operate automatically for the desired throughput. ▪ The PrepMaster utilizes new 4″ OD "flow homogenizer" columns for a relative capacity ratio up to 165 times that of usual prep columns. As a result, the PrepMaster accepts injection volumes of over 100 milliliters with a demonstrated collection efficiency of 90-98% at purity levels approaching 100%. ▪ In recent applications work, a gallon (almost 4 liters!) of rectified turpentine was automatically injected over a 30 hour instrument running time. 1733 milliliters of α-pinene and 701 milliliters of β-pinene were collected with both components having a purity of over 98% (1046 ml of the unwanted components were collected in the bypass trap.) In another run, 970 milliliters of C_8, C_9 and C_{10} methyl esters were separated on the PrepMaster in 7 hours with 906 milliliters collected. The purity of the C_8 and C_{10} components was 99.8% and the C_9 purity was 99.2%. This work would have taken 6 months on a conventional preparative gas chromatograph. Sound interesting? Find out the full story on alcohols, hydrocarbons, and other applications from your local F & M representative and write us for the new product bulletin on the F & M Model 775 PrepMaster. ▪ 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.

F&M®

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

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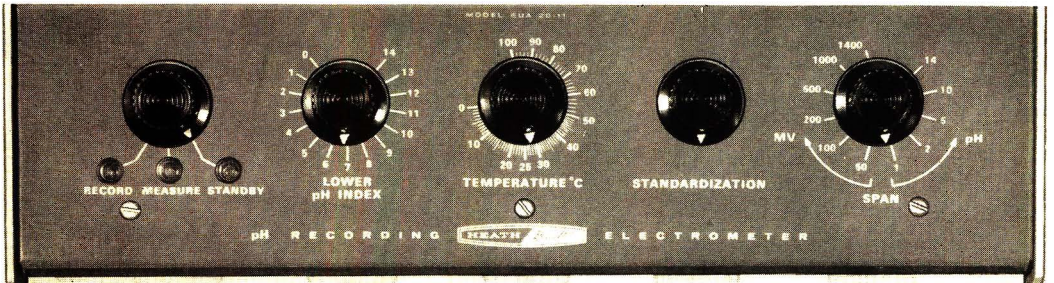

You are looking at the Control Center of the New Heath-Built Recording pH Meter . . . .

Compare These Versatile Features

• *Multi pH Ranges.* Full-scale pH spans of 1, 2, 5, 10, and 14. Any 1 pH unit, 2 pH units, etc. over entire pH region of interest can be switched for full scale on 10″ scale or recorder chart.

• *Multi MV Ranges.* Full-scale millivolt spans of ± 50, 100, 200, 500, 1000 and 1400. There are 14 calibrated 50 mv increments of zero suppression that can be switched in on all millivolt spans.

• *Direct Reading.* pH is read directly from a 10″ scale; expanded ranges are made direct reading by 6 interchangeable scales (e.g. 6.000-8.000 pH, 0-250 millivolts, etc.). No interpolation necessary.

• *Versatile Recording Speeds.* Chart with 10″ grid on 120′ roll moves at selected rates. Standard rate of 2″/min.; other chart speeds as low as 1″/hr. and as high as 12″/min. are available with interchangeable motors.

• *Scale Readability.* 0.1% of full-scale span (e.g. 0.001 pH on span of 1/pH, 0.01 pH on span of 10 pH, etc.).

• *Highly Accurate.* Better than 0.5% of any calibrated full-span, 0.005 pH on span of 1.

• *Temperature Compensation.* Calibrated 0 to 100° C manual control. May be automatically controlled by accessory Thermistor probe.

• *Modular Construction.* EUW-301 consists of Heath Servo-Chart Recorder & a special pH Module. It was designed by Dr. Howard V. Malmstadt, Professor at the University of Illinois.

• *Completely Assembled & Tested.*

• *Special Educational Discount Available* — Write for details.

⟨It Measures 1 pH On A Full 10″ Scale⟩ And It Sells For Just $300!

HEATH Built

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Name _____
(Please Print)
Address _____
City _____ State _____ Zip _____

Prices & specifications subject to change without notice. EK-175

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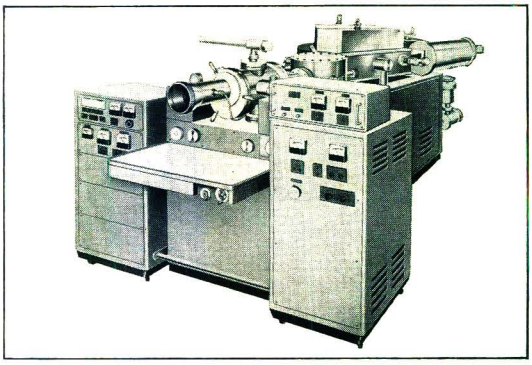

mass

High Resolution (M/ Δ M)
Spark Ion Source — 5,000
Electron Bombardment Ion Source — 20,000

The JEOL (Japan Electron Optics Laboratory Co.) Double Focusing Mass Spectrometer, JMS-01U is an unconventional Mattauch type instrument. It features, in one instrument, the use of either or both types of ion sources — spark and electron bombardment, and either or both detection methods — photographic and electrical. This flexibility allows high resolution analysis of metals and semiconductor impurities and high molecular weight organic structures. The basic analyzer tube is very easily adjustable through a unique mechanism for ion beam focusing and intensity control to attain exceptionally high resolution, sensitivity and reproducibility. Direct sample inlet and reservoir type heated inlet systems are optionally available as well as a peak matching device and emission outlet. Specially designed and convenient front panel controls assure simple operation. JEOLCO (U.S.A.), Inc. has established a fully staffed servicing network in the United States to provide technical assistance and assure continuous trouble-free service. For complete technical and sales information please call or write JEOLCO (U.S.A.), Inc., 461 Riverside Avenue, Medford, Massachusetts 02155, telephone 396-6241, area code 617.

JEOLCO

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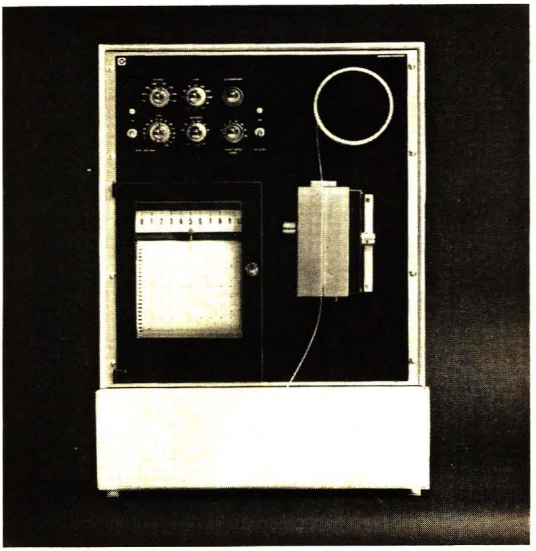

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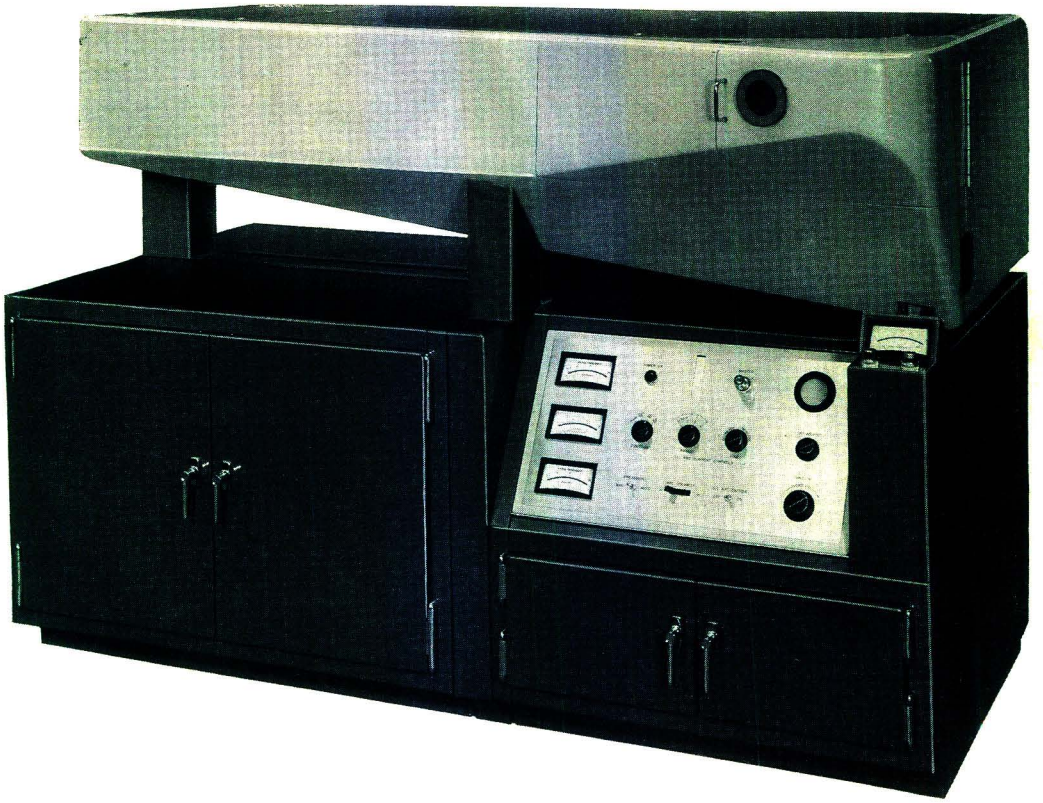

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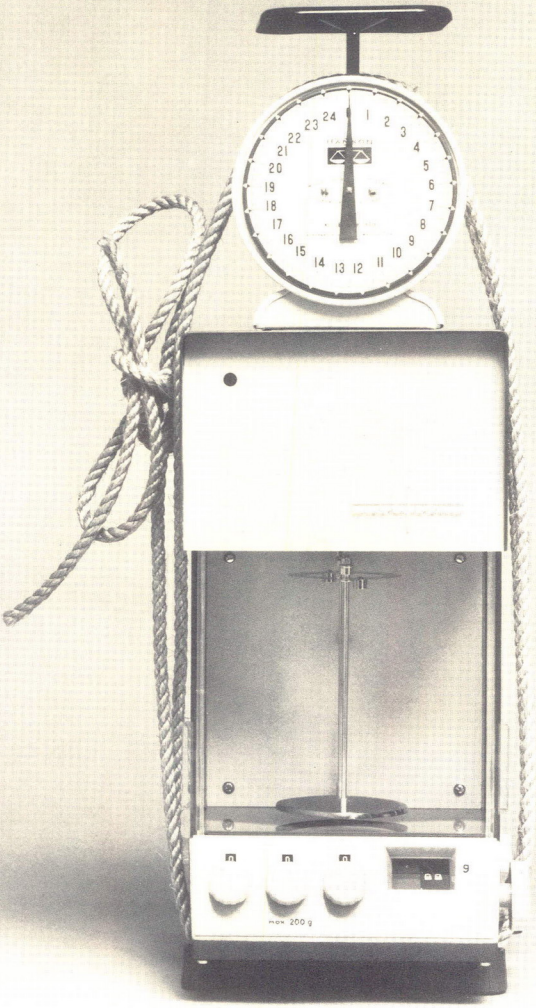

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Fig. 1–Macro reading: 14.0 grams plus

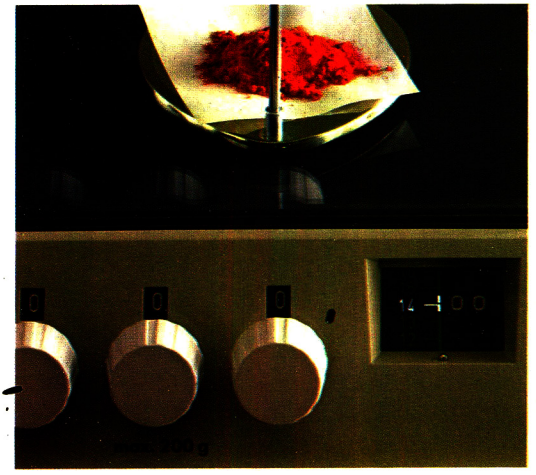
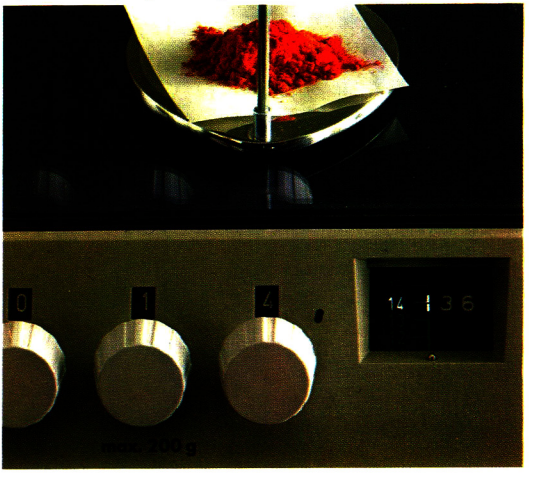


Fig. 2–Fine-weighing: 14.1436 grams



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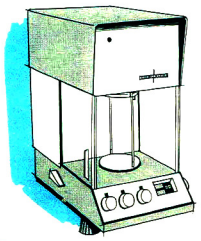

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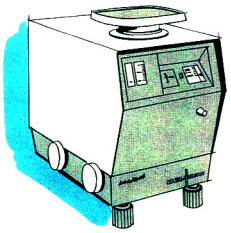
Reproducibilty	±0.05 mg	±0.05 mg	±0.01 mg

(*) Capacity with standard tare. Mechanical capacity (built-in weights) is without tare.



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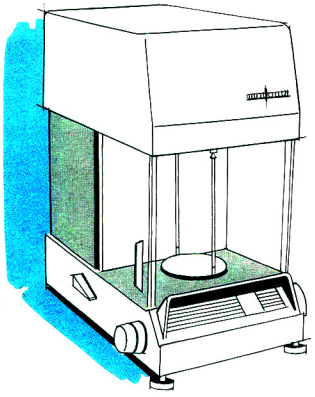

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Readability (digital)	1 mg	0.1 mg	0.1 mg	1 mg	*
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Built-in Weights	10-190 g	1-199 g	1-99 g
Optical Range	10 g	1 g	1 g
Mechanical Tare Range	10 g	1 g	1 g
Readability (digital)	1 mg	0.1 mg	0.1 mg
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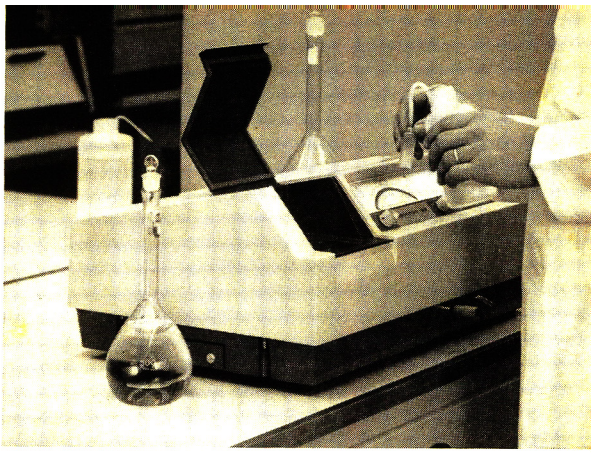

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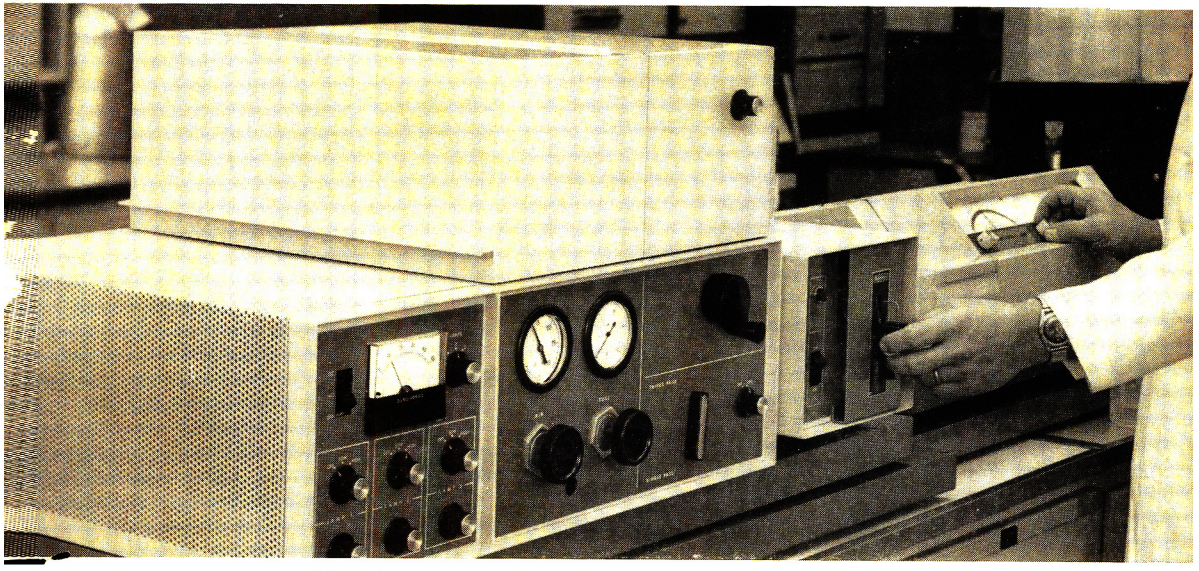

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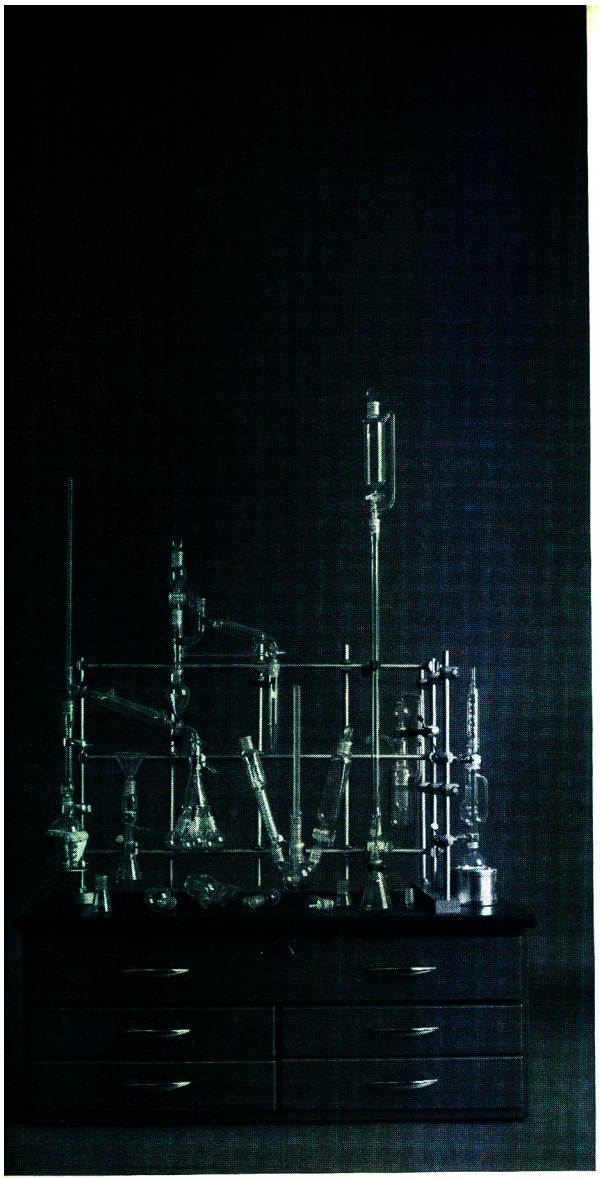



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Clinical Chemistry. Principles and Technics. *Richard J. Henry. xxiv + 1128 pages. Hoeber Medical Division of Harper and Row, 49 East 33rd St., New York 16, N. Y. 1964. $24.50.*

Reviewed by Clifford B. Walberg, Los Angeles County General Hospital, Los Angeles 33, Calif.

The purpose of this book, as indicated by the author in the preface, is "to present in a reasonably complete fashion, the principles and technics of clinical chemistry." The field of clinical chemistry has become so extensive and the literature so voluminous and filled with divergent and controversial opinions, that there has long been a need for a comprehensive reference work on the subject. The author has succeeded in preparing a book that fills this need. Its 29 chapters cover the field of clinical chemistry from the fundamentals of photometry, instrumentation, collection and preservation of specimens, and quality control to the methodology of almost all commonly requested biochemical tests. It is regrettable that the subjects of toxicology and endocrinology (except thyroxine) have been omitted from this fine work, but it is understandable since each of these would fill a volume in itself.

Each chapter concerning methods begins with an extensive review of the literature covering historical information related to reagents and technics, many of which have been abandoned by most workers, but which are still mentioned in many books on clinical biochemistry. This correlation of the literature alone will save the reader many hours of library work, and will quickly orient the reader to the discrepancies and problems involved in many analytical technics. The author does not hesitate to expose erroneous information, ideas, and opinions which are firmly entrenched in the literature. He attempts to clarify and eliminate these by pointing out the sources and some conditions which prevailed at the time of first publication (bilirubin and hemoglobin are outstanding examples). Old established methods are correlated with newer methods and the author's choice is given with reasons for his selection based on personal experience. The methods of choice are presented clearly and completely in step-wise fashion. Of special value is the section of "Notes" following each method in which emphasis is given to important details necessary for the success of the method but which are often omitted in text books or in original publications. Absorption curves are given wherever they help to explain points made in the text.

Undoubtedly the choice of methods will not meet with the approval of all workers in the field. However, the impression is given that all of these methods have been thoroughly investigated and successfully used in the author's laboratory. The advantages and shortcomings of these methods as compared to others are recognized.

The author personally abstracted over 15,000 references and has presented over 6900 of these. Throughout this book are many tables and charts, notable particularly for the quality of information which they impart at a glance (a complete list of commercially available spectrophotometers and flame photometers, a chart on hemoglobin and derivatives with absorption maxima and minima, etc). In addition, the appendix contains much useful information that, to the reviewer's knowledge, does not appear in any other one available source. The material includes lists of adsorbents, resins, desiccants, pH indicators, and manufacturers of commonly used equipment, plus instructions for preparing buffers and pH reference standards.

The book is well organized, clearly written and will serve as a reference for anyone associated with clinical chemistry whether he is a laboratory director, pathologist, technologist, instructor, or research worker.

New Biochemical Separations. *A. T. James, L. J. Morris, editors. ix + 424 pages. D. Van Nostrand Co., Inc., 120 Alexander St., Princeton, N. J. 1964. $12.50.*

Reviewed by Paul B. Hamilton, Alfred I. du Pont Institute of The Nemours Foundation, Wilmington, Del.

This is a very worthwhile book. Its 17 chapters include a tremendous amount of information while keeping within the small book class, relative to the more usual type of compendium. Each chapter contains the appraisal and summary of important papers, the choice of which has been selective. The information has been put together in a compact but very readable style. In short, it achieves its aim admirably, namely, to present in well organized form the information from good papers on the subjects covered. Each chapter is excellent in its own right.

Chapter 1 discusses methods for the detection and estimation of radioactive compounds separated by gas liquid chromatography. Both discontinuous and continuous methods of counting and the apparatus necessary for each are considered. Chapter 2 summarizes the gas liquid chromatographic procedures for the separation, identification, and estimation of steroids; alkaloids and sugars; Chapter 3 is limited to GLC determination of the coenzyme A esters. Chapter 4 discusses GLC of the bile acids. Chapter 5 summarizes experience to date in the GLC determination of amino acids.

Chapters 6 and 7 discussed gel filtration of proteins, peptides, amino acids, and the fractionation of polysaccharides.

Chapter 8, on the characterization of protein hydrolysates and amino acids in biological materials by thin layer chromatography (TLC), contains a great deal of detailed information on the separation of both free and DNP-amino acids. Chapter 9 on the chromatography of the alkaloids discusses their separation on both paper and thin layer chromatography. Chapter 10 considers TLC of steroids; Chapter 11 is concerned with TLC and ion exchange chromatography of the triterpenoid compounds and Chapter 12 condenses a great deal of information of TLC of bile acids and their derivatives.

Chapter 13 reviews the use of hydroxyapatite as an adsorbent for TLC in the separation of lipids and proteins. Chapter 15 is concerned with the separation of phospholipids and glycolipids, largely by TLC. Chapter 16 reviews the information on the chromatographic analysis of polar lipids on silicic acid impregnated paper and Chapter 17 describes counter current distribution of lipids.

Chapter 14, chromatography on impregnated adsorbents, is the most outstanding, not only for what has been done, but for its imaginative probing into new fields and for suggesting new possibilities. The first part deals with silver nitrate impregnated adsorbents as a means of separating by TLC similar compounds differing in degree and type of unsaturation. The second part, also TLC, considers the separation of polyhydroxy compounds

on adsorbents impregnated with glycol-complexing agents. As the author rightly asserts, given the principle of impregnating the adsorbent with compounds for specific purposes, the field has not yet even been scratched.

It is to be hoped that the editors will turn their attention to other methods such as ion exchange, density gradient centrifugation, differential dialysis, membrane separations, etc. in future publications.

Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives. *Academic Press, Inc., 111 Fifth Ave., N. Y. and London, England. 1964.*

Vol. II. Insecticides. *xvii + 619 pages; $23 regular; $20 subscription.*

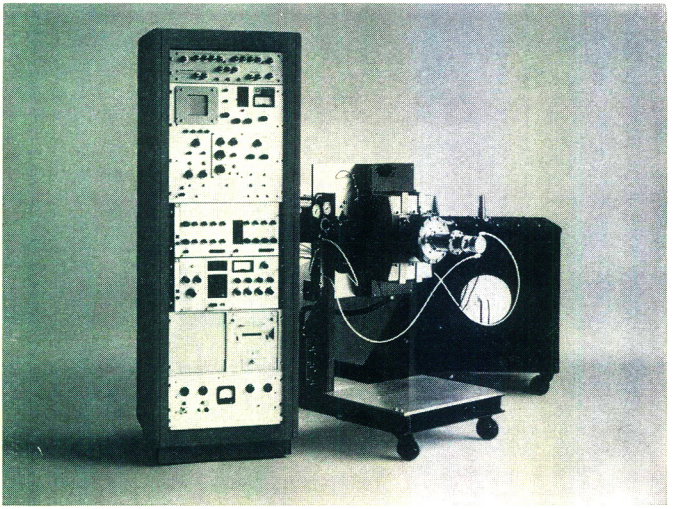
Vol. III. Fungicides, Nematocides, Soil Fumigants, Rodenticides, and Food and Feed Additives. *xii + 237 pages; $12 regular; $10 subscription.*

Reviewed by Milton S. Schechter, U. S. Dept. of Agriculture, Entomology Research Division, Pesticide Chemicals Research Branch, Beltsville, Md.

These two volumes are part of a four volume series, the first of which on "Principles, Methods, and General Applications" appeared in 1963. Forty-seven of the most important insecticides, miticides, acaricides, etc. are covered in Vol. II and fourteen fungicides, five nematocides and soil fumigants, two rodenticides and three food and feed additives in Vol. III.

These volumes are the only collection of recent, detailed, analytical methods available on such a wide variety of pesticides and food and feed additives besides the well-known "Methods of Analysis of the Association of Official Agricultural Chemists." Hence, like the latter, they will be a necessity in any laboratory concerned with the analysis of either formulations or residues of this important class of compounds.

The methods for each pesticide and food additive have been written by leading authorities who have taken great pains to select one or more of the best procedures for formulations and also for residues. In virtually every case, the structural formula, empirical formula, name, source of analytical standard, biological properties, history, physical properties, chemical properties (including the synthesis in some cases), formulations, formulation analysis, residue analysis, and references are covered. The structural formulas and figures for apparatus are very clear and well done. Although the sensitivity, precision, and recovery to be expected are indicated in some instances, it would have been better if this information had been given for all of the methods so that the analyst would know what is reasonable to expect. However, this is not too serious since this information can be obtained by consulting the original references. A more serious shortcoming is that, except for Thiodan, colorimetric methods for the chlorine-containing and for some of the phosphorus-containing insecticides are emphasized and recommended without a gas chromatography procedure being described in detail. In most laboratories having suitable gas chromatographs, conventional spectrophotometric or colorimetric procedures have been displaced by gas chromatographic methods wherever possible. However, some references are given to the recent gas chromatography



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literature and Volume I contains a whole chapter on the gas chromatography of pesticides.

The last volume in this series will be Volume IV on herbicides. It would be highly desirable, if it is at all possible, to include in this volume a bibliography of references to new methods and literature pertaining to each of the pesticides or food additives described in the earlier volumes.

It is difficult to see how any laboratory engaged in the analysis of formulations or residues of pesticides, or food and feed additives can afford to be without these volumes. They are as up-to-date as any text can be without making them a loose-leaf type.

In summary, Dr. Zweig and his contributing authors have done an excellent job in compiling this set of volumes on analytical methodology in an important and fast-growing field and they should be considered as highly recommended reference works and working tools.

Gas Analysis by Gas Chromatography. *P. G. Jeffrey and P. J. Kipping. xi + 216 pages. Macmillan Co., 60 Fifth Ave., New York 11, N. Y. 1964. $10.*

Reviewed by Theodore Christos, Explosive Research Center, Bureau of Mines, U. S. Department of the Interior, Pittsburgh, Pa.

This is the first text to be written dealing specifically with gas analysis by gas chromatography. According to the authors, they "include reference to compounds that are normally transferred to a chromatograph in the gaseous state, and are present in such samples in amounts that warrant determination." There is no special emphasis on the determination of trace amounts, but suggestions are included in appropriate portions of the text.

The authors have stressed the practical aspect of gas chromatography; therefore, a theoretical treatment has been omitted. A standard electronic circuit for thermal conductivity detectors has been included, but complete electronic circuitry for ionization detectors is not shown. The two chapters on detectors contain a critical evaluation of the applicability of the various types for specific gases.

The text is divided into three parts. Part I describes sample transfer systems, detectors, and apparatus and discusses gas solid and gas liquid chromatography. The description of sample transfer systems is thorough. The treatment of solid adsorbents is explained and some stationary liquid

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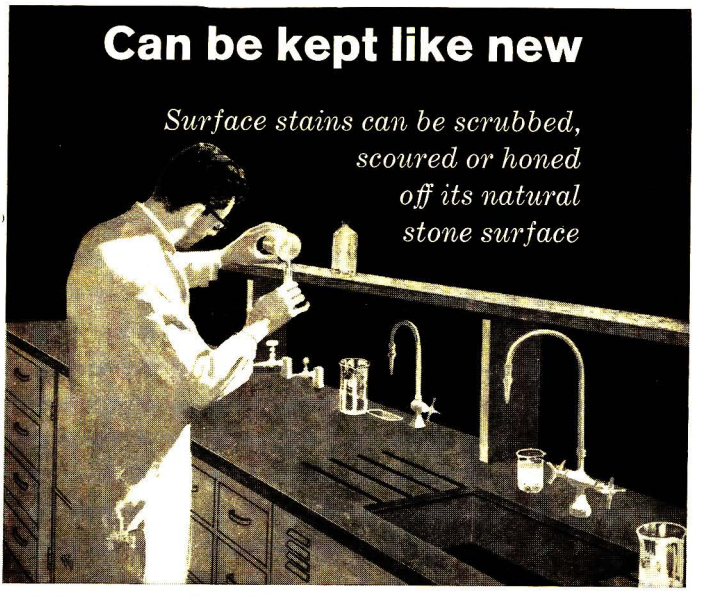

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phases used for gas analysis are presented with reference to the gases for which they are suitable. Part II covers the determination of individual gases. There are excellent discussions of the separation of hydrogen and its isotopes and the separation of nitrogen compounds. A chapter deals with the separation of the common gases—i.e., oxygen, nitrogen, methane, carbon monoxide, and carbon dioxide. Other chapters cover the hydrocarbon gases, sulfur compounds, and halogen compounds. There is also a chapter on water, hydrogen cyanide, cyanogen, silanes, boranes, and germanes. Part III discusses the application of gas chromatography to gaseous mixtures containing the common inorganic gases and methane. There is a brief discussion of engine exhaust gas and sludge digestion gas.

The authors have outlined the operating conditions for various separations at the ends of the chapters. The examples shown will be especially helpful to those beginning to analyze gases by gas chromatography. A careful study of any chapter will save the analyst the time necessary to determine the conditions for a satisfactory analysis.

Each subject discussed contains references to the original papers. The subject index is excellent and thus provides ready searching. An author index is also provided.

The book not only fills a need for a text on gas analysis by gas chromatography, but can be used as a ready reference manual.

Spectra-Structure Correlation. *John P. Phillips. ix + 172 pages. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 10003. 1964.*

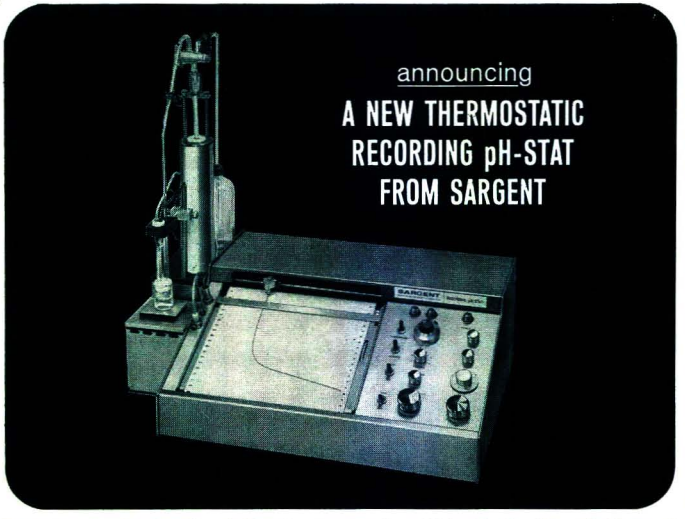
Reviewed by J. M. Vandenbelt, Research Division, Parke, Davis & Co., Ann Arbor, Mich.

The photometric revolution has occurred in one generation. Absorption spectra are now used in the chemical work of every laboratory from early undergraduate to technical institute, from first reaction to product assay. Every aid to efficiency in all this action is significant; Professor Phillips helps to provide it in this book.

His aim is "the analysis of spectrophotometric data." His range is from far ultraviolet to far infrared. Absorption spectra in each part of the range are examined for best contribution to the structure analysis of the main categories of chemical compounds.

These categories are: Hydrocarbons, Compounds with Oxygen Function, Compounds with Nitrogen Functions, Heterocycles, Organic Compounds Containing Halogen, Sulfur, Phosphorus, Silicon, or Boron, Inorganic Compounds, and Complex Materials. A description and evaluation of the spectra of each of these forms a chapter.

There are a number of subdivisions in each. For example, the chapter on "Compounds with Nitrogen Functions" takes up Amines, Amides and Imides, Double Bond from Nitrogen to Carbon, Nitrogen, or Oxygen, and Nitriles and Related Compounds. The spectral characteristics of each group in the regions of far ultraviolet, ultraviolet–visible, near infrared, infrared, and far infrared are examined in turn for properties and applications. This arrangement permits comparison of the relative merits of each type of spectrum for the particular group, and encourages the valuable concept that



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studies employing more than one type of spectrum tend to give more information and certainty than any one alone. At the end of the chapter there is a summary table, giving the author's opinion as to the most distinctive regions of the spectrum for a group.

To present a reasonable exposition of the chemical spectra of five regions in 172 pages, including an introductory chapter and 16 pages of Author and Subject Indexes, requires careful selection, a sure touch, and a compact style. These are evident.

The author has had to rely heavily on the literature in order to encompass so much material. As a result, some aspects of the original conclusions may have been shaded or changed. For example, in a discussion of the trisubstituted benzenes, it is stated that "the maxima lie at wavelengths close to those found in the most displaced monosubstituted benzene of the three possibilities." This of course should read "the most displaced corresponding band in the spectra of the disubstituted compounds containing the same groups." A weakness, inherent in a short treatment, is the lack of attention which can be given to band number, shapes, intensities, and spectrum contours, and implications which derive from these.

The introductory chapter describes wavelength ranges, gives definitions, types of instruments, the mechanisms of absorption, spectrophotometric sources, solvent and other effects, and discusses the accuracy of spectra. It is shown from collections of published ultraviolet data on a simple compound that the accuracy of some work is unbelievably poor. This is more the result of carelessness or incompetence at the bench than of instrument failure. The author tends to discount the quality of early absorption work. The reviewer respectfully submits that it is not necessarily bad since the advent of the Beckman spectrophotometer.

In summary, this volume provides a clear outline of spectral use and structure implications. The material covered is fundamental. It will be particularly appreciated by those who wish to expand their knowledge in a field quickly, or those who have tended to work mainly with one type of spectrum and would benefit if they could use the others also.

Stability Constants of Metal-Ion Complexes. Section I: Inorganic Ligands. *Lars Gunnar Sillén, compiler;* **Section II: Organic Ligands.** *Arthur E. Maytell, compiler. xviii + 754 pages. The Chemical Society, Burlington House, London W1, England. 1964. $23.*

The first edition of this book was published as "Stability Constants of Metal-Ion Complexes, and Solubility Products of Inorganic Substances, Part I, Organic Ligands," and "Part II, Inorganic Ligands," Special Publication No. 6, 1957, and Special Publication No. 7, 1958, respectively. The present edition, Special Publication No. 17, contains both parts bound in one volume. Both sections have been brought up-to-date by the inclusion of all data published up to the end of 1960 and of some data which have appeared from 1961 to 1963. The scope of the inorganic section has been extended to cover redox equilibria and extraction of inorganic ligands into nonaqueous solvents.

It has been the policy of the compilers to attempt to read each paper in the original. Equilibrium constants quoted are usually those given by the authors. In addition to the tables of stability constants, the book has indexes of inorganic ligands, organic ligands, and metals.

Systematics of the Electronic Spectra of Conjugated Molecules: A Source Book. *John R. Platt and Co-workers. viii + 342 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N. Y. 10016. 1964. Paperbound, $6.95; Clothbound $10.95.*

This book is a collection of the original papers from the Laboratory of Molecular Structure and Spectra, Department of Physics, at the University of Chicago. All of the papers are bound together by a common approach which according to the authors might be called "chemical systematics" or the "chemical perturbation" approach. The essential idea and rationale of this approach is described explicitly in five of the papers. All of the contributions have been published before, many in the *Journal of Chemical Physics.*

Practical Handbook on Spectral Analysis. *V. S. Burakov, A. A. Yankovskii. xiv + 190 pages. Macmillan Co., 60 Fifth Ave., New York 11, N. Y. 1964. $12.*

This is an edited translation of the original Russian "Prakticheskoye rukovodstvo po spektral'nomu analizu," published in 1960 by Izdatel'stvo Akedemii nauk B.S.S.R., Minsk. The book was translated by R. Hardbottle and edited by S. Tolansky.

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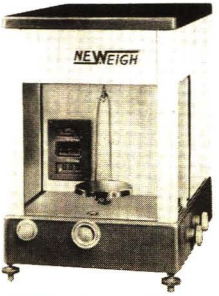

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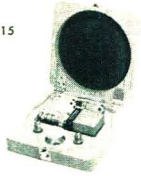

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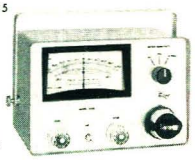

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Major practical problems of visual photographic methods of spectra analysis are covered in this volume. The main standard instruments and reliable methods for the analysis of ferrous and nonferrous alloys are described. Atlases of spectra and tables of spectral lines are given. Chapters deal with light sources, visual methods, photographic methods, quantitative procedures, spectral analysis of powders and solutions, and setting up a spectral analysis laboratory.

Temperature Measurement Thermocouples, *C96.1-1964. American Standards Association. Instrument Society of American, 530 William Penn Place, Pittsburgh 19, Pa. $4.50; to ISA members, $3.*

This standard was developed after five years of study and research by the ASA-C96 Committee on Temperature Measurement Thermocouples and is based on the original work of ISA Recommended Practices Committee (SD-RP1) on Thermocouples and Thermocouple Extension Wires. In addition to definitions of terminology, this new standard includes coding practices, temperature EMF tables, and procedures for fabrication, selection, checking, and installation for six widely-used types of thermocouples.

Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives. Vol. IV. Herbicides, *Gunter Zweig, editor. xiii + 269 pages. Academic Press, Inc., 111 Fifth Ave., New York, N. Y. 10003. 1964. $10 subs.; $12, reg.*

Thirty different herbicides and plant growth regulators that are widely used are covered in this volume. Experimental methods for formulation and residue analyses and other data such as chemical and biological properties and history of development for the compounds are included. The individual procedures have been written by the originators of the method or by experts in the field. The following herbicides are covered: Alanap, ametryne, 3-amino-*s*-triazole, atratone, atrazine Carbyne, isopropyl-*N*-(3-chlorophenyl) carbamate, Dacthal, Dalapon(sodium), *S,S,S*-tributyl phosphorotrithioate, 2,4-dichlorophenoxyacetic acid, Eptam, Falone, isopropyl *N*-phenylcarbamate, maleic hydrazide, monuron, diuron, neburon, Prometone; prometryne, Propazine, Randox, Sesone, silvex, simazine, Stam, Tillam, 2,4,5-trichlorophenoxyacetic acid, and Vegadex.

Engineering Units and Physical Quantities. *H. S. Hvistendahl. viii + 132 pages. St. Martin's Press. Inc., 175 Fifth Ave., New York 10, N. Y. 1965. $5.*

This book was written for those people engaged in work in the physical and mechanical sciences. It contains the various systems of units—metric and English—used by engineers, with particular reference to the International MKSA system and to ISSO recommendations. The first three chapters deal with definitions and basic principles; quantity calculus, quantity arithmetic, and conversion of units; and systems of units. Following this are chapters on the units of heat and thermodynamics; units of electricity and magnetism; and dimensional analysis and the laws of simulitude. A chapter of Tables of Conversion includes 19 pages of tables. The final chapter deals with vector calculus symbols and notations.

Standard Aqueous Electrode Potentials and Temperature Coefficients at 25° C. *A. J. de Bethune. N. A. S. Loud. 19 pages. Clifford A. Hampel, 8501 Harding Ave., Skokie, Ill. 60077. 1964. Paperbound. $1.95 + 8 cents postage.*

This booklet provides a theoretical introduction, discusses chemical applications and includes tables of thermodynamic properties of water and the chemical elements. This is said to be the most complete compilation of electrode potentials ever assembled and the first one to include temperature coefficients and thermal emf's explicitly. It contains the electrode potential data for 467 reactions of 90 elements.

U. S. Government Publication

The following can be obtained from the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402.

Analysis of Essential Nuclear Reactor Materials. *Clement J. Rodden, ed. xiii + 1280 pages. 1964. Paper Cover. $4.25.*

This book just released by the U. S. Atomic Energy Commission supersedes Dr. Rodden's earlier book "Analytical Chemistry of the Manhattan Project," National Nuclear Energy Series, Dev. VIII, Vol. 1, McGraw-Hill Book Co., 1950. The book has been written to provide the analytical chemist with the in-

formation needed to carry out many analyses involved in nuclear technology.

The first chapter, Uranium by C. J. Rodden, 157 pages, covers the chemistry of uranium and its compounds, methods of separation, and methods of determination. Five hundred references to the literature are given. Following this are three chapters: Plutonium by C. F. Metz and G. R. Waterbury, 134 pages, 242 references; Thorium by R. Z. Bachman, C. V. Banks, 55 pages, 186 references; and Beryllium by C. J. Rodden, 56 pages, 123 references. These chapters consider the general chemistry of the element in question, methods of dissolution and separation, methods of determination; and, in the case of beryllium, analysis of impurities in the element.

Chapter 5, Alloys and Ceramics by R. W. Bane, 83 pages, 208 references, includes analytical methods for aluminum, zirconium, stainless steel, molybdenum, bismuth, and fissium alloys as well as methods for ceramics and plutonium alloys. Chapter 6, Expended Reactor Fuels by G. L. Booman, J. E. Rein, 49 pages, 101 references, gives methods of analysis of irradiated fuels with emphasis on proven methods.

Chapter 7, Graphite by F. E. Clark, 35 pages, 114 references, gives analytical methods for that element, while Chapter 8, Boron by M. W. Lerner, J. Rynasiewicz, 51 pages, 340 references, gives detailed separation and determination procedures for boron. Chapters 9 and 10, Heavy Water by C. E. Anderson, D. G. Ebenhack, 28 pages, 26 references, and Reactor Coolants by W. C. Judd, D. Dutina, D. J. Rodden, 58 pages, 43 references, are followed by the longest chapter in the book (181 pages, 625 references), Trace Elements by M. W. Lerner. This chapter describes the "danger coefficient, K" which is used to calculate the ability to absorb neutrons by contaminants in nuclear technology, and gives detailed procedures or references to published procedures for contaminants. The last five chapters of the book deal with specific methods and cover 352 pages and provide more than 800 literature references. These chapters and authors are: Spectrochemical Methods by H. R. Mullin, C. G. Goldbeck; Mass Spectrometry by A. E. Cameron, C. M. Stevens; Radiochemical and Nuclear Methods by S. A. Reynolds; Electrometric Methods by W. N. Carson, Jr.; and X-Ray Spectrometric Methods by C. G. Goldbeck.

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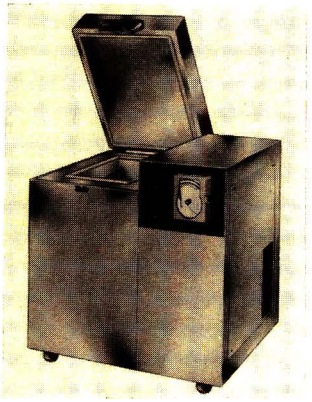

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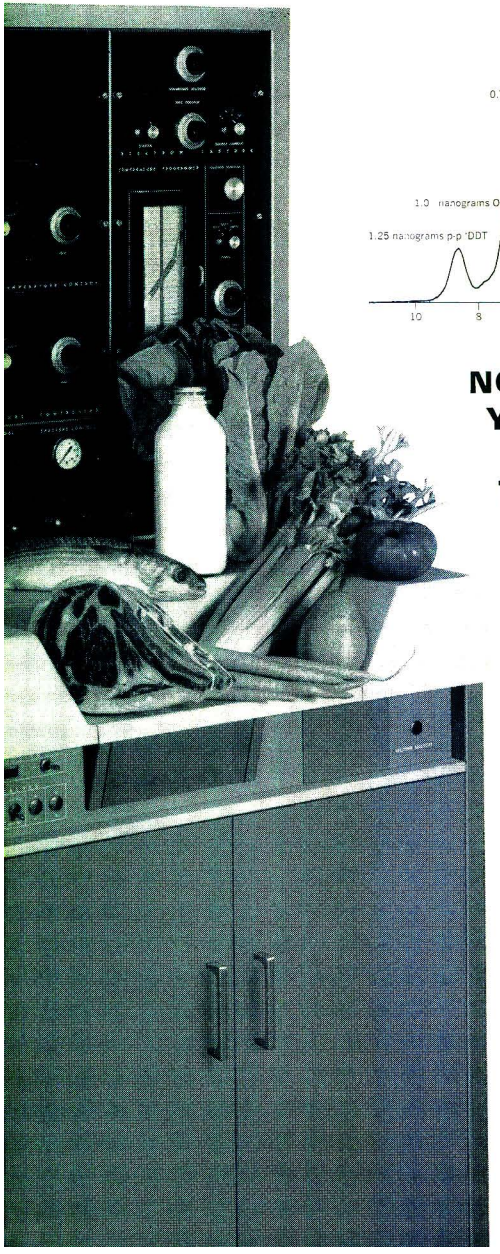

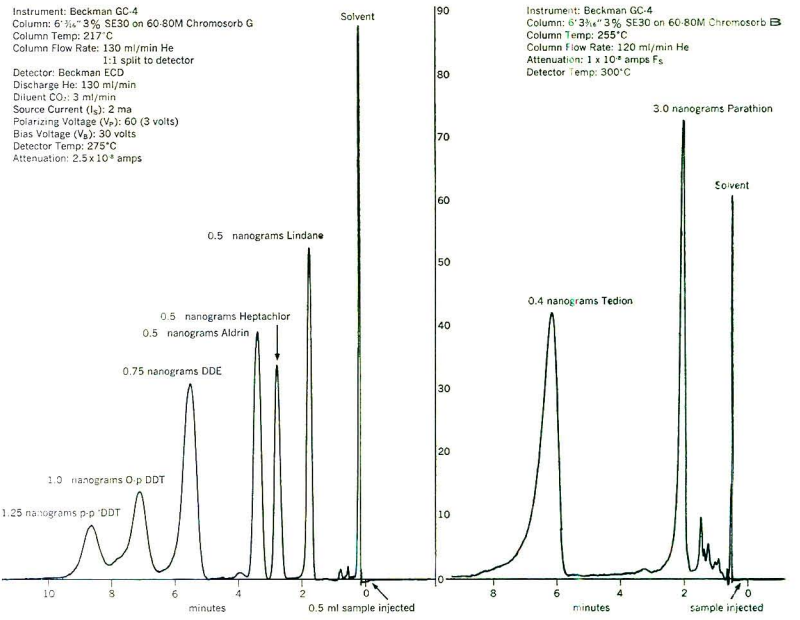

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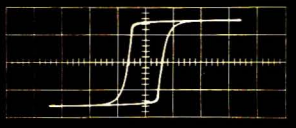

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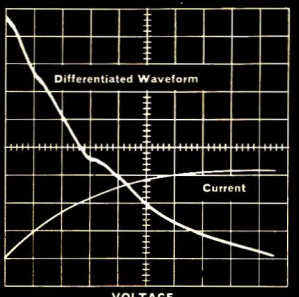

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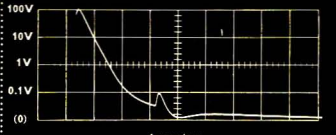

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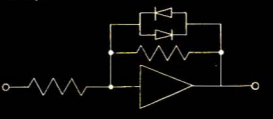

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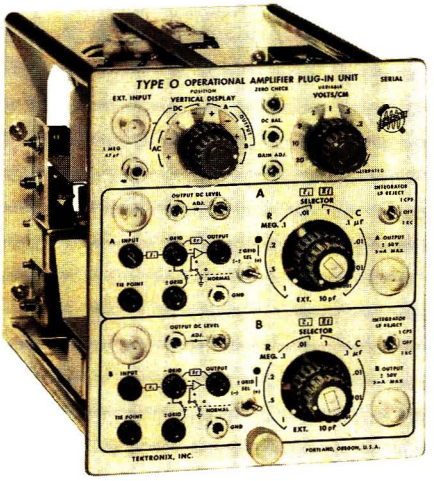

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Using this new Operational Amplifier Unit in your Tektronix Oscilloscope, you can perform precise operations of integration, differentiation, function generation, linear and non-linear amplification.

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You can use the Type O Unit as a gated integrator . . . as a high-input-impedance amplifier . . . as a bandpass amplifier . . . as a constant-current-drive amplifier . . . as a peak-memory amplifier . . . as a function generator . . . as a capacitance-measuring device . . . as a low-current measuring device . . . and for many and varied other specialized operations—some performed *with* external circuitry and some *without.*

CHARACTERISTICS

The Type O Unit contains two complete operational amplifiers and one complete vertical preamplifier.

Each operational amplifier features 15 mc open-loop gain-bandwidth product, open-loop dc-gain of 2500, selectable input and feedback impedances, drift rejection for ac integration. The output of one operational amplifier can be applied to the input of the other for combined operations.

The vertical preamplifier can be used independently or to monitor the output of either operational amplifier. In a Tektronix Type 540-Series Oscilloscope, the passband is dc-to-25 mc, the risetime is 14 nsec, and the maximum calibrated sensitivity is 50 mv/cm.

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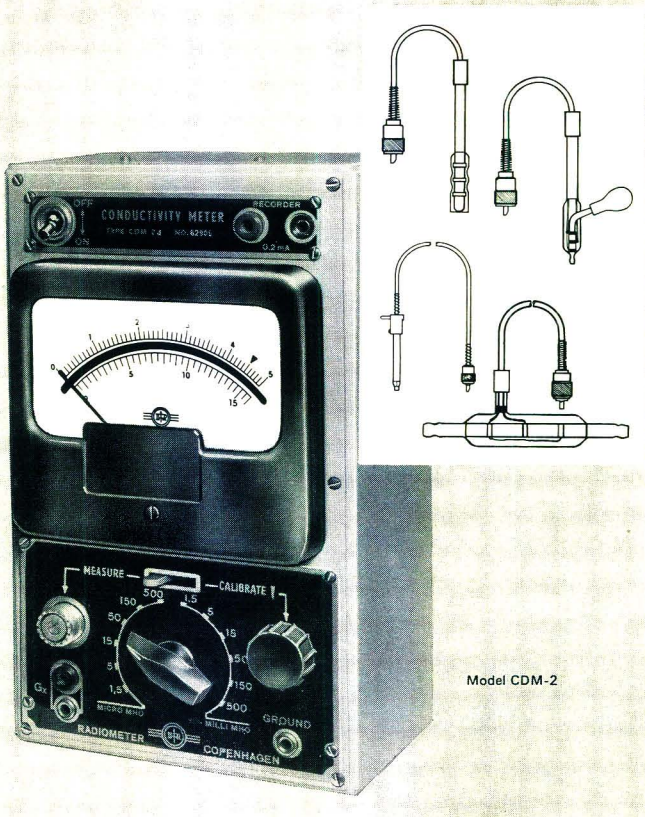

Model CDM-2

Direct reading CONDUCTIVITY METER *by RADIOMETER*

The Radiometer Model CDM-2 has been designed with laboratory requirements in mind. Without any sacrifice in accuracy it has been made more flexible and simpler to operate than the conventional conductivity bridge—and covers the *complete* range of conductivities.

Direct readings on 12 ranges are displayed instantly on a hand drawn illuminated mirror scale with an accuracy of better than ±1% on most ranges and ±2% at the extremes of conductivity.

A choice of conductivity cells makes CDM-2 ideal for all normal laboratory conductivity measurements as well as conductometric titrations. Available cells cover either immersion, flow, or pipette applications—all on grounded or ungrounded media.

Output terminals are provided for connection to recorders for continuous measurement, or to automatic titrators for automatic conductometric titrations.

Write for complete descriptive literature and prices.

RANGES: (12 complete full scale ranges)

0 - 1.5 - 5 - 15 - 50 - 150 - 500 micromhos.

0 - 1.5 - 5 - 15 - 50 - 150 - 500 millimhos.

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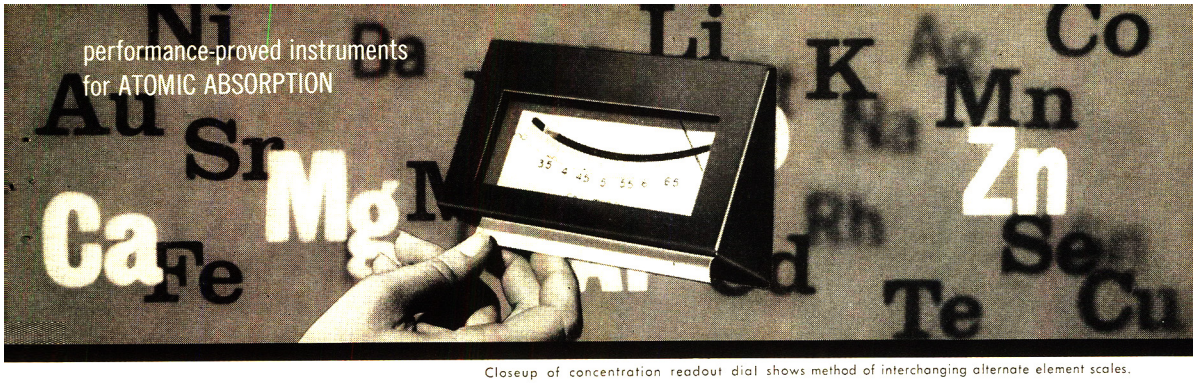

Closeup of concentration readout dial shows method of interchanging alternate element scales.

NEW, COMPACT ATOMIC ABSORPTION SPECTROPHOTOMETER FROM PERKIN-ELMER AT $2,900!

The new Model 290 is designed to make available all the advantages of atomic absorption at the lowest possible cost. The Model 290:

- Determines up to 30 metallic elements with a detection limit of less than 1 ppm.
- Reads out *directly in concentration.*
- Provides quantitative precision better than 1% of the amount present.
- Makes successive determinations in less than 15 seconds per sample.
- Requires as little as 0.1 ml of sample solution.
- Operates with complete freedom from spectral interferences and a minimum of matrix interferences.
- Is simple to operate.

Fast and precise, the Model 290 is designed for laboratories where large numbers of samples must be analyzed for a moderate quantity of elements, or where many persons must use the instrument. Interchange between one element and another is simplified by P-E's *new multi-element hollow cathode sources,* now available in Ca-Mg and Cr-Cu-Co-Fe-Ni-Mn combinations.

Compact (25″ x 15″ x 12″) and self-contained, the Model 290 reads out concentration directly on a five-inch meter, which incorporates interchangeable scales. No conversion tables or calculations are required. An AC system eliminates spectral interference. The grating monochromator insures high energy. Gas controls are built in. The stable, almost inaudible pre-mix burner handles higher dissolved solids than any other burner. The instrument can be used with an external recorder, which will also read out in concentration. The Model 290 handles many elements impossible of determination by flame photometry. In the analysis of alkalis and alkaline earths, the Model 290 outperforms flame photometry in precision, accuracy and specificity.

The Model 290 is backed up by free customer training courses at Perkin-Elmer. For complete information, including specifics on the Model 290 applied to your needs, write the Perkin-Elmer Corporation, 702 Main Avenue, Norwalk, Connecticut.

(Prices subject to change without notice.)

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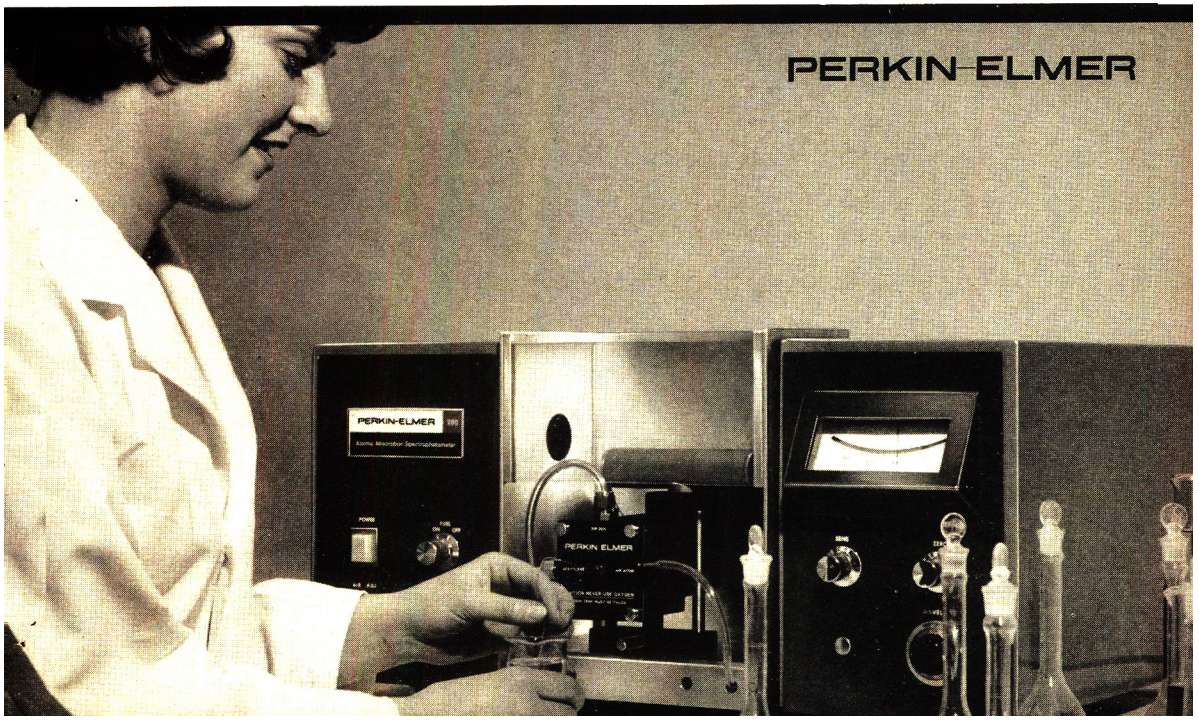
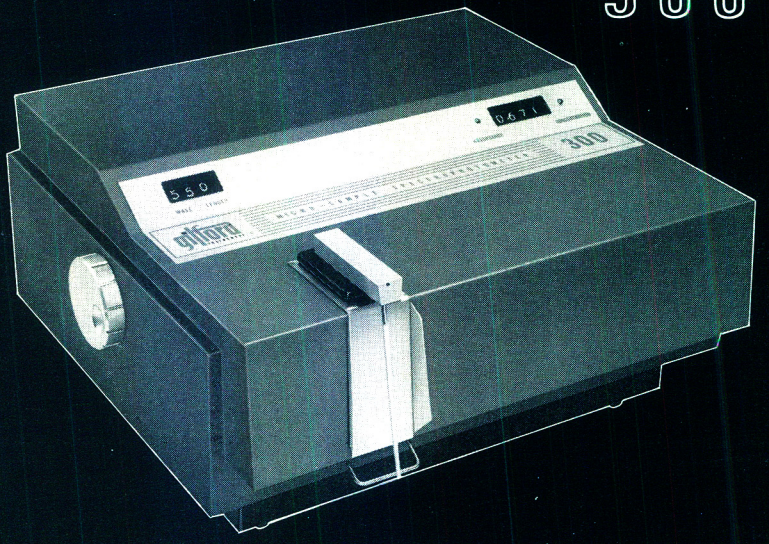


ANNOUNCING..... the GILFORD 300



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MATHESON Compressed Gas Notes

Now available for prompt shipment: Cyanogen, Nickel Carbonyl, Deuterium, tech. grade

Cyanogen $(CN)_2$

Cyanogen, also called Dicyan and Oxalonitrile, is a colorless, flammable, toxic gas at room temperature and atmospheric pressure with a characteristic almond-like odor. It is supplied in 8 oz., 2 lb. and 5 lb. cylinders as a liquefied gas under its own vapor pressure of about 60 p.s.i.g. at 70°F. Cyanogen has a minimum purity specification of 98.5% by volume. The following is a typical analysis of the gas as supplied by Matheson:

	Vol.
Cyanogen	99.14%
Hydrogen Cyanide	3200 ppm
Carbon Dioxide	0.5%
Chlorine	nil
Water	nil
Nitrogen	trace
Hydrogen Chloride	nil
Cyanogen Chloride	400 ppm

Physical constants (partial listing) of Cyanogen are as follows:

Molecular Weight	52.04
Vapor Pressure@ 70°F.	60.1 p.s.i.g.
Specific Volume, 70°F., 1 atm.	7.4 cu. ft./lb.
Boiling Point @ 1 atm.	–6.1°F. (–21.17°C.)
Freezing Point @ 1 atm.	–18.2°F. (–27.9°C.)
Density, Liquid @ b.p.	0.9537 g./cc.
Critical Temperature	259.8°F. (126.55°C.)
Critical Pressure	855.5 p.s.i.a. (58.2 atm.)
Latent Heat of Vaporization @ b.p.	5.778 kcal./mole
Specific Heat, Gas Cp, 15°C., 1 atm.	0.4095 cal./g/°C.
Specific Heat, Gas Cv, 15°C., 1 atm.	0.3260 cal./g/°C.
Specific Heat Ratio, Cp/Cv	1.256
Viscosity, Gas, 20°C.	107 micropoises
Surface Tension @ b.p.	21.98 dynes/cm.
Heat of Dissociation	77±4 kcal./mole
Trouton's Constant	22.94
Heat of Formation	73.8 kcal./mole
Flammability Limits in Air	6—32%

Because cyanogen burns with a very hot flame it is of interest as a gas for welding and cutting heat-resistant metals, as a rocket and missile propellant when mixed with an oxidizing agent such as Ozone or Fluorine, as a fumigant, and as an intermediate in many organic chemical syntheses.

Recommended Controls

Single Stage Regulator: Matheson #19C-160
Needle Valves: Matheson #57-160 and #59

Nickel Carbonyl $Ni(CO)_4$

Nickel Carbonyl is a volatile, toxic, mobile liquid with a musty odor. It melts at –25°C. and boils at 43°C. Its vapor pressure at 68°F. is 315 mm. Hg.; specific gravity at 17°C., 1.32. Its molecular weight is 170.73. It is supplied in 1, 5, 10, 25, and 150 lbs. quantities in cylinders pressurized with carbon monoxide to 15 p.s.i.g. at 68°F. Cylinders containing 25 and 100 lbs. of Nickel Carbonyl are supplied with a goose-neck eductor tube. Nickel Carbonyl is practically insoluble in water and does not react with water or aqueous acids or alkalies. It is highly soluble in many organic solvents, such as ethanol, ether, benzene, and chloroform. In Nickel Carbonyl, the four carbonyl groups form a tetrahedral arrangement and are linked covalently to the metal through carbon rather than oxygen. Its properties reflect this unusual coordination structure. Nickel Carbonyl begins to decompose at 50°C. into Nickel and Carbon Monoxide. In many reactions, the properties of Nickel Carbonyl are those of Nickel and Carbon Monoxide. Thus Nickel Carbonyl, when reacted with Bromine, gives Nickel Bromide and Carbon Monoxide. However, with Grignard reagents its reactions are those of Carbon Monoxide. Nickel Carbonyl is oxidized rapidly by atmospheric Oxygen to Nickel Oxide, with liberation of Carbon Monoxide. Nickel Carbonyl is used as a catalyst in carbonylation reactions. It is also used (in the Mond process) as a way to refine Nickel. Nickel Carbonyl has been used to obtain metallic mirrors and to coat objects with a thin film of Nickel.

Recommended Controls

Needle Valve: Matheson #50-320
Lecture Bottle Control: Matheson #31

Deuterium, Technical Grade D_2

Now at a new lower price.

This heavier, stable isotope of ordinary hydrogen is a colorless, odorless, flammable gas. It is shipped as a non-liquefied gas in high pressure steel cylinders at varying pressures depending on the quantity packaged. Cylinder sizes are 7, 14, 50, 100, 500 and 1000 liters. Matheson's technical grade Deuterium has a minimum purity of 98.0 atom percent. (Matheson also offers Deuterium as a 99.5 atom percent gas.)

Physical constants (partial listing) of technical grade Deuterium are as follows:

Molecular Weight	4.032
Specific Volume (70°F., 1 atm.)	97 cu. ft./lb.
Boiling Point @ 1 atm.	23.59°K. (–417.1°F.) (–249.5°C.)
Triple Point	18.71°K. (–425.9°F.) (–254.4°C.)
Freezing Point @ 121 mm. Hg	18.58°K. (–426.1°F.) (–254.5°C.)
Specific Gravity (Hydrogen=1)	2.0
Density, Gas (32°F., 1 atm.)	0.01122 lb./cu. ft.
Critical Temperature	38.35°K. (–390.55°F.) (–234.75°C.)
Critical Pressure	241.55 p.s.i.a. (16.432 atm.)
Latent Heat of Fusion @ Triple Point	52.3 cal./mole
Latent Heat of Sublimation @ 18.58°K.	355.4 cal./mole
Latent Heat of Vaporization @ b.p.	293 cal./mole
Flammable Limits in Air	5-75% (by volume)

Deuterium is used in tracer applications, in reaction rate studies, and exchange reaction studies, i.e., reactions in which one or more deuterium atoms trade places with light hydrogen atoms in some ion or molecule.

Recommended Controls

Two Stage Regulator: Matheson #8-350
Single Stage Regulators: Matheson #1L-350, #1H-350 and #36
Needle Valves: Matheson #50-350, #52-350 and #31

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Data Sheets which include prices are now available on these three gases. Check coupon for data sheets you desire.

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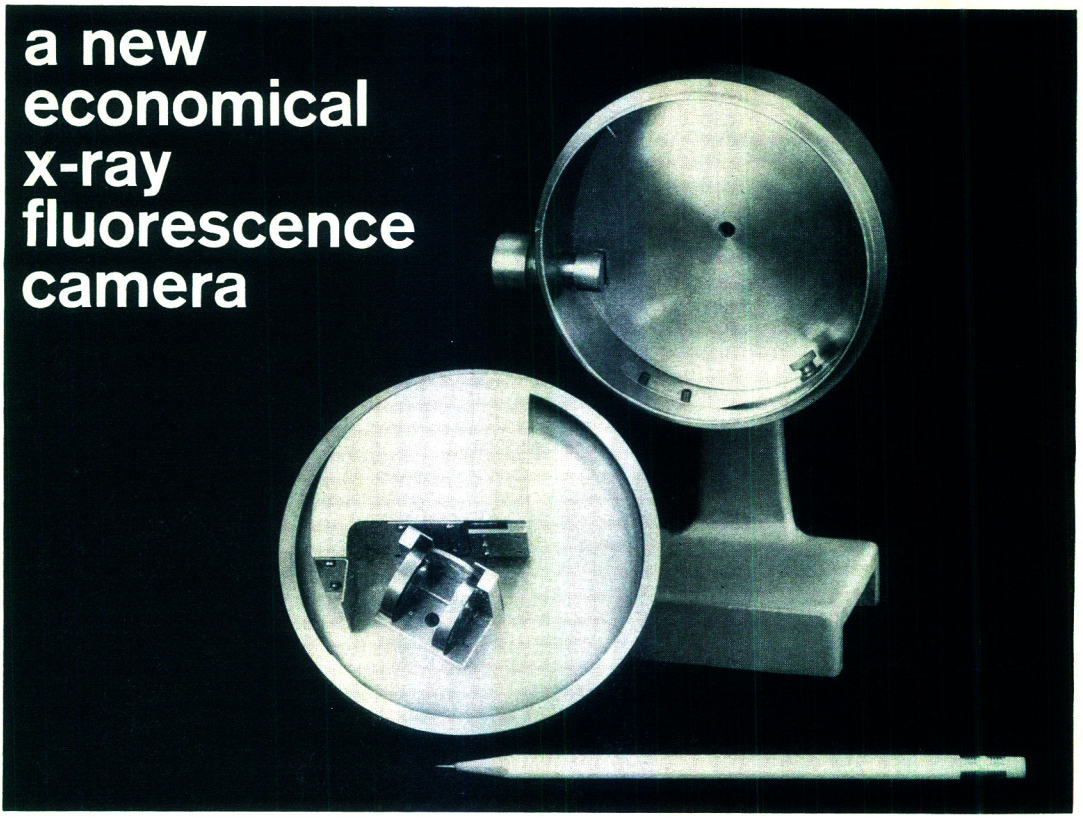
a new economical x-ray fluorescence camera



What it is

The x-ray fluorescence camera identifies the elements making up the major proportion of unidentified materials. It is a companion piece to the x-ray powder diffraction camera, making use of the same photographic films and processing and the same x-ray sources. The complete fluorescence spectrum can be obtained from specimen in 60 minutes. ☐ The fluorescence camera uses either 'white' or 'monochromatic' x-rays to cause the elements of the specimen to give off their own characteristic 'monochromatic' x-rays. These in turn are diffracted by a single crystal of a known material, which is incorporated in the instrument. As a result, the x-ray pattern which is read directly on the film, from a fluorescence camera, is due entirely to various "colors" of x-rays, originating from the specimen of the unidentified material.

How it is used

The specimen is placed in a holder. Under a safelight in a darkroom, a strip of ordinary 35mm x-ray film is cut about 7″ long, inserted in the camera and held in place by a spring clip. The lid of the camera is then pressed in place. Once the lid is in place, the unit is light tight and sufficiently vacuum tight. The unit is then placed on the camera track, clamped in place, connected to a vacuum pump, if necessary, and an exposure made in the same manner as used in preparing diffraction patterns. Alignment is not critical, because the height and most of the width of the x-ray source is used. ☐ Elements having an atomic number of 22 or higher may be made to fluoresce and will be registered on film. Using a sodium chloride diffracting crystal and a vacuum of the order of 1mm of mercury, potassium, calcium and scandium may be detected also.

What it costs

Though small, compact and the "economy" model of the industry, this x-ray fluorescence camera is manufactured by our instruments division to rigid quality standards. All parts are made of brass, with the exception of the aluminum specimen holder. The finish in all cases is smooth machine finish, with dull nickel plating. ☐ For more detailed information about the x-ray fluorescence camera, write us on your letterhead. We'll need to know your present x-ray power unit and its model number. Cameras can be supplied, ready to use, with Norelco or GE equipment, at no extra charge. ☐ If you have an immediate need for the camera, why wait... send your order today. Remember to send all information requested above. Oh, and don't forget the check. Make it out to Analtech, Inc.

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Also: Our Seminar and Workshop on TLC and "UNIPLATE" **/ May 3-4** in San Francisco, Calif. **/ May 24-25** in Houston, Texas

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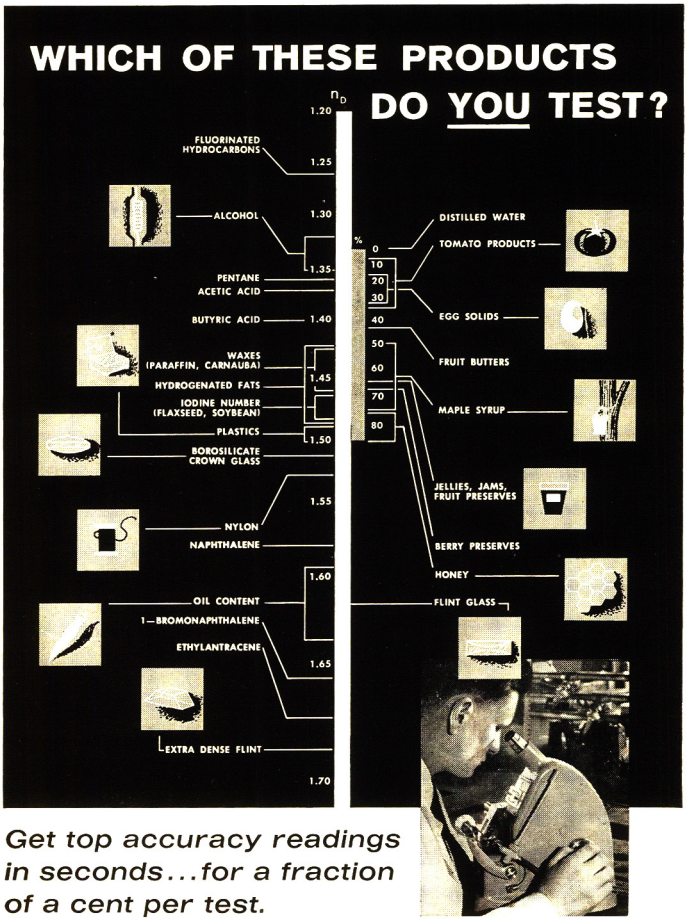
the EDITOR'S column

L. T. Hallett, Editor

TO AN ANALYTICAL CHEMIST, the composition of a material is its most meaningful property. Realizing the importance of standards and reference materials, ANALYTICAL CHEMISTRY has kept abreast of the latest developments (ANAL. CHEM. 31, 1934 (December 1959); 32, 19A (September 1960); 36, 23A (November 1964).

The most recent of these papers is a Report for Analytical Chemists that summarizes events at the Symposium on Standard Reference Materials at the 148th National ACS meeting in Chicago on September 3, 1964. The standard reference materials distributed by the National Bureau of Standards and the American Petroleum Institute were discussed. In addition, the work being carried out at the Oak Ridge Research Materials Information Center, the National Academy of Sciences, the International Union of Pure and Applied Chemistry, the Manufacturing Chemists' Association, the American Society for Testing and Materials, and the International Standards Organization was described.

In addition to these programs the efforts of the United States Pharmacopeia date back to 1931, when approval was given for a lot of digitalis for use in the U.S.P. assay procedure for digitalis. The program has grown to the point where it now includes 157 standards, and it is expected that 42 additional standards will be prepared for use with the U.S.P. monographs when U.S.P. XVII becomes official in September 1965. In addition to the current 157 U.S.P reference standards, a set of six U.S.P. melting point standards is distributed, and 72 U.S.P. steroid reference standards are distributed for use in paper chromatography.



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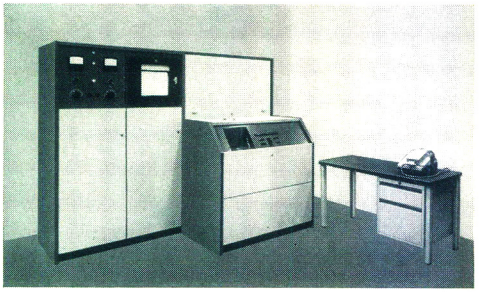
ELECTRONIC DEVICE PRODUCES SURPRISING ACCURACIES IN AUTOMATIC CHEMICAL ANALYSES



A new automatic X-ray spectrograph has recently been introduced which is virtually a foolproof electronic analytical chemist. The new Norelco apparatus—PW 1212, is a sequentially operating spectrometer capable of automatically providing qualitative and quantitative analyses of any group or combination of elements from Fluorine to Uranium. The new apparatus is fast in response and flexible in adaptability, consequently it is suited for production analysis and routine testing in most industries. As a fully automatic device, it will repetitively analyze four samples in a single loading for as many as fifteen elements. A total of twenty-four elements can be selected, and fifteen of these are analyzed automatically in sequential order.

Automatic operation of the entire apparatus is controlled by insertion of pre-programmed color-coded pegboards. Operation is completely automatic after goniometer positions are indexed and four samples are manually inserted. The apparatus will shift from one sample to the next until each loading of four samples is completely analyzed. Stand-by pegboards can be pre-programmed for various matrices and are inserted in seconds to match the analytical problem at hand.

The entire apparatus is multi-functional and readily responds to either *automatic operation*—for repetitive, routine analyses; *semi-automatic operation*—for large numbers of non-routine samples for which pre-programmed pegboards can easily be interchanged; and *manual operation*, in which the apparatus is used as a basic analytical tool to study the chemical spectrum of a sample whose contents may not be entirely known.

The PW 1212, as an automatic sequential spectrometer is designed to provide three distinct services: to perform with an uncanny degree of accuracy, repetitive reliability and unbelievable speed; eliminate the possibility of human error; and minimize the time and concentration required of personnel in attendance. For any unknown or contaminated sample, the apparatus can be operated under vacuum to scan the complete spectrum of a specimen. In any mode of operation, element detection is exceedingly sensitive with parts per million discrimination...dependent upon sample material and matrix.

Performance data from a stainless steel mill attest to the analysis time of 1½ minutes to complete seven determinations in which the specimen was compared to a standard. The deviation is expressed in plus or minus percentages.

Element	*% Element, ± Std. Deviation*	*Time of Analysis*
Mo	0.33% ± 0.003%	4 Sec.
Cu	0.16% ± 0.006%	10 Sec.
Ni	0.52% ± 0.004%	4 Sec.
Mn	2.13% ± 0.02%	10 Sec.
Nb	0.49% ± 0.006%	10 Sec.
Cr	9.09% ± 0.07%	4 Sec.
Si	1.25% ± 0.03%	20 Sec.

In determining the recovery possibilities in reprocessing foundry slag, the PW 1212 was used. Silicates containing valuable elements usually prove to be rather difficult to determine by wet-chemistry methods. The pre-programmed PW 1212 Spectrograph routinely analyzes slag samples for five elements, unattended... within 1½ minutes.

In the production of cements, deviations from a norm were easily and almost instantly recognized by the PW 1212, by reading out the variations in the mix from the prescribed standard before shipment. This is the essence of meticulous quality control, completed with amazing accuracy in lightning-fast time.

Additional analytical data are now being routinely supplied by the instrument. These include the determination of fluorine and sodium in alumina, analysis of copper and copper base alloys, presence of metals in lubricating oils and the analysis of plain carbon steels.

The apparatus may be linked with computers to read directly in any prescribed units of measurement such as percentages, micrograms per milliliter, etc. Likewise, information can be fed from the computer to hoppers or controls which automatically determine the flow of raw materials into the mix. This and other types of work not previously performed, approach the ultimate in completely controlled chemical processing.

Accept this invitation to discuss the adoption of this technology to improvement of your products or processes. Information is available from:

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See the Norelco PW1212 at the Philips Electronics exhibit—Booths 2 and 3, Pittsburgh Analytical Conference—March 1 - 5.

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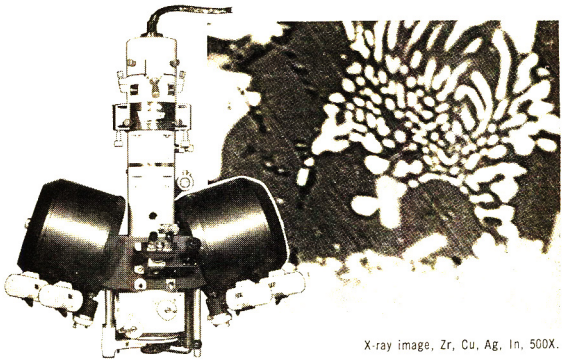
EDITOR'S COLUMN

The National Formulary reference standards program was started more recently than the U.S.P. program, but it has been in operation for more than 20 years. Ninety-one materials are now distributed as N.F. standards.

The World Health Organization authentic chemical substances program was begun in 1957, and it now includes eight substances in addition to 13 W.H.O. melting point reference substances. Active work is currently in progress to make available 14 new substances. The World Health Organization also sponsors a wide array of international standards for biological assays and tests of serums, toxins, vaccines, enzymes, and endocrine principles. These are used mainly for the preparation of national secondary standards for the standardization of products for both human and veterinary use.

In preparing each of the U.S.P., N.F., and W.H.O. standards, a somewhat similar approach is used. Samples of the pure or otherwise representative materials are obtained as gifts, or through purchase on the open market. They are subjected to a preliminary analysis to verify their suitability for the intended purpose. Phase solubility analysis and thin layer chromatography prove useful in this preliminary examination. If a material proves useful for further study, a multilaboratory collaborative evaluation study is arranged, with each laboratory carrying out one or more determinations. The results are then compiled into a report, using statistical analysis if necessary. For the standards subjected to microbiological evaluation, statistical evaluation is absolutely necessary, while for some chemical substances the statistical treatment might be superfluous. After approval of the appropriate standards committees, the materials are packaged and labeled, and are stored under conditions of long stability while being held for distribution.



X-ray image, Zr, Cu, Ag, In, 500X.

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New scanning system gives uniformly high x-ray sensitivity over 400 x 400 micron area • 18° take-off angle for minimizing fluorescence corrections • Large specimen chamber — fully accessible and readily removable • Sensitive spectrometers give high resolutions and peak-to-background ratios • Unique high resolution specimen current image • Variable speed plug-in specimen and spectrometer motor drives • Viewing parts and fluorescent screen permit simple beam alignment at any voltage • Automatic collodion x-ray window for light elements • Coaxial light optics.

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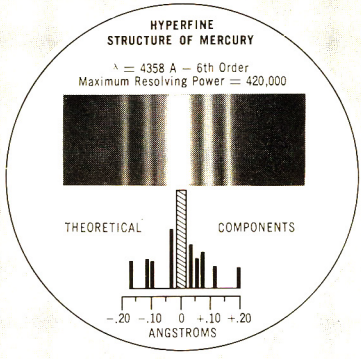
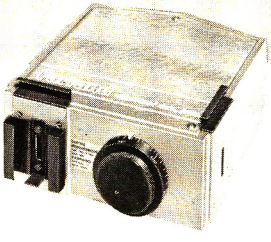


Theoretical resolving power of a Farrand Master Diffraction Grating reflecting the efficiency of Farrand Replicas.



Write for descriptive literature

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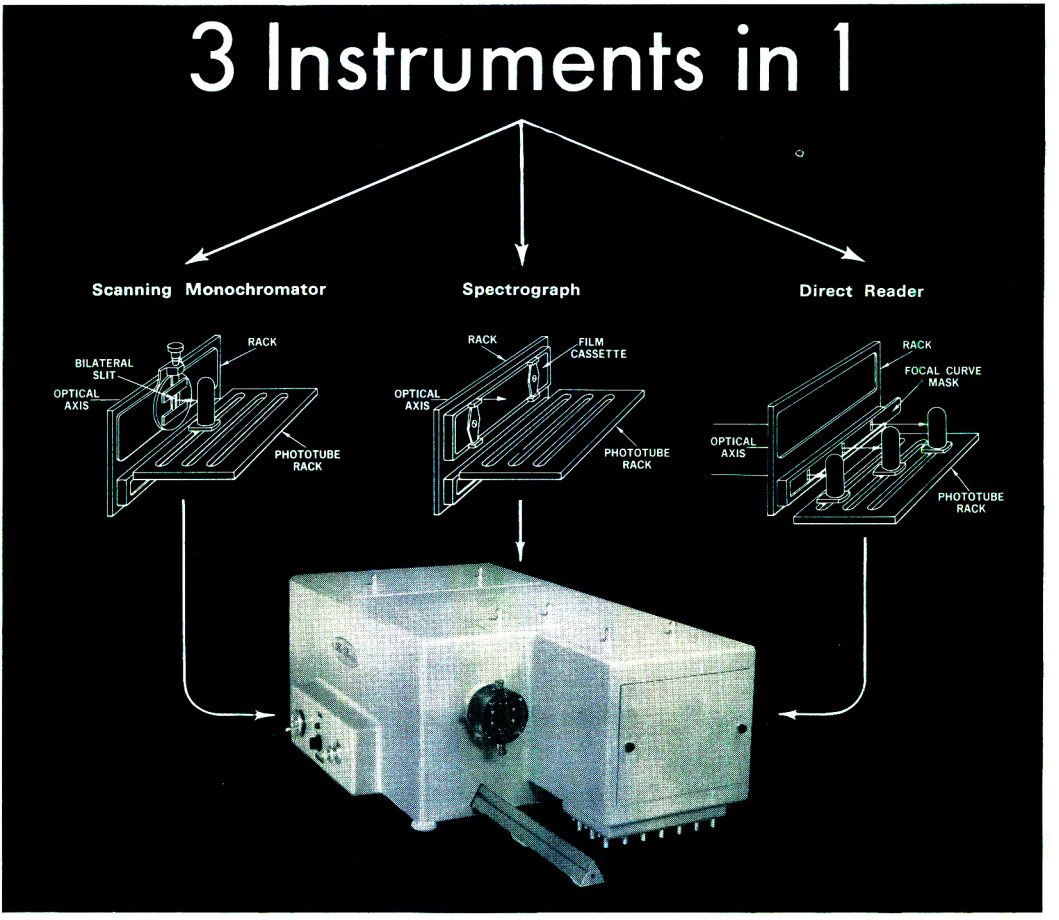

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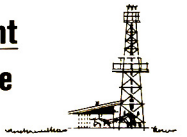

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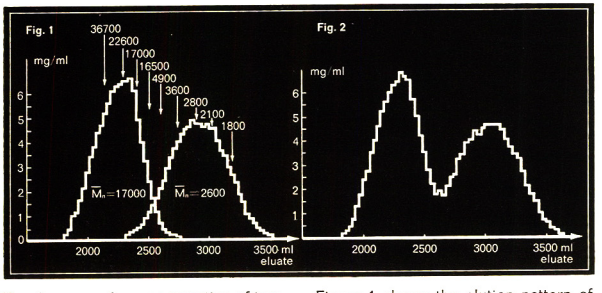

The diagrams show a separation of two fractions with $\bar{M}_n$ 17,000 and 2,600 respectively, chromatographed on two Sephadex G-100 and G-25 columns connected in series.

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Figure 2 demonstrates the elution pattern of the dextran mixture.

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*For proteins the fractionation range is larger. P. Andrews, Biochem. J. 91:222, (1964).

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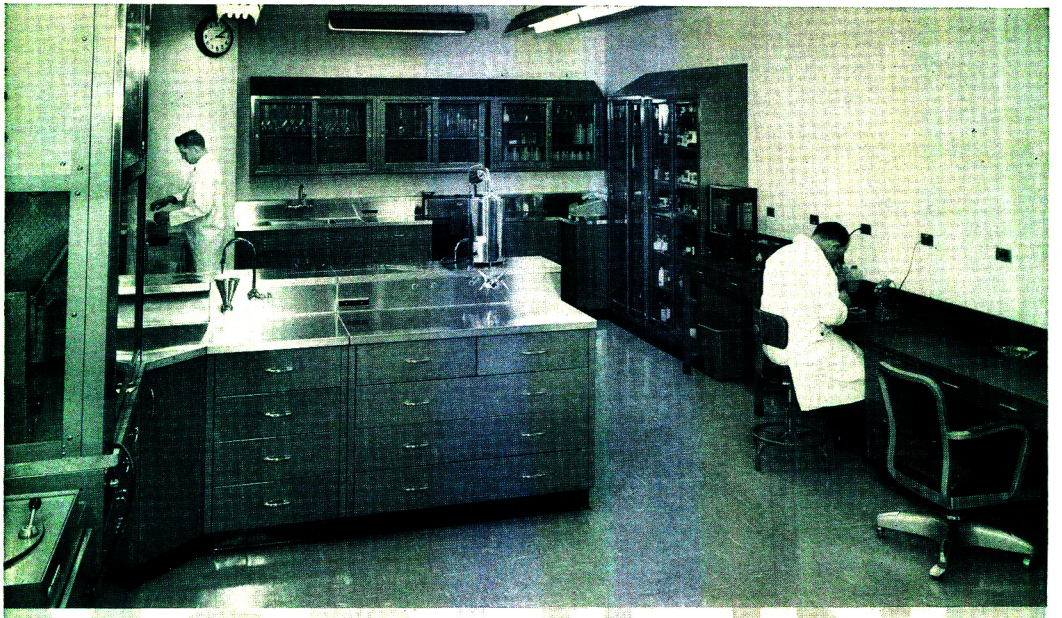

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National Steel's Research Center Has Important Analytical Functions

As one might expect, the major analytical effort at the new Research and Development Center of the National Steel Corporation is with materials produced in and otherwise related to steel making. However, this does not mean that the work is narrow in scope. Advances in blast furnace technology, the advent of new steelmaking and refining methods, the continual modernizing of rolling and plating practices—all have given rise to new analytical problems and requirements.

The research and development center is located at Weirton, West Virginia, about five miles from one of National Steel's principal operating divisions, Weirton Steel Company. Approximately 100 people are employed at the Center, of whom eight constitute the analytical procedures group. This group treats a wide variety of analytical problems which cannot be considered as routine, and in doing so it employs modern instrumental techniques and wet chemical procedures.

Specialized instruments which are used by the group are:

- Emission spectrographs
- Absorption spectrometers
- Electron beam microprobe analyzer
- X-ray diffraction and fluorescence apparatus
- Mass spectrometer
- Vacuum fusion analyzer

The Center has other equipment which can be brought into play to assist in making difficult or unusual analyses: An electron microscope, a differential thermal analyzer, and metallurgical microscopes.

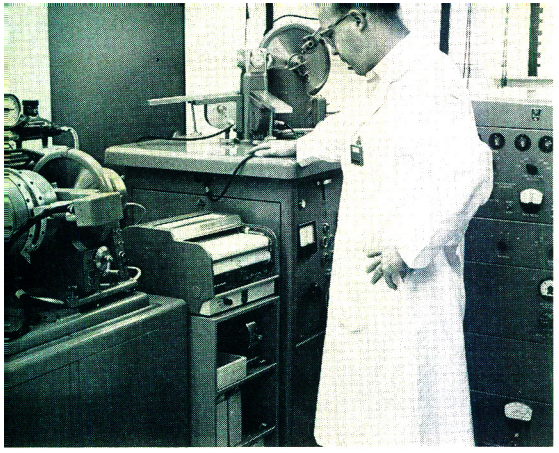
Much of the work at the Center is related to the production of tin plate, since this material is a basic part of National Steel's product mix. Correspondingly, a considerable part of the analytical effort is related to studies of the factors which promote corrosion resistance and improve the appearance of tin plate and other coated products. Organic lacquers and joint cements also are evaluated for their utility in can manufacture; infrared techniques have proved useful in these evaluations.

Although accuracy is a prime requisite in measuring the small differences in metallics and metalloid levels which significantly affect the properties of steel, speed of analysis is also important in the execution

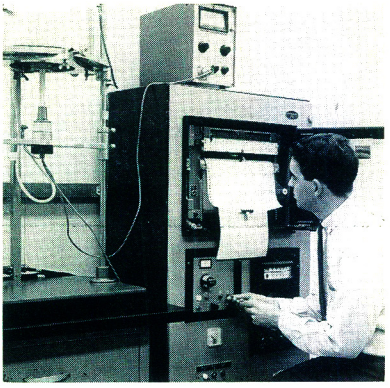


Electron Beam Microprobe Analyzer is used for the identification of inclusions in steel, determination of diffusion-derived composition gradients in metals, and studies of surface defects on steel sheet and tin plate

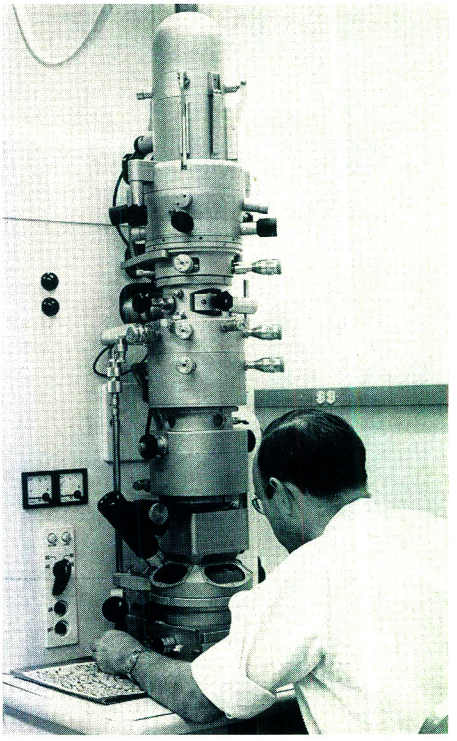
LABORATORY OF THE MONTH



X-Ray Diffraction and Vacuum-Path Fluorescence are used for the analysis of metals, surface coatings, and slags, and the identification of inclusion particles extracted from steel sheet. In addition, orientation studies on rolled products are performed by these methods

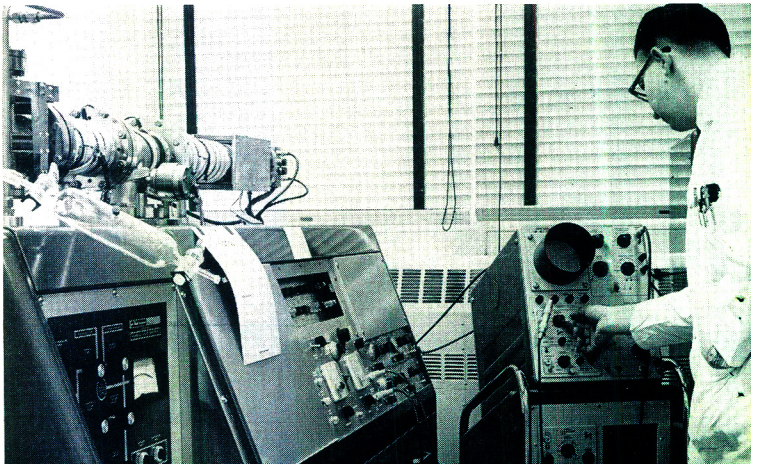


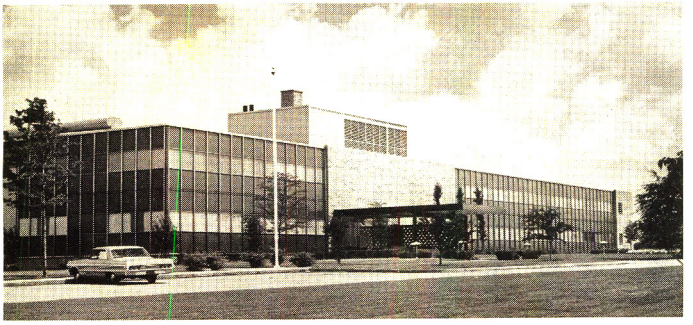
Differential Thermal Analyzer determines the thermal effects which accompany changes in refractory materials on heating. Refractories are important because they constitute a major cost in the steelmaking shop



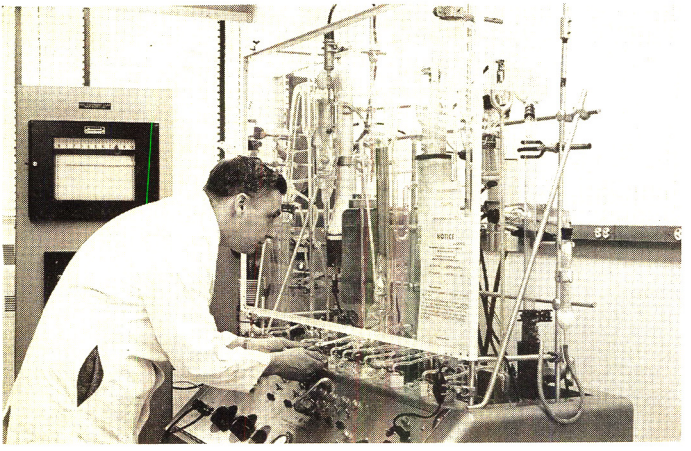
Electron Microscope is used to furnish valuable information on the structure of tin plate

Time-Of-Flite Mass Spectrometer is used as a referee in routine gas analysis, as a device for the identification of unknown gases, and as a means of studying the pyrolysis of organic materials





National Steel's New Research and Development Laboratory has a total of 75,000 square feet of floor space, and contains a machine shop, a library, and offices



Vacuum Fusion Apparatus is used for routine determinations of oxygen and nitrogen in steel and determinations of the separate oxide contents of steel

of some research projects. For this reason, the plate-type spectrograph which has been in service in the laboratory since 1961 has been augmented recently by installation of an RCI Direct Reading Spectrometer. This instrument has been equipped with 23 channels so that it can give rapid analyses of steel, cast iron, and sinters for the elements usually specified, as well as for a number of elements which at present are largely of research interest only. Provision has been made for installation of a vacuum path assembly at a later date so that analyses can be obtained for carbon and sulfur. These elements are now determined by combustion techniques.

When possible, statistical methods are employed to facilitate the development of analytical techniques and the interpretation of analytical results. The cooperation of the computer laboratory is invaluable in this work.

Equally important to National Steel is the continued improvement in product quality and manufacturing techniques for automotive steels. Weldability, strength, ductility, and surface finish are affected by the chemistry of the steel, by the nature of non-metallic inclusions, and by surface treatments such as pickling. These items are under constant study, and the studies generate much analytical work, both routine and novel in nature.

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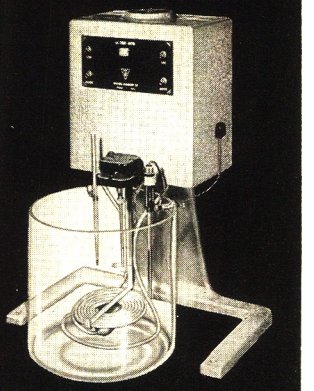

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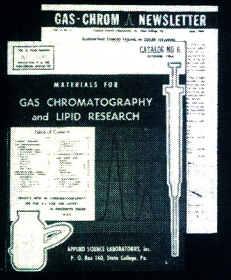

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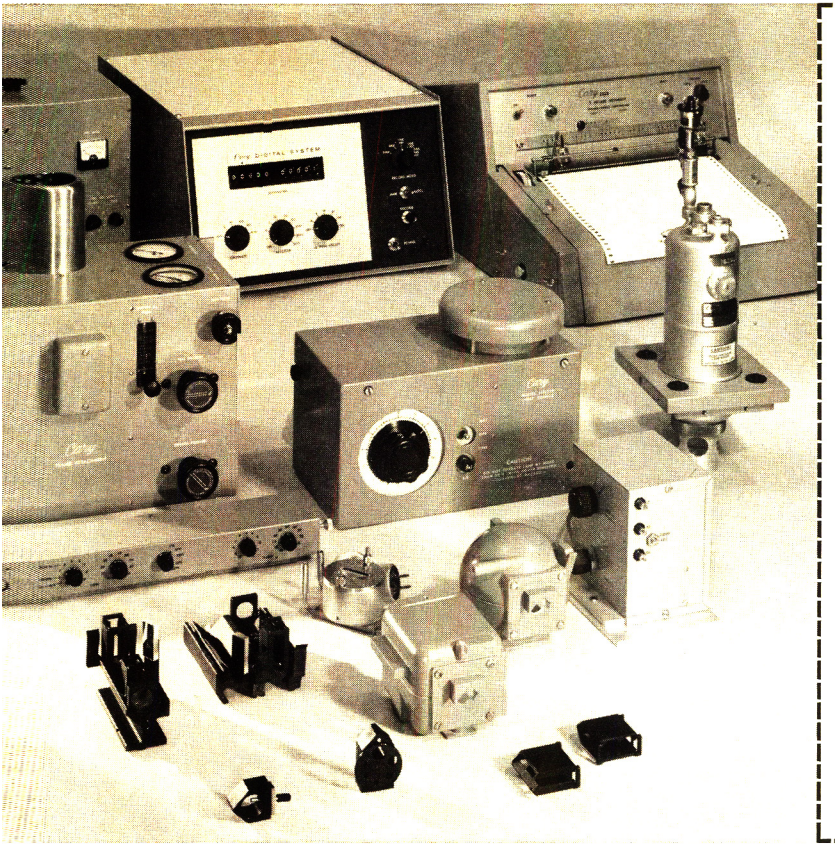

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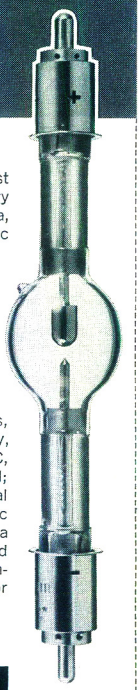

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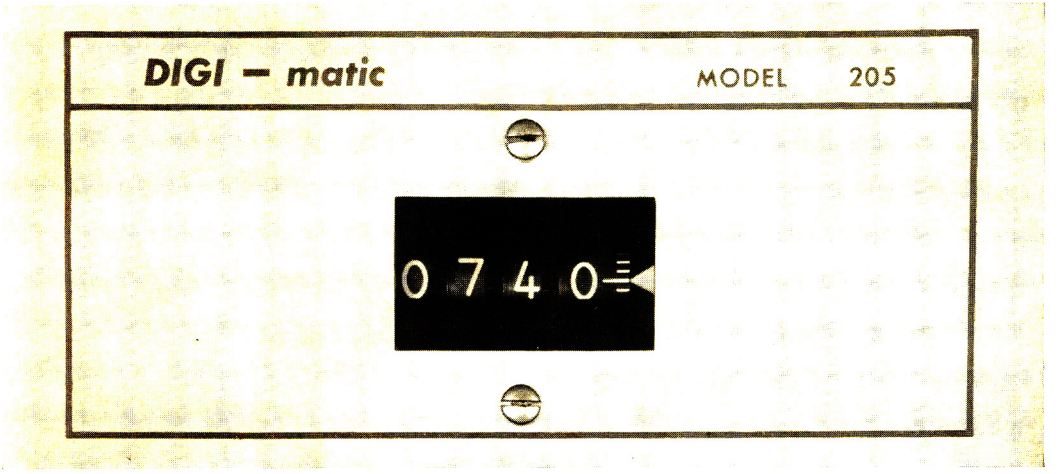

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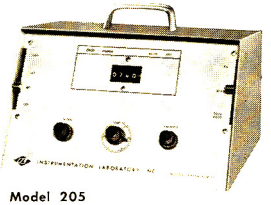

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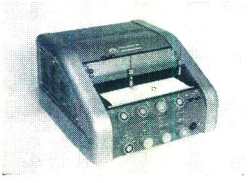

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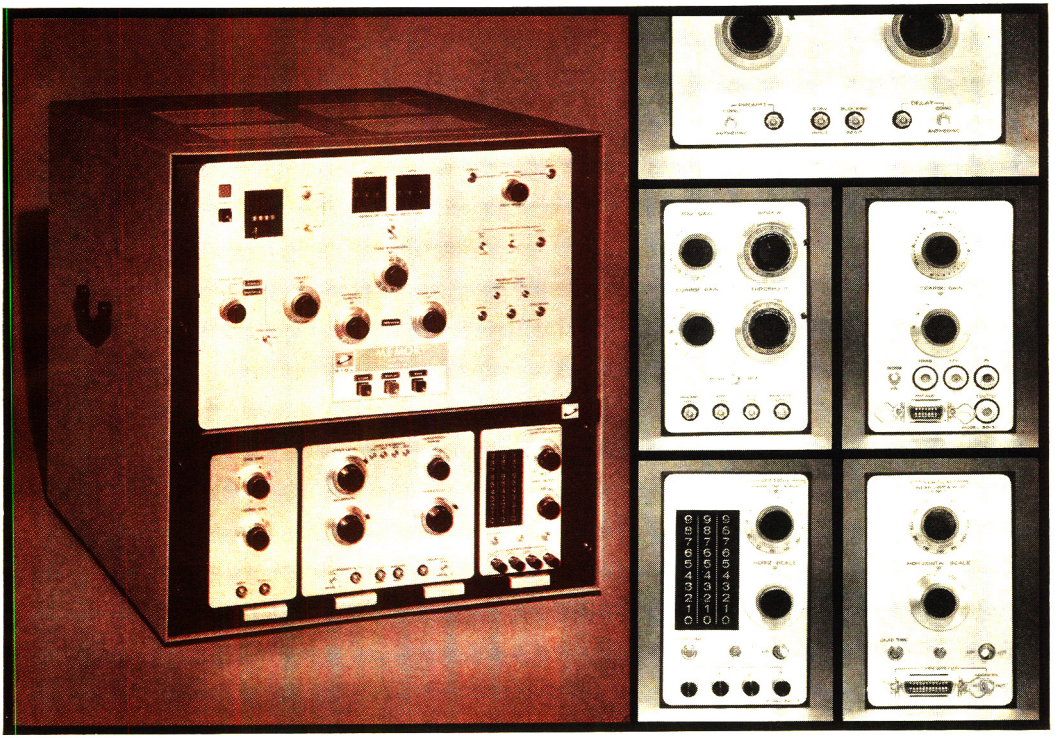

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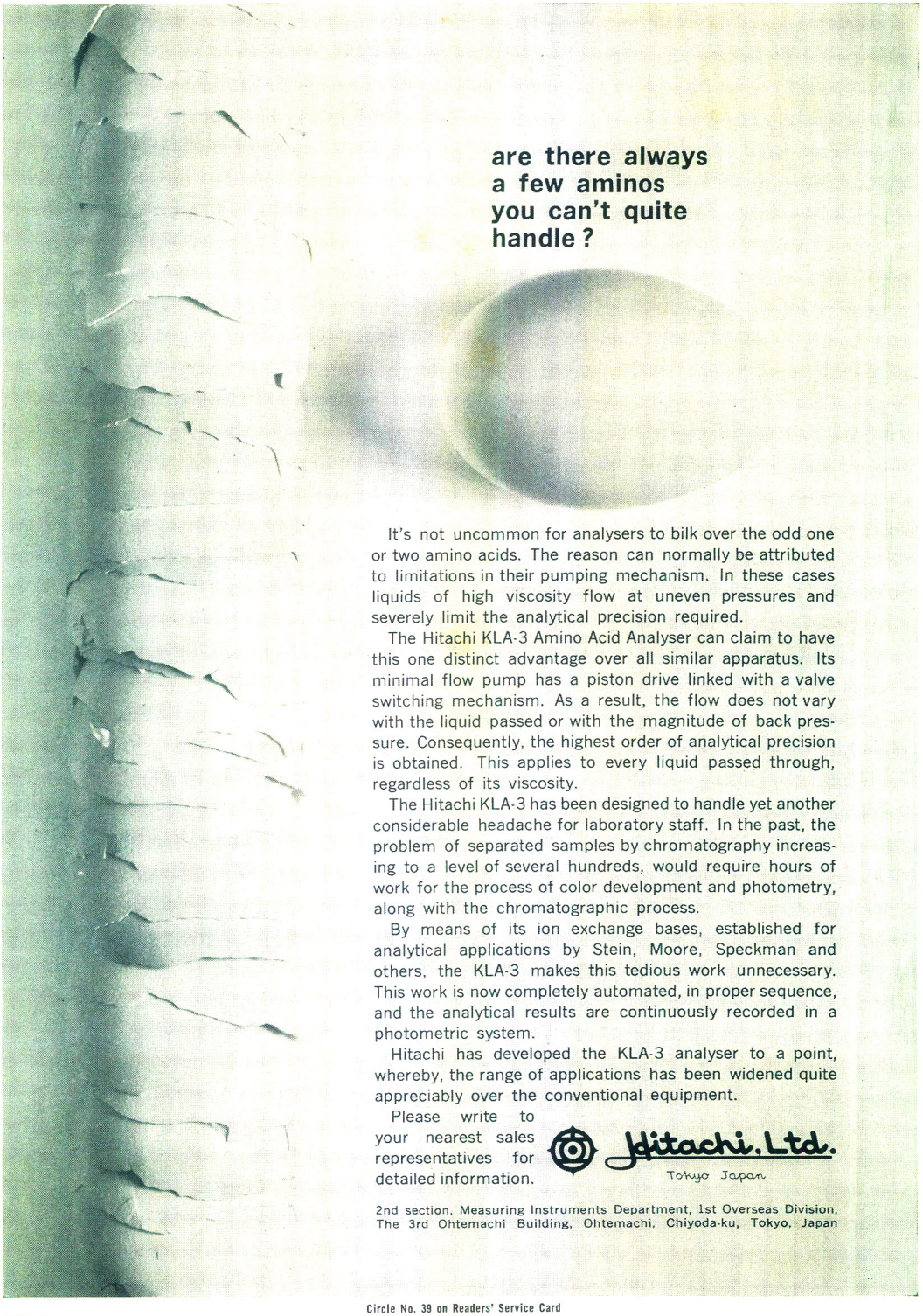

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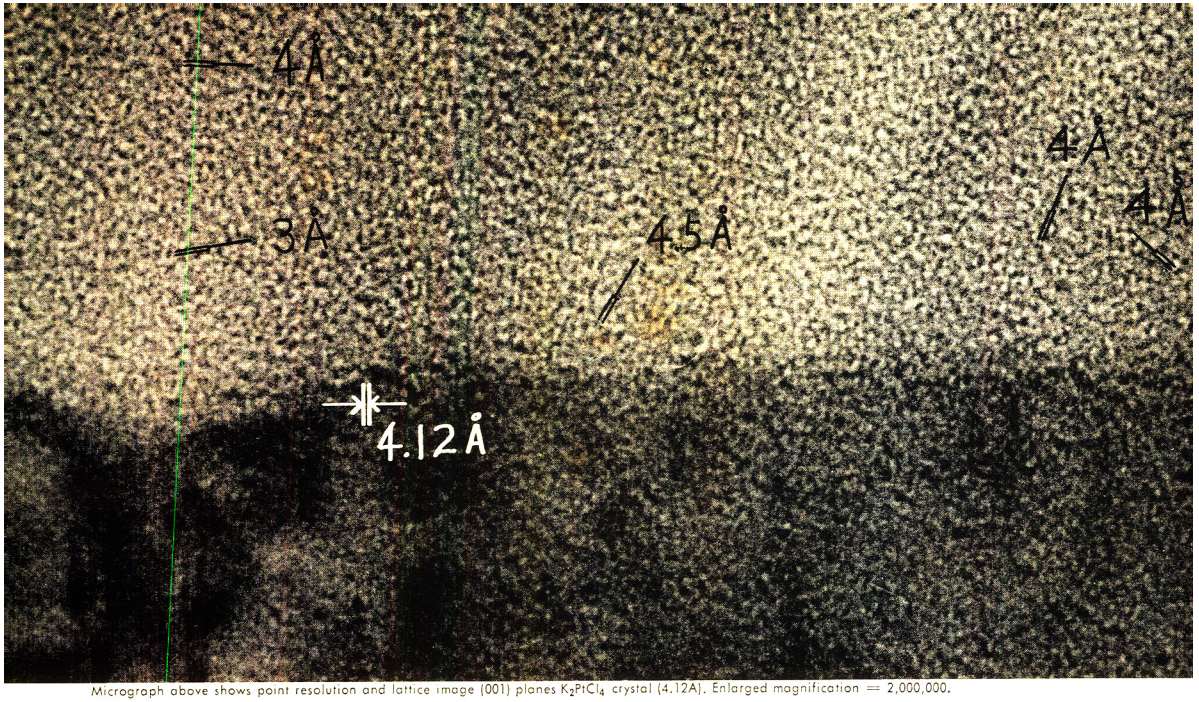

Micrograph above shows point resolution and lattice image (001) planes K_2PtCl_4 crystal (4.12A). Enlarged magnification = 2,000,000.

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As research in the life sciences and solid state physics accelerates, ultra high resolution electron microscopy assumes an increasingly important role as a source of fundamental new information. Recently, scientists at the Hitachi Central Research Laboratory have announced new discoveries in electron optics which are being incorporated in their latest designs. The five electron micrographs below of a tiny (0.05 micron) hole in collodion film were taken at equal intervals during a four minute period. They demonstrate the remarkable performance of the new Hitachi HU-11B Electron Microscope.

Careful measurements on the original plates indicated (a) At the direct magnification of 250,000, better than 5Å resolution was maintained for each exposure (b) Electronic stability was better than 2 in 10^6 for four minutes (c) The specimen contaminated at a rate of less than 0.5 angstroms per minute.

With this constancy of performance, ultra high resolution micrographs can now be obtained similar to that shown above. The (001) lattice image of K_2 Pt Cl_4 Crystal with 4.12 Å spacing is resolved while on the same plate point-to-point resolution of particles as close as 3Å is obtained. This is the highest point resolution yet demonstrated by any electron microscope, approaching the dimensions of single atoms.

A complete set of these micrographs and details on the Model HU-11B can be obtained from the Perkin-Elmer Corporation, Distributor Products Department, 702 Main Avenue, Norwalk, Conn., exclusive sales and service representative for Hitachi Electron Microscopes in North America.

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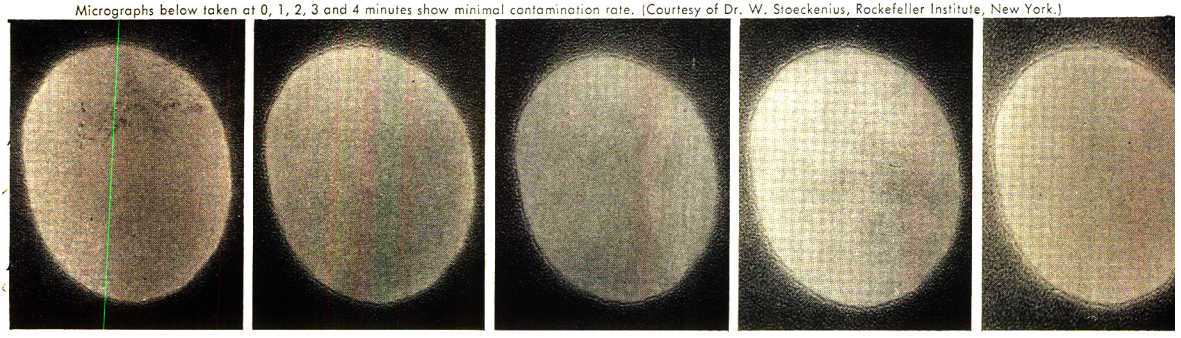
Micrographs below taken at 0, 1, 2, 3 and 4 minutes show minimal contamination rate. (Courtesy of Dr. W. Stoeckenius, Rockefeller Institute, New York.)



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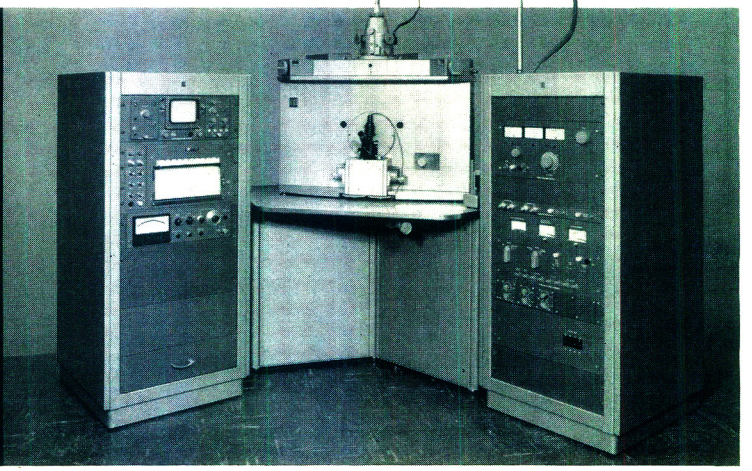

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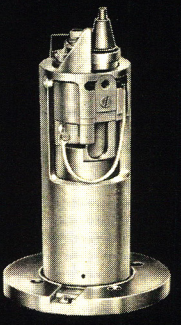
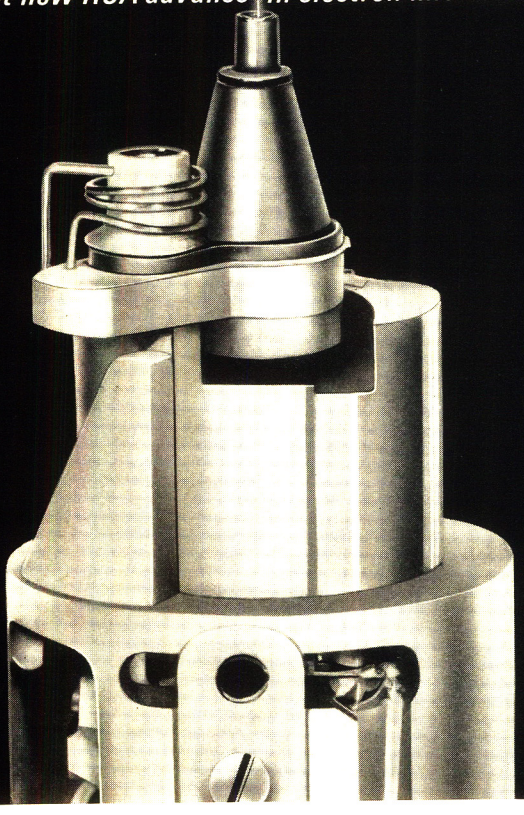
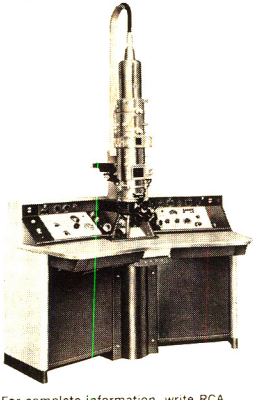
Another important new RCA advance in electron microscopy!







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VANGUARD

NEW MODEL 885 GLASS PLATE SCANNER FOR THIN LAYER CHROMATOGRAPHY

The Model 885 Glass Plate Scanner now extends the range and versatility of the Model 880 Low Background Autoscanner for applications involving the assay of thin layer chromatograms. Designed as an accessory system to operate in conjunction with the Autoscanner, the Model 885 provides a convenient, low cost system for assaying TLC glass plates with unequalled accuracy and sensitivity. The compact design of Model 885 allows it to be operated atop the Model 880 Autoscanner so that no additional bench space is required.

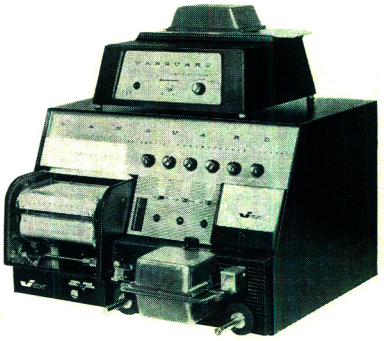
Utilizing the electronics of the Model 880 Autoscanner, the Model 885 provides 2 pi windowless detection for tritium, carbon-14, sulphur-35 and other beta-emitting radioisotopes. A pushbutton transmission provides 10 scanning speeds identical to those available on the Model 880 Autoscanner, assuring absolute correlation between the glass slides and recorder chart paper. An automatic marking system places a distinctive "pip" on the chart record to denote the beginning and end of each TLC plate. This assures accurate location of radioactive zones.

Model 885 is furnished with three interchangeable stainless steel collimators of ½ cm., ¼ cm., and ⅛ cm. width to meet varying requirements of chromatogram resolution while maintaining maximum detection sensitivity. Standard glass plates from ½"—2½" wide and up to 12" in length may be scanned.

To facilitate the scanning of either paper or TLC chromatograms, an automatic power and gas control system incorporated in the Model 885 Glass Plate Scanner switches both electronics and counting gas supply from the Model 880 to the Glass Plate Scanner when power is applied.

To further increase the versatility of the Model 885 Glass Plate Scanner, the Model 880 ADS digital integration system may also be used to provide quantitative evaluation with digital presentation of radioactive zones.

For additional information on the new Model 885 Glass Plate Scanner, write Vanguard, P. O. Box 244, LaGrange, Illinois, or one of the local sales offices.



Model 885 shown atop the Model 880 Autoscanner



Model 885
Glass Plate Scanner

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by Ralph H. Müller

Hardware, Gimmicks, and Ideas

INDUSTRY IS TAKING A HARD LOOK at research and development to decide whether its value is a myth or a fact or how much of each. *Fortune* magazine for January 1965 contains a penetrating analysis of the question. The authorities quoted by *Fortune* are the top executives of large corporations and, without exception, they are scientists with impressive records of research accomplishments. This article is timely, interesting, and provocative. It reveals a number of surprising facts—for instance, the large percentage of unhappy scientists and engineers who can find little of merit in management, and the increasing dismay of management at the prima donna attitude of some of its scientists. One gains the impression that all the problems will be solved, particularly because they are recognized as being studied with great care. According to one research director, "One of the greatest myths of industrial research has been that if you spend enough money something wonderful will happen." Another angle expressed by a corporation president is "On the difficulty of finding good research directors, one just has to hope that a candidate will turn up in every epoch."

The impressive and incomparable achievement of American industry has been accomplished largely by continuing research and development. Industry has every intention of keeping things that way.

It would be a happy state of affairs if the general status of all research and development could be appraised and an orderly adjustment be made despite the many difficulties. The trouble lies with definitions. The word "development" is simple enough. It may be rapid, normal, retarded, stunted, or even malignant. Research, on the other hand, is one of the most ill-defined words in current use. It is creeping into our grade schools. An inspired teacher informs Timmie that he is about to do research. After consulting three arithmetic books, his research confirms the fact that the sum of nine and nine is eighteen, and nothing but. Have you read a paper recently in which essentially the same thing was done, possibly with vectors, matrices, or Bessel functions? Instrumentation, to which we have been hopelessly committed for years, is contributing heavily to a new definition of research and compounding its sins. By the turn of the century, much of what passes for research today will be obsolete. Even now, we do not have to make measurements. In many instances, the data are printed out, recorded on tape, punched on I.B.M. cards or fed directly to a computer. We do not bemoan this state of affairs, in fact, we have been guilty of developing a few of these things. What we do know and predict will happen in those coming 35 years is that the data collecting type of research will no longer attract the inquiring minds. We may be forced to rely on ideas, new ideas, obscure phenomena, unfashionable notions. Rewards, support, and grants will not be readily forthcoming and the dogged investigator will run the constant danger of discovering something brand new. When that time arrives, the instruments, recorders, and computers can take over and a fresh group of recruits will be on hand to carry the banners.

Many gifted people in government, industry and the academic world are seeking better means of fostering the entire scientific effort. It just happens that not too long ago they killed off one of our best bets—the Ivory Tower. The embers under its pyre have died out, the drums no longer beat, and the excited natives are now formed into quiet orderly teams and committees. It is a mild form of heresy to suggest that the institution had some merit and that no completely successful substitute has been found. To suggest this gives the impression that one favors the return of the bustle, spats, Malacca canes, or five-cent nickels.

More than ever we need unhampered inquiry and plenty of idea men and we should not have to wait until one of them wins a Nobel Prize or establishes an entirely new industry before we help him. How do we find such people? They are not in the ordinary R and D category, certainly not in P and G (promotion and gimmicks) nor in the H and D (hardware and delivery). There is no certain clue in the number of degrees they hold. Any research professor knows very well that some of the most brilliant students often lack the curiosity, detachment, and willingness to dream which characterize the trial blazer. We suggest a profitable manner of search for such a person. It has a parallel in our Anglo-Saxon legal tradition—trial or judgment by "one's" peers. Let all our learned scientific and engineering societies poll their members once each year for their joint nomination of such people in the various disciplines and broadcast the results. When you want to know the merits of a Cadillac or Volkswagen or a Volvo, you do not write to General Motors, to West Germany, or to Sweden—you ask the man who owns one. Any scientist worthy of the name can at once mention a dozen people in his field whose work is inspiring, original, and has contributed heavily to his own thinking. Will the members cooperate in such a poll? They had better for they have a large stake in the outcome. We propose to seek a grant to study this proposal because - - - Oh, oh, here comes a committee.

It's a hazardous undertaking needing a latter-day Diogenes. No one has expressed the dangers better than E. J. Tangerman, Editor of *Product Engineering* whom we quote in full, with permission of the editor and publisher.

THE CREATIVE CATERPILLAR*

There is in France a race of caterpillars which has a very specialized way of finding food. When a colony gets hungry, its members line up, each hooking his tentacles into the tail of the caterpillar ahead. And off they go, the lead caterpillar doing the searching and guiding. The rest just follow the leader.

(Continued on page 118 A)

* *From "Horizons Regained." E. J. Tangerman. McGraw-Hill. Inc. New York, New York, 1964.*



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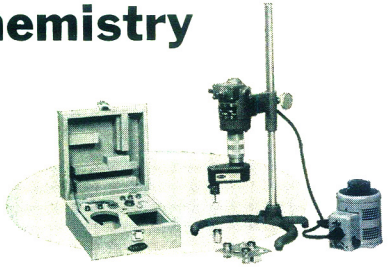



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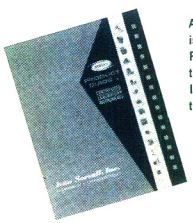

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INSTRUMENTATION

Once there was a zoologist who wondered about this caterpillar chain. Was the leader smarter, a better food-finder, was there a "pecking order"—or was the leader just the caterpillar who happened to be in front when the trek for food began? The zoologist worked a chain into a circle and got the lead caterpillar lined up with the tail-end one. The "leader" promptly hooked on, and the chain started to go round and round. Not until a week later, when one caterpiller died of hunger and broke the circle did the chain begin to cover ground again.

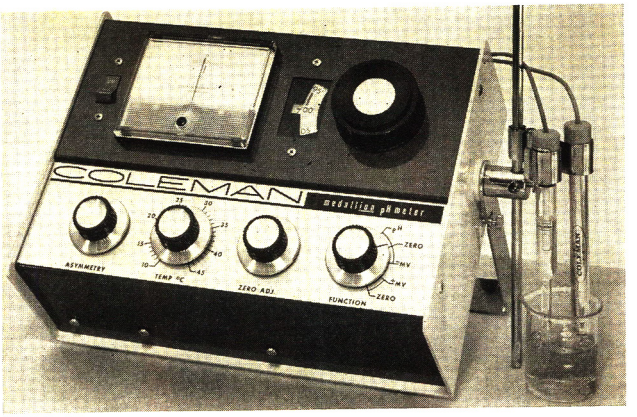
Imagine how a creative caterpillar would upset this colony. What if he were to come up with the idea that each caterpillar strike out on his own? Imagine the pressure to get him back into line. First the other caterpillars: "Why are you doing this to us?" "Don't you like to eat regularly?" "What's the matter with things as they are?" "What was good enough for Grandpa is good enough for us." "So you think you know more than the caterpillar council." "Your idea is no good, or some other caterpillar would have thought of it long ago."

Then the lead caterpillar: "What are you trying to do, show me up?" "Is this loyalty?" "After all I've done for you, you do this to me." "Why don't you just forget the whole thing—or don't you like it here?"

They can certainly make a creative caterpillar feel like a worm. And if he tries to turn, as rebellious worms do, obstacles will be put in his way. Nobody will know the proper procedure, the papers will be missing, there will be dark warnings of banishment—they may even threaten to feed him to the birds, because his ideas are for the birds anyhow.

But let's say he keeps right on turning—and begins to get somewhere. The whole colony will promptly clamp onto his tail, applying another traditional philosophy of "all for one and one for all." They may even get him to sign a patent release to make sure he doesn't just take off on his own. And they'll hang back, letting him not only lead but also drag them along as well, mentally as well as physically.

Moral: If you break the chain, what happens to you is your own fault. A light in your eye will only attract the birds. ■



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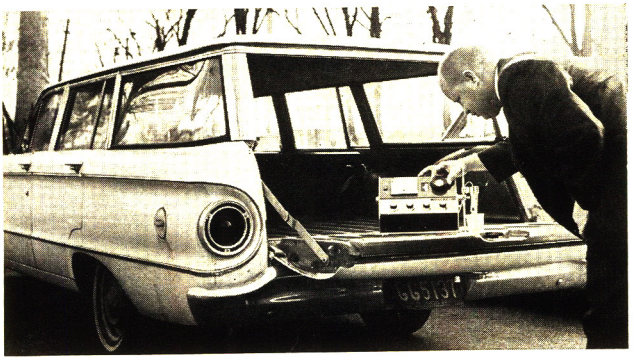

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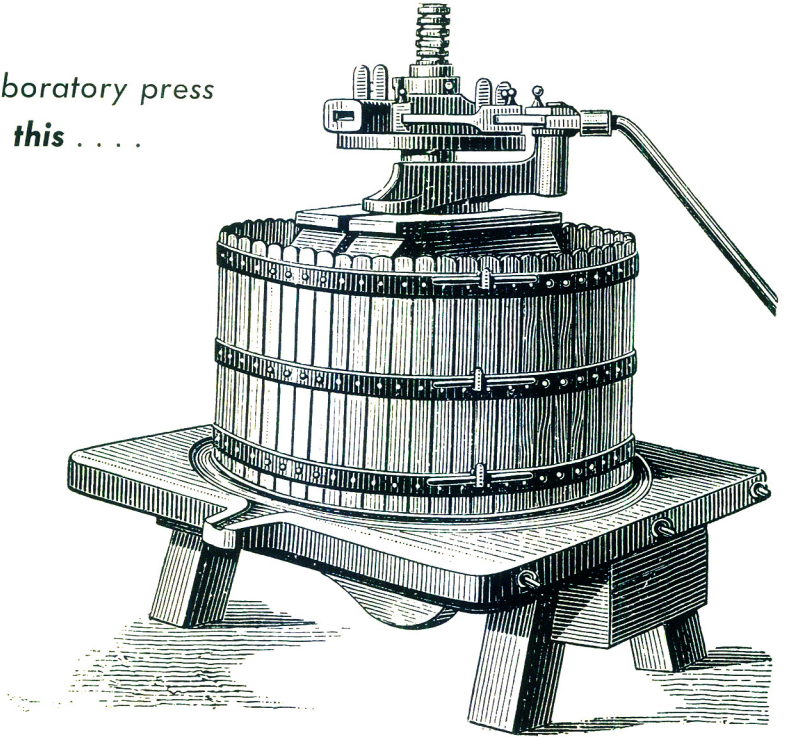

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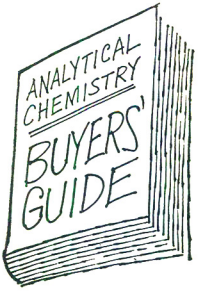

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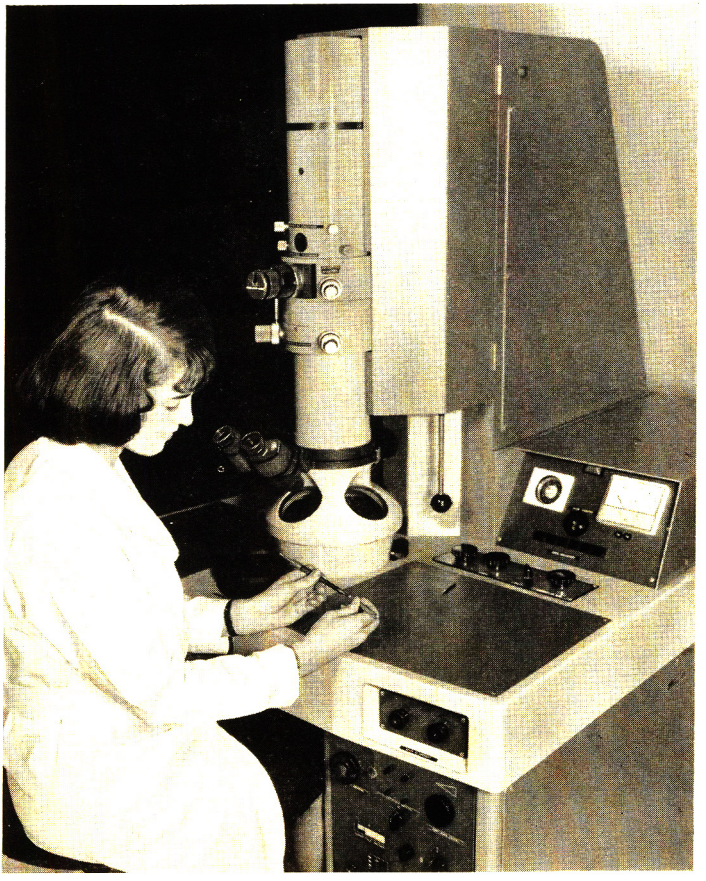

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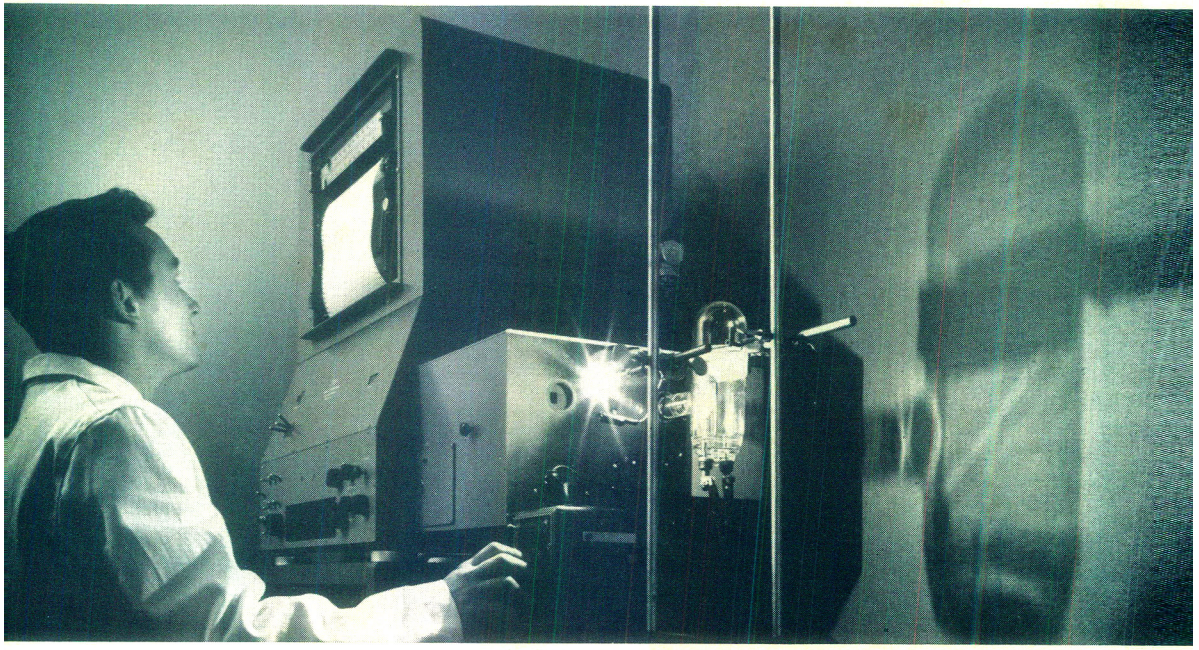

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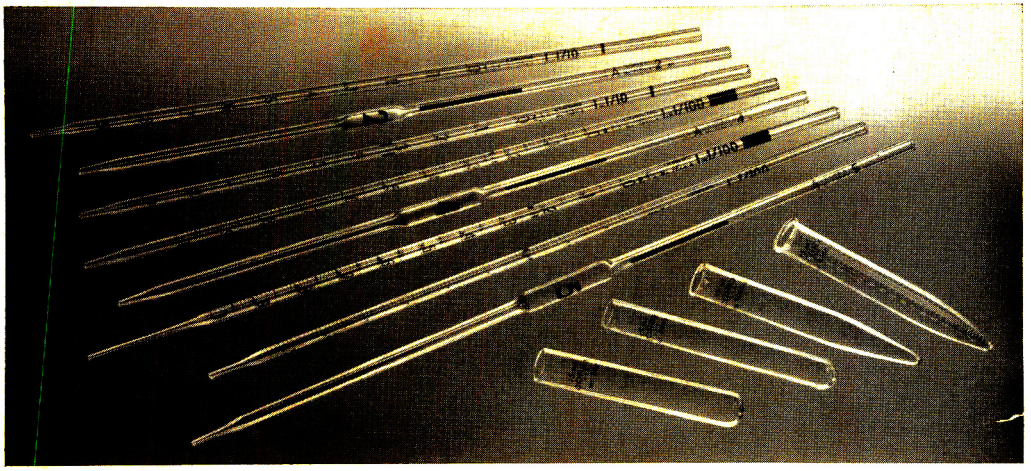

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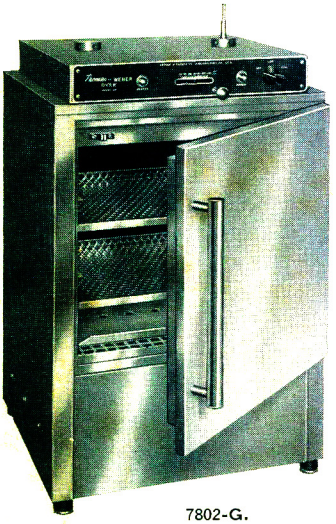

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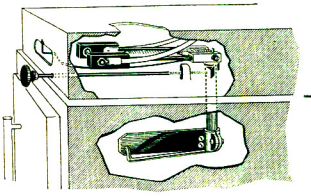

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The Tutorial System

THE TUTORIAL SYSTEM at Oxford and Cambridge has been for several centuries the preferred method of education in Britain. Its excellence has rarely been questioned. However, developments in Britain since World War II expressed by a lack of industrial growth and efficiency and the present phenomenal growth of technological colleges have caused considerable discussion in educational circles as to the aims of education in Britain. Industry reports that the traditional narrow specialization at Oxford and Cambridge is poor preparation for the young man entering business or industrial research. In addition, it is extremely difficult to enter these two institutions. It is not surprising therefore, that the technical colleges are flourishing and new ones are being founded as it appears they are needed for training in the neglected fields of applied science.

It is significant that Oxford has appointed a commission headed by Lord Franks, Provost of Worchester College, to examine the aims and results of the tutorial system as related to modern needs in education. This self-examination by such a venerable institution founded in the 12th century is a commendable project. They are not only looking at their own procedures but are asking prominent people in all segments of British life to give opinions that they hope will permit constructive adaptation of the tutorial system to present-day British professional and industrial needs. The study is not undertaken to solve a crisis for there is none; hence, the commission intends to gather and digest its information over a period of two years.

Unfortunately in education today there seems to be widening gap between the scholar and the technical expert and it is hoped that with skill and understanding this gap can be narrowed to the benefit of education and research in all disciplines.



Generalized Chronopotentiometric Potential-Time Equations and Their Application to Quasi-Reversible Processes

LARRY B. ANDERSON[1] and DANIEL J. MACERO
Department of Chemistry, Syracuse University, Syracuse, N. Y.

▷ **A general potential-time relationship for quasi-reversible first-order electrode reactions without kinetic complications, which allows the use of concentrations other than zero for both the oxidized and reduced forms, is derived. A similar equation is derived for the potential-time relation for the reverse process upon reversal of the current at or before the transition time. The significance of the equations is discussed and suggestions are made for their application to the determination of $k_{s,h}$, α, and $E^{\circ\prime}$.**

In recent years, there have been many excellent treatments of chronopotentiometric potential-time equations for various electrode reaction schemes (*2, 4, 6, 7, 9, 11*). In almost all of these, however, attention has been focused on completely reversible and/or completely irreversible processes. Very little consideration has been given to intermediate or quasi-reversible electron transfer processes. In an important paper dealing with the interpretation of chronopotentiometric potential-time curves, Reinmuth (*9*) has touched upon the type of relation to be expected for such intermediate processes in the absence of any kinetic and catalytic effects. He uses this relationship to define the practical limits of application of the simple totally reversible and totally irreversible chronopotentiometric equations.

In the present work, we have considered a more general potential-time relationship for quasi-reversible, first-order electrode reactions without kinetic complications. This equation allows the use of concentrations other than zero for both the oxidized and reduced forms. A similar equation is derived for the potential-time relation for the anodic process upon reversal of the current. The equations given here are written for the case where a reduction process is followed by reoxidation. They apply equally well, of course, to an oxidation process followed by a reduction. A discussion is given of the significance of these equations and suggestions are made for their application to the determination of the quantities $k_{s,h}$, α, and $E^{\circ\prime}$.

[1] Present address, Department of Chemistry, University of North Carolina, Chapel Hill, N. C.

THEORY

In the case of a first-order electrode reaction

$$O + ne^- \rightleftharpoons R \qquad (1)$$

the rate of the reaction may be described in terms of the current as

$$i_o/nF = k_{s,h}\theta^{\alpha}[C_{OS} - C_{RS}/\theta];\ 0 < t \leqslant \tau \qquad (2)$$

$$-i_o'/nF = k_{s,h}\theta^{\alpha}[C_{OS} - C_{RS}/\theta];\ 0 < t' \leqslant \tau \qquad (3)$$

The surface concentrations of R and O used in Equations 2 and 3 must be obtained by solution of the boundary value problem describing voltammetry at constant current under conditions of semi-infinite linear diffusion. Various aspects of the solution of this differential equation have been discussed by Sand (*10*), Karaoglanoff (*4*), Berzins and Delahay (*2*), Testa and Reinmuth (*12*), and King and Reilley (*5*). In the appendix the expressions for C_{OS} and C_{RS} have been substituted into Equation 2 and the resulting equations rearranged to yield the expression:

$$\left[1 - \frac{b}{\theta} - \frac{S\pi^{1/2}D^{1/2}}{2\tau^{1/2}k_{s,h}\theta^{\alpha}}\right]\left(\frac{\theta}{\theta + 1}\right) = f(t)$$

where

$$S = \begin{cases} 1 & 0 < t \leqslant \tau \\ -a & 0 < t' \leqslant \tau' \end{cases} \qquad (4)$$

and

$$f(t) = \begin{cases} t^{1/2}/\tau^{1/2} & ;\ 0 < t \leqslant \tau \\ \dfrac{(\tau + t')^{1/2} - (1 + a)t'^{1/2}}{\tau^{1/2}} & ;\ 0 < t' \leqslant \tau' \end{cases}$$

This is the expression for the time dependence of the potential during the course of a chronopotentiometric wave. The equation takes a simpler form in two limiting cases—reversible or diffusion control of the rate and irreversible or electron transfer control.

Reinmuth has shown (*9*) that, if Condition 5 holds, the electrode reaction may be considered to be electrochemically reversible.

$$1 - b \geqslant 5\, i_o/2nFk_{s,h}C_o^{\circ};\quad 0 < t \leqslant \tau$$
$$1 - b \geqslant 5\, i_o'/2nFk_{s,h}C_o^{\circ};\quad 0 < t' \leq \tau' \qquad (5)$$

Applying this criterion to Equation 4, the following time dependence of the potential is obtained:

$$E = E_{1/2} + \frac{RT}{nF}\ln\left[\frac{\tau^{1/2} - t^{1/2}}{b\tau^{1/2} + t^{1/2}}\right];\quad 0 < t \leqslant \tau \qquad (6a)$$

$$E = E_{1/2} + \frac{RT}{nF} \times \ln\left[\frac{\tau^{1/2} - (\tau + t')^{1/2} - (1 + a)t'^{1/2}}{b\tau^{1/2} - (\tau + t')^{1/2} - (1 + a)t'^{1/2}}\right];\quad 0 < t' \leqslant \tau \qquad (6b)$$

If, on the other hand, Condition 7 holds, the current will be controlled by the rate of electron transfer and the process is irreversible.

$$1 \ll b + \frac{i_o}{nFC_o^{\circ}k_{s,h}\theta^{\alpha}};\quad 0 < t \leqslant \tau$$
$$1 \ll b - \frac{i_o'}{nFC_o^{\circ}k_{s,h}\theta^{\alpha}};\quad 0 < t' \leqslant \tau' \qquad (7)$$

Under these conditions, Equation 4 is found to yield the following potential-time expression.

$$E = \frac{RT}{\alpha nF}\ln\left[\frac{2k_{f,h}^{\circ}\tau^{1/2}}{\pi^{1/2}D_o^{1/2}}\right] + \frac{RT}{\alpha nF} \times \ln\left[1 - (t/\tau)^{1/2}\right];\ 0 < t \leqslant \tau \qquad (8a)$$

$$E = \frac{RT}{(1-\alpha)n'F} \times \ln\left[\frac{D^{1/2}\pi^{1/2}a}{2k_{b,h}{}^{\circ}\tau^{1/2}}\right] + \frac{RT}{(1-\alpha)n'F} \times \ln\left[\frac{\tau^{1/2}}{b\tau^{1/2} + (\tau + t')^{1/2} - (1+a)t'^{1/2}}\right]$$

$$0 < t' \leqslant \tau' \quad (8b)$$

In any of these equations, b may be expressed in terms of either the measured concentrations $C_R{}^{\circ}$ and $C_O{}^{\circ}$ or τ and τ' as defined in the glossary. In the usual chronopotentiometric experiment, the initial concentration of species R is zero, and the potential of the working electrode before application of the current is near the decomposition potential of mercury. When the current is applied, the potential swings very rapidly to the decomposition potential of the electroactive species, causing drastic changes in the double layer and surface of the electrode. These rapid potential excursions are avoided by maintaining finite concentrations of both R and O in the solution (or the amalgam). The potential-time equations for the general concentration ratio, b, are required to plot the resulting E-t data.

DISCUSSION

Equation 4 completely describes the potential-time relationship for a first-order electrode reaction in which mass transfer is limited to linear diffusion. The assumption is made here that the rate of the reaction and hence the current are limited only by two series processes, mass transfer and electron transfer. If either of these processes may be considered fast with respect to the other, the general relation simplifies to either Equation 6 or Equation 8. If both processes have comparable rates, Equation 4 must be dealt with directly.

It is readily seen that for each value of the potential, E, there is a corresponding value of $f(t)$ determined by the kinetic constants $k_{s,h}$ and α, and the equilibrium potential, $E^{\circ\prime}$. To illustrate this dependence, Figure 1 has been constructed for $D_O = 10^{-5}$ sq. cm. per second; $\tau = 25$ seconds, $b = 1$, and $a = \sqrt{2}$. These curves were calculated by assuming a value of E, substituting it into the left-hand side of Equation 4, and solving for t (or t').

From this construct, it is apparent that changes in the equilibrium potential cause a shift of the entire curve along the potential axis without affecting the shape or separation of the forward and reverse curves. A decrease of $k_{s,h}$, on the other hand, increases the separation of the forward and reverse curves—i.e., the processes become more irreversible.

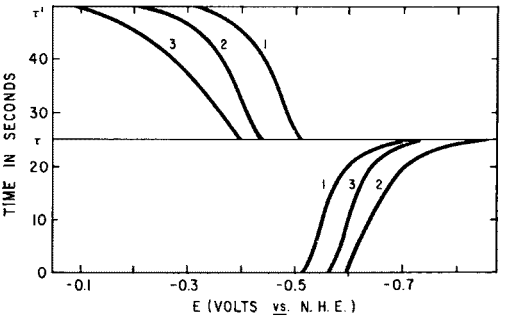

Figure 1. E-t curves calculated from Equation 4 illustrating the dependence of waveform on kinetic parameters $k_{s,h}$ and α

Changes in $E^{\circ\prime}$ result in translation of curves with no changes in slope or shape

Curve	α	$k_{s,h}$	$E^{\circ\prime}$
1	0.5	10^{-3}	−0.500
2	0.5	10^{-4}	−0.500
3	0.7	10^{-4}	−0.500

The symmetry of the curves is affected by changes in α; an increase in α decreases the slope of the forward curve and increases that of the reverse curve.

Practical application of Equation 4 is another matter. A method is required for selecting those values of the constants $E^{\circ\prime}$, $k_{s,h}$, and α which gives the best approximation to the experimental potential-time curve. Two general approaches are discussed here: an iteration method of fitting the complete equation to the data by successive approximations, and a short-cut method which is less accurate but can be used to make a reasonable first estimate.

Iteration Method. Several values of the potential and time must first be taken from the experimental chronopotentiometric curve (eight points spread evenly along the S-shaped curve are usually sufficient) and the transition time. From τ and each value of t (or t'), a value may be calculated for the right-hand side of Equation 4 which will be called $[f(t)_{\text{obsd}}]_i$. This set of functions of time are the experimentally observed quantities to be used as reference points for the iteration process.

The iteration process begins with the assumption of an initial value of each of the constants $E^{\circ\prime}$, $k_{s,h}$, and α. The numerical value of the left-hand side of Equation 4 is then calculated for each experimental value of E. These values are called $[f(t)_{\text{calcd}}]_i$. The two sets of $f(t)$ values are then compared and a numerical value is assigned to the agreement between these sets. The value of one of the constants $E^{\circ\prime}$, $k_{s,h}$, or α, say $E^{\circ\prime}$, is then changed slightly and a new set of $[f(t)_{\text{calcd}}]_i$ values computed. That value of $E^{\circ\prime}$ which gives the better agreement between $[f(t)_{\text{obsd}}]_i$ and $[f(t)_{\text{calcd}}]_i$ is retained and the iteration process continued by now changing in order $k_{s,h}$ and α. After each change of $k_{s,h}$, a new best fit must be found for $E^{\circ\prime}$. Similarly after each change of α, a new best fit must be found for both $E^{\circ\prime}$ and $k_{s,h}$. This results in an enormous number of checks for a best fit. For example, if it were necessary to undertake only 10 trials to obtain a best fit for each of the variables, the total number of checks for best agreement would be $10 \times 10 \times 10$ or 1000. When the best agreement between the calculated and observed $f(t)_i$ values has been reached, the "best" values of $E^{\circ\prime}$, $k_{s,h}$, and α have been assumed.

It must now be decided what constitutes the "best fit" of the calculated to the observed values of $f(t)$. The most common criterion for a best fit is the sum of the squares of the differences between the calculated and the observed data.

$$A = \sum_i \{[f(t)_{\text{obsd}}]_i - [f(t)_{\text{calcd}}]_i\}^2 \quad (9)$$

A familiar case is the least squares method of fitting a straight line to experimental data (*8*). Unfortunately, it is not feasible to obtain an explicit expression for the best fit of Equation 4 to experimental data, and consequently a trial and error procedure must be employed. The values of $E^{\circ\prime}$, $k_{s,h}$, and α sought are those for which Equation 9 is a minimum.

As has been mentioned above, changes in $E^{\circ\prime}$ and $k_{s,h}$ cause a translation of the E-t curve parallel to the potential axis, while α is more closely related to the slope, dE/dt, of the curve. Because of this, Equation 9 is found to be a poor criterion for the best value of α. In

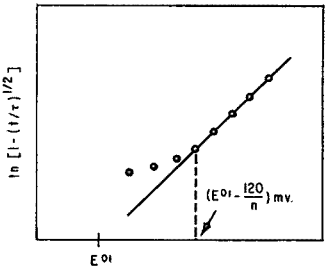

Figure 2. E vs. ln f(t) for irreversible Equation 8a applied to data from quasi-reversible chronopotentiogram

Nearly irreversible case

this case Equation 10, the sum of the squares of the differences in slope of the lines drawn between successive points on the two curves, is found to be more sensitive in establishing the best value of α.

$$\sum_i \left\{ \frac{[f(t)_i - f(t)_{i-1}]_{obsd} - [f(t)_i - f(t)_{i-1}]_{calcd}}{E_i - E_{i-1}} \right\}^2 \qquad (10)$$

The procedure described is excessively time-consuming and tedious when fitting Equation 4 to experimental curves by hand calculations. With the use of a digital computer to speed up the arithmetic manipulations, however, the iteration process becomes not only practicable but even simpler than graphical methods. Macero and Anderson (*7*) have described a general computer program for the treatment of reversible and irreversible chronopotentiometric data. This has been modified to accomplish the iteration process described above. The detailed FORTRAN program will be described elsewhere (*1*) along with experimental applications of the technique.

In the case of a quasi-reversible process it is not necessary to have both a forward and reverse curve in order to establish the best values for $E^{\circ\prime}$, $k_{s,h}$, and α. This can be done by obtaining the best fit of Equation 4 to either a forward or a reverse curve. This procedure allows the determination of a value for the formal reduction potential in cases where only the forward (or only the reverse) wave can be obtained under the experimental conditions employed. These correspond to the cases where the cathodic wave is obscured by the evolution of hydrogen, or the anodic wave is obscured by the dissolution of mercury. This is a rather surprising result, since the application of the corresponding totally irreversible equations (Equations 8a and 8b) yields estimates of $k_{f,h}^\circ$ and of α but not of $E^{\circ\prime}$. This is because the quasi-reversible process does not exhibit a linear shift of $E_{1/2}$ with $\ln(i_o/C_o^\circ)$ and an additional degree of freedom, the curvature, is available for the estimation of $E^{\circ\prime}$.

Consideration of Equation 4 indicates that the best approximation of $E^{\circ\prime}$ at a fixed current density is obtained when $k_{s,h}$ is large ($\approx 10^{-2}$ cm. per second). This approximation becomes less certain as $k_{s,h}$ becomes small ($\approx 10^{-4}$cm. per second) and when Equation 7 holds, it is no longer possible to estimate $E^{\circ\prime}$ from a single experimental curve. On the other hand, $k_{s,h}$ and α are determined with the most accuracy when the overvoltage is largest—i.e., when $k_{s,h}$ is smallest. When Equation 5 holds, no estimates may be made of $k_{s,h}$ and α.

Therefore both kinetic and equilibrium information can be obtained from the same data only if the rate process is controlled by both diffusion and charge transfer. The determination of $E^{\circ\prime}$ using two irreversible curves, one forward and one reverse, is possible when $\alpha + (1 - \alpha) = 1$. This imposes a symmetry condition on the two curves and allows estimation of the $E^{\circ\prime}$ from the intersection of the cathodic and anodic branches of the E *vs.* $\ln i_o/C^\circ$ plot.

Short-Cut Method. Delahay (*3*) has pointed out that for all points on the potential-time curve more than $\frac{120}{n}$ mv. from the equilibrium potential, the rate of the back reaction may be neglected. Practical use may be made of this fact by simply neglecting those points for which $|E^{\circ\prime} - E|$ is less than $\frac{120}{n}$ mv. and applying the totally irreversible equation to the remaining points. In Figure 2 is shown a portion of a typical E *vs.* $\ln[f(t)]$ plot. The back process can be considered to be negligible about halfway up the curve.

$$C_R = C_R^\circ + \frac{2i_o t^{1/2}}{nFD_R^{1/2}\pi^{1/2}} \exp\left(-\frac{x^2}{4D_R t}\right) - \frac{i_o x}{nFD_R} \operatorname{erfc}\left(\frac{x}{2D_R^{1/2}t^{1/2}}\right) \qquad (A1)$$

This is the point at which $E = \left[E^{\circ\prime} - \frac{120}{n}\right]$ mv. The upper points all lie on a straight line and are best described by the equation for the totally irreversible process, Equation 8a. This line has a slope of $RT/\alpha nF$ and an intercept equal to $\frac{RT}{\alpha nF} \ln\left[\frac{2\,k_{f,h}^\circ \tau^{1/2}}{\pi^{1/2} D_o^{1/2}}\right]$.

When the overvoltage is small, as is the case in Figure 3, $k_{f,h}^\circ$ and α may still be estimated by drawing the asymptote to the experimental points where $E = \left[E^{\circ\prime} - \frac{120}{n}\right]$ mv., and applying Equation 8a to this line. These methods are approximate and are less desirable than the general iteration method.

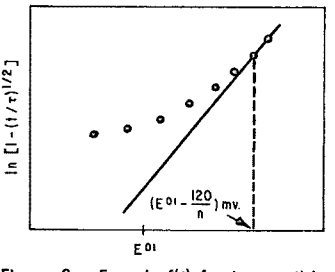

Figure 3. E vs. ln f(t) for irreversible Equation 8a applied to data from quasi-reversible chronopotentiogram

Nearly reversible case

In summary, Equation 4 describes a first-order electrode process in which the rate is controlled by both diffusion and electron transfer. Analysis of this equation and the limiting cases of totally reversible and totally irreversible processes yields insight into the reduction process. Application of these relationships, particularly with the aid of machine computation, will allow the investigation of a large number of quasi-reversible processes hitherto neglected.

APPENDIX

Expression for C_R during Forward Process When C_R° Is Not Zero. By making the substitution $Q_R = C_R - C_R^\circ$, and then expressing Fick's second law and the boundary conditions in terms of Q_R rather than C_R, the expression for Q_R as a function of x and t is readily obtained. From this the desired expression for C_R is obtained—i.e.,

Since it is the surface concentration which is of interest this reduces to

$$C_{Rs} = C_R^\circ + \frac{2i_o t^{1/2}}{nFD_R^{1/2}\pi^{1/2}} \qquad (A2)$$

Expression for C_R after Current Reversal When C_R° Is Not Zero. From Fick's second law we have

$$\frac{dC_R}{dt} = D_R \frac{d^2C_R}{dx^2}$$

and from Equation A1

$$(C_R)_{t=\tau} = C_R^\circ + \frac{2i_o\tau^{1/2}}{nFD_R^{1/2}\pi^{1/2}} \exp\left(-\frac{x^2}{4D_R\tau}\right) - \frac{i_o x}{nFD_R} \operatorname{erfc}\left(\frac{x}{2D_R^{1/2}\tau^{1/2}}\right) \qquad (A3)$$

In this case the boundary conditions are:

$\lim_{x\to\infty} C_R = C_R^\circ$ and $\frac{i^{\circ\prime}}{nF} = D_R\left(\frac{dC_R}{dx}\right)_{x=0}$

Again the above differential equation and boundary conditions may be transformed into expressions in Q_R. The solution is now

$$Q_R = \frac{2i_o(\tau+t')^{1/2}}{nFD_R^{1/2}\pi^{1/2}}\exp\left[-\frac{x^2}{4D_R(\tau+t')}\right] - \frac{i_o x}{nFD_R}\operatorname{erfc}\left[\frac{x}{2D_R^{1/2}(\tau+t')^{1/2}}\right] - \frac{2(i_o+i_o')(t')^{1/2}}{nFD_R^{1/2}\pi^{1/2}}\exp\left(-\frac{x^2}{4D_R t}\right) + \frac{(i_o+i_o')x}{nFD_R}\operatorname{erfc}\left[\frac{x}{2D_R^{1/2}(t')^{1/2}}\right] \quad (A4)$$

Substituting again for Q_R and setting $x = 0$, we obtain $C_{RS} = C_R^\circ + \frac{2i_o}{nFD_R^{1/2}\pi^{1/2}}\left[(\tau+t')^{1/2} - (1+a)(t')^{1/2}\right]$ (A5)

Expression for C_O after Current Reversal. By means of the substitution $C_O = C_O^\circ - Q_R$ and the assumption that $D_O = D_R = D$ it can be shown that at the electrode surface

$$C_{OS} = C_O^\circ - \frac{2i_o}{nFD_R^{1/2}\pi^{1/2}}\left[(\tau+t')^{1/2} - (1+a)(t')^{1/2}\right] \quad (A6)$$

Derivation of Equation 4 for Forward Process. The expression for the concentration of the oxidized form during the forward process when C_O° is not zero is well known (3).

$$C_{OS} = C_O^\circ - \frac{2i_o\tau^{1/2}}{nFD_O^{1/2}\pi^{1/2}} \quad (A7)$$

If Equations A2 and A7 are substituted into Equation 2, the following result is obtained:

$$\frac{i_o'}{nF} = k_{s,h}\theta^\alpha\left[C_O^\circ - \frac{2i_o t^{1/2}}{nFD_R^{1/2}\pi^{1/2}} - \frac{C_R^\circ}{\theta} - \frac{2i_o t^{1/2}}{nFD_R^{1/2}\pi^{1/2}\theta}\right]$$

Multiplying both sides by $\frac{nFD_O^{1/2}\pi^{1/2}}{2ik_{s,h}\theta^\alpha}$ gives

$$\frac{D_O^{1/2}\pi^{1/2}}{2k_{s,h}\theta^\alpha} = \frac{nFD_O^{1/2}\pi^{1/2}C_O^\circ}{2i_o} - t^{1/2} - \frac{nFD_O^{1/2}\pi^{1/2}C_R^\circ}{2i_o\theta} - \frac{D_O^{1/2}t^{1/2}}{D_R^{1/2}\theta}$$

Grouping like terms, and assuming $(D_R/D_O)^{1/2} = 1$ yields

$$\frac{D_O^{1/2}\pi^{1/2}}{2k_{s,h}\theta^\alpha} = \frac{nFD_O^{1/2}\pi^{1/2}}{2i_o}(C_O^\circ - C_R^\circ/\theta) - \left(\frac{\theta+1}{\theta}\right)t^{1/2}$$

Rearranging and multiplying both sides by $\left(\frac{\theta}{\theta+1}\right)$ gives

$$\left[nFD_O^{1/2}\pi^{1/2}(C_O^\circ - C_R^\circ/\theta) - \frac{D_O^{1/2}\pi^{1/2}}{2k_{s,h}\theta^\alpha\tau^{1/2}}\right]\left(\frac{\theta}{\theta+1}\right) = \frac{t^{1/2}}{\tau^{1/2}}$$

Finally, substituting $C_O^\circ = \frac{2i_o\tau^{1/2}}{nFD_O^{1/2}\pi^{1/2}}$ from the Sand equation, the final form of the equation is obtained:

$$\left[1 - \frac{C_R^\circ}{C_O^\circ\theta} - \frac{D_O^{1/2}\pi^{1/2}}{2k_{s,h}\theta^\alpha\tau^{1/2}}\right]\left(\frac{\theta}{\theta+1}\right) = \left(\frac{t}{\tau}\right)^{1/2} \quad (2)$$

Derivation of Equation 4 after Current Reversal. Substituting Equations A6 and A7 into Equation 3 one obtains:

$$\frac{-i_o'}{nF} = k_{s,h}\theta^\alpha\left\{C_O^\circ - \frac{2i_o}{nFD^{1/2}\pi^{1/2}}\left[(\tau+t')^{1/2} - (1+a)(t')^{1/2}\right]\right\}$$
$$\left\{-C_R^\circ/\theta - \frac{2i_o}{nFD^{1/2}\pi^{1/2}\theta}\left[(\tau+t')^{1/2} - (1+a)(t')^{1/2}\right]\right\}$$

Multiplying both sides by $\frac{nFD^{1/2}\pi^{1/2}}{2i_o k_{s,h}\theta^\alpha}$ and regrouping terms gives:

$$\frac{-D^{1/2}\pi^{1/2}a}{2k_{s,h}\theta^\alpha} = \frac{nFD^{1/2}\pi^{1/2}}{2i_o}\left[C_O^\circ - C_R^\circ/\theta\right] - \left(\frac{\theta+1}{\theta}\right)\left[(\tau+t')^{1/2} - (1 \mp a)(t')^{1/2}\right]$$

Multiplying both sides by $\left(\frac{\theta}{\theta+1}\right)\tau^{1/2}$, substituting $\frac{nFD^{1/2}\pi^{1/2}}{2i_o\tau^{1/2}} = C_O^\circ$, and rearranging terms yield the final form:

$$\left[1 - \frac{C_R^\circ}{C_O^\circ\theta} - \frac{a\pi^{1/2}D^{1/2}}{2k_{s,h}\tau^{1/2}\theta^\alpha}\right]\left(\frac{\theta}{\theta+1}\right) = \frac{(\tau+t')^{1/2} - (1+a)(t')^{1/2}}{\tau^{1/2}} \quad (3)$$

NOMENCLATURE

a	= ratio of reverse to forward currents
b	= $\frac{C_R^\circ}{C_O^\circ} = \left[(1+a)\left(\frac{\tau'}{\tau}\right)^{1/2} - \left(1+\frac{\tau'}{\tau}\right)^{1/2}\right]$
C_O, C_R	= concentration of O and R, respectively, at any time t and distance x from electrode surface
C_O°, C_R°	= initial concentrations of O and R
C_{OS}, C_{RS}	= concentrations of O and R, respectively, at electrode surface at any time t
D_O, D_R	= diffusion coefficients of O and R, respectively
D	= common value of diffusion coefficient for both O and R
E	= potential of working electrode
$E^{\circ\prime}$	= formal potential
$E_{1/2}$	= half-wave potential (see Equation 8)
erfc	= complement of the error function
exp	= natural exponential function
F	= Faraday
i_o, i_o'	= forward and reverse current densities, respectively
$k_{f,h}^\circ$, $k_{b,h}^\circ$	= standard heterogeneous rate constant for forward and backward processes
$k_{s,h}$	= heterogeneous rate constant at $E = E^{\circ\prime}$
ln	= natural logarithmic function
n	= number of electrons transferred in an electrochemical reaction
O	= oxidized species
R	= reduced species
t	= time
t'	= $(t - \tau)$
T	= temperature
x	= distance from electrode surface
θ	= $\exp\left[\frac{nF}{RT}(E^{\circ\prime} - E)\right]$
τ, τ'	= forward and reverse transition times, respectively
α	= electron transfer coefficient

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An Instrument for Cyclic Voltammetry

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▷ An instrument has been designed for cyclic voltammetry utilizing electronic DC-coupled switching which will accept either fast or slow sweep signals. Provision is made for one-half-, one-, two-cycle, and free-running operation. Controlled electrode D.C. level is adjustable over approximately a five-volt range. It can be made to sweep in either the positive or negative direction from the rest position. A switching arrangement is provided which, in conjunction with a staircase sweep, will eliminate charging current effects at a mercury electrode. This allows determination of reversibly reduced substances to a sensitivity of approximately 10^{-7}M.

APPARATUS for cyclic voltammetry which have been recently described utilize operational amplifier circuits for sweep potential control and for current amplification. Davolio, Guerzoni, and Papoff (*6*) have described an instrument suitable for oscilloscopic readout. It imposes a free-running triangular signal which can be varied over a wide range of sweep rates with accurately determined adjustable D.C. level. Buck and Eldridge (*4*) have designed an instrument capable of producing free running triangle or step potential or current signals. Alden, Chambers, and Adams (*1*) have developed an instrument which provides a slow triangular signal to be used with recorder readout. It can be used for either single or repetitive sweeps. It is the purpose of the present paper to describe an instrument which, like those mentioned above, makes use of operational amplifiers, but which incorporates all-electronic D.C.-coupled switching which makes it quite versatile in operation. In addition, a sampling device is described which permits exclusion of charging current when fast sweeps are used. This involves the use of a staircase sweep, with current measurements made after decay of charging current (*9*).

The function of the major components of the apparatus can be understood from the block diagram of Figure 1. The basic sweep signal is generated as a sawtooth wave form. This may be either a linear or staircase signal. Its period may be short as a few milliseconds for very high sweep rates, or may be as long as desired for slow sweep experiments. The basic positive going signal is inverted at unity gain. Both positive and negative signals are presented to the sweep gate. The function of the sweep gate is to synthesize the desired sweep signal by correct choice of positive and negative signal segments. The following types of sweep are convenient and are provided: single sweep, positive or negative; cycle, positive then negative; one one cycle, negative then positive; two cycle, positive-negative sequence; two cycle, negative-positive sequence; continuous operation with either positive or negative initial sweeps. D.C. level adjustment of the controlled electrode potential is also accomplished in the sweep gate. Provision is made for adjustment over approximately a five-volt range, making available the range of potentials, anodic and cathodic, which is of interest in electrochemical experiments.

The function of the gate signal generator is to provide the command signals to the two sides of the sweep gate. In continuous operation, for example, this amounts to two square wave trains, 180° out of phase. In the gate signal generator, the decision is made about the duration of the sweep—i.e., half cycle, one cycle, etc.

The signal from the sweep gate is accepted by the potential control amplifier and is imposed on the electrolysis cell in a conventional operational amplifier arrangement. The sweep generator and gate produce a sweep signal which initially moves positive, then negative. This is the sequence usually desired for work with mercury electrodes, since the sweep is imposed on the counter electrode while the controlled electrode remains at virtual ground. This will be called the reducing mode of operation. For anodic voltammetry, it is convenient to have the controlled electrode start at a negative rest potential and move positive. This sequence, termed the oxidizing mode, is conveniently obtained by including an optional unity gain inverter in front of the potential control amplifier.

The current amplifier uses a stabilized operational amplifier with the controlled electrode held at virtual ground. Output sensitivities of 1, 10, 100, and 1000 μa. per volt are provided. When a linear sweep is used, the current

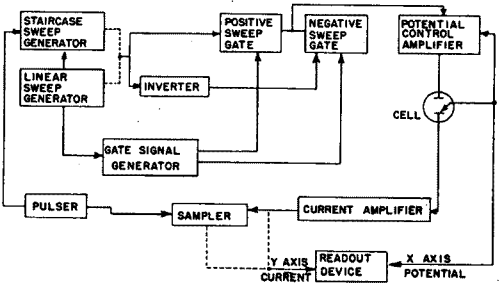

Figure 1. Block diagram of apparatus

amplifier output can be taken directly to the readout device. If the staircase sweep is used, the current signal must be subjected to switching in the sampler to eliminate the charging current spikes.

The sampler accepts the current signal from the current amplifier and a pulse train synchronized with the steps of the staircase signal. It samples the current signal a few microseconds before a step is applied to the cell. This sample is stored in a holding circuit and is applied continuously to the readout device during almost the entire duration of the succeeding step. Just at the end of the next step, the signal holder is discharged and a new sample is accepted.

A brief description of each of the sections of the instrument is given below. A detailed schematic diagram can be obtained by mail from the writer.

Power Supplies. D.C. power in the instrument is furnished by two Philbrick R-100B ±300-volt supplies and one larger ±250-volt supply. Because the 300-volt supplies are more stable and offer less hum, they have been used throughout where stability and freedom from noise is critical. The 250-volt supply is used in the less critical pulse circuitry. Nearly all parts of the instrument powered by the 250-volt supply would operate without modification from a 300-volt supply.

Filament current is obtained by stepping down the output from a Sola 110-volt regulating transformer. The considerable line voltage fluctuations in our laboratory make this necessary; quite likely it would not be necessary in a building with better wiring. Filaments in the sweep gate are run from a D.C. supply.

Sweep Generator. The instrument has been used exclusively with oscilloscope readout; accordingly the sweep generators which are described provide relatively fast sweeps with short periods. Slower sweeps with longer periods would be entirely compatible with the other components of the instrument if recorder readout were desired.

The sweep generator is an operational amplifier integrator (Philbrick K2W). Sweep rate is in part determined by selection of input resistance to the integrator. Current being integrated is supplied from the stabilized dual power supply. A sawtooth wave form is generated by discharging the integrating capacitor with a thyratron. To obtain the thyratron discharge pulse, the sweep wave form is scanned by a Schmitt comparator. This also serves as the time marker pulse in the gating circuitry. Sweep length can be adjusted by adjusting the comparison voltage in the Schmitt circuit. In order to keep the thyratron filaments away from the K2W input to avoid pickup of 60 c.p.s. noise, it is necessary to generate a negative-going sweep. It is convenient, however, to arrange the sweep generators so that the linear and staircase sweeps are entirely interchangeable. Since the basic staircase signal is positive-going, the basic linear sweep is inverted, using a unity-gain operational amplifier (K2W). By combining selection of sweep input resistance with variable attenuation in the sweep gate, sweep rates from 2 to 100 volt per second are available.

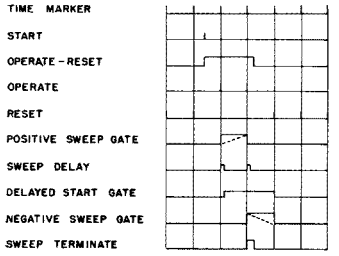

Figure 2. Timing sequences, gate signal generator

The staircase sweep generator is a modified diode pump circuit, described by Kramer (*8*). The necessary pulse train input for staircase generation is obtained from a General Radio Type 1217B pulser. The discharge pulse formed in the linear sweep generator is used to terminate the staircase sweep also. This ensures that current samples will be taken at randomly chosen potentials in free running polarograms to avoid loss of detail due to the periodic sampling process. The signal produced has a step rise time of about 4 μsec. and a tilt of about 0.4%.

The basic sweep signal chosen, linear or staircase, is inverted (K2W) and the D.C. level of both positive- and negative-going signals is adjusted by a cathode follower arrangement to permit them to be put together to form a coherent triangle.

Gate Signal Generator. As indicated above, this component provides two signals. One of these controls the positive sweep transmission gate, the other controls the negative gate. These signals are generated by a pair of bistable multis, each capable of furnishing an Open or a Close gating signal to the corresponding transmission gate. When the sweep is not in use, both gating multis are in the Close condition. To illustrate the operation of this component, consider the action to produce a one-cycle sweep. Timing sequences are shown in Figure 2.

A train of pulses, produced in the sweep generator and synchronized with the basic sweep signal, designated Time Marker pulses, serves as the basic timing reference. When the sweep is being used, a logic gate passes them as Operate pulses to operate the gating multis. When the sweep is not in use, another logic gate uses these pulses as Reset pulses to hold all components in their rest conditions.

When the operator closes the switch to start the sweep, his action probably will not coincide with the start of one of the sweep signals. This is indicated by the position of the Start pulse relative to the Time Marker pulses. Accordingly, the Start command must be accepted and held until the start of the next sweep signal. At this time, an Operate pulse is directed to the positive gating multi to put it in the Open condition. The second Operate pulse must be directed to the positive gating multi to Close it and simultaneously to the negative gating multi to Open it. Since this generates one complete sweep cycle, the third Time Marker pulse, as well as successive Time Markers, appearing after the Start pulse is directed in the Reset circuit to return all components to their rest conditions. In Figure 2, two Operate pulses are shown appearing at the time of a two-pulse vacancy in the Reset train.

The operator's action generates a Start pulse which triggers a bistable multi to form the Operate-Reset gating signal. The Operate condition of this signal is the third line of Figure 2. The Reset is the reciprocal and is taken from the other side of the multi. These two signals actuate logic gates to provide Operate and Reset pulses, respectively.

The positive gating multi is connected directly to the Operate logic switch and is opened by the first Operate pulse and closed by the second. When sweeps longer than one cycle are used, the positive gating multi is opened by all odd numbered pulses and closed by all even numbered pulses. To avoid scrambling the halves of the sweep signal, the negative gating multi must be opened by even numbered pulses and closed by odd numbered pulses. To get the negative gating multi out of phase from the positive gating multi, the Operate pulses actuating the negative gating multi are passed through an additional logic gate which is itself opened by the first Operate pulse. This is done by using the Operate pulses to trigger a univibrator set to produce a pulse quite a bit wider than the Operate pulses. The trailing edge of this Sweep Delay pulse opens the Delayed Start Gate which passes the second and all successive Operate pulses to the negative gating multi to produce the Negative Sweep Gate signal.

When a one-cycle sweep is desired, the trailing edge of the Positive Sweep Gate triggers a univibrator to produce the Sweep Terminate pulse which

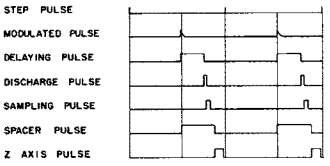

Figure 3. Timing sequences, sampler

returns the Operate-Reset multi to its original condition. As shown in Figure 2, the next Time Marker pulse appears in the Reset train and returns all multis to their original conditions. If a single sweep polarogram is desired, the Sweep Terminate pulse is triggered by the first Operate pulse. For two-cycle operation, the trailing edge of the Positive Gate signal is divided by two to produce a Sweep Terminate pulse on appearance of the fourth Operate pulse. In continuous operation, the Sweep Terminate pulse is produced by the operator pressing the start switch a second time.

Sweep Transmission Gate. This consists of two unidirectional diode transmission gates operating into a common load resistor. Signal attenuation to the level suitable for the cell is accomplished by taking a portion of the drop across this resistor. The attenuated signal is taken to a long tailed cathode follower fitted with potentiometer in its cathode circuit. Resistance values are chosen to permit adjustment of the D.C. level of the controlled electrode over the desired range without appreciable variation in signal attenuation.

Potential Control Amplifier. The signal from the sweep gate is applied to the noninverting input of an operational amplifier (Philbrick SK2V) if the reducing mode is desired. The output of this amplifier is applied to the auxiliary electrode. The reference electrode signal is brought to the inverting input of the amplifier and to the X-axis of the readout. Using the reference electrode signal this way imposes a limitation on the input impedance of the readout device, but eliminates the problem of removing the offset of the potential control amplifier. In practice, there has been no difficulty with aqueous systems using either an X-Y recorder for conventional polarography or an oscilloscope for cyclic voltammetry. Dimethylsulfoxide and acetonitrile have been used with fiber type reference electrodes filled with silver in the appropriate solvent. No difficulties are experienced when the reference electrode is taken to the X-axis of an oscilloscope with one-megohm input impedance.

When the oxidizing mode of operation is desired, the sweep signal is first taken to an operational amplifier inverter (SK2V) and then to the potential control amplifier described above.

Current Amplifier. A stabilized operational amplifier (Philbrick USA-3) is used in the conventional way for a current amplifier for the 1000, 100, and 10 μa/volt ranges. To obtain 1 μa./volt sensitivity with the staircase sweep, it is necessary to use a second stage (SK2V) with a gain of ten because of the frequency response demands imposed by the raw current signal from the staircase electrolysis.

Sampler. Figure 3 illustrates the timing sequences in the sampler. The Step pulse, from the General Radio 1217B pulser, is used as the time marker for the sampler. This pulse actuates a relaxation oscillator, Schmitt trigger time modulation arrangement with univibrator pulse shaping to produce a time-Modulated pulse which occurs at an adjustable time near the end of each step. The variable time modulation arrangement is required to permit a change in step width in the signal generator. The leading edge of the Modulated pulse triggers a univibrator to generate a 240-μsec. Delaying pulse. The trailing edge of the Delaying pulse is similarly used to trigger a 20-μsec. Discharge pulse, the trailing edge of which triggers a 40-μsec. Sampling pulse. The Modulated pulse also is used to trigger a 350-μsec. Spacer pulse, the trailing edge of which triggers the 90-μsec. Z-Axis pulse.

This sequence of events produces three trains of pulses which are fixed in time with respect to each other, the Discharge pulse followed almost immediately by the Sampling pulse, followed 50 μsec. later by the Z-Axis pulse. These pulses can be adjusted as desired relative to the steps of the staircase signal.

The raw current signal appears at the input of a diode transmission gate. During the period of the Sampling pulse, the gate is open to the current signal. At this stage, the sampled current signal carries the desired information as the maximum D.C. level of quite large pulses. If this signal were taken directly to the oscilloscope, it would be impossible to operate at very high sensitivity without saturating the scope amplifier. To avoid this difficulty, the sampled signal is taken to a boxcar holder. As described above the Discharge pulse is timed to discharge the holder sharply just before a new sample is taken. The resulting signal is taken to the scope Y-axis after D.C. level adjustment in a long-tailed cathode follower with glow tube coupling.

The oscilloscope trace is turned on once during each step for a period of 90 μsec. by the Z-Axis pulse. This arrangement prevents the scrambling of the polarogram by either the shifting of the potential with the appearance of the next sweep step or by the discharge spike from the holder. Since the trace is illuminated for only 90 μsec. during the course of a step, this prevents possible damage to the scope phosphor when the sweep is stationary between polarograms. It also provides a convenient way to synchronize the sampling circuit with the sweep circuit. The sweep is displayed on the scope and the sampler modulation is adjusted till the Z-axis spot falls at the foot of the step. The pulse circuitry is sufficiently stable that adjustment is rarely needed except when it is desired to change the step width.

EXPERIMENTAL

Reagents. Solutions were prepared with water from the metal house still which had been run through a mixed bed deionizer. The KCl used was reagent grade, once recrystallized from deionized water. Cd(II) stock solutions were standardized by electrogravimetry. Solutions were deaerated with tank nitrogen from which traces of oxygen were removed by contact with reduced alkaline anthraquinone sulfonate. At the highest sensitivity, it was necessary to add a small amount of Na_2SO_3 to remove the last traces of oxygen.

Instrument Performance. The major sections of the instrument have been in satisfactory routine use for about a year. Its stability is such that it is normally unnecessary to make any adjustments except when the sweep signal is changed. The only day to day calibration required is of the oscilloscope and of the polarization rate, if an accurate value is required.

The precision of measurements with this instrument is comparable to that of similar instruments. As an example of the precision obtained in the midportion of the normal operating range of concentrations, the measurement of peak heights obtained with 0.1m*M* Cd(II) at a hanging mercury drop electrode may be cited: at 40 volt/sec., the standard deviation was 5.7%; at 20 volt/sec., 2.1%; at 10 volt/sec., 2.4%; at 4 volt/sec., 2.9%; at 2 volt/sec., 0.8%. Similar figures for anodic voltammetry at platinum electrodes have been published elsewhere (*10*).

The sensitivity of the instrument is quite dependent upon the nature of the electrode and the electrode reaction being used. It is, of course, greatest with a mercury electrode and a reversible system. In this case, the limiting factor is the noise level in the sweep signal generator. This noise, predominately 60 c.p.s., has a peak-to-peak value of approximately 0.5 mv. When this is impressed across the double layer capacitance of the mercury electrode, an A.C. current signal is obtained which is not compensated by the staircase switching scheme. Its magnitude varies with the electrode area and the potential imposed. With a

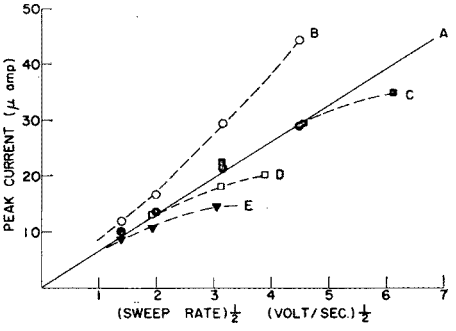

Figure 4. Comparison of linear and staircase sweeps

0.102mM Cd(II) in 0.10M KCl; hanging mercury drop electrode' 0.031 cm.² area; 25.0° C.

- A. Solid line, theoretical curve; solid circles, corrected linear sweep peak currents
- B. Uncorrected linear sweep peak currents
- C. Uncorrected staircase sweep peak currents, 1-msec. step
- D. Uncorrected staircase sweep peak currents, 2-msec. step
- E. Uncorrected staircase sweep peak currents, 4-msec. step

single DME drop of approximately 0.03 cm.² area in 0.1*M* KCl, the noise current varies from 0.1 to 0.5 μa., depending upon the potential imposed. In practice this limits the range of detection to about $10^{-7}M$ when Cd(II) is being electrolyzed. An attempt was made to carry out determinations at the 10^{-6} to $10^{-7}M$ level by electrolyzing Cd(II) solutions at a DME, using a continuous cyclic sweep of 10 volt/sec. with 2-msec. step widths. To assess the validity of the results, the assumption is made that the peak-to-peak height for a cyclic sweep arranged symmetrically about the half-wave potential is equal to twice the peak height for a single linear sweep. Knowing the diffusion coefficient for Cd(II) in 0.1*M* KCl, the electrode area and other necessary constants, the peak height to be expected for a single sweep experiment can be calculated from Equation 1 and doubled according to the assumption being made. For $2 \times 10^{-7}M$ Cd(II), the value expected is 0.08 μa. The measured value was 0.06 μa. For $6 \times 10^{-7}M$, 0.24 μa. would be expected and 0.3 μa. was measured. At the potential of the Cd(II) peak, the noise level is approximately 0.15 μa. A measurement is feasible because a number of cycles during the latter part of the lives of several drops can be photographed with the camera stopped back somewhat. This permits a sufficient bandwidth reduction to surmount the difficulty of the unfavorable signal to noise ratio.

The lower limit for analysis of reversibly reduced substances with this instrument is approximately $10^{-7}M$. For comparison, Cooke, Kelley, and Fisher have been able to determine cadmium to about the same level with their controlled potential derivative polarograph (*5*). Barker and Jenkins have stated that the limit of detection for the square wave polarograph is $2 \times 10^{-7}M$ (*3*). Using the pulse polarograph, Barker and Gardner have been able to carry out determinations with the normal pulse technique to $10^{-7}M$ and with the derivative pulse technique, to $10^{-8}M$ (*2*).

Use of Staircase Sweep. A discussion of the use of a staircase sweep to reduce the effect of double layer charging current has been presented previously (*3*). This is quite effective when sweep rates greater than one volt/sec. are used with mercury electrodes. It is not very helpful with platinum electrodes because of the large noncapacitative background currents. A comparison of the use of a linear sweep and of a staircase sweep with theoretically expected behavior on mercury electrodes is summarized in Figure 4. The line *A* represents peak current expected from theory. It is calculated from Equation 1, using the conditions of the experiments being compared (*7*)

$$i_p = 2.72 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \quad (1)$$

where i_p is peak current in amperes; *A*, area is cm.²; *C*, concentration in moles/cm.³; *n*, number of electrons/mole for the couple involved; *v*, sweep rate in volt/sec.; *D*, diffusion coefficient in cm.²/sec. A value of 7.15×10^{-6} cm.²/sec. was used for diffusion coefficient of Cd(II) in 0.10*M* KCl (*11*).

Line *B* represents measured values, using a linear sweep and measuring peak heights from zero current. The solid circles represent measurements taken with a linear sweep, but with graphical correction for the blank. The solid squares of *C* represent peak currents measured with a staircase sweep with 1-msec. steps, peak heights measured from zero current, the same procedure used to get the data for line *B*. Line *D* is made up of measurements of peak height from zero current using a staircase sweep with 2-msec. steps. Line *E* represents similar measurements with a 4-msec. staircase.

It is evident that the use of a staircase sweep is effective in reducing capacitance current effects and that, within limits, results obtained with the staircase sweep are in agreement with the theoretical relationship. One measure of effectiveness in eliminating capacitance effects is the difference between lines *A* and *B* in Figure 4 since results with the staircase sweep are in good agreement with the theoretical curve. From another point of view, the capacitance component of peak current at a sweep rate of 10 volt/sec. is about 8 μa. For a cyclic sweep, this would be about 16 μa., about 200 times the peak current measured for $2 \times 10^{-7}M$ Cd(II) with a staircase sweep under similar conditions.

It can be seen in Figure 4 that as the sweep rate is increased, a negative deviation from the theoretical relationship is observed. Furthermore, the linear relationship between (sweep rate)$^{1/2}$ and peak current is lost quicker as the step width is increased. This is attributed to the fact that as the steps are made larger, the staircase becomes progressively a poorer approximation to the linear sweep assumed in the derivation of Equation 1. The point at which the deviation becomes large is apparently partly dependent upon the width of the polarographic peak. With the broad peaks encountered in voltammetry with irreversible systems, a 10 volt/sec. sweep with 3-msec. steps causes no appreciable error. In practice, with reversible systems, it is convenient to use 2- or 3-msec. step widths at low sweep rates and to use 1-msec. steps at rates of 15 volt/sec. and higher.

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Digital Computer Program for Calculation of Molecular Formulae

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▷ **A digital computer program is described which calculates all molecular formulae that correspond to a given set of elemental analyses. All formulae are printed that have calculated elemental percentages which, for each element, differ from the experimentally found values by less than any previously specified amount. Provision is made for the inclusion of elements for which no analytical figures have been obtained.**

THE PROCESS of searching for molecular formulae which are consistent with a given set of elemental percentage compositions and the associated experimental errors is usually a laborious task. Where the number of elements present is large, the relevant "anticomposition" tables simply do not exist, and when several elements thought to be present have no analysis figures, the amount of work entailed in finding even a few possible formulae can be prohibitive.

We here give details of a digital computer program, written in FORTRAN, which calculates and prints all possible molecular formulae that correspond, as closely as desired by the operator, to the given elemental percentage composition.

At present, two versions of the program are in use; these vary primarily in the Input/Output routines. The first version uses the IBM 1620 computer (minimum core storage 20,000), with the "AFIT improved FORTRAN" (*1*) processor; this version accepts a maximum of 10 different elements in any one search. A compressed deck (250 cards) of this program can be run on any IBM 1620 equipped with card reader and typewriter output. The second version, which is reproduced here, was written for the IBM 1620 with FORTRAN II-D, and with little modification can be run on larger and faster computers such as the IBM 7094. This version at present accepts a maximum of 8 elements, but the number can be increased when more core storage is available by expanding only the dimension statements.

BRIEF DESCRIPTION OF THE PROGRAM

A. Elements with Analyses. Molecular formulae are considered which contain an integral number (n_1) of atoms of the first element. The number of atoms of each succeeding element must then fall within the range

$$\frac{n_1A_1}{A_j}\cdot\frac{(P_j+\epsilon_j)}{(P_1-\epsilon_1)},\ldots\ldots,\frac{n_1A_1}{A_j}\cdot\frac{(P_j-\epsilon_j)}{(P_1+\epsilon_1)}$$

where A_j, P_j, ϵ_j are the atomic weight, the found percentage, and the assigned experimental error for the jth element.

Initially n_1 is set equal to one, and the above range for each element in turn is tested to see whether it contains one or more integers. If this condition is not satisfied, n_1 is increased by one and the process is repeated. Eventually, either n_1 exceeds the highest number to which it is desired to search and the program terminates, or a value of n_1 is found such that the above range contains at least one integer for each element.

B. Elements without Analyses. The sum of the calculated percentages of all the elements without analyses must lie within the limits

$$[100-\Sigma(P_i+\epsilon_i)]\text{ and }[100-\Sigma(P_j-\epsilon_j)]$$

(The summations extend over all elements with analyses.) All combinations of these elements which comply with this restriction are considered.

C. Printed Formulae. Only formulae which have an even number of odd-valenced atoms are printed.

D. Unsaturation Number. The unsaturation number is given by

$$u=\frac{\Sigma(V_j-2)n_j}{2}+1$$

Where n_j is the number of atoms having valency V_j in the molecular formula.

DATA INPUT TO THE PROGRAM

Card	Format	Data
1	30H	For comments, identification, etc.
2	2I2, I4	Number of elements for which analyses are known; number of elements for which analyses are not known; number of atoms of the first element to which it is desired to test.

The remainder of the cards fall in one of two classes.

If the Analysis Is Known.

Card A	Format A2, F10.5,I2	Symbol of element (left justified), Atomic Weight, and Valency.
Card B	Format 2F5.2	Experimental percentage and error. The error will usually be set at the value of the precision of the analysis.

If the Analysis Is Not Known.

Card A as above
No Card B

All elements with analyses must precede those without analyses, and the experimental percentage for the first element must exceed its associated error. If C and H are known it will generally be convenient to place them first, in that order. If the percentage of only one element is known, the list of possibilities may, of course, become very large.

OUTPUT

The program prints the identification comments, the symbols of the elements entered as data, the experimental percentages, and the allowable errors for each element.

Valid formulae are then printed, together with the calculated percentages for every element and, where appropriate, the difference between the calculated and experimental percentages. These figures are truncated after the second decimal place. The molecular weight and the "unsaturation number" follow. The latter entry gives the number of double bonds or rings in the formula found, subject to the following qualifications.

PROGRAM LISTING

```
      DIMENSION AW(8),L(8),P(8),ER(8),SPU(8),SPL(8),PU(8),PL(8)
      DIMENSION ASW(7),LS(7),A(7),JA(7),SYM(8),SIM(8)
      DIMENSION EP(8),BU(8),NG(8),AX(8),ASG(8)
      DIMENSION AL(8),AU(8),SL(8),SU(8),NL(8),NU(8),TP(8)
    1 PRINT 2
    2 FORMAT (///26HMOLECULAR FORMULAE PROGRAM//)
      NL(2)=0
      NU(2)=0
      READ 3
      PRINT 3
    3 FORMAT (30H)
      PRINT 4
    4 FORMAT (//55X,4HM.W.,8X,12HUNSATURATION)
      READ 5,N,M,MJ
    5 FORMAT (2I2,I4)
      AB=MJ
      NT=N+M
      READ 6,(SYM(K),AW(K),L(K),P(K),ER(K),K=1,N)
    6 FORMAT (A2,F10.5,I2/2F5.2)
      IF (M)7,8,9
    9 DO 10 K=1,M
      READ 11,SIM(K),ASW(K),LS(K)
   11 FORMAT (A2,F10.5,I2)
      ND=N+K
      L(ND)=LS(K)
      ASG(K+1)=ASW(K)
   10 SYM(ND)=SIM(K)
    8 PRINT 12,(SYM(K),K=1,NT)
   12 FORMAT (10(3X,A2,2X))
      PRINT 13,(P(K),K=1,N)
      PRINT 13,(ER(K),K=1,N)
   13 FORMAT (/10(F7.2))
      YI=100.
      ZI=100.
      DO 14 K=1,N
      SPU(K)=P(K)+ER(K)
      SPL(K)=P(K)-ER(K)
      PU(K)=SPU(K)/AW(K)
      PL(K)=SPL(K)/AW(K)
      YI=YI-SPU(K)
      ZI=ZI-SPL(K)
      AL(K)=PL(K)/PU(1)
      AU(K)=PU(K)/PL(1)
      SL(K)=AL(K)
   14 SU(K)=AU(K)
      MP=M+1
      AX(1)=0.
      ASG(1)=0.
      AC=1.0
   15 DO 16 K=1,N
      NL(K)=AL(K)+0.9999
      NU(K)=AU(K)
      IF (NL(K)-NU(K))16,16,17
   16 CONTINUE
      IF (M)7,18,19
   19 W=AW(1)*AC
      X=0.
      WL=W/SPU(1)
      WU=W/SPL(1)
      Y=YI*WL
      Z=ZI*WU
      DO 20 K=2,MP
   20 AX(K)=0.
   21 IF (X-Y)22,23,23
   22 K=1
   24 X=X-ASG(K)*AX(K)+ASG(K+1)
      AX(K)=0.
      AX(K+1)=AX(K+1)+1.
      IF (X-Z)21,21,25
   25 IF (K-M)26,17,7
   26 K=K+1
      GO TO 24
   17 DO 27 K=1,N
      AL(K)=AL(K)+SL(K)
   27 AU(K)=AU(K)+SU(K)
      AC=AC+1.
      IF (AC-AB)15,15,28
   28 PRINT 29,SYM(1),MJ
   29 FORMAT (///24HSEARCH COMPLETE THROUGH ,A2,I4)
      PAUSE
      GO TO 1
   23 DO 30 K=1,M
      JA(K)=AX(K+1)
   30 A(K)=JA(K)
   18 NG(1)=AC
      DO 31 K=2,N
   31 NG(K)=NL(K)
   32 JE=0
      DO 33 K=1,N
      JE=JE+NG(K)*(L(K)-2)
      IF (NG(K))38,33,33
   33 CONTINUE
      IF (M)7,34,35
   35 DO 36 K=1,M
   36 JE=JE+JA(K)*(LS(K)-2)
   34 JO=JE/2*2-JE
      JE=JE/2
      IF (JO)38,37,38
   38 IK=2
   39 NG(IK)=NG(IK)+1
      IF (NG(IK)-NU(IK))32,32,40
   40 NG(IK)=NL(IK)
      IK=IK+1
      IF (IK-N)39,39,41
   41 IF (M)7,17,22
   37 AMW=0.
      DO 42 K=1,N
      BU(K)=NG(K)
   42 AMW=AMW+BU(K)*AW(K)
      IF (M)7,43,44
   44 DO 45 K=1,M
   45 AMW=AMW+ASW(K)*A(K)
   43 DO 46 K=1,N
      TP(K)=BU(K)*AW(K)*100./AMW
      EP(K)=TP(K)-P(K)
      SP=ABSF(EP(K))
      IF (SP-ER(K))46,46,38
   46 CONTINUE
      IF (M)7,48,49
   49 DO 50 K=1,M
      ND=N+K
      TP(ND)=A(K)*ASW(K)*100./AMW
   50 NG(ND)=JA(K)
   48 PRINT 52,(NG(K),K=1,NT)
   52 FORMAT (////10(I5,2X))
      PRINT 13,(TP(K),K=1,NT)
      PRINT 13,(EP(K),K=1,N)
      JE=JE+1
      PRINT 53,AMW,JE
   53 FORMAT (51X,F12.5,8X,I4)
      GO TO 38
    7 PRINT 54
   54 FORMAT (5HERROR)
      STOP
      END
```

For the purpose of this program all ionic bonds are treated as covalent—e.g., the nitrogen atom in an amine salt or a nitroalkane should be regarded as pentavalent. Each time an atom occurs in a molecule in a valency state two higher than the valency entered as data for that element, one must be added to the computed unsaturation number. When the search is completed, the message SEARCH COMPLETE THROUGH M X is printed, where M is the symbol of the first element, and X is the number through which it was desired to test. A new search may then be initiated by depressing the start button.

MOLECULAR FORMULAE PROGRAM

DEMONSTRATION

C	H	N	O	M.W.	UNSATURATION
77.80	6.10				
.20	.20				
11	10	2	0		
77.62	5.92	16.45	0.00		
−.17	−.17			170.21630	8
12	11	1	1		
77.81	5.98	7.56	8.63		
.01	−.11			185.22817	8
13	12	0	2		
77.97	6.04	0.00	15.98		
.17	−.05			200.24004	8

SEARCH COMPLETE THROUGH C 15

EXAMPLE

Found: C, 77·80; H, 6·10.%

The compound probably contains C, H, N, O. Set limits of C ± 0.20; H ± 0.20 (for example). The following cards would be used as input (the letter "b" signifies a blank column):

CARD NO.	(Column 1) ↓	
1	DEMONSTRATION	(identification card)
2	b2b2bb15	(i.e., 2 elements with analyses; 2 elements without analyses; and will test to C_{15}).
3	Cbbb12.0112bb4	Cards for carbon
4	77·80b0·20	
5	Hbbbb1·00797b1	Cards for hydrogen
6	b6·10b0·20	
7	Nbbb14·0067bb3	Card for nitrogen
8	0bbb15·9994bb2	Card for oxygen

The Output is given above. This search required 2.2 minutes; the actual calculation time was less than 25 seconds.

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Continuous Titrations with a Tubular Mercury–EDTA Electrode

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▷ A previously reported continuous automated potentiometric titrator with direct readout is extended to titrations of metal ions with EDTA. The sensor electrode, a tubular platinum electrode, is plated with metallic mercury and serves as indicator electrode for the titrations when the potential is established by the presence of low concentrations of Hg(II) in the titration mixture. The present study is confined to the concentration range 0.04 to 0.003M in order to obtain both direct readout and simplicity of operation. The titrator's performance is evaluated for different metals that are titratable at pH 10 and shows a relative standard deviation of 0.5%. The electrode is not satisfactory for titrations at pH 5.

THE TUBULAR platinum electrode (TPE) has recently been introduced as an analytical device (*5*). It has been adapted for use in a continuous (*4*) potentiometric titrator (*3*) that meters a sample stream at a constant flow rate, and that controls and measures the flow rate of a reagent stream that is kept chemically equivalent to the sample. The flow rate of the reagent stream is then taken to be proportional to the concentration of the sought-for substance in the sample stream.

In the present study, the continuous titrator has been adapted to chelometric titrations with EDTA. The theory and application of the mercury–EDTA indicator electrode have been extensively discussed from both a theoretical and experimental point of view by Reilley and Schmidt (*14, 15*). Additional uses of the mercury electrode as a p*M* indicator electrode for direct titrations (*13, 16*), for back-titrations (*11, 13*), and for determination of stability constants of metal–EDTA complexes (*16, 21, 22*) have been reported. Fritz has developed methods utilizing masking agents to increase the specificity of the titration (*7*). Ringbom treats the relationship of the end point break and accuracy of titrations for potentiometric chelometric methods (*18*). Barnard, Broad, and Flaschka (*1*) treat the mercury indicator electrode in an extensive review of the applications and uses of EDTA. In a later review (1962), Schmidt considers specifically the applications of the mercury indicator electrode (*19*). Recently the possibility of automating the potentiometric EDTA titration was considered (*20*).

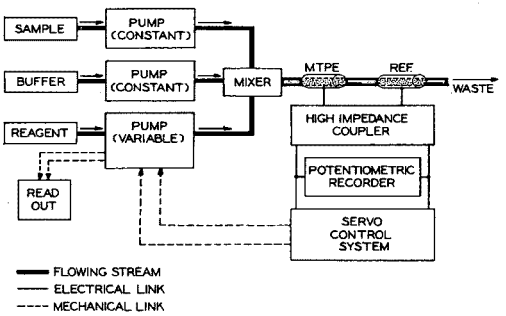

Figure 1. Block diagram of titrator

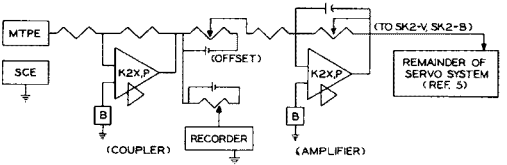

Figure 2. Modifications to the servo unit

For "remainder of servo system," see Reference 3

In the present study, a mercury-coated tubular platinum electrode (MTPE) has been used as the indicator electrode in the continuous titrator (*3*), rather than the mercury drop or pool type that was described in the above references. Kolthoff and Verzyl introduced the mercury-plated platinum electrode in 1923 (*10*), and Siggia and coworkers applied it recently to chelometric titrations (*23*). Gold (*15, 20*) and silver (*8, 9*) amalgams have also been used as indicator electrodes for chelometric titrations.

DESCRIPTION OF EQUIPMENT

Operation of Titrator. The fundamental principle on which the titrator operates is that separate streams containing sample and reagent are pumped together and passed through the indicator and reference electrodes. A servo unit controls the reagent pump speed to keep the resultant stream at a preselected equivalence point potential. Once the servo has adjusted the flow rate of the reagent stream to attain equivalence, the pump speed is presented numerically as a measure of the concentration of the sample stream. By adjusting the interval over which the pump speed is measured, the titrator can be calibrated with a standard sample so that subsequent sample concentrations may be read out directly.

Modifications to Titrator. Figure 1 is a block diagram of the previously reported titrator, modified for EDTA titrations. The reagent stream (an EDTA solution in buffer), the sample stream (a solution of the metal ion to be determined), and buffer stream (containing more concentrated buffer) are combined to produce the main stream that flows through the electrodes. The buffer stream is needed for ionic strength (*vide infra*) and pH control during titration. The buffer and sample pumps are respectively 23 and 56 r.p.m. constant speed peristaltic pumps (New Brunswick Scientific Co., New Brunswick, N. J., Models PA-23, PA-56), and the reagent pump is a variable speed peristaltic pump (Model 500-1200, Harvard Apparatus Co., Dover, Mass.). The New Brunswick pumps use 0.081-inch Silastic tubing and the Harvard pump uses two 0.040-inch Silastic tubes. Flow rates are, respectively, 5.82, 14.2, and 6.5 to 14.8 ml./min. The mixer (constructed of Teflon) combines and mixes the three individual streams immediately upstream from the MTPE. Downstream from the MTPE is a flow-through saturated calomel reference electrode (SCE). The signal from these electrodes is coupled through a high impedance to the servo unit of the titrator and also to a potentiometric recorder—to prevent current drain at the electrodes. The impedance coupling has been changed from the original titrator, as have other parts of the servo unit, to provide both greater signal amplification and greater amplifier stability—requirements dictated by the smaller magnitude of the break in the titration curve obtained with the EDTA system.

Figure 2 is a schematic of the servo unit with the high impedance coupling. The principal changes that were made provide greater stability by using a chopper-stabilized operational amplifier in the high impedance coupler and increased stabilized amplification (gains of approximately 100). The voltage amplifying-current boosting section and the remainder of the servo unit remain unchanged from the previous titrator. The coupling and amplifying stages utilize K2-W and K2-P operational amplifier and chopper stabilizer combinations while the amplifier-booster stage utilizes a SK2-V, SK2-B combination (Geo. A. Philbrick Researches, Inc., Boston, Mass.). Neither the readout system nor the system for measuring pump speed has undergone any modification. A capacitor in the amplifier stage is used to damp the response to sharply changing signals (primarily due to pick-up of electrical interferences from the laboratory).

A grounded TPE (0.50 inch long, 0.060-inch i.d.) is inserted into the flowing stream immediately before the MTPE assembly. This electrode reduces the pick-up of a.c. signals and noise by the sensor electrode, which would cause erratic behavior in the servo.

Preparation of Electrode. The mercury-coated TPE assembly is shown in Figure 3. The TPE is plated with mercury by the procedure outlined below, adapted from that of Ramaley, Brubaker, and Enke (*12*), and modified by Blaedel and Strohl (*6*). The TPE (0.45 inch long × 0.060-inch i.d.) is sealed into soft glass, as shown in Figure 3. After annealing, the electrode assembly is cleaned by successive boilings in cleaning solution (H_2SO_4–$Na_2Cr_2O_7$) and dilute perchloric acid, and then is washed with distilled water. Dilute perchloric acid is pumped through the assembly while the electrode is cathodized to the point of gassing for about 15 minutes against a platinum counter electrode. After cathodization (with evolution of hydrogen), small slugs of pure polarographic mercury are passed through the electrode, which becomes coated. The TPE is kept cathodic with respect to the counter electrode during the introduction of mercury. Completion of the surface coating is signaled by cessation of hydrogen evolution. After washing with distilled water, the electrode is mounted in the titrator.

In Figure 3, the branch to vacuum serves to accumulate stray bubbles from the flowing stream (usually introduced by changes of sample). When the branch becomes filled with gas, it is withdrawn to vacuum. The mercury coating may be renewed periodically simply by passing drops of fresh mercury from the reservoir through the MTPE.

Comparison of Mercury Pool Electrode and MTPE. The characteristics of EDTA titrations utilizing a mercury pool electrode have been discussed by Reilley and Schmidt (*14*). The mercury pool electrode consists of a massive amount of mercury while the MTPE has only a surface coating. A comparison of the two electrodes was obtained by using both simultaneously on the same titration.

A 0.003*M* solution of $Ca(NO_3)_2$ in 150 ml. of ammonia buffer [0.3*M* in NH_3 and 0.15*M* in $(NH_4)_2SO_4$] was placed in a 250-ml. beaker containing a mercury pool electrode. A SCE was bridged to the solution. A peristaltic pump was used to circulate the beaker contents through a MTPE (0.45 inch long, 0.060-inch i.d.) and back into the beaker. During the titrations, both electrodes were measured with respect to the same SCE using a selector switch and a Leeds & Northrup pH meter (Leeds & Northrup Co., Philadelphia, Pa., No. 7410) as a

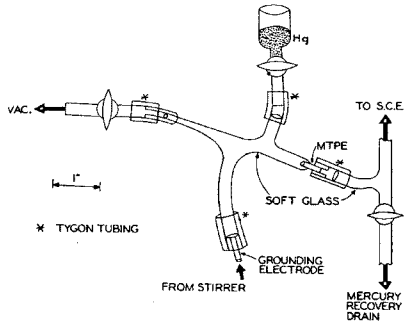

Figure 3. MTPE assembly

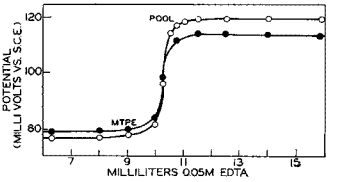

Figure 4. Comparison of titration curves—mercury pool and MTPE

5.0 ml. of 0.1*M* $Ca(NO_3)_2$ in 150 ml. of 0.3*M* NH_3–0.3*M* NH_4^+ buffer. Hg(II)–EDTA indicator ion at 10^{-6}*M*

millivoltmeter to give the titration curves shown in Figure 4. The curve for the mercury pool electrode is similar in shape to that obtained by Reilley and Schmidt (*14*).

The break of the MTPE is smaller than that for the mercury pool. After preparation, the mercury coating requires about half an hour at titration conditions to stabilize, after which the properties do not change. In practice new mercury is applied about twice a month.

THEORY OF CONTINUOUS TITRATIONS WITH MTPE

Selection of Conditions for Constant Equivalence Point Potential. Reilley and Schmidt (*14*) have discussed in detail the factors which determine the potential of the mercury electrode during the course of a titration. Ringbom has developed a method of calculating the p*M* during titration by use of conditional stability constants (*17*). The basic equation relating the potential of the mercury electrode to the p*M* during a titration through the formation constants of the HgY^{-2} complex (K_{HgY}) and of the MY^{-2} complex (K_{MY}), as given by Reilley and Schmidt (*14*) is:

$$E = E_{Hg}^{\circ} + 0.0296 \log (M^{+2}) + 0.0296 \log \frac{(HgY^{-2})\ (K_{MY})}{(MY^{-2})\ (K_{HgY})} \quad (1)$$

These authors point out that the observed potential is limited and/or altered by several factors not appearing in Equation 1, such as ionic strength, complexation effects of the buffer, and pH. However, this simplified equation suffices to explain the behavior of the continuous titrator.

It is important to recognize that the continuous titrator titrates to a selected end point potential, and not to an inflection point. In order to achieve reproducibility, titration conditions must be chosen to keep the end point potential invariant with changes in sample concentration and reagent pump speed. While these requirements are unique to continuous titrators, they are not difficult to achieve.

For this reason, a sample stream (containing metal ion and in some cases acid to prevent precipitation, but of negligible ionic strength and acidity compared to the other two streams) and a buffer stream (1.0*M* NH_3–1.0*M* NH_4^+) are pumped at constant rate in all cases to give a resultant stream whose gross ionic strength is practically constant (0.29*M* NH_3–0.29*M* NH_4^+). If the EDTA reagent stream is also made 0.29*M* in NH_3 and 0.29*M* in NH_4^+, it may be added in any proportion to the other two streams without changing the ionic strength or pH significantly. The resultant stream will then have a constant ionic strength and pH, independent of the metal ion concentration in the sample (if its ionic strength is small compared to 0.29*M*) and independent of reagent pumping rate.

In the simplified Equation 1, the term

$$(HgY^{-2})/(MY^{-2})$$

appears. In batchwise titrations to an inflection point, this ratio does not change appreciably through the inflection region and does not significantly affect the shape of the inflection. In the continuous titrator, the ratio must be kept constant at the equivalence point, regardless of the metal ion concentration in the sample; otherwise the end point potential becomes dependent upon sample size. Constancy of the ratio is achieved by addition of Hg(II) indicator ion (about 10^{-6}*M*) to the reagent solution. Since the flow rate of reagent at equivalence point is proportional to the concentration of the metal ion in the sample, the ratio $(HgY^{-2})/(MY^{-2})$ will be constant for all samples.

A slight dependence of equivalence point electrode potential upon concentration does occur. The concentration of free metal ion at the equivalence point does depend upon sample size, and does affect the equivalence point potential in a way not shown in Equation 1. Fortunately, the magnitude of the effect is small, and its neglect causes errors of only about 1.5 mv. or less over the range of sample concentrations handled by the titrator.

The potential at half titration—i.e., 50% of equivalence, with metal ion in excess—is determined by the formation of an Hg(II)–NH_3–EDTA complex (*14*). It is given by

$$E = E_{Hg}^{\circ} + 0.0296 \log \frac{(NH_3HgY^{-2})\ (K_{MY})\ [1 + (H^+)/K_a]}{(NH_3)_t (K_{NH_3HgY^{-2}})(K_{HgY^{-2}})} \quad (2)$$

Here, t denotes total or formal concentration, and K's are stability constants. The potential past the equivalence point, in the presence of excess EDTA, is given by

$$E = E_{Hg}^{\circ} + 0.0296 \log \frac{(NH_3HgY^{-2}) \cdot (\phi)\ [1 + (H^+)/K_a]}{(NH_3)_t (Y)_t (K_{NH_3HgY^{-2}})\ (K_{HgY^{-2}})} \quad (3)$$

Here ϕ is the ratio (total free chelate)/(Y^{-4}). The potential at half titration in the presence of excess metal depends upon the specific metal ion being titrated. Past the equivalence point the potential depends only on the concentration of buffer, EDTA, and pH, and is independent of the metal ion being titrated. These observations are verified in the experimental titration curves of Figure 5.

Titration Curves. The feasibility and characteristics of the titration of a specific metal ion (at a given concentration) can be predicted by recording a titration curve for a particular sample solution. Reagent pump speed is varied manually and plotted against observed electrode potential to give a titration curve analogous to a conventional batchwise titration curve, as shown for various metals in Figure 5. The curves are similar in shape to those obtained with the mercury pool electrode.

These titration curves are used to select the equivalence point potential empirically at the midpoint of the steepest portion of the curve. At concentrations of 0.005*M* or greater for all

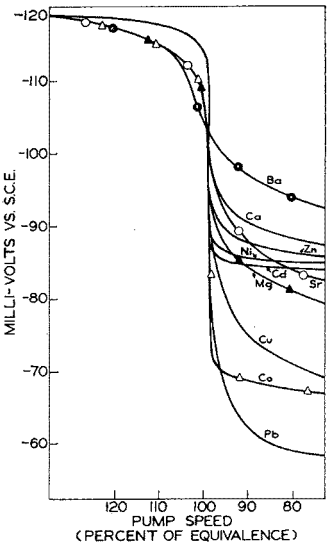

Figure 5. Manual titration curves for various metals

0.007M metal ion solution at 14.2 ml./min. 0.01M EDTA in buffer, pH 9.7

metals except Ba, the curves are sufficiently steep so that selection of the equivalence point potential is not critical for servo control purposes.

EXPERIMENTAL

Operation of Titrator. The titrator reported previously operates over about a twofold range of sample concentrations for a given reagent solution. This limitation is imposed by the range of available pump speeds. A fundamental assumption in the design of the titrator is that the equivalence point potential does not shift over the twofold concentration range. As long as the equivalence point potential remains nearly constant, all titrations are made to the true equivalence point.

The equivalence point potential for a particular metal ion may be chosen from a single titration curve made with a sample of approximately mid-range concentration. After the equivalence point potential has been selected, the end point band width and control band potentials are adjusted as described in the previous publication (*3*). Calibration is performed with a standard sample, and the readout time interval is adjusted to make the readout (counts accumulated) numerically equal to the standard sample concentration. The equipment is then used for titration of a series of samples or continuous monitoring of a sample stream.

In EDTA titrations at lower concentrations, the slope of the titration curves is not great and the selection of the equivalence point potential and band widths becomes more critical. The problems and techniques associated with continuous titrations at low concentrations (ranging down to metal ion concentrations of 0.00005*M*) will be considered in a subsequent publication.

Reagents. Buffer solution was prepared to contain 1.0*M* NH_3 (Du Pont) and 0.5*M* $(NH_4)_2SO_4$ (J. T. Baker Chemical Co.). For titrations of Ba, Sr, and Co, 1.0*M* NH_4NO_3 (J. T. Baker) was used instead of the $(NH_4)_2SO_4$.

EDTA titrant at 0.01*M* and 0.05*M* was prepared by dissolving the disodium dihydrate salt in 0.29*M* NH_3 and 0.29*M* NH_4^+ made by diluting the stock buffer solution with distilled water. The reagent solution was also made approximately $10^{-6}M$ in Hg(II) by the addition of 1 ml. per liter of a 0.001*M* solution of $Hg(NO_3)_2 \cdot H_2O$ (Allied Chemical and Dye Corp.).

Metal ion stock solutions were prepared at 0.1*M* by dissolving appropriate weights of the following reagent grade salts in water or a slight excess of HNO_3 if necessary: $Co(NO_3)_2 \cdot H_2O$ (Mallinckrodt), $Ba(NO_3)_2$ (Mallinckrodt), $Cd(NO_3)_2 \cdot 4H_2O$ (Mallinckrodt), $Sr(NO_3)_2$ (Mallinckrodt), $Zn(NO_3)_2 \cdot 6H_2O$ (Mallinckrodt), $Cu(NO_3)_2 \cdot 3H_2O$ (Mallinckrodt), $CaCO_3$ (Mallinckrodt), $Pb(NO_3)_2$ (Allied Chemical and Dye Corp.), $MgSO_4$ (Allied Chemical and Dye Corp.), and $Ni(NO_3)_2 \cdot 6H_2O$ (Mallinckrodt). Stock solutions were standardized by titration against a standard EDTA solution, prepared from the disodium dihydrate salt according to the procedure of Blaedel and Knight (*2*), and using the method outlined in the Baker Chemical Company Handbook (*1*).

Sample solutions of the metal ions were prepared for titration by volumetric dilution of the stock solutions.

Performance of Titrator. To study the precision with which continuous EDTA titrations could be performed, a series of samples of a particular metal ion was prepared over the titratable concentration range. The samples were then titrated in random order with respect to concentration. The experimental concentration (as determined from the titrator) was divided by the known concentration (as determined from the dilution data) to give a concentration ratio whose theoretical value is unity if the direct readout procedure is valid. Figure 6 is a plot of this ratio for a series of calcium samples ranging from 0.0035 to 0.0072*M*. The relative root mean squared deviation of the 27 titrations from the theoretical value of unity is 0.6%, which is taken to be the standard error of the continuous titration. Table I summarizes the precision which was obtained for other representative metal ions at pH 10, and the conditions under which the titrations were performed.

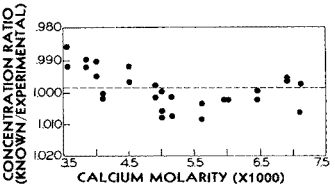

Figure 6. Performance of titrator on calcium samples

27 samples of Ca(II) ranging in concentration from 0.0035 to 0.0072M, titrated with 0.01M EDTA. Computed rel. std. dev. is 0.64%

DISCUSSION

The study reported here was confined to the pH 9.7 in ammonia buffer. While the stability of the electrode is excellent under the conditions described in the paper, attempts to extend the study to acid conditions at pH 5 (with acetic acid or hexamethylenetetramine buffers) were unsuccessful. Under these conditions, the electrode did not stabilize and did not exhibit constant potential with respect to time. Instead, as the electrode aged, the magnitude of the equivalence point break decreased nearly to zero after 3 to 4 hours of use. A similar decay was noted with a mercury pool electrode in the flowing stream where a surface film seemed to form. This effect apparently causes no difficulties in batchwise titrations [as performed by Reilley and Schmidt (*14*)] and is not noted in any of the numerous publications on potentiometric EDTA titrations.

Table I. Precision of EDTA Titrations for Various Metal Ions

Sample composition					Conditions		
EDTA molarity	Metal ion	Concn. range, *M*	No. of samples	Rel. std. dev., %	Eq. pt. potential,[a] mv.	Band widths, mv. Eq. pt.	Control
0.01	Cd(II)	0.003–0.007	30	0.32	−105	3.2	26
0.01	Ba(II)	0.003–0.007	31	0.79	−106	3.6	11
0.01	Zn(II)	0.003–0.007	16	0.49	−104	3.4	22
0.01	Ca(II)	0.003–0.007	27	0.64	−106	4.2	23
0.01	Cu(II)	0.003–0.007	41	0.61	−96	4.4	36
0.05	Cu(II)	0.015–0.035	31	0.55	−96	6.2	41
0.05	Ca(II)	0.015–0.035	13	0.40	−105	5.3	28
0.05	Mg(II)	0.015–0.035	32	0.42	−104	6.5	38
0.05	Ni(II)	0.015–0.035	29	0.32	−103	9.4	25

[a] Against the SCE.

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Controlled-Potential Coulometric Titration of Uranium(VI) in Aqueous Solutions of Sodium Fluoride

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▷ A method has been developed for the controlled-potential coulometric titration of U(VI) in aqueous solutions of NaF. The method involves the coulometric reduction of U(VI) to U(IV) at −1.000 volt *vs.* S.C.E. in neutral or slightly acid 0.75*M* NaF. The relative standard deviation is no greater than 0.5%; the relative error is +0.2 to +0.3% at the 6-mg. level. Reasonable amounts of Cr(III), Cu(II), Mo(VI), and Zr(IV) do not interfere. Mole ratios at least as large as 1:1 for Fe(III) to U(VI) and 5:1 for Al(III) to U(VI) can be tolerated. The method was applied to a number of synthetic reactor-fuel dissolver solutions.

RECENTLY DEVELOPED complex fuel elements contain a number of alloying elements,—for example, zirconium, molybdenum, nickel, iron, chromium, and aluminum. New methods are thus required for the determination of uranium in various types of the highly radioactive spent fuel elements.

Controlled-potential coulometric titrations are especially adaptable to remote manipulator-type operations. At the Oak Ridge National Laboratory, U(VI) is determined routinely by controlled-potential coulometric titration in 0.5*M* H_2SO_4 (*8*); Fe(III), Mo(VI), and other cations interfere when present in more than trace amounts. Zittel and associates (*12*, *13*) developed methods in which sodium tripolyphosphate ($Na_5P_3O_{10}$) is the supporting electrolyte; these methods permit the determination of U(VI) in the presence of large amounts of Mo(VI) and small amounts of Fe(III), Th(IV), and other cations. Shults and Dunlap (*9*) developed a tri-*n*-octylphosphine oxide extraction procedure that isolates U(VI) from a number of interfering cations. Subsequently, U(VI) is determined by controlled-potential coulometric titration in 0.5*M* H_2SO_4. Booman and Holbrook (*2*) investigated other procedures for extracting U(VI) and titrating it coulometrically. Verbeek, Moelwyn-Hughes, and Verdier (*11*) describe a polarographic method for U(VI) that can tolerate excess Fe(III); the supporting medium is neutral 0.75*M* NaF. Two waves exist; the first ($E_{1/2}$ = −0.65 volt *vs.* S.C.E.) coalesces with the second ($E_{1/2}$ = −0.95 volt *vs.* S.C.E.). Consequently, the height of the composite wave is used to determine the diffusion current. Because the reactions that occur in polarography and controlled-potential coulometric titrimetry are similar, it was decided to evaluate sodium fluoride as a supporting electrolyte for coulometric titrimetry.

The reduction of U(VI) in neutral (or slightly acid) solutions of NaF was studied. Conditions were established for the quantitative controlled-potential coulometric reduction of U(VI) in aqueous solutions of NaF. Possible interferences were checked, and the precision and accuracy of the method were determined. The method was applied with various degrees of success to a number of typical synthetic, reactor-fuel dissolver solutions. These studies did not include the effects of fission products of radiation.

EXPERIMENTAL

Apparatus. Coulometric Titrator, ORNL Model Q-2005, controlled-potential (*7*); used for all coulometric studies. The calibration, use, and care of this instrument are described (*6*).

A mechanically stirred mercury cathode and a saturated calomel reference electrode (S.C.E.) were used in a conventional coulometric cell (*8*). The Vycor tubes, which are normally used as membranes and which contain the platinum wire or counter electrode and the S.C.E., were replaced by fritted tubes that contained a 3% (w./v.) agar–5% (w./v.) K_2SO_4 plug (*13*).

pH Meter, Beckman Model G; used to measure the pH of the solutions to be titrated.

Reagents. Supporting Solutions of Sodium Fluoride; prepared from analytical-reagent grade sodium fluoride. After addition of the prepared test portions to these media, pH adjustments were made with 30% (w./v.) solution of NaOH. All other reagents used in the preparation of the test portions were ACS-approved grade.

Standard Solutions of U(VI); prepared by dissolving portions of National Bureau of Standards standard sample No. 950 U_3O_8 in ~7.5*M* HNO_3, destroying the nitrate by fuming with H_2SO_4, and diluting the resulting solution to volume with 0.5*M* H_2SO_4. The final solution was standardized volumetrically by potentiometric ti-

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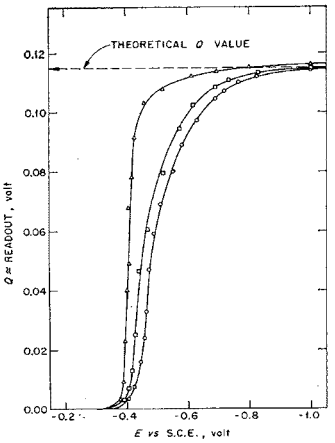

Figure 1. Effect of NaF concentration on coulometric reduction of U(VI)–U(IV)

[5.66 mg. of U(VI), 10 ml. of electrolyte, pH = 7]
△ 0.50M NaF
□ 0.75M NaF
○ 1.00M NaF

tration with standard ferric sulfate solution (*4*).

Procedure. Preparation of Test Portion for Titration. Into a 50-ml. Vycor beaker that contains 5 ml. of $3M$ H_2SO_4, pipet from the sample a test portion that is estimated to contain about 6 mg. of U(VI). Add 5 drops of concentrated HNO_3. Evaporate the solution to near dryness; do not bake the residue. After the residue is cool, add sufficient 5% (w./v. hydroxylamine hydrochloride (~5 drops) to reduce Cr(VI) to Cr(III). Transfer the solution to the titration vessel, using a wash of $0.75M$ NaF; use a total volume of 10 ml. of the NaF solution to effect the transfer. Add 3 drops of a saturated solution of sulfamic acid. Add dropwise 30% (w./v.) NaOH until the color of the basic U(VI), which appears after the addition of each drop, persists but disappears in 15 to 30 seconds; avoid an excess of reagent. Using a pH meter, adjust the pH to the value between 6.5 and 7.0 with $1.0M$ NaOH and/or $0.5M$ H_2SO_4. (The suitability of pH buffer solutions was not studied.) Exception: When Cu(II) and/or large amounts of Al(III) (~5 mg.) and Fe(III) (~20 mg.) are present, adjust the pH to 5.5. Wash the electrodes of the pH meter with a minimum amount of $0.75M$ NaF.

Coulometric Titration of U(VI). Add 7.5 ml. of mercury to the titration cell, place the cell in position, and sparge the solution 5 minutes with a brisk stream of helium. Maintain a helium blanket over the test solution during the following electrolysis. Prereduce the solution at −0.300 volt *vs.* S.C.E. until the current decreases to 50 μa.; then zero the integrator. Exception: When Cu(II) is present, prereduce the solution at −0.210 volt *vs.* S.C.E. Coulometrically reduce U(VI) to U(IV) at −1.000 volt *vs.* S.C.E. until the current again decreases to 50 μa. Via Faraday's laws ($n = 2$) and from the readout voltage of the integrator, calculate the amount of U(VI) titrated.

RESULTS AND DISCUSSION

Choice of Titration Conditions. Curves are given in Figures 1, 2, and 3 that relate readout voltage, which is a measure of the quantity of current consumed during electrolysis, with controlled electrode potential when U(VI) is reduced electrolytically in several supporting media. Data for these curves were obtained by making the reduction in the usual manner except that periodically throughout the electrolysis the potential was adjusted to a value which caused cessation of current. The readout voltage (proportional to current consumed or extent of reaction) and electrode potential were recorded, and the electrolysis was then continued. Curves plotted from a series of such data are especially useful in comparing supporting media with each other and in establishing optimum electrode potentials, because they relate extent of reaction with electrode potential under actual titration conditions.

Uranium(VI) in an aqueous solution of NaF can be reduced electrolytically at a mercury cathode; a 2-electron change occurs during the overall reduction. As the curves in Figure 1 indicate, the potential of the U(VI) → U(IV) reduction varies considerably with change in NaF concentration. The same curves also show that the potential of the U(VI) → U(IV) reduction in $0.50M$ NaF is very close to the reduction potential of UO_2^{+2} in acid media (−0.325 volt *vs.* S.C.E. in $0.5M$ H_2SO_4) (*8*). Fluoride ion in concentration greater than $0.50M$ is required to avoid premature reduction of U(VI). The curves for $0.75M$ and $1.00M$ NaF confirm this observation. In $1.00M$ NaF, the U(VI) → U(IV) reduction appears to be slower and to require a more negative reduction potential for the complete electrolytic reduction of U(VI) than in $0.75M$ NaF. Interference from the reduction of hydrogen ion could result.

Figure 2 indicates that U(VI) can be reduced in $0.75M$ NaF over the pH range from 5.5 to 7.0 without significant loss in current efficiency. However, practical as well as theoretical considerations dictate that the pH be controlled carefully. At pH 6 or lower the electrolytic cell is attacked by hydrofluoric acid. Even in neutral or slightly acid media, the Vycor tubes specified in the conventional cell assembly are stable for only two or three days. Under the same conditions, fritted glass tubes are

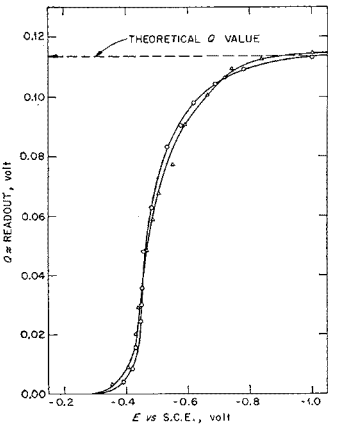

Figure 2. Effect of pH on coulometric reduction of U(VI)–U(IV) in 0.75M NaF

[5.59 ml. of U(VI), 10 ml. of 0.75M NaF]
○ pH 7.0
△ pH 5.5

satisfactory for six weeks to several months. However, at pH <5.5 the fritted tubes are stable for only a few days. When a fritted tube is damaged, the duration of a titration is long and background currents are high. One damaged fritted tube had a resistance of 100,000 ohms across the cell to the mercury cathode; the resistance of an undamaged tube is about 4000 ohms.

Sodium diuranate precipitates at pH >7.0 and coprecipitates with Fe (III) and Al(III) at pH <7.0. Even when coprecipitation does not occur, there is the possibility of sorption of the U(VI) on the hydrous gel formations. Under such conditions, titrations are prolonged, do not attain a reasonable background current, and give erratic results. Consequently, when these elements are present, the pH is controlled between 5.5 to 6.5 depending on the amount of Fe(III) and Al(III) present.

During the course of a titration, the pH of the solution increases. High U(VI) concentration could result in loss of pH control through the following proposed mechanism:

$$UO_2^{+2} + 4\ F^- \rightleftarrows UO_2F_4^{-2} \qquad (1)$$

$$UO_2F_4^{-2} + e \rightarrow UO_2F_4^{-3} \qquad (2)$$

$$H_2O + 2\ UO_2F_4^{-3} \rightarrow UO_2F_4^{-2} + UF_4\downarrow + 4\ OH^- \qquad (3)$$

Equation 3 shows the production of OH^- during the course of the reaction. Under this condition, a more basic medium results. The fluorouranium (V) complex was not identified. However, the precipitation of the reduction product, UF_4, is readily observed. This proposed mechanism is similar to that

Table I. Typical Results of Coulometric Titration of Standard Solutions of U(VI) in 0.75M NaF

Aliquots of U(VI) solutions titrated by procedure in text

N[a]	U(VI), mg. Taken	U(VI), mg. Found	Rel. std. dev., %	Rel. error, %	Average time/ titration, min.
11	5.45	5.45	0.18	0.00	24
5	6.05	6.06	0.17	+0.17	18
6	6.67	6.69	0.33	+0.30	27
4	9.07	9.03	0.23	−0.44	23

[a] N = number of titrations.

Table II. Results of Coulometric Titration of U(VI) in 0.75M NaF in Presence of Various Common Anions

Aliquots of U(VI) solutions titrated by procedure in text

Anion[a] Identity	Concn. in test solution, M	U(VI), mg. Taken	U(VI), mg. Found	Rel. error, %	N^b
SO_4^{-2}	0.03	5.45	5.46	+0.18	12
	0.11	5.45	5.45	0.00	6
	0.18	5.45	5.43	−0.37	2
Cl^-	0.10	6.42	6.45	+0.47	2
	0.20	6.42	6.45	+0.47	2
NO_3^-[c]	0.02	5.45	5.47	+0.37	3
	0.13	6.42	6.44	+0.31	3
	0.26	6.42	6.45	+0.46	3
	0.48	6.42	6.44	+0.31	3
	0.60	6.42	6.47	+0.78	2
	1.10	6.42	6.47	+0.78	1

[a] Each anion was added as the acid before the addition of NaF solution and final pH adjustment.
[b] N = number of titrations.
[c] Five drops of a saturated solution of sulfamic acid was added to each test portion that contained NO_3^- to destroy all nitrite.

Table III. Results of Coulometric Titration of U(VI) in 0.75M NaF in Presence of Some Common Cations

Aliquots of U(VI) solutions titrated by procedure in text

Cation[a] Identity	Amt. in test solution, mg.	U(VI) found, mg.	N^b	Rel. std. dev., %	Rel. error, %
		U(VI) Taken, 6.05 mg.			
Fe(III)	2.5	6.07	6	0.2	+0.3
	5.0	6.04	5	<0.1	−0.2
	7.5	6.04	5	0.2	−0.2
	10.0	6.02	5	0.3	−0.5
	20.0	6.04	4	0.5	−0.2
	25.0	6.05	5	0.5	0.0
	30.0	6.05	6	0.2	0.0
	40.0	6.23	4	1.6	+3.0
		U(VI) Taken, 6.42 mg.			
Al(III)	1.0	6.40	7	0.8	−0.3
	2.0	6.36	5	0.7	−0.9
	5.0	5.98	2	...	−6.9
Cr(III)	1.0	6.43	2	...	+0.2
Cr(VI)[c]	1.0	6.40	5	0.3	−0.3
Cu(II)[d]	1.0	6.42	2	...	0.0
	2.6	6.40	4	...	−0.3
Mo(VI)	0.3	6.43	3	...	+0.2
	0.5	6.46	5	0.6	+0.6
	1.0	6.41	8	2.0	−0.2
Ni(II)	0.5	6.44	1	...	+0.3
	1.0	6.45	2	...	+0.5
	2.5	6.45	3	...	+0.5

[a] Each cation was added at the beginning of the sample preparation; see text.
[b] N = number of titrations.
[c] Cr(VI) prereduced to Cr(III) by the addition of 5% (w./v.) $NH_2OH \cdot HCl$; see text.
[d] Cu(II) requires careful prereduction; see text.

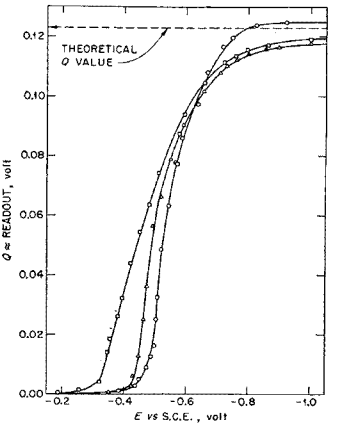

Figure 3. Effect of Fe(III) concentration and pH on coulometric reduction of U(VI)–U(IV) in 0.75M NaF

[6.05 mg. of U(VI), 10 ml. of 0.75M NaF]
□ 2.5 mg. of Fe(III), pH 6
△ 2.5 mg. of Fe(III), pH 7
○ pH 7

suggested by Booman, Holbrook, and Rein (*3*) for the reduction of UO_2^{+2} in a citrate-buffered medium.

Figure 3 indicates the action of an ion that forms a more stable fluoro complex than does U(VI) and the effect of pH on such competition. When Fe(III) is present, U(VI) reduces at a less negative potential (more UO_2^{+2} is present) and requires a longer titration time. These effects are accentuated by low pH. The practical significance of such a condition is twofold. Should the U(VI) be prematurely reduced, low results would be observed. A longer titration time tends to give high results. Under particular conditions, the two effects can cancel.

The conditions established for this study were as follows: 0.75M NaF, pH 6.5 to 7.0, prereduction at −0.300 volt *vs.* S.C.E., and reduction at −1.000 volt *vs.* S.C.E. These conditions allow for minor variations in pH, potential of the S.C.E., power supply fluctuations, and traces of interfering cations. However, when Al(III), Cu(II), and Fe(III) are present in more than trace amounts, a lower pH and a less negative prereduction potential may be required.

Precision and Accuracy. The precision and accuracy of the method, determined on solutions that contained U(VI) in 0.75M NaF, are indicated in Table I. The results show a relative standard deviation no greater than 0.5% in the range from 5 to 7 mg. of U(VI). For larger amounts, the results become unreliable, because UF_4 coagulates on the electrodes and settles out on the

mercury cathode. The cell resistance increases, and the duration of the titration is prolonged.

The average duration of the reduction of U(VI) in sodium fluoride solution is 18 to 27 minutes. This time is somewhat longer than that required for the reduction of U(VI) in H_2SO_4 solution, which is 15 to 20 minutes (*8*). The disproportionation rate of U(V) to U(IV) and U(VI) is accelerated by H^+ and SO_4^{-2} concentrations. Apparently, in neutral fluoride media the rate is lower than in the commonly used 0.5*M* H_2SO_4 media. The longer time required for the U(VI) reduction in sodium fluoride solution results in decreased precision as compared with the precision of the titration in H_2SO_4 solution.

Interferences. Table II presents results obtained when known amounts of U(VI) in 0.75*M* NaF medium were titrated in the presence of each of several common anionic contaminants. Sulfate in reasonable concentration does not interfere, and chloride at concentration less than 0.2*M* interferes only slightly. Nitrate in concentration less than 0.6*M* does not interfere provided sulfamic acid is added to destroy the nitrite that is usually present along with nitrate. Since the interference of sulfate is negligible, repeated fumings in H_2SO_4 minimize interferences by chloride and nitrate.

The effects of a limited number of cationic contaminants on the U(VI) reduction in 0.75*M* NaF were studied; Table III shows the results. Trace quantities of Fe(III), Al(III), Cr(III), and Mo(VI) do not interfere. In addition, small amounts of Cr(VI) can be reduced to Cr(III) with hydroxylamine hydrochloride (see Preparation of Test Portion). Directions for minimizing the interference of Ni(II) are given above (see Titration of Sample). Under these stated conditions, Ni(II) and Cr(VI), when present in trace amounts, do not interfere.

Larger quantities of Fe(III) and Al(III) cause unreliable results. The pK_1 values for the stability constants for the fluorides of Fe(III) = −5.3, of Al(III) = −6.1, and of UO_2(II) = −4.5 (*5*). In competition with Fe(III) and Al(III) at mole ratios of 25:1 for Fe(III) to U(VI) and 6:1 for Al(III) to U(VI), the UO_2(II) would be relatively uncomplexed and would tend to be reduced prematurely. In addition, coprecipitation and/or sorption of U(VI) with the hydrated oxides of Fe(III) and Al(III) occur when large quantities of these ions are present.

Application of Procedure to Synthetic Dissolver Solutions. The compositions of the various synthetic dissolver solutions to which the method was applied have been reported previously (*1, 9, 10*). Table IV summarizes the results obtained; these results include values for the precision and error. The method has the advantage that U(VI) can be determined in 0.75*M* NaF in the presence of 0.5*M* Fe(III), ~0.9*M* Al(III), and ~0.07*M* Mo(IV). In contrast, U(VI) in 0.5*M* H_2SO_4 cannot be determined satisfactorily in the presence of >0.2*M* Fe(III), >0.5*M* Al(III), or trace amounts of Mo(VI) (*13*).

The method is applicable for the determination of U(VI) in the following dissolver solutions: Consumer Public Power Reactor, Experimental Boiling Water Reactor, Fermi Reactor, and Molten Salt Reactor. The method can be used for the approximate determination of U(VI) in dissolver solutions of the Foreign Research Reactor type, 14

Table IV. Results of Coulometric Titration of U(VI) in 0.75M NaF in Presence of Various Synthetic Dissolver Solutions

Aliquots of U(VI) solution added to dissolver solution and sample titrated by procedure given

U(VI), mg. Taken	U(VI), mg. Found	Rel. std. dev., %	Rel. error, %	N[a]	pH	Av. time/ titration min.
		CONSUMER PUBLIC POWER				
		(1 ml., 1:25[b])				
3.34	3.34	0.22	0.00	7	6.8	23
6.05	6.04	0.15	−0.17	8	6.9	30
6.42	6.44	0.28	+0.31	9	7.0	27
6.67	6.68	0.49	+0.15	11	6.9	45
12.09	12.09	0.37	0.00	14	6.7	45
		EXPERIMENTAL BOILING WATER				
		(1 ml., 1:1[b])				
3.34	3.37	0.72	+0.89	7	6.7	21
6.05	6.06	0.70	0.17	5	6.7	32
9.07[c]	9.03	0.40	−0.44	9	6.8	25
9.07[d]	9.02	1.90	−0.55	6	6.8	40
		(1 ml., no dilutions)				
9.07	8.92	1.07	−1.66	8	6.7	49
		FERMI				
		(1 ml. 1:50[b])				
3.49	3.48	1.52	−0.29	7	6.9	33
5.00	5.10	0.65	+2.00	5	7.0	25
6.17	6.19	0.36	+0.32	5	6.9	36
6.67	6.73	0.72	+0.78	8	6.7	36
12.09	12.07	0.26	−0.17	17	6.6	41
		(2 ml., 1:50[b])				
9.07	9.14	0.30	+0.77	4	7.0	35
		FOREIGN RESEARCH				
		(1 ml., 1:1[b])				
3.34	3.3	17	0	4	4.8	35
6.05	6.01	1.32	−0.65	5	4.5	50
9.07	8.84	3.2	−1.4	5	5.5	55
12.09	11.90	2.0	−1.7	7	4.5	38
		MOLTEN SALT				
		(5 ml., 0.2*M* in molten salt)				
3.00	3.05	1.66	+1.66	6	6.7	32
6.39	6.37	1.59	−0.30	5	6.7	36
8.04	8.00	0.38	−0.50	5	6.5	42
		(5 ml., 0.2*M* in molten salt, 0.15 mmole of NaF added)				
3.05	3.12	0.33	+2.0	5	6.5	30
		N. S. SAVANNAH[e]				
		(1 ml., 1:20[b])				
3.34	3.32	1.20	−0.60	6	5.7	40
6.67	6.67	1.16	0.00	6	5.6	40

[a] *N* = number of titrations.
[b] Designates v./v. dilution.
[c] Cell resistance less than 4000 ohms; see text.
[d] Cell resistance greater than 10,000 ohms; see text.
[e] Careful prereduction of Cr(VI) required; see text.

mg. of Al(III) per 7 mg. of U(VI), and the *N.S. Savannah* type. The latter's combination of interferences due to mole ratios of 0.7:1 for Cr(III) to U(VI), 1.5:1 for Fe(III) to U(VI), and 0.3:1 for Ni(II) to U(VI) in its dissolver solution demands very exact pretreatment of the sample to minimize their combined effects.

Dissolver solutions of the Army Package Power Reactor type, which contain a 40:1 mole ratio of Fe(III) to U(VI), and of the Consolidated Edison Reactor type, which contain a 17:1 mole ratio of Th(IV) to U(VI), were not amenable to the method. In the latter solution, Th(IV) interferes in the $3M$ H_2SO_4 with fuming by precipitating as $Th(SO_4)_2$; when the $0.75M$ NaF is added, it interferes by precipitating as ThF_4.

This investigation indicates the need for the development of a cell assembly that withstands acid fluoride solution. Also, there is need for a supporting medium from which Fe(III) and Al(III) do not precipitate. The medium $Na_5P_3O_{10}$ (6% w./v.)–NaF (sat.) was examined briefly; it appears to be promising.

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Determination of Uranium and Americium-Curium in Urine by Liquid Ion Exchange

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▷ Exchange of Th, Pa, U, Np, Pu, Am, Cm, and Cf from various concentrations of HNO_3 and HCl to liquid ion exchangers was determined. Both anion and cation exchangers were used; the former was triisooctylamine (TIOA), while the latter was di-2-ethylhexyl phosphoric acid (HDEHP). Tests with TIOA indicated preferential and rapid removal of U from other actinides, and in a mixture of Pu(III) and Np(IV), Np was extracted to TIOA. The reagent also separated Pa^{233} from the parent Np^{237}. HDEHP extracted more than 90% of all eight actinides from an acid solution adjusted in the pH range 4 to 5. At higher acidities—e.g., $4N$ HNO_3—all the actinides are extracted except Am, Cm, and Cf. Procedures were developed for analysis of U^{235} and Am^{241}–Cm^{244} in urine. Tracer recoveries were greater than 90% and decontamination factors were sufficiently high for other actinides. Detection limits by direct alpha counting were 0.3 d.p.m. for 250-ml. urine samples. Overall recoveries, through electrodeposition techniques, were 84 ± 10% for U^{235} and 89 ± 6% for Am^{241}.

ANALYTICAL METHODS to determine actinides separately and as mixtures are needed more as production of transplutonium elements increases.

Liquid ion exchange is a relatively new technique for chemical analysis. With this technique, an aqueous sample and organic reagent dissolved in an inert solvent are thoroughly mixed. Nuclides as anions and cations are substituted at exchange sites in the immiscible organic phase, in a manner similar to absorption by solid ion exchangers (*3*, *4*). An advantage is the rapidity of both absorption and desorption of ions.

A survey of the literature showed limited use of liquid ion exchange for analytical procedures, particularly for analysis of actinides in urine. Previous tests at the Savannah River Plant with HDEHP resulted in a method to separate Ca and Sr (*2*). This reagent and TIOA were further studied to develop analytical techniques for the actinides Th through Cm.

EXPERIMENTAL

Reagents. HDEHP from Union Carbide Chemical Co. was purified by washing with $4N$ HNO_3 and water prior to use. TIOA from Bram Chemical Co. was not purified before use.

TIOA–xylene, 10%, and HDEHP–toluene, 20%, were satisfactory dilutions for the reagents, and are henceforth referred to as TIOA and HDEHP. For exchange reactions, equal volumes of organic and aqueous solutions were used unless otherwise specified.

Procedure. Actinides were tested separately with the anion and cation exchangers. Ten-milliliter samples of individual actinides were shaken vigorously for 1 minute and allowed to settle. Small aliquots of the aqueous samples were counted for alpha and/or gamma activity before and after exchange.

No attempt was made to adjust actinide valences initially. Each spike solution was evaporated to dryness with the same acid used for dissolution in the test.

RESULTS

Anionic Complex Formation (TIOA). Results of initial tests with TIOA and aqueous solutions are summarized in Table I, including the probable valence of each actinide. Only U^{238} and Pa^{233} were removed from

3*N* HCl. Neptunium-237 exchanged quantitatively from 8*N* HCl. Am^{241}, Cm^{244}, and $Cf^{250-252}$ did not form exchangeable anionic complexes with HCl.

Alpha counting indicated that Th^{232} did not absorb in TIOA from HCl. Gamma counting showed some removal of daughter products. Recounts of aqueous solutions following extraction showed buildup of gamma to the original activity within 1 to 2 days. The Th^{232} chain was probably broken at Po^{216}, based on this rapid buildup and the known exchange of the chloride complexes to anion resins (*7*).

Although there was greater than 96% exchange of Np^{237} from 8*N* HCl and Pu^{239} from 4*N* HNO_3, valence adjustments were necessary to separate these two actinides. TIOA will absorb the chloride complex of Np(IV), but not that of Pu(III) (*8*). These valences were attained by reduction with either ammonium iodide (*6*) in concentrated (12*N*) HCl or freshly prepared ferrous sulfamate (*8*) in 4*N* HNO_3. After this reduction, more than 95% of Np^{237} and less than 5% of Pu^{239} exchanged to TIOA.

Table I shows a possible separation of Np^{237} and its daughter Pa^{233}. Further extractions of Np^{237} showed removal of 90% of Pa^{233} from 4.5*N* HCl solution. More than 99% of Pa^{233} was removed from solution in two extractions with TIOA; no Np^{237} was exchanged under these conditions. U^{235} and its daughter Th^{231} were also separated by extraction of a 3.5*N* HCl solution with TIOA; the 0.084-m.e.v. Th^{231} remained in aqueous solution. U^{235} was completely stripped from TIOA in 1 minute with an equal volume of water.

Cation Removal (HDEHP). Results of initial tests with HDEHP are shown in Table II. The rapidity of exchange of the actinides was demonstrated by removal of all Am^{241} from aqueous solution to HDEHP in approximately 1 second of vigorous shaking. More than 90% of all eight actinides were removed from the original sample to the organic phase from acid solution at pH 4 to 5. Because HDEHP is an acid reagent which contributes to acidity of solutions, the pH described is the equilibrium pH attained after extraction. More than 90% of Np, Pa, U, and Pu and 75% of Th were removed from 4*N* HNO_3, based on alpha counting of aliquots. Americium–curium were stripped from HDEHP with 4*N* HNO_3. Plutonium was stripped from HDEHP with 1*M* oxalic acid.

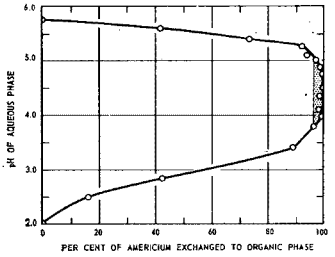

Figure 1. Am^{241} from oxidized urine solution extracted into 20% HDEHP-toluene

Shaded area shows >95% between pH 3.7 and 5.1; 100% is exchanged at pH 4.5

APPLICATIONS

Determination of Enriched Uranium in Urine. Wet ash (oxidize) a 250-ml. volume of urine with 16*N* nitric acid and 30% hydrogen peroxide. Dissolve the white residue in 50 ml. of 3.5*N* HCl and extract with an equal volume of TIOA for 2 minutes. Extract the aqueous solution with 25 ml. of TIOA in a second separatory funnel. Combine the organic phases (75 ml.) and wash with 15 ml. of 3.5*N* HCl to remove traces of other actinides and inorganic salts. Strip the U^{235} from the organic phase by shaking with two 25-ml. volumes of distilled water. Evaporate and planchet the water for alpha counting. U^{235} can be electrodeposited by the method of Boni (*1*), radioautographed, and the tracks counted to obtain greater sensitivity.

Separation of Np^{237} and Pu^{239} in Urine. Because the urine salts were more soluble in dilute HNO_3 than in concentrated HCl, the ferrous sulfamate reduction method was used. Wet ash 250 ml. of urine with nitric acid and hydrogen peroxide; reduce the residue with freshly prepared ferrous sulfamate (*8*); exchange the Np^{237} from 4*N* HNO_3 to TIOA.

Determination of Am–Cm in Urine. Americium was quantitatively removed from urine salts solutions as shown in Figure 1. More than 95% of Am was exchanged to the organic phase when the aqueous equilibrium pH was 3.7 to 5.1. Curium exchanged in the same pH range. More than 99% of Am–Cm was exchanged at pH 4.5. A similar curve was obtained with aqueous solution containing tracer only. (Californium, the other trivalent actinide, was not available in sufficient quantity for studies other than those values shown in Tables I and II.)

Although a 4*N* HNO_3 strip solution of the organic phase showed good chemical recovery, based on gamma counting of Am–Cm, the effective recovery by alpha counting was only about 60% because of self-absorption in solids accompanying the actinides. A TTA (10% thenyltrifluoroacetone in toluene) extraction was necessary to remove solids (see Discussion).

The pH control is critical in both HDEHP and TTA extractions. Methyl orange indicator was used successfully for adjustment of pH for both extractions. A standard solution at pH 4.5, verified by pH meter measurement, should be used for color comparison. Ten drops of 1% methyl orange were added to all samples.

The Am–Cm procedure is as follows: wet ash 250 ml. of urine with nitric acid and hydrogen peroxide. Dissolve the white residue in 50 ml. of 4*N* HNO_3 and extract with 50 ml. of HDEHP to remove contaminating actinides. Evaporate the sample solution to dryness and dissolve the residue in 1 ml. of concentrated HNO_3 and 50 ml. of distilled water. Add methyl orange indicator and concentrated NH_4OH, dropwise, until the solution is yellow. Extract for a few seconds with 50 ml. of HDEHP. Add NH_4OH until the color

Table I. Eight Actinides Extracted into 10% TIOA–Xylene

Aqueous solution	Per cent extracted							
	Th^{232}(IV)	Pa^{233}(V)	U^{238}(VI)	Np^{237}(V)	Pu^{239}(IV)	Am^{241}(III)	Cm^{244}(III)	$Cf^{250-252}$(III)
HCl								
1*N*	<10	0	58	0	0			
2*N*	0	14	94	0	0	0	0	0
3*N*	0	58	98	0	0			
4*N*	0	85	>99	0	21	0	0	0
6*N*	0	95	>99	56	31			
8*N*	9	>99	>99	98	39	0	0	0
HNO_3								
4*N*	55	22	66	20	96	0	0	0

Table II. Eight Actinides Extracted into 20% HDEHP–Toluene

Aqueous solution	Per cent extracted							
	Th^{233}(IV)	Pa^{233}(V)	U^{238}(VI)	Np^{237}(V)	Pu^{239}(IV)	Am^{241}(III)	Cm^{244}(III)	$Cf^{250-252}$(III)
Distilled H_2O (pH 4 to 5)	93	97	>99	96	>99	>99	>99	>90
HNO_3								
2*N*	70	97	>99	81	>99	0		
4*N*	75	97	>99	96	>99	0	0	0
8*N*	82	97	>99	95	>99	0		
HCl								
2*N*	82	90	96	63	92	0		0

is that of the standard pH 4.5 solution. Extract for 1 minute and discard the aqueous portion. Strip the Am–Cm from the organic phase with two 25-ml. volumes of 4*N* HNO_3.

Evaporate the 50 ml. of 4*N* HNO_3 solution. Dissolve the residue in 1 ml. of 16*N* HNO_3 and 50 ml. of distilled water. Add methyl orange and shake with 50 ml. of TTA for 20 minutes. Discard the aqueous solution and strip the Am–Cm from the organic phase with three 25-ml. 1-minute extractions with 4*N* HNO_3. Evaporate the 75 ml. of 4*N* HNO_3, planchet, and count for alpha activity. Alternatively, the electrodeposition technique of Dupzyk and Bigg (*5*) can be used to attain greater sensitivity.

DISCUSSION

The U^{235} procedure was first developed using spiked aliquots of composite urine. To account for variations in individual urines, 30 samples from individuals were spiked at 3000 d.p.m. and analyzed in either 150- or 250-ml. aliquots. Recoveries for these samples were 91 ± 5% (relative standard deviation). Decontamination factors (DF's) for the other actinides were greater than 10^3. Although Pa^{233} partially exchanges with U^{235}, it is not detected by alpha counting. The solids on the final planchets weighed less than 5 mg.

Samples spiked with 10 d.p.m. of U^{235} were analyzed both by direct plancheting and alpha counting, and by electrodeposition and alpha counting. Twelve electrodeposited samples were recovered at 84 ± 10%, while recoveries by plancheting were 98 ± 10%.

The U^{235} procedure is also a good method for removing uranium from a sample prior to analyses of other radionuclides. An average of only 0.06% of U^{235} remained in aqueous solutions after the extractions. This procedure, followed by ferrous sulfamate reduction, should offer an excellent sequential analysis scheme for U, Np, and Pu.

The previous liquid ion exchange study in this laboratory (*2*) resulted in exchange of Ca to HDEHP at the same equilibrium pH found to be optimum for Am–Cm. Tests showed no extraction of Ca^{45} and good extraction of Am–Cm with TTA. The extraction with this reagent was necessary to separate the two actinides from the alkali earths. Without the TTA step, the final Am–Cm planchets contained approximately 70 mg. of self-absorptive solids, representing the normal alkali content of 250 ml. of urine in the form of oxides. After TTA separation of Am–Cm and subsequent stripping and plancheting, the solids content was less than 5 mg.

The single extraction of 4*N* HNO_3 with HDEHP in the Am–Cm procedure resulted in DF's for the other actinides of greater than 500, except for Th which showed a DF of greater than 200. The DF's can be improved by a second 1-minute extraction of the 4*N* HNO_3 solution.

Both the U^{235} and the Am–Cm urine procedures are sufficiently quantitative and specific, and both are more rapid than procedures reported in the literature. After a case of suspected uptake of a specific actinide each method can be modified to yield even quicker results. Urine volumes can be reduced and the DF step can be eliminated in the Am–Cm procedure. The TTA separation may also be omitted for a sample with enough activity for gamma counting.

Two 250-ml. urine samples containing Am^{241} were wet ashed and extracted directly by the TTA portion of the procedure. The recovery of Am^{241} was less than 35%, indicating that the previous HDEHP extraction cannot be eliminated.

The sensitivity by direct plancheting is limited in both procedures by standard alpha counting statistics Approximately 0.3 d.p.m. ± 0.3 d.p.m. (90% confidence limit) of either U^{235} or Am–Cm can be detected after 2 hours of counting. Increasing the volume of urine will increase the sensitivity of the U^{235} procedure, but additional modifications will be necessary in the Am–Cm procedure to reduce the Ca and Mg contamination.

Electrodeposition, radioautographing, and track counting are more sensitive than alpha counting methods. The U^{235} overall recovery was 84 ± 10% by the method of Boni (*1*). The Am^{241} overall recovery for 10 samples was 89 ± 6% by the method of Dupzyk and Bigg (*5*), with a plating area of 0.3 sq. cm. and current density of 1.3 amperes per sq. cm.

Beyond the applications discussed above, the technique of liquid ion exchange certainly appears to offer a wide scope of possibilities. One such slight modification has been a method to enable the determination of U^{235} and Pu^{239} in those aluminum alloys used as fuels for irradiation.

ACKNOWLEDGMENT

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Rapid and Nondestructive Analysis of Sulfur and Calcium by Radioactivation and Photoneutron Counting

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▶ A method is described for the activation analysis of sulfur and calcium by the assay of 5.1-minute sulfur-37 and 8.8-minute calcium-49 using photoneutron counting. Both sulfur-37 and calcium-49, formed by neutron capture in sulfur and calcium, respectively, decay with the emission of high energy (>3 m.e.v.) gamma rays which cause emission of photoneutrons from a D_2O reservoir incorporated in a neutron counting assembly. The photoneutron activity is proportional to the content of the sulfur-37 or calcium-49 in the sample, the activity being ~20 c.p.m. per mg. of sulfur and ~1100 c.p.m. per mg. of calcium, when the sample is irradiated to saturation at a flux of 10^{13} neutrons/cm.^{2}-second. Sensitivities of ~0.5 mg. for sulfur and ~10 μg. for calcium were obtained. Sulfur and calcium in samples containing various proportions of these elements were analyzed with satisfactory precision. The use of the method for the rapid determination of sulfur and calcium in complex matrices, without any chemical processing and by a simple and versatile apparatus, is discussed.

RADIOACTIVATION ANALYSIS of sulfur is generally based on the formation of either S^{35} or P^{32} by irradiation with reactor neutrons (*4, 6, 10*). These nuclides are pure β-ray emitters and their assay is generally possible only after radiochemical processing of the irradiated sample and preparation of the purified fraction in a form suitable for β-ray counting. Only in limited cases, for example in organic substances, where the main matrix (C, H, O, and N) does not become activated, can P^{32} be determined without separation, provided that the radioactivation of other components is at a very low level. With S^{35} a direct method cannot be used at all because of the low energy of its beta rays. For these reasons the methods for analysis of sulfur have been described as unsatisfactory (*6*).

The same applies to the radioactivation analysis of calcium. The main radioactive nuclide produced upon neutron irradiation is Ca^{45} which is also a pure soft β-ray emitter, and its assay is possible only after chemical separation (*10*).

Table I lists the reactions relevant to activation analysis and the properties of the radioactivities induced by reactor neutrons in sulfur and calcium.

The table clearly shows up the difficulties which might arise in analyzing complex samples for their sulfur and calcium content. A major source of interference in the analysis of sulfur via P^{32} is the formation of P^{32} from chlorine by the reaction $Cl^{35}(n, \alpha)P^{32}$ and from phosphorus by $P^{31}(n, \gamma)P^{32}$ (*10*). While the contribution from phosphorus, which has a large neutron capture cross section (200 mb.) may be partly discriminated against by the use of a thermal neutron absorber (*12*), that arising from chlorine cannot be eliminated. Chlorine must therefore be determined independently and the corresponding interference subtracted. When S^{35} is used for the analysis of sulfur, chlorine might interfere by the reaction $Cl^{35}(n, p)S^{35}$. Duplicate irradiations of sample and standards, with and without thermal neutron absorbers—e.g., cadmium—are necessary for the evaluation and subtraction of the chlorine contribution, and the possibility of introducing serious errors is considerable. Other problems are the prolonged irradiations needed (≫ 1 hour, because of the long half lives), radiochemical separation, and the long counting period necessary for the assay of S^{35} and P^{32}. Other nuclides, except S^{37} which will be discussed below in detail, are not suitable for the analysis of sulfur, because of low activation and absence of gamma rays (P^{33}), very short half life (P^{34}), or excessive interference (Si^{31}-produced in a larger proportion from silicon).

The use of S^{37} for the analysis of sulfur appears promising at first sight since the S^{37} gamma ray has an outstandingly high energy, 3.1 m.e.v., which should make it easy to resolve it from lower energy gamma rays by using a γ-ray spectrometer. However, this method is handicapped by relatively poor sensitivity due to the very low isotopic abundance of S^{36} and its small neutron capture cross section. Analysis by S^{37} has been reported only in cases

Table I. Reactor Induced Reactions and Radioactivities in Sulfur and Calcium

Reaction	Abundance of target nuclide, % (*13*)	Cross section mb.[a]	Properties of product (*13*) $T_{1/2}$	Radiations, m.e.v.
Sulfur				
$S^{34}(n,\gamma)S^{35}$	4.22	260	86.7-day	β^- 0.167; no γ
$S^{36}(n,\gamma)S^{37}$	0.0136	140	5.1-min.	β^- 4.3, 1.6; γ 3.09
$S^{32}(n,p)P^{32}$	95.0	60[b]	14.5-day	β^- 1.71; no γ
$S^{33}(n,p)P^{33}$	0.76	(65)[b]	25-day	β^- 0.238; no γ
$S^{34}(n,p)P^{34}$	4.22	(0.63)[b]	12.4-sec.	β^- 5.1, 3.2, 1.0; γ 2.1, 4.0
$S^{34}(n,\alpha)Si^{31}$	4.22	2.5[b]	2.64-hour	β^- 1.48; γ 1.26
Calcium				
$Ca^{44}(n,\gamma)Ca^{45}$	2.06	700	165-day	β^- 0.254; no γ
$Ca^{46}(n,\gamma)Ca^{47}$	0.0033	300	4.7-day	β^- 2.0, 0.69, γ 0.5, 0.81, 1.30
$Ca^{48}(n,2n)Ca^{47}$	0.185	(0.25)[b]		
$Ca^{48}(n,\gamma)Ca^{49}$	0.185	1100	8.8-min.	β^- 2.0, 1.0, 0.5; γ 3.1, 4.0, 4.7
$Ca^{44}(n,p)K^{44}$	2.06	(0.08)[b]	22.3-min.	β^- 4.91, 2.71, 2.44, 0.7 γ 1.13, 1.74, 2.07, 2.48, 3.6
$Ca^{40}(n,\alpha)Ar^{37}$	96.97	(6.7)[b]	34.3-day	K capture; no γ
$Ca^{44}(n,\alpha)Ar^{41}$	2.06	(0.035)[b]	1.83-hour	β^- 2.5, 1.2; γ 1.3

[a] When not marked cross sections are given for thermal neutrons.
[b] Effective cross sections with fission spectrum neutrons according to ref. (*11*). Values in parentheses are only estimated.

[1] Visiting scientist from the Philippine Atomic Research Center, Quezon City, Philippines.

where the sulfur content is high and other γ-ray emitters are absent (*7*). Although other activities, if present, usually emit low energy gamma rays which can be discriminated against electronically, the 3.1-m.e.v. peak of S^{37} can only be resolved when the other activities are not more than about 10 times more intense than S^{37}; otherwise, sum peaks may mask the 3.1-m.e.v. peak, or the high background might overload the detector and paralyze it for a considerable fraction of the counting time. Another drawback in using S^{37} is the likelihood of strong interference from chlorine by the reaction $Cl^{37}(n,p)S^{37}$.

The difficulties encountered in the activation analysis of calcium can be inferred from Table I. Although production of Ca^{45} by a neutron flux takes place exclusively from calcium, Ca^{45} cannot be used conveniently for the analysis (*6*) because of its unfavorable nuclear properties, viz. the absence of gamma rays, decay by low energy beta rays, long half life and low production rate. The other neutron-produced radioactive isotopes of calcium are Ca^{41}, Ca^{47}, and Ca^{49}. Ca^{41} is practically useless for activation analysis, being of $\sim 10^5$-year half life and decaying only by K-capture. Its production is thus extremely low and its detection difficult. Ca^{47} has favorable nuclear properties but the extremely low isotopic abundance of Ca^{46} makes it practically impossible to detect it. Ca^{49} decays with the emission of high energy gamma rays which should make it easy to detect and identify it with the aid of a discriminator or a pulse height analyzer; however, it is produced from Ca^{48} which has a low isotopic abundance, so that in complex samples where calcium is a minor constituent the Ca^{49} peak may be masked by sum peaks or there may be overloading and partial paralysis of the detectors.

A possibility of overcoming interferences in the assay of S^{37} and Ca^{49} is to use radiochemical separation. However, this is difficult because of the short lives of these nuclides. A recent report (*5*) quotes a separation taking 22 minutes prior to the assay of Ca^{49} or its daughter 57.5-minute Sc^{49}.

The circumstances discussed above suggest that most of the problems can be solved by using a γ-ray detector insensitive to energies below the range in question, viz. ~3 m.e.v. One possibility is to use a pair-spectrometer, which responds to gamma rays above the threshold for pair production, viz. 1.02 m.e.v. However, because of the possible presence of many nuclides emitting gamma rays with energies above 1.02 m.e.v., this detector will not have a high degree of specificity for complex samples, and additional assignment by half life might be cumbersome. Another possibility is to count the photoneutron emission caused by the gamma rays in beryllium or deuterium, the thresholds for this process being 1.67 and 2.23 m.e.v., respectively. Here there are far fewer sources of interference, especially in the case of deuterium, since the number of radionuclides which can be produced by neutron irradiation and which emit gamma rays of energies above 2.23 m.e.v. is relatively small. Further, only nuclides with half lives in the range 10 times shorter or 10 times longer than those of S^{37} and Ca^{49} need be of concern, which eliminates most nuclides except a few fission products. Thus photoneutron counting is highly specific, and in conjunction with decay rate measurements it can be used for the nondestructive activation analysis of sulfur and calcium.

Table II. Production and Properties of S^{37}

Half life: 5.1 min.
γ-ray energy: 3.09 m.e.v.; abundance: 90% of disintegrations

Reactions	Abundance of target nuclide, %	Cross sections, mb.
$S^{36}(n,\gamma)S^{37}$	0.0136	140
$Cl^{37}(n,p)S^{37}$	24.47	0.24[a]
$Ar^{40}(n,\alpha)S^{37}$	99.60	(0.56)[a]

[a] Effective cross section with fission spectrum neutrons (*11*). Value in parenthesis is estimated (*11*).

The present work is based on the counting of photoneutrons in deuterium. This method was previously applied to the analysis of sodium (*2*) and is presently also being developed for analysis of manganese (*3*).

Detector. The most suitable apparatus for detecting the high energy gamma rays is a neutron counting assembly embedded in a heavy water matrix in which the photoneutron emission takes place and which also serves to moderate the neutrons for efficient detection.

Sample. The only condition required of the sample is that it should not be too bulky and should not contain large amounts of neutron absorbing materials, so as to minimize systematic errors due to self-shielding. The presence of neutron emitters in the sample, or their formation during the irradiation, would give results which are too high and attention should be given to eliminating them before the analysis if possible, although both types of interferences can be checked experimentally and corrected for.

Irradiation Conditions. During the neutron irradiation S^{37} can also be formed from chlorine and argon, according to the reactions given in Table II. Argon, a gas and a rare element, should not cause any interference in practice. Chlorine, on the other hand, is very abundant, and a well thermalized neutron flux is important when small amounts of sulfur are assayed in a sample with a large amount of chlorine. Alternatively, thermal neutron absorbers can be used in duplicate irradiations to obtain the net thermal neutron effect. In the analysis of calcium by Ca^{49} the problem of a foreign source of this nuclide does not arise.

The duration of the irradiation should be adjusted to the approximate sulfur or calcium content. In general, irradiations longer than 2 half lives—i.e., 10 minutes for sulfur and 17 minutes for calcium—will not add significantly to the sensitivity and accuracy of the analysis, and will only increase the probability of interferences from long-lived photoneutron sources like 2.58-hour Mn^{56} or 15-hour Na^{24}.

Counting Conditions. The yield of photoneutrons is highest when the sample is placed at the center of a large D_2O tank. Efficient neutron detection is then possible by surrounding the sample with a ring of thermal neutron detectors immersed in the heavy water.

When the only photoneutron sources are S^{37} or Ca^{49}, an integral count over one or two half lives (depending on the background level) will give the highest sensitivity and precision. If more than one component is present the decay must be followed long enough to permit the subtraction of the other components, which are most probably long lived—e.g., Mn^{56} and Na^{24}.

EXPERIMENTAL

Samples were weighed, sealed in small (~2 cc.) polyethylene vials, and positioned in a reproducible geometry in the standard pneumatic tube irradiation containers ("rabbits"). The samples were irradiated for 10 minutes in the pneumatic tube facility of the Israel Research Reactor IRR-1 at a thermal neutron flux of 7.4×10^{12} neutrons/cm.^{2}-second. The fast fission flux (fission spectrum neutrons) was 2.4×10^{12} neutrons/cm.^{2} - second. Counting started about 1 minute after the end of irradiation.

The irradiated sample was placed at the center of a 1-liter polyethylene bottle containing heavy water (>98% D_2O) and surrounded by a ring of six $B^{10}F_3$ proportional counters. This assembly was embedded in a 40- × 40- × 40-cm. paraffin block shielded externally by a cadmium screen, a layer of lead, and borated paraffin bricks to reduce the background. The pulses from the counters were amplified and fed to a recording electronic scaler. The γ-ray effect in the BF_3 counters, resulting in low energy pulses, was discriminated against by introducing

Table III. Production and Properties of Ca^{49}

Half life: 8.8 minutes

γ-rays:

Energy, m.e.v.	Abundance (% of disintegrations)
3.10	89
4.05	10
4.68	0.6

Reaction	Abundance of parent	Cross section
$Ca^{48}(n,\gamma)Ca^{49}$	Ca^{48} 0.185%	1100 mb.

an electronic bias. The background of the system during the experiments was about 10 c.p.m. A more detailed description of the apparatus and other pertinent data on the operational and checking procedure were previously published (*2*).

RESULTS

The photoneutron activity of the irradiated samples was followed until it had decayed completely. The half lives observed were in agreement with the published values, viz. 5.1 and 8.8 minutes for S^{37} and Ca^{49}, respectively (Tables II and III). The activity of the 57.5-minute Sc^{49} daughter of Ca^{49} was not observed even when large activities of Ca^{49} were present in the sample. This was expected since Sc^{49} does not emit photons of energies greater than 2.23 m.e.v.

A series of calibration measurements for sulfur analysis was made by irradiating varying amounts of elemental sulfur, in the range 15 to 115 mg. The photoneutron activity was found to be proportional to the sulfur content. The activity was 11.20 ± 0.32 c.p.m. per mg. of sulfur irradiated for 10 minutes at a neutron flux of 7.4×10^{12} neutrons/cm.^{2}-second (Table IV). The corresponding saturation activity at 10^{13} neutrons/cm.^{2}-second was 19.9 c.p.m. Similarly, different amounts of $CaCO_3$ and $CaHPO_4$ containing 0.3 to 30 mg. of calcium were irradiated and counted. The photoneutron activity was proportional to the calcium content. The activity was 449.64 ± 10.4 c.p.m. per mg. of calcium at a flux of 7.4×10^{12} neutrons/cm.^{2}-second (Table V). The corresponding value at saturation, using a flux of 10^{13} neutrons/cm.^{2}-second was 1124.7 c.p.m In no case was self shielding or flux depression observed in the samples irradiated.

The detection efficiency of the counting system—i.e., the number of disintegrations of S^{37} or Ca^{49} necessary to produce a photoneutron pulse was measured using Na^{24} as an internal standard. The latter has a detection efficiency of one neutron count for every 2.447×10^4 disintegrations (*2*).

Table IV. Calibration of Photoneutron Count Rate for Sulfur Analysis

Wt. of S (mg.)	Observed neutron count[a]	Neutron count per mg. S	Count rate per mg. S at end of 10-min. irradiation (c.p.m.)
14.650	469	32.01	11.33
36.225	1120	30.92	10.93
52.050	1701	32.68	11.55
65.885	2008	30.48	10.76
81.275	2500	30.76	10.86
102.095	3241	31.74	11.22
105.000	3463	32.98	11.65
114.600	3657	31.91	11.27
		Mean:	11.20
		Std. dev.:	±0.32 (±2.57%)

[a] A 5-minute integral count starting 1 minute after a 10-minute irradiation at a flux of 7.4×10^{12} n/cm.^{2}-sec.

Known amounts of sulfur or calcium were mixed with known amounts of sodium and irradiated in the pneumatic tube. The photoneutron counts due to Na^{24} and Ca^{49} or S^{37} were obtained from the decay curve. Using the known detection efficiency of Na^{24} the amount of Ca^{49} or S^{37} was calculated. The photoneutron counting efficiencies of S^{37} and Ca^{49} were 1.07×10^4 and 1.66×10^4 disintegrations per photoneutron counted, respectively (Table VI). These values were in general agreement with the estimated photoneutron yield based on the $D(\gamma, n)H$ excitation function (*8*).

Samples of various amounts of S, Ca, and their mixtures were prepared, irradiated for 10 minutes, and counted. The results of the sulfur and calcium determinations are given in Tables VII, VIII, and IX. Photoneutron activities from samples containing S, Ca, Na, Mn, or natural uranium are shown in Figure 1.

This method of analysis was also applied to soils, plants, rubber, and mineral oils and yielded satisfactory results. As an example, results of the sulfur analysis of mineral oils are given in Table X. In this particular case a large weight of oil was used, about 9 grams, to compensate for the low sulfur content of the oil. Internal standards ("spikes") of sulfur were used to calibrate the measurements.

Table V. Calibration of Photoneutron Count Rate for Calcium Analysis

Wt. of Ca (mg.)	Observed neutron count rate at end of 10-min. irradiation (c.p.m.)	Observed count rate per mg. Ca at end of 10-min. irradiation (c.p.m.)
$CaCO_3$		
0.602	268	445.18
1.120	504	450.00
7.250	3314	457.10
10.171	4651	457.28
$CaHPO_4$		
0.290	122	450.52
0.651	292	448.54
1.290	593	459.69
4.809	2175	452.28
9.574	4362	455.60
14.528	6550	450.85
21.609	9528	440.92
30.353	13615	448.55
	Mean:	449.644
	Std. dev.:	10.4 (2.3%)

Measurements of the interference of the chlorine and argon are given in Table XI. The experimental values do not agree with the calculated ones, indicating the need for re-evaluation of the corresponding cross sections (*9*).

Table VI. Detection Efficiency of S^{37} and Ca^{49} by Photoneutron Counting

Sample composition, mg.			Neutron counts per min. per mg. at end of 10-min. irradiation			Ratio disintegrations per neutron count[a]	
Na	Ca	S	Na	Ca	S	Ca	S
2.965	17.710	...	892	210	...	1.73×10^4	...
2.705	74.525	...	880	219	...	1.660×10^4	...
2.821	80.620	...	849	226	...	1.609×10^4	...
2.738	90.534	...	860	221	...	1.645×10^4	...
2.184	...	145.060	859	...	4.96	...	1.178×10^4
0.970	...	156.685	845	...	5.44	...	1.074×10^4
0.630	...	160.002	870	...	5.80	...	1.007×10^4
0.440	...	158.325	851	...	5.75	...	1.016×10^4

Mean $1.662 (\pm 0.052) \times 10^4$; $1.069 (\pm 0.078) \times 10^4$

[a] Absolute disintegration rate of S^{37} and Ca^{49} calcd. using value 2.447×10^4 disintegration/photoneutron count for Na^{24} (*2*).

DISCUSSION

Precision and Sensitivity. It has already been mentioned (*1–3*) that the main source of error in nondestructive activation analysis using photoneutron or delayed neutron counting is irradiated flux variations. The reactor flux itself may vary, and there may be differences between the irradiation fluxes through the sample and the standard with which it is compared. Errors due to weighing of samples and instability of the counting assembly are minor when care is paid to precision. Errors due to statistics depend on the amount of the element sought that is present in the sample, on the intensity of the irradiation flux, and on the background of the counting assembly. The precision obtained under present conditions was ~2.5% for both sulfur and calcium. This can be regarded as satisfactory for activation analysis, for which a precision of 2 to 5% is expected. The precisions reported for Na (*2*) and Mn (*3*) using the same method were ~2% and ~1%, respectively, but these cases are notable for their high photoneutron yield and long half lives, which result in improved statistics.

The detectabilities—i.e., the standard deviation when the sample count equals the background—were ~ 660 μg. for sulfur and 16.5 μg. for calcium, when a single 10-minute irradiation was made at a flux of 10^{13} neutrons/cm.^{2}-second and the counting was done at a background of 10 c.p.m. It is more practical to state a sensitivity level when the relative standard deviation is 10%. The corresponding values are 7.7 mg. for sulfur and 190 μg. for calcium when the irradiation time is 10 minutes. These figures refer to the statistical counting error using a single photoneutron count taken for 1 minute. By integrating the count over an extended period, the precision and sensitivity increase correspondingly. In practice an increase of a factor of 10 is attainable for both calcium and sulfur.

Further improvements are possible using higher neutron fluxes, or repeating the irradiation and counting several times. The use of a larger D_2O container will increase the photoneutron yield, and a more efficient neutron detector array can be used; both will result in better sensitivity and precision.

Accuracy. The tests of accuracy shown in Tables VII and VIII indicate a general agreement with the precision of the method (given in Tables IV and V). Systematic errors due to self-shielding were not studied, but such effects can be dealt with by the use of internal standards, as pointed out previously (*2*).

Interferences. Spurious neutron counts might arise from several different origins. Photoneutron emission caused by high energy γ-ray sources like Mn^{56}, Na^{24}, and fission products, may be subtracted by following the decay and stripping the decay curve. Figure 1 gives an idea of the comparative interferences of this kind.

Beryllium, if present in substantial amounts, might interfere by undergoing photodisintegration with gamma rays of ≥1.67 m.e.v. emitted by active sample components. The interference of this source as well as (α, n) reactions and spontaneous fission can be deter-

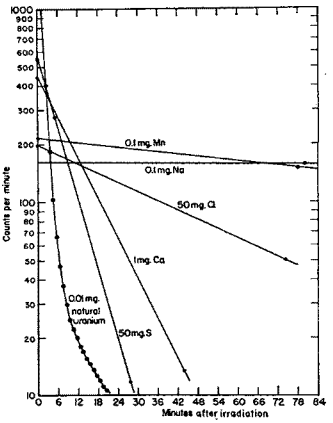

Figure 1. Comparison of photoneutron count rates from different sources after a 10-minute irradiation

Table VII. Some Results of Sulfur Determinations

Sulfur content, mg.		Error	
Present	Found[a]	(mg.)	(%)
351.35	355.74	+4.39	+1.25
246.28	294.75	+3.47	+1.41
201.38	199.73	−1.65	−0.82
150.11	146.31	−3.80	−2.53
101.26	97.80	−3.46	−3.42
50.32	53.41	+3.09	+6.14
25.61	25.30	−0.31	−1.21
10.87	11.43	+0.56	+5.15
5.23	5.17	−0.06	−1.15
2.66	2.49	−0.17	−6.39
1.22	1.34	+0.12	+9.84
0.54	0.68	+0.14	+25.93

[a] Samples irradiated for 10 minutes and counted 1 minute after irradiation for 5 minutes each in a single determination. A value of 31.7 counts/mg. obtained from calibration measurement (of 3 standards) was used to calculate the results.

Table VIII. Some Results of Calcium Determinations

Calcium content, mg.		Error	
Present	Found[a]	(mg.)	(%)
50.352	50.592	+0.267	+0.53
28.633	28.979	+0.346	+1.21
15.282	15.229	−0.053	−0.35
5.215	5.257	+0.042	+0.81
1.200	1.217	+0.017	+1.42
0.832	0.814	−0.018	−2.16
0.321	0.288	−0.033	−1.03
0.125	0.151	+0.026	+2.08
0.082	0.070	−0.012	−14.63

[a] Conditions same as Table VII except a value of 1396 counts/mg. obtained and used to calculate results.

Table IX. Analyses of Mixtures of Sulfur and Calcium

Sample composition, mg.		S/Ca ratio	Determination by photoneutron counting			
			S		Ca	
S	Ca		(mg.)	% error	(mg.)	% error
100.343	1.034	97.044	95.828	−4.5	1.164	+12.6
50.888	0.897	56.731	55.061	+8.2	0.982	+9.5
24.955	0.979	25.490	21.636	−13.3	0.893	−8.8
9.853	0.999	9.863	[a]	...	1.065	+6.6
0.999	0.995	1.004	[a]	...	0.943	−5.2
0.998	5.385	0.1853	[a]	...	5.207	−3.3
0.999	10.928	0.09142	[a]	...	11.267	+3.1

[a] Resolution of sulfur from decay curve was not possible.

Table X. Determination of Sulfur in Mineral Oil

	Sulfur content (%)	
Wt. of sample (g.)	Conventional analysis[a]	Activation analysis and photoneutron counting[b]
8.850495	0.067	0.052, 0.057
8.492900	0.063	0.047, 0.049
8.540710	0.043	0.044, 0.042
8.440600	0.200	0.190, 0.203
8.557755	0.19	0.211, 0.225
9.142090	0.23	0.203, 0.205
8.275275	0.19	0.202, 0.205
8.516755	0.21	0.214, 0.216
8.879660	0.22	0.231, 0.223
8.484135	0.19	0.212, 0.205
		0.218, 0.211

[a] Analyses performed by Chemical Testing Laboratory, Technion Research and Development Foundation Ltd., using I.P. 61/61 procedure of the Institute of Petroleum, in which sulfur is converted by combustion in a bomb to SO_4^{-2} and weighed as $BaSO_4$.

[b] The two values given represent independent detns. Each sample was irradiated for 10 minutes at a neutron flux of ~7.4 × 10^{12} n/cm.^{2}-sec. and counted for 5 minutes. A calibration value of 28.0 counts/mg. sulfur was used to calculate the results. A relative error of 10% was obtained in each detn.

mined from their different rates of decay and subtracted, or, more efficiently, the same sample can be irradiated again and counted in the neutron counting assembly in which the D_2O has been replaced by natural water. Delayed neutron emission, due to its short half life (< 1 minute) is of no practical concern, since a ~5-minute delay will result in the complete decay of this source. If a delay in counting cannot be permitted the delayed neutron effect can be subtracted by counting with natural water, as mentioned above.

The extent of mutual interference of calcium and sulfur in samples containing both elements is seen in Table IX.

Another possible source of interference in the analysis of sulfur is chlorine, and to a much lesser degree, argon. Table XI shows the extent of formation of S^{37} from these sources. Since chlorine might be more abundant than sulfur in many types of samples, its effect would mask that of sulfur. The use of a well thermalized neutron flux is then important. Another possibility is to irradiate the sample behind a thermal neutron absorber—e.g., cadmium—and the difference will represent the net thermal effect due to neutron capture in sulfur. A minor source of interference is the high energy gamma ray of 37.3-minute Cl^{38}, of $\sim 10^{-2}$% abundance, which may give rise to photoneutrons (*9*), but because of the large difference in half lives, it can be corrected for by following the decay. The interference of argon is small as can be seen from the fact that 10 cc. of air present in the sample contribute only ~1 c.p.m., when irradiated for 10 minutes at a flux of 10^{13} neutrons/cm.^{2}-second. These problems do not exist for Ca^{49} which is formed exclusively from calcium.

Table XI. Formation of S^{37} from Different Sources [Using Mixed Neutron Flux of 7.4×10^{12} Thermal and 2.4×10^{12} Fission Spectrum Neutrons per cm.^{2} per sec.]

Reaction	Photoneutrons/min./mg. parent after 10-min. irradiation: Calcd.	Exptl.
$S^{36}(n,\gamma)S^{37}$	11.1	11.2 ± 0.3
$Cl^{37}(n,p)S^{37}$	10.2[a]	3.4 ± 0.3
$Ar^{40}(n,\alpha)S^{37}$	84.0[a]	6.0 ± 0.5

[a] Based on estimated cross sections quoted in Table II according to (*11*).

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Application of Galvanic Cell to Measurement of Oxygen-Consuming Enzyme Systems

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▶ **The application of a galvanic cell oxygen analyzer to the study of oxidative enzyme systems is discussed. Comparisons are made of results obtained on three enzyme-substrate systems using the Warburg manometric technique, spectrophotometry, and the galvanic cell with a bucking potential circuit. Agreement of kinetic data, high sensitivity, and versatility suggest that the galvanic cell is applicable in the analysis of oxidative systems. Data are presented which demonstrate that the galvanic cell can be used to measure changes in oxidative systems which consume less oxygen than can be measured by conventional manometry or which involve no change in the ultraviolet or visible spectrum of reactants or products.**

THE METHOD most commonly used in the study of oxidative reactions is the Warburg manometric technique (*8*). The spectrophotometer has also been used in studies of oxidative reactions when the solutions are translucent and there are changes in either the visible or ultraviolet spectra (*6*). Polarographic techniques in which the reduction of oxygen is measured when proper potentials are applied are also used to measure oxidative reactions. The dropping mercury electrode (*2*) is the system usually associated with the term polarography, however, the oxygen electrode (*1*) and the galvanic cell oxygen analyzer (*3–5*) are variants of the polarographic technique.

Mancy (*4*) described a galvanic cell which utilized a membrane enclosed chamber containing electrodes and supporting electrolyte. Lipner (*3*) described a bucking potential circuit which resulted in a marked increase in sensitivity when used with the Mancy galvanic cell.

The purpose of this study was to investigate the applicability of the galvanic cell to oxidative enzyme systems and to establish the limits of accuracy, sensitivity, and the reproducibility of this apparatus. (The galvanic cells were constructed by E. J. Highsmith and the bucking potential circuits by F. Jordan of the Department of Biological Science, Florida State University, Tallahassee, Fla.) Oxidative systems chosen for study were ones which allowed direct comparison of data obtained with the galvanic cell, Warburg, and spectrophotometer. The tyrosinase oxidation of tyrosine to dopachrome was applicable for study with all three instruments. The tyrosinase oxidation of 3,4-dihydroxyphenylalanine (DOPA) to dopachrome was too rapid for accurate manometry and was measured only with the galvanic cell and spectrophotometer. The reaction catalyzed by snake venom L-leucine oxidase to the corresponding alpha keto acid was measured with the galvanic cell and the Warburg but

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Table I. Calculated Apparent K_ms

Instrument	Reaction: Snake venom L-leucine oxidase	Tyrosinase-tyrosine	Tyrosinase-DOPA
Galvanic cell	0.95×10^{-3}	2.03×10^{-4}	6.61×10^{-4}
Warburg	1.07×10^{-3}	2.29×10^{-4}	...
Beckman DK	...	1.77×10^{-4}	5.89×10^{-4}
Literature values	1×10^{-3} (Singer and Kearney, 1950)	$1.9 \times 10^{-4} \pm 0.4$ (Osaki, 1963)	...

Table II. Cell Constants

Membrane	μl. O_2/mv./ml.
1.0-mil polyethylene	0.107
1.0-mil Teflon	0.092
0.5-mil Teflon	0.044

could not be measured directly with the spectrophotometer because no significant change in the ultraviolet or visible spectrum of the reactant or product occurs.

EXPERIMENTAL

Instrumentation. A galvanic cell equipped with a bucking potential circuit and with a Beckman linear recorder was used to measure initial rates of oxidation in all systems studied (*3*). Polyethylene membranes, 1.0-mil (obtained from O. L. Dube, Precision Scientific Co., Chicago, Ill.) were employed for all studies except as otherwise noted. The cells had a diameter of 1 cm. and when in use the membranes had an effective area of approximately 16 mm.^{2} The micro-Winkler method was used to determine the equivalence of oxygen concentration to voltage generated (cell constant) (*3*). Three identical galvanic cells were used to facilitate the operation. A switching device allowed the recorder to monitor any of the three cells. A rate could be recorded from one cell while the other two chambers were being prepared for subsequent runs. Care must be taken that oxygen does not become a limiting factor. When cold solutions, or solutions that had been tightly stoppered, were introduced into the cell chamber, it was necessary to aerate the solutions. This was done by aspiration through a syringe when the solution was introduced into the cell chamber. Because there is very little surface exposed to the air, there is insufficient diffusion of oxygen into the solution to influence the rate observed during the first several minutes.

The choice of a cell membrane is important since the rate of diffusion of oxygen through the membrane determines the voltage output of the cell circuit. A comparison of three membranes, 1.0-mil polyethylene, 1.0-mil Teflon (Du Pont), and 0.5-mil Teflon was made to determine the membrane best suited for the cell.

A limitation imposed on the use of the galvanic cell is noise which may be introduced by erratic stirring and temperature fluctuation. The former can be reduced by rapid stirring at the membrane surface and the latter by using a large volume reservoir as a source of constant temperature water for the jacketed reaction chamber. These factors have been more extensively treated by Mancy (*5*).

A Beckman DK spectrophotometer was used to measure the oxidative activity of tyrosinase. The formation of dopachrome was observed spectrally at 475 mμ. The Warburg was used to measure the oxygen consumed in the tyrosinase–tyrosine and snake venom–L-leucine oxidations. A paper accordion carbon dioxide trap was used for the snake venom catalized oxidations to trap carbon dioxide formed because of instability of the alpha keto acid product.

Materials. L-Leucine was used as the substrate for snake venom–L-amino acid oxidase. Lyophilized *Agkistrodon p. pisciworous* (moccasin) venom was used without purification (obtained from Ross Allen's Reptile Institute, Inc., Silver Springs, Fla.). Enzyme solutions contained 62.5 mg. venom/5 ml. buffer. L-tyrosine and L-DOPA were used as substrates for tyrosinase. A crude mushroom preparation was the source of the tyrosinase activity (obtained from Earl Frieden, Department of Chemistry, FSU, Tallahassee, Fla.). All substrate and enzyme solutions were prepared in 0.1*M* phosphate buffer, pH 7.1.

Measurements. Velocities (v) were determined when both the enzyme (E) and the substrate (S) concentrations varied. The rates plotted represent the mean of the observations. Values obtained for replicate runs differed by no more than ±10% from the mean and all slopes were determined using the method of least squares. Apparent Michaelis-Menten constants (K_m) were calculated from the data collected with each instrument. The K_ms were compared because they are independent of the units of the rate constants. The enzyme was added to fixed volumes and the assumption was made that small changes in volume did not appreciably alter concentrations. Rates measured by the galvanic cell as spectrophotometer were initial rates, observed within seconds after the reaction began. Since the Warburg technique does not lend itself to determination of initial rates, a velocity curve was constructed from six readings made at 10-minute intervals for the tyrosinase oxidation of tyrosine. The snake venom catalyzed oxidation of L-leucine was difficult to measure manometrically because of high substrate inhibition necessitating that velocities be determined from three readings made at 5-minute intervals.

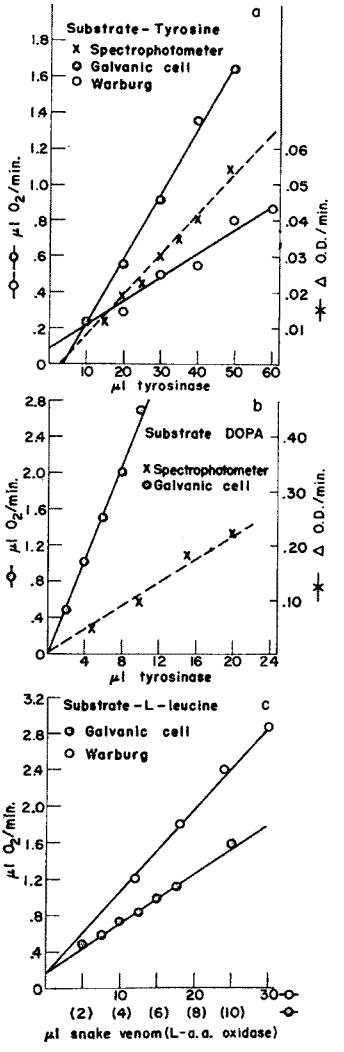

Figure 1. Linear response obtained with spectrophotometer, galvanic cell, and Warburg with increasing enzyme concentration

a. Tyrosinase oxidation of tyrosine (10^{-2}M)
b. Tyrosinase oxidation of DOPA (10^{-3}M)
c. Snake venom oxidation of L-leucine (10^{-3} M).

Enzyme added to 1.0 ml. in galvanic cell, 2.0 ml. in spectrophotometer and 3.0 ml. in Warburg

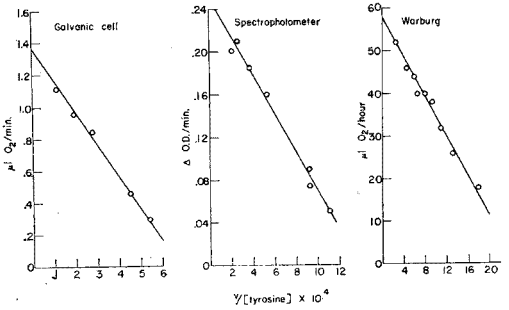

Figure 2. v vs. v/S plots used to calculate the K_ms for tyrosinase oxidation of tyrosine

30 μl. of enzyme added to 1.0 ml. substrate in galvanic cell, 15 μl. enzyme added to 2.0 ml. substrate in spectrophotometer, and 50 μl. enzyme added to 3.0 ml. substrate in Warburg

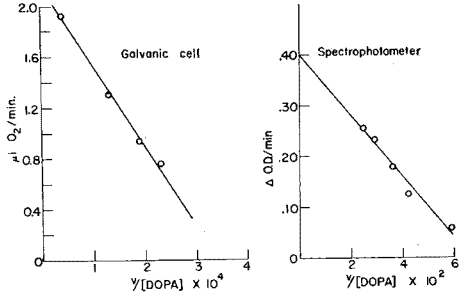

Figure 3. v vs. v/S plots used to calculate the K_ms for tyrosinase oxidation of DOPA

5 μl. enzyme added to 1.0 ml. substrate in galvanic cell, 25 μl. enzyme added to 2.0 ml. substrate in spectrophotometer

In all comparative studies the same stock solutions of enzyme and substrate were used. Most runs were made in triplicate on the Warburg and galvanic cell and in duplicate on the spectrophotometer.

RESULTS

The linearity of the response of the galvanic cell and the other two instruments is indicated in Figure 1. The tyrosinase catalyzed oxidation of tyrosine and DOPA is indicated in Figures 1*a* and 1*b*, respectively. In the oxidation of tyrosine to dopachrome there is an initial lag during which tyrosine is oxidized to DOPA (*6*). The rate achieved after this induction period is plotted in Figure 1*a*. The rate of oxidation of L-leucine as catalyzed by the L-amino acid oxidase is indicated in Figure 1*c*. This system has been described and it is known that the substrate inhibits at high concentrations (*7*). Apparent K_ms calculated from the data obtained for the oxidations studied are listed in Table I. *v vs. v/S* plots were used for the calculation of the K_ms and are shown in Figures 2 to 4. Figures 2 and 3 illustrate the tyrosinase oxidation of tyrosine and DOPA, respectively. Figure 4 shows the snake venom oxidation of L-leucine. The high substrate inhibition is clearly indicated.

The comparison of a 1.0-mil polyethylene, 1.0-mil Teflon, and 0.5-mil Teflon membrane is shown in Figure 5. These results expressed in mv. per min. *vs.* enzyme concentration indicate the greater response obtained with the thinner membrane and parallel the cell constants for the three membranes listed in Table II. The 0.5-mil Teflon membrane was the most sensitive membrane tested and gave reproducible results over a range of 0.05 μl. to 1.0 μl. per ml. However, above this range of concentrations of oxygen the response of the cell became erratic. The 1.0-mil Teflon and polyethylene membranes both gave reproducible results in the system.

Calibration of the 1.0-mil polyethylene membrane demonstrated the linearity of cell output over an extended range of oxygen concentrations (Figure 6). The cell constant for this membrane was determined to be 0.107 μl. of O_2 per mv. per ml. and to have an output of 0.32 μa. or 9.84 mv. per μl. of O_2 per ml. The cells were used no more than five days. Newly prepared cells had the same response characteristics as the old and the data obtained were accumulated over several weeks with no apparent loss of reproducibility. There was no significant difference between the response of the 1.0-mil polyethylene and 1.0-mil Teflon membranes. At the same oxygen concentration the voltage change for the 0.5-mil Teflon membrane was twice that measured with the thicker membranes.

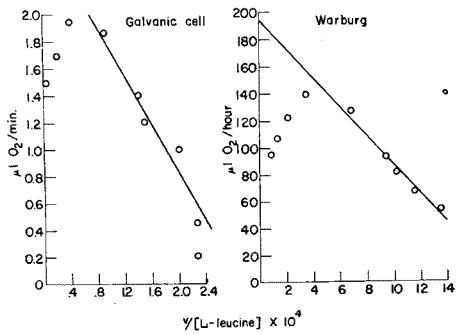

Figure 4. v vs. v/S plots used to calculate the K_ms for snake venom L-amino acid oxidase oxidation of L-leucine

10 μl. enzyme added to 1.0 ml. substrate in galvanic cell, 15 μl. enzyme added to 3 ml. substrate in Warburg

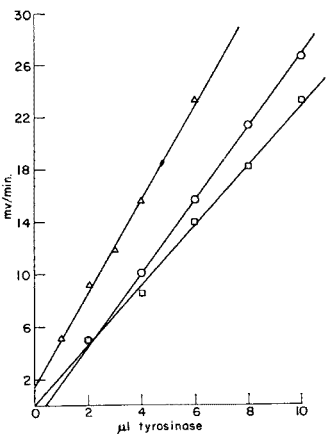

Figure 5. Comparison of 1.0-mil polyethylene (0–0), 1.0-mil Teflon (□–□) and 0.5-ml Teflon membrane (△–△)

Rate of tyrosinase catalyzed oxidation of tyrosine (10^{-3}M) is plotted vs. enzyme concentration

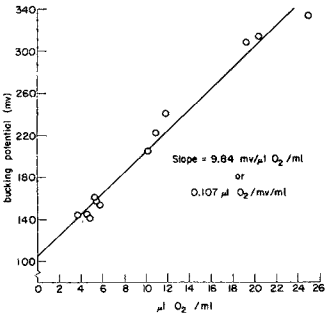

Figure 6. Determination of equivalence of measured potential to oxygen present (cell constant) for 1.0-mil polyethylene membrane

DISCUSSION

The galvanic cell with bucking potential circuit is a sensitive and rapidly responding device, well suited for measuring the total amount of oxygen or rates of oxygen consumption or production. The sensitivity of this apparatus may be varied by choice of membrane since the cell constant is a function of the steady state diffusion current which is dependent on both membrane thickness and permeability. With the 1-mil polyethylene membrane the cell output was linear over a greater than 50-mv. span and therefore changes in oxygen concentration of from 0.1 to 5.0 μl. of O_2 per mv. were within the sensitivity limits of this membrane.

The galvanic cell proved to be as sensitive as the spectrophotometric method and superior to the manometric technique. Agreement of the K_ms demonstrates that the data obtained with the galvanic cell is comparable to that obtained with other instruments and by other workers (*6*, *7*). The galvanic cell has a reproducibility of not less than ±10% and all three cells used were identical in response characteristics.

The greater sensitivity of the galvanic cell over the Warburg technique is apparent when one recognizes that with the former apparatus the total volume of the reactants is 1 ml. and that the rate is determined (after 1 minute equilibration) in 15 sec. to 1 minute. In the case of the Warburg technique a 3-ml. volume was used and readings over a minimum of 20 minutes were required before a rate could be determined. Since about 3 times as much oxygen per minute was consumed and 20 minutes had elapsed before a rate could be determined, we estimated the galvanic cell to be at least 60 times more sensitive than the Warburg under the conditions described. This increase in sensitivity of the galvanic cell over conventional manometry is not significant if the reaction gives consistent data over an extended period of time, 30 to 60 min.; however, many systems do not lend themselves to measurements over long periods.

The use of the Warburg technique in determining optimum reaction conditions is severely limited. Since several determinations are made simultaneously, predictions must be made as to the most favorable concentrations of reactants and much effort may be expended before the data indicating the next step are obtained. The galvanic cell eliminates the necessity for long-range predictions of reaction conditions since each determination is made individually; the data are quickly presented and conclusions as to the necessary modifications can be made on the basis of this data.

In addition to allowing accurate data to be obtained quickly the galvanic cell has the advantage of being set up quickly. In contrast, the Warburg technique requires that all the reactants be present in the vessels (even though physically separated), the vessels placed on the manometers, the manometers placed on the instrument, and the flasks brought to the desired temperatures. The time required for these steps, a minimum of 15 minutes as opposed to a one-minute equilibration to constant temperature for the galvanic cell, often rules out the study of enzymes that denature easily and the study of many biological systems.

A distinct advantage of the galvanic cell is that it measures the change in oxygen concentration of the reaction system and eliminates the variable of diffusion of gas into the liquid which is present in the Warburg system. Also the galvanic cell measurements are not sensitive to changes in outside barometric pressure which can severely hamper the performance of the Warburg.

The use of the galvanic cell also proved to be highly favored over the manometric technique in studying the snake venom catalyzed oxidation of L-leucine, a system exhibiting high substrate inhibition. The concentration of substrate needed to maintain the enzyme at saturating levels for 1 minute was considerably less than to maintain saturating conditions for 20 minutes permitting more latitude in the range of substrate concentrations.

Rapid reactions cannot be studied with the Warburg. The oxidation of DOPA by tyrosinase occurred so rapidly that after mixing of the enzyme with the substrate, 2- and 4-minute readings did not provide meaningful data because the reaction had gone too far.

The basic assumption in the application of Michaelis-Menten kinetics is that the data is derived from initial rate measurements. The galvanic cell provides initial rates while such measurements are not possible with the Warburg technique. Initial rates with the latter technique are derived by extrapolation. Thus the need to consider such detrimental factors as product inhibition, failure of enzyme saturation with substrate, depletion of essential co-factors and inactivation of the enzyme by the conditions of the reaction are obviated when the galvanic cell is used.

The necessity of measuring initial rates of oxidative reactions was illustrated by the observations made by Osaki (*6*) on the tyrosinase–tyrosine system. He found an induction period increased by increasing substrate concentration and decreased by increasing enzyme concentration, and confirmed in the course of this study. There is an oxidative reaction during the induction period which was observed, and measured with the galvanic cell, but barely perceptible using the Warburg technique and not detectable with the spectrophotometric technique. Lack of such pertinent information might well lead to misinterpretations of data with incorrect mechanisms being proposed.

Use of the spectrophotometric technique has similar advantages to those of the galvanic cell in regard to speed with which the data can be obtained, ease of operation, and measurement of initial rates. However, application of the spectrophotometer to the measurement of oxidative reactions is limited since there must be a measurable change in the absorption spectrum of either the substrate or product, or a coupling system must be added, thus introducing an additional source of potential error. This limitation is illustrated by the study of the oxidation of L-leucine, a reaction not accompanied by any spectral change. Other problems can arise because of sensitivity of one or more components of the reaction to irradiation by visible or ultraviolet light. Also the requirement that the solutions be translucent severely limits the use of this technique in the study of biological systems.

The galvanic cell provides immediate rate information, an ability to measure oxygen consuming systems which cannot be measured otherwise, a choice of sensitivity ranges by variation of membranes, and conservation of expensive reactants. Furthermore, if one wishes to use manometric techniques, the galvanic cell may be employed as an excellent survey instrument. Enzyme–substrate concentrations acceptable for the Warburg can be determined by a few preliminary analyses in the galvanic cell with maximum conservation of time and materials. Applications to the study of rates of oxygen consumption in biological systems have been sug-

gested (*5*). These applications are now feasible as routine procedures with the present apparatus (*3*).

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Decay of Cesium-137 Determined by Absolute Counting Methods

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▶ **Precise decay data for Cs^{137} have been determined by absolute counting techniques aided by a rapid method for the carrier-free separation of Ba^{137m}. The following values for the decay parameters were obtained: half-life of Ba^{137m}, 2.554 ± 0.003 minutes; total internal conversion coefficient of the 662 k.e.v. transition, 0.1100 ± 0.0011; K-conversion coefficient, 0.0894 ± 0.0010; branching ratio for the decay of Cs^{137} to Ba^{137m}, 0.952 ± 0.010; ratio of 662 k.e.v. γ-ray emission to Cs^{137} disintegration rate, 0.857 ± 0.009. The relative uncertainty of ~±1% obtained for the latter ratio should make possible the absolute assay of Cs^{137} by γ-ray spectrometry to ±2% or better.**

BECAUSE Cs^{137} is a prominent long-lived fission product and a very useful γ-ray standard, there has been a demand for accurate measurements of its radioactivity. These measurements have been complicated by uncertainties in the decay scheme. Values reported for the branching ratio to the 662 k.e.v. level in Ba^{137} vary from 0.92 to 0.97. Also there has been some uncertainty in the total internal conversion coefficient for the 662 k.e.v. transition. Altogether the uncertainty in the 662 k.e.v. γ-ray abundance in the Cs^{137} decay has limited the accuracy with which Cs^{137} can be assayed by γ-ray measurements to about 5%.

A direct determination of the total internal conversion coefficient, α, of the 662 k.e.v. transition in Ba^{137} was made by counting simultaneously conversion electrons and γ-rays from Ba^{137m} sources and is reported here. This determination of α was combined with absolute β- and γ-ray measurements of a Cs^{137} stock solution to yield a new and more precise value for the 662 k.e.v. γ-ray abundance and a value for the β-branching ratio to the 662 k.e.v. level in Ba^{137}. These new values have been incorporated in the decay scheme shown in Figure 1.

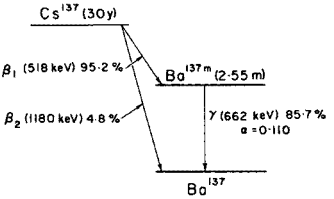

Figure 1. Decay scheme for Cs^{137}

EXPERIMENTAL

Chemical Procedures. Cs^{137} containing no detectable Cs^{134} was obtained from Oak Ridge National Laboratory. It was purified further by $La(OH)_3$ scavenges and by elution from Dowex-50 with 1*N* HCl (*2*, *25*). From the eluate a stock solution was prepared of about 0.2 mc. of Cs^{137} per ml. in 1*N* HCl. The specific activity of this solution was >1 mc. per mg. cesium. Part of a γ-ray spectrum of this solution taken with a lithium-drifted germanium γ-ray spectrometer (*28*) is shown in Figure 2 together with a spectrum of the same material with 2.0% Cs^{134} added. From these spectra it was concluded that there was less than 0.02% Cs^{134} in the Cs^{137}.

A method was developed for the rapid separation of carrier-free samples of Ba^{137m}. This method made use of the adsorption of Cs^{137} on $Co_2Fe(CN)_6$ (*10*).

$Co_2Fe(CN)_6$ adsorption columns were prepared as follows: about 2 ml. each of $K_4Fe(CN)_6$ solution, water, $CoSO_4$ solution, and water were passed in turn through small (0.03 cm.^{2} × 6 cm.) columns of Dowex-1. In this way $Co_2Fe(CN)_6$ was distributed throughout a column which permitted a reasonable flow rate. Cs^{137} stock solution was fed onto the column and >99% of the cesium was adsorbed. The column was washed with 2 ml. of 1*N* HCl and a period was allowed for growth of the Ba^{137m} daughter. Then a Ba^{137m} milking consisted of flowing 1*N* HCl through the column and collecting individual drops of the effluent. Ba^{137m} was eluted promptly and sharply and a separation factor from Cs^{137} of $>10^5$ was achieved.

Ba^{137m} sources suitable for $4\pi\beta$ counting were prepared by evaporation of small samples of the eluate onto gold coated collodion films. These films could be placed very close to an infrared lamp without damage. The time required for a Ba^{137m} milking and source preparation usually was <5 minutes.

Gamma-Ray Measurements. The γ-ray emission rate of the Cs^{137} stock solution was obtained from accurately weighed samples sealed in glass ampoules measured in a TPA Mk. II (well-type) ionization chamber (*5*, *26*). The response of this chamber was determined as a function of γ-ray energy using nuclides which had been standardized by $4\pi\beta$–γ coincidence counting (*3*). Response curves were obtained for ampoules in three different containers: 0.002-inch Al, 0.016-inch Cd, and 0.048-inch Cd lined with 0.005-inch Ta. The latter two source holders were designed for use when it is necessary to absorb out x-rays accompanying electron capture or internal conversion, but they are also useful in that they provide three partially independent response curves for checking the precision of the method.

Ba^{137m} Counting. The Ba^{137m} sources were counted in a system consisting of a $4\pi\beta$-proportional counter sandwiched between two 3 inch × 3 inch NaI γ-ray detectors (*3*). Essentially all (≥99.9%) of the conversion electrons were detected in the $4\pi\beta$ counter (*17*). The γ-ray emission rates of the sources were determined by direct comparison

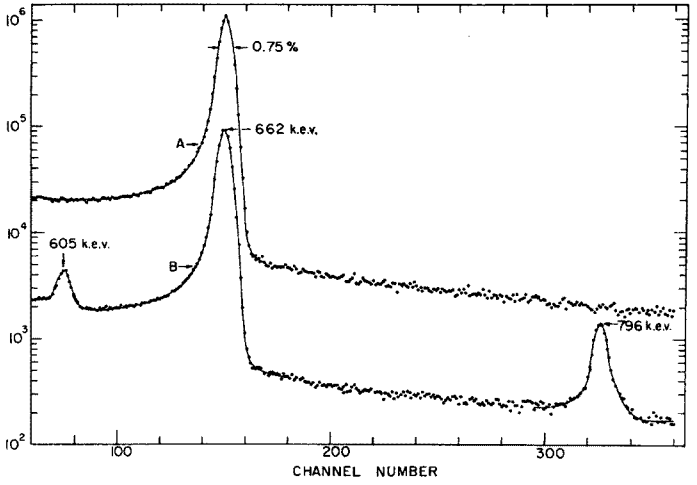

Figure 2. γ-Ray spectra of Cs^{137}

A. Stock solution, using lithium-drifted germanium detector
B. Sample with 2% Cs^{134} added

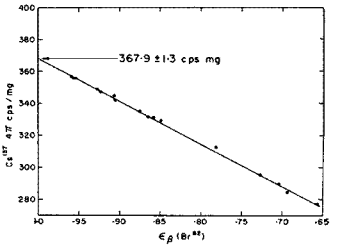

Figure 3. Plot of 4π counting rate due to Cs^{137} vs. 4π counting efficiency for Br^{82} for sources of Cs^{137} Br^{82}

with similar sources of Cs^{137} accurately weighed from the stock solution. The counting rates in both the $4\pi\beta$ and γ-ray counters were followed for about 20 Ba^{137m} half-lives to look for any Cs^{137} contamination.

Cs^{137} Counting. One method used for determining the absolute total electron emission rate of the Cs^{137} stock solution was the $4\pi\beta$–γ efficiency tracing technique (*4, 18*) with the use of Br^{82} as tracer. In this method a series of sources is prepared of Br^{82} combined with Cs^{137} as CsBr and with varying quantities of inactive CsBr carrier added. The efficiency for 4π counting Br^{82} is measured by the coincidence method. The contribution of the Br^{82} activity to the $4\pi\beta$ counting rate for each source is computed and subtracted from the observed $4\pi\beta$ counting rate. This net counting rate is due to Cs^{137} and is plotted *vs.* the measured Br^{82} 4π counting efficiency for each source (Figure 3). Extrapolation by least-squares to 100% efficiency gives the total electron emission rate. A 0.15% correction was applied for the detection of 662 k.e.v. γ-rays in the $4\pi\beta$ counter (*29, 35*).

The second method adopted for determination of the electron emission rate of the Cs^{137} stock solution was $4\pi\beta$ counting. Several very thin Cs^{137} sources were prepared by the (non-quantitative) electrospraying technique (*6, 17*) from a solution of CsCl in ethanol. These sources were $4\pi\beta$ counted and a self-absorption correction of 0.5% was applied (*17*). The γ-counting rates for these sources were compared with the γ-ray emission rate of the stock solution in the same manner as for the Ba^{137m} counting. From these data the electron emission rate of the Cs^{137} stock solution was calculated. The relative standard deviation for the mean of the ratios of electron emission rate to γ-ray counting rate for the electrosprayed sources was only $\pm 0.1\%$.

RESULTS AND DISCUSSION

Gamma-Ray Measurements. The ionization chamber response curve for the 0.016-inch Cd source holder is shown in Figure 4. Similar curves were obtained for the other two source holders. Since these curves were obtained with samples for which the absolute disintegration rates had been determined to $\sim \pm 0.2\%$, their accuracy depends upon the reliability of the γ-ray abundances used. Since these in turn depend upon accurate branching ratios and internal conversion coefficients very few nuclides are available for which they are known to 0.3% or better. Data for the nuclides shown in Figure 3 came from the Nuclear Data Sheets (*20*) plus references (*30*) for Ce^{139} and (*15*) for Nb^{95}. The points for Sc^{46} and Co^{60} are plotted at the mean energies for the two γ-rays in each case. The point for Na^{22} is the response for annihilation radiation after subtracting the response for the 1277 k.e.v. γ-rays obtained from the Co^{60} response. Where applicable, corrections were made for branching ratios, internal conversion, low-abundance γ-rays, and bremsstrahlung. The latter correction was estimated from measurements with pure β-emitters.

The response for 662 k.e.v. γ-rays was obtained by quadratic interpolation in the appropriate response function for each sample holder. For Cs^{137} samples absorption in the steel wall of the well of the ionization chamber rendered the response to the Ba K-x-rays following internal conversion negligible even for the Al holder. The bremsstrahlung correction amounted to about 0.1% in the Al holder and less in the other two holders. From the uncertainties in the interpolations, the consistency of the results obtained with the three holders and among samples, and the accuracy of the primary standardizations, a relative error of $\pm 0.7\%$ was estimated for the determination of the γ-ray emission rate of the Cs^{137} stock solution. The relative standard deviation of the individual measurements was less than $\pm 0.1\%$

Internal Conversion Coefficient of 662-k.e.v. Transition. After making small corrections for dead-time losses

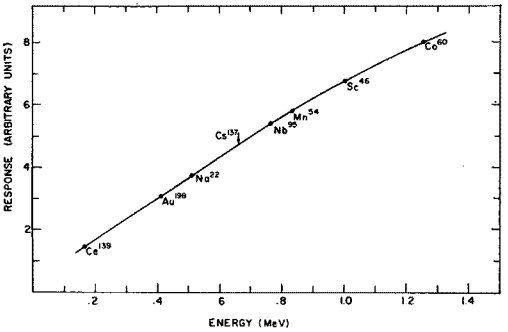

Figure 4. Ionization chamber curve of response *vs.* γ-ray energy for 0.016-inch cadmium sample holder

the minute Cs^{137} contamination in the Ba^{137m} sources ($< 3 \times 10^{-5}$ initially) was subtracted together with the backgrounds. Weighted least-squares fits were made to the decay data for both the $4\pi\beta$ and γ-ray counters over the first 10 half-lives. The ratio of $4\pi\beta$ to γ-ray counting rates was taken to be the ratio of their respective intercepts from the leasts-quares analyses. A correction of (1.6 ± 0.3)% was applied for the response of the $4\pi\beta$ counter to the 662 k.e.v. γ-rays (*29, 35*) to get the ratio of conversion electron to γ-ray counting rates. This ratio, corrected for the γ-ray counter efficiency obtained from the comparison with accurately weighed samples of the stock solution, gave directly the total internal conversion coefficient, $\alpha = e/\gamma = 0.1100 \pm 0.0011$. Allowances for possible systematic errors of ± 0.6% in the γ-ray calibrations and ± 0.3% in the conversion electron measurements were added and the sum combined in quadrature with a relative standard deviation of ± 0.3% to obtain the quoted error of ± 1.0%. A value of 0.813 ± 0.003 for the K/total conversion line intensity ratio was measured for us by J. S. Geiger with the use of the Chalk River $\pi\sqrt{2}$ β-spectrometer (*31*). Applying this measurement to our value for α, the K-conversion coefficient, α_K, was calculated to be 0.0894 ± 0.0010. This and other conversion coefficient determinations (*1, 7–9, 11–13, 16, 19, 21, 23, 32–34, 36*) are listed in Table I, where it is seen that a considerably smaller error has been obtained with the present direct method. The theoretical K conversion coefficient for an M4 transition was obtained from Sliv and Band (*27*) by numerical interpolation. The agreement between the present value and theory is satisfactory since the latter is uncertain by 1 to 3%. A brief discussion of this result has been submitted to Nuclear Physics (*31*).

Ba^{137} Half-Life. The half-life of Ba^{137m} calculated from the results of the least-squares analyses of both β- and γ-counting rates for two runs was 2.554 ± 0.003 minutes. The error includes an allowance of ±0.1% for possible systematic errors, which probably is generous since the Cs^{137}/Ba^{137m} ratio was $< 3 \times 10^{-5}$ initially and none of the results from the two completely independent counting systems was outside this limit.

Cs^{137} 662-k.e.v. γ-Ray Abundance. The total electron emission rate for the Cs^{137} stock solution as determined by the tracer technique and $4\pi\beta$ counting agreed to 0.4% with relative standard deviations of ±0.3% (Figure 3) and ±0.2%, respectively. The value obtained for the internal conversion coefficient was combined with the measured γ-ray emission rate of the stock solution to calculate the conversion electron emission rate. This was then subtracted from the mean of the total electron emission rate determinations to get a value for the Cs^{137} disintegration rate of the stock solution. The ratio of the measured γ-ray emission rate to this Cs^{137} disintegration rate was 0.857 ± 0.009. The same ratio within ~0.1% with essentially the same error was obtained from similar measurements on a Cs^{137} solution distributed for an intercomparison by the International Atomic Energy Agency. Again, a large part of the error quoted is the allowance for systematic error in the determination of the γ-ray emission rate. This γ-ray abundance is about 4% higher than the value of 0.82 ± 0.03 reported by Rider and Peterson (*24*). The smaller uncertainty of the present result should make possible the absolute assay of Cs^{137} by γ-ray spectrometry to ±2%.

In addition to the measurements reported above, the γ-ray emission rates of three sources were measured with a calibrated NaI γ-ray spectrometer. The result is not completely independent of the ionization chamber measurements since the same primary standardizations served to determine the response functions of both instruments. Nevertheless it was gratifying to note that the NaI spectrometer measurements gave the same γ-ray abundance within 0.5% as that quoted above but with a somewhat larger overall relative uncertainty (~ ±1.5%).

Cs^{137} β-Branching Ratio. The β-branching ratio for the decay of Cs^{137} to Ba^{137m} is $(1+\alpha)$ times the γ-ray abundance or 0.952 ± 0.010. This value is compared with earlier measurements (*7, 14, 21–23, 34, 36*) in Table II.

Table I. Values Reported for Internal Conversion Coefficients of 662-k.e.v. Transition

Reference	α	α_K
Townsend *et al.* (*32*)	0.12	
Osoba (*21*)		0.081
Mitchell and Peacock (*19*)		0.118
Waggoner (*33*)		0.097 ± 0.003
Heath and Bell (*11*)		0.095 ± 0.005
Dolishnyk *et al.* (*9*)		0.11 ± 0.01
Azuma (*1*)		0.096 ± 0.005
Wapstra (*34*)		0.092 ± 0.006
McGowan and Stelson (*16*)		0.095 ± 0.008
Ricci (*23*)	0.114 ± 0.022	
Yoshizawa (*36*)		0.0976 ± 0.0055
Hultberg and Stockendahl (*13*)		0.093 ± 0.006
deVries *et al.* (*8*)		0.093 ± 0.005
Hultberg *et al.* (*12*)		0.095 ± 0.004
Daniel and Schmitt (*7*)	0.114 ± 0.03	0.093 ± 0.003
This work	0.1100 ± 0.0011	0.0894 ± 0.0010
Theoretical value (*27*)		0.092

Table II. Values Reported for Branching Ratio to Ba^{137m}

Reference	Reported value
Osoba (*21*)	>0.95, <0.98
Peacock and Mitchell (*22*)	0.95
Langer and Moffatt (*14*)	0.92
Wapstra (*34*)	0.97
Ricci (*23*)	0.952 ± 0.003
Yoshizawa (*36*)	0.924 ± 0.008
Daniel and Schmitt (*7*)	0.935 ± 0.002
This work	0.952 ± 0.010

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The authors are grateful to W. J. Edwards for making some NaI γ-ray spectrometer measurements, to G. T. Ewan for the use of his lithium-drifted germanium γ-ray spectrometer, to J. S. Geiger for his careful measurement of the internal conversion line ratios, to G. W. Parker, ORNL, for supplying the special purity Cs^{137}, and to S.C. Misra, E. A. Ouellette and B. A. Risto for their assistance in these experiments.

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Coupled Reaction System for Determination of Transaminase Enzymes

Application to Glutamic Oxaloacetic Transaminase

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▷ **The determination of transaminase activity with a versatile coupled enzyme reaction system and the automation of the determination are presented. The dependence of instrument response upon enzyme activity is linear. The interferences associated with the determination of glutamic oxaloacetic transaminase (GOT) in 0.2-ml. samples of serum and tissue homogenates are studied. Elimination of the interferences through the use of gel filtration is demonstrated. The standard deviation is 23 Karmen units, or 2% relative, whichever is greater, for samples containing 0 to 1600 Karmen units of GOT.**

THE ANALYTICAL APPLICATIONS OF enzyme-catalyzed reactions can be greatly extended through the use of coupled reactions. Unfortunately, as the number of coupled reactions is increased, the overall specificity of the method decreases whereas the purity of the reagents required and the number of possible interferences generally increase. Thus, the interferences and limitations associated with coupled enzyme reactions must be studied carefully in any application to complex samples if full advantage of the enzyme analysis is to be realized.

This paper presents a coupled reaction system for the determination of transaminases utilizing the reactions shown below:

$$\text{Amino acid} + \alpha\text{KG} \xrightleftharpoons{\text{GXT}} \text{keto acid} + \text{glutamate} \quad (1)$$

$$\text{Glutamate} + \text{NAD} \xrightleftharpoons{\text{GDH}} \alpha\text{KG} + \text{NADH}_2 + \text{NH}_4^+ \quad (2)$$

$$\text{NADH}_2 + \underset{\text{(blue)}}{\text{dye-ox}} \xrightleftharpoons{\text{PMS}} \text{NAD} + \underset{\text{(colorless)}}{\text{dye-red}} \quad (3)$$

In Reaction 1, a transaminase enzyme catalyzes the transfer of an amino group from an amino acid to α-ketoglutarate (αKG), converting αKG to glutamate and the amino acid to a keto acid. In Reaction 2, the oxidation of glutamate by nicotinamide adenine dinucleotide (NAD) to give αKG, reduced NAD ($NADH_2$), and NH_4^+ is catalyzed by glutamic dehydrogenase (GDH). Finally in the third reaction, $NADH_2$ reduces an oxidized dye (dye-ox) to give NAD and reduced dye (dye-red) in the presence of phenazine methosulfate (PMS). When the concentrations of the amino acid, αKG, NAD, GDH, dye-ox and PMS are not rate-limiting, the rate of dye reduction is proportional to the activity of the transaminase enzyme. The reduction of the blue dye is measured as the decrease in absorbance at 600 mμ.

The amino acid required depends upon the transaminase to be determined. For determination of the clinically important glutamic oxaloacetic transaminase (GOT), aspartic acid is required. Alanine as a substrate permits the determination of glutamic pyruvic transaminase (GPT). GXT is a term used in this paper to denote a general transaminase.

The determination of transaminase activity in tissues and biological fluids is of considerable interest and is the basis for important routine tests in the clinical laboratory (*10*). Although most work has been limited to only a few transaminase systems, studies have shown that many transaminases are present in animal tissues (*3, 7*). In this paper, the coupled reaction system described above is applied to the determination of GOT and, in principle, should permit the determination of many other transaminase activities simply by changing the amino acid substrate. The automation of the determination is described. Interferences in human serum and tissue homogenates are studied and eliminated through the use of gel filtration.

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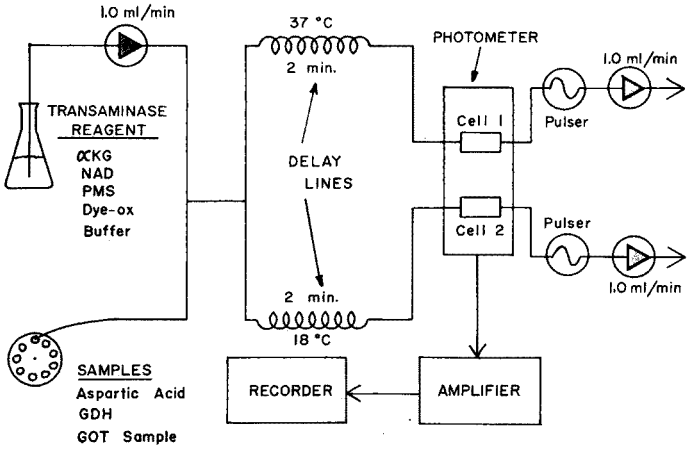

Figure 1. Equipment for the determination of GOT activity

The method presented in this paper has been used routinely to continuously monitor transaminase activities in column effluents during the separation of isoenzymes on ion exchange gels (*4*), and also to study the distribution of transaminases in tissue homogenates.

EXPERIMENTAL

Apparatus. An instrument has been described which makes it possible to automate the determination of GOT (*2*, *5*). A schematic outline is given in Figure 1.

Reagents. Phosphate Buffer. Mix 420 ml. of 0.1*M* Na_2HPO_4 and 80 ml. of 0.1*M* KH_2PO_4 to give 500 ml. of 0.1*M* buffer, pH 7.4.

Aspartic Acid. Add 10.65 grams of L-aspartic acid (Sigma grade, Sigma Chemical Co., St. Louis, Mo.) to 90 ml. of phosphate buffer, adjust the pH to 7.4 with 1*N* NaOH, and dilute to 200 ml. with phosphate buffer. Stored in a refrigerator, the reagent is stable for at least 1 month.

αKG. Add 2.94 grams of α-ketoglutaric acid (free acid, Sigma) to 140 ml. of phosphate buffer, adjust to pH 7.4 with 1*N* NaOH, and dilute to 200 ml. with phosphate buffer. The reagent is stable for at least 1 month in a refrigerator.

Dye Solution. Dissolve 34 mg. of 2,6-dichlorophenolindophenol (grade I, Sigma) in 100 ml. of distilled water. This solution is stable for 1 week at room temperature.

Transaminase Reagent. Add 200 mg. of NAD (grade III, Sigma), 4 ml. of αKG, 6 mg. of PMS (Sigma), and 20 ml. of dye solution to 80 ml. of phosphate buffer. The reagent is evacuated with an aspirator before use to remove dissolved air. It is stable for 1 day at room temperature.

GDH. Process 5 ml. of GDH (Sigma, type II, in 50% glycerol, containing 20 mg. of protein per ml.) by the gel filtration procedure described later.

Procedure. An enzyme sample (serum or tissue homogenate) diluted with GDH and buffered amino acid solution is metered at a constant rate (1.0 ml. per minute) and mixed with a reagent stream as shown in Figure 1. The reagent stream, also metered at 1.0 ml. per minute, contains optimum concentrations of all of the other components necessary for reaction. The resultant reaction stream is split into two delay lines, one at 37° C. and the other at 18° C. After a delay of two minutes, the reaction stream in each line flows through a photometer cell. The absorbance difference between the cells is measured and recorded by a differential filter photometer and is proportional to the GOT concentration. Provisions are made in the photometer and amplifier for setting zero and for calibrating with a standard sample so that the recorder chart will read directly in any desired enzyme units. Samples are introduced automatically at the rate of 20 per hour by a sample turntable. [A detailed description of instrument use can be found elsewhere (*2*, *5*).]

Sample Purification by Routine Gel Filtration. Enzyme samples (serum or tissue homogenate) are passed through a dextran gel column to remove low-molecular-weight substances which interfere in the transaminase determinations. The column procedure has been described (*5*). Routinely, 5.0 ml. of the specimen (serum or homogenate) is put through a 11- × 2-cm. column of Sephadex G-50 (coarse, block form) which has been equilibrated with phosphate buffer. The 5.0-ml. specimen is quantitatively collected in a 20-ml. fraction and diluted to 25 ml. according to a simple procedure (*5*). The fraction routinely collected in this manner quantitatively contains the enzyme activity in phosphate buffer free from low-molecular-weight interferences (below about 10,000) as will be shown later. The preparation requires only a few minutes and one technician can process many samples simultaneously (*5*). The gel technique is modifiable to process very small samples, but this particular study required that many experiments be performed on each sample, and it was therefore more convenient to process large sample volumes.

GDH reagent is also purified by Sephadex separation, using the procedure described above for the enzyme samples.

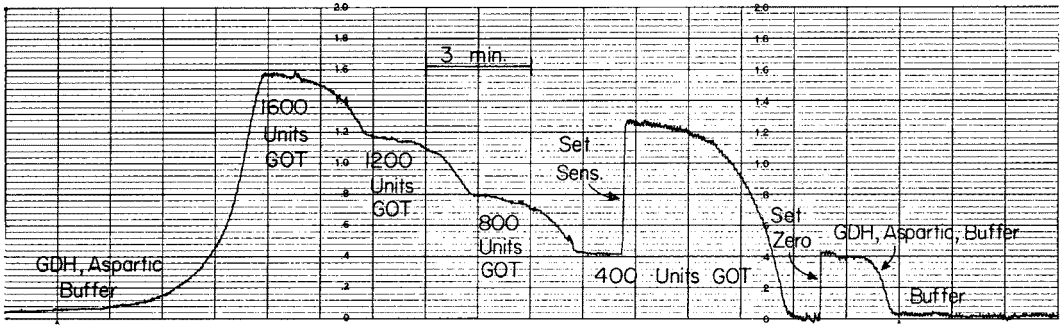

Figure 2. Recording of a series of diluted serum samples

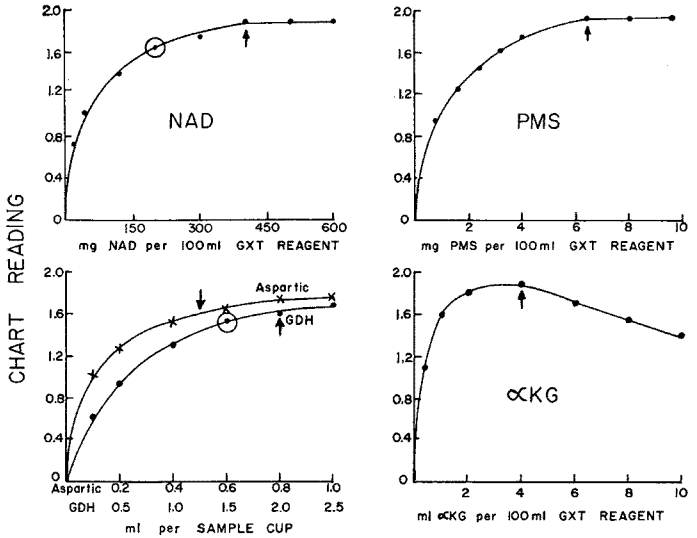

Figure 3. Dependence of response on NAD, PMS, GDH, αKG, and aspartic

SAMPLE SIZE. Routine samples are prepared by diluting 1.0 ml. of serum processed by gel filtration (0.2 ml. of original serum sample) with 1.5 ml. of GDH, 0.5 ml. of L-aspartic acid, and 2.0 ml. of phosphate buffer. Tissue homogenates are diluted into the activity range of serum samples before use. When the volumes of samples or other reagents are varied, enough buffer is added to bring the final volume in the sample cup to 5.0 ml.

BLANK. The instrument baseline is set by running a blank sample, prepared by mixing 1.5 ml. of GDH, 0.5 ml. of aspartic acid, and 3.0 ml. of phosphate buffer. The blank sample takes into account any transaminase activity contained as contamination in the GDH.

RESULTS

Figure 2 is a record of the type of response obtained with the enzyme analyzer. From right to left, a baseline was established with only buffer in the sample cup. Next, a blank sample was introduced, and at steady state, the instrument was set to zero. After setting the blank, a series of four dilutions on the same serum sample was run. The original serum sample contained 1200 Karmen units of GOT per ml. as determined by an accepted routine colorimetric procedure (*6*, *8*).

The first dilution (corresponding to 0.067 ml. of the original serum, or to 400 Karmen units in a 0.2-ml. sample) was used for calibration, and was run longer than the other dilutions, to permit setting the sensitivity to give a reading of about 0.4 chart unit. For this sample, the chart reading is constant within about 0.01 chart unit, corresponding to 20 Karmen units in a 0.2-ml. serum sample. Finally, the remaining three dilutions were run for 3 minutes each, a time selected for routine determinations, which was generally long enough just to reach steady state. The chart reading corresponding to each sample was therefore taken at the end of its 3-minute interval (*5*).

A plot of chart readings (ordinates) against the known values of the diluted serum samples gives a straight-line working curve that extrapolates through the origin within experimental error. The standard deviation of the five individual points (including the origin) from the straight line is ±23 Karmen units of GOT, which may be regarded as a measure of the precision of the procedure for samples ranging from 0 to 1600 units. This is a relative standard deviation of about 2% for samples in the upper third of the range. This precision compares with that obtained for other applications of this enzyme analyzer (*2*, *5*).

STUDY OF REAGENT CONDITIONS

The effect of the concentration of each component upon the rate of dye reduction at constant enzyme activity was studied to determine the optimum conditions for each reagent. In each case, all components except the one under study were at the following concentrations: 400 mg. of NAD (except 200 mg. for GDH and aspartic acid studies), 6 mg. of PMS, and 4.0 ml. of αKG in 100 ml. of transaminase reagent; and 0.5 ml. of aspartic acid and 1.5 ml. of GDH in 5.0-ml. sample cup. All samples contained 1.0 ml. of Sephadex prepared serum (0.2 ml.) which had 350 Karmen units (*6*, *8*) of GOT.

The results are shown in Figure 3. A nonrate-limiting region of concentration was obtained for the aspartic acid, NAD, GDH, and PMS. The response goes through a maximum for αKG, which is a substrate for Reaction 1 and a product in Reaction 2. A maximum rate is obtained when the rate of Reaction 1 is maximum with a minimum amount of product inhibition of Reaction 2. Even though the αKG concentration may limit the rate of Reaction 1, linearity is still obtained with the system because the αKG is recycled by Reaction 2 and its concentration does not change during the measurement. The same argument would hold true for the NAD in Reactions 2 and 3, but high concentrations are required to inhibit Reaction 3.

The optimum concentrations given in the section on reagents were selected from the data in Figure 3 and are shown by the arrows. The linearity between the recorder response and enzyme activity is evidence that the reagent conditions are optimal. For routine enzyme analysis, NAD and GDH were set at slightly suboptimal concentrations (circled in Figure 3) to conserve these reagents, a condition which did not adversely affect the linearity of the response.

STUDY OF INTERFERENCES

When the coupled reaction system was used to determine transaminase activity in samples which had not been processed by gel filtration, a response was obtained even when the amino acid substrate was omitted from the sample cup. Such residual activity has been found in variable amounts in all serum samples and tissue homogenates studied. It can, therefore, be regarded as a general interference which must be removed by gel filtration prior to the assay of transaminase as described in this paper.

Several experiments were performed to study the nature of this residual activity and to test for other interferences. Five-milliliter aliquots of a serum pool—made by pooling 200 serum specimens from patients with cancer, most of whom were being treated with chemotherapy—were frozen. Aliquots were thawed and used in the following studies. The serum pool had 14 units (Karmen) of GOT (*6*, *8*), which falls within the normal range. A pathological serum pool (PSP) was used because it seemed best suited for interferences that could be expected in clinical applications.

Removal of Residual Activity by Gel Filtration. Five milliliters of the

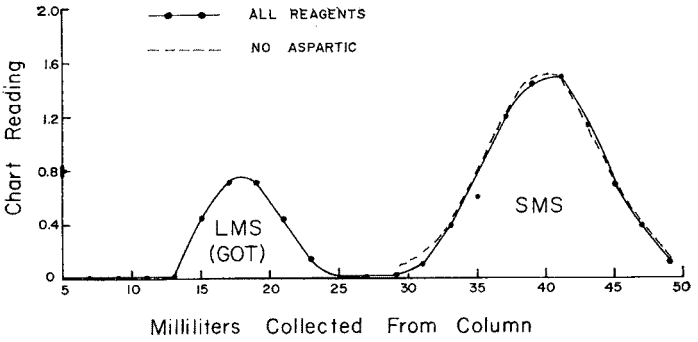

Figure 4. Separation of GOT activity from small molecular size fraction on Sephadex G-50

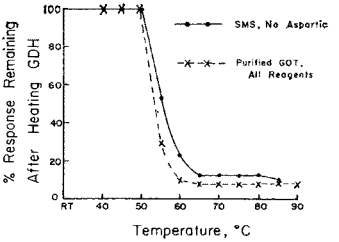

Figure 5. Effect of heating GDH on the responses

PSP were put through a gel column identical to that described for the routine procedure and they were followed by 45 ml. of the phosphate buffer. Twenty-five 2-ml. fractions were collected from the column. Each fraction was assayed for GOT as previously described, using 0.4 ml. of each fraction as the sample. The results are shown in Figure 4.

Two peaks of apparent GOT activity were eluted from the column. Because in gel filtration the substances of large molecular size (LMS)—protein for example—are eluted first, the first peak is the actual GOT activity. The second peak, which contains substances of small molecular size (SMS), is not GOT activity. Also, as shown in Figure 4 by the dotted line, the SMS peak was obtained equally well when aspartic acid was omitted from the sample cups in the assay, showing that the SMS peak was not GOT. The LMS fractions required aspartic acid in the assay to give activity.

When purified GOT (3.0*M* ammonium sulfate–ketoglutarate–maleate suspension, Sigma Chemical Co.) was added to the SMS or LMS fractions, 100% of the added GOT activity was recovered. Thus, neither peak contained inhibitors.

Study of the Dependence of SMS Activity on Various Reagents. The SMS peak was collected as a single 10-ml. fraction (35 to 45 ml. in Figure 4) from several aliquots of PSP and used to determine the reagents required for the SMS fraction to give a response. The amount of SMS sample in the sample cup was varied with certain components omitted from the transaminase reagent or sample cup.

With all reagents included, a linear response with sample size was obtained. No significant response was obtained without GDH or NAD, and only a very small response was obtained with no αKG. As shown in Figure 4, about the same response could be obtained with or without aspartic acid in the sample cup.

The requirements for αKG, GDH, and NAD strongly suggest that the SMS response involves some enzymic reactions, as opposed to some nonspecific chemical activity which reduces the dye or some reagent component. Such a response could be explained by the presence of substrates in the SMS peak which react with enzymes in the GDH. The requirement for αKG suggests that some of the response is transamination. The GDH does have a small amount of GOT activity, but only enough to account for a small fraction of the response with the SMS peak. Other transaminases have not been identified in the GDH reagent. The small response with no αKG could come from direct reaction of GDH with substrates. GDH is known to react with many different substrates (*9*) some of which might be contained in serum or tissue samples. While, in this particular case, the interfering enzymic activity was in a reagent (GDH), it is worth noting that similar variable blank activity could come from substrates and enzymes contained in the serum or tissue homogenates used as samples. Residual activity has also been observed in other procedures (*1*).

The presence of a residual activity in the transaminase method presented here demonstrates the limitations (loss of specificity and purity of reagents required) which are frequently associated with the direct application of coupled enzyme reactions. Gel filtration is a useful means of extending the applications of coupled enzyme reactions by greatly reducing these limitations.

Effect of Heat on GDH Reagent. Because GDH was the only source of enzymes in the study of the dependence of SMS activity of various reagents, further studies were made to evaluate the requirement of GDH. GDH solutions which had been heated at various temperatures for 10 minutes were used in two ways: to assay the activity of purified GOT (Sigma) according to the routine procedure described; and to assay the response of 1.2 ml. of SMS fraction as described in the SMS reagent study, but with the aspartic acid omitted from the sample cups. In both cases, the amount of GDH added was limiting so that any decrease in GDH activity would result in a proportional decrease in the overall rate. The results are shown in Figure 5. No attempt was made to run blanks for each point, so the slight residual activity above 65° C. does not mean that the GDH activity was not completely destroyed.

That the heat destruction curves were essentially the same in each series shows that the GDH activity itself was required in both the GOT and SMS assays. That is, if some of the response from the SMS fraction had been due to some activity (enzymic) contained in the GDH which was not GDH or did not require GDH, the heat destruction for SMS would have been different, and the SMS response might have persisted, even after the destruction of GDH.

ABBREVIATIONS

GDH = glutamic dehydrogenase
GOT = glutamic oxaloacetic transaminase
GPT = glutamic pyruvic transaminase
GXT = general transaminase
αKG = α-ketoglutarate
LMS = large molecular size
NAD = nicotinamide adenine dinucleotide
$NADH_2$ = reduced NAD
PMS = phenazine methosulfate
PSP = pathological serum pool
SMS = small molecular size

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Preconcentration of Trace Elements by Precipitation Ion Exchange

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▷ A new approach to preconcentration of trace elements, precipitation ion exchange, is demonstrated whereby matrix and traces are sorbed on a cation exchange column, the matrix is precipitated by concentrated HCl, and traces are then eluted with additional HCl. The separation is based on the insolubility of the matrix and the low selectivity of the traces in 12.2M HCl. Many trace elements were found to be concentrated in greater than 90% yields, matrix-free or with only small amounts of matrix from NaCl, KCl, $BaCl_2$, $SrCl_2$, and AgCl.

ION EXCHANGE methods of separation are generally based on differences in selectivity of the various species for the resin, and preferential separations may be further effected in some cases by complexation of the ionic species in solution (*7*) or by the use of chelating resins (*4*).

For the simultaneous separation of many elements at the trace level from large amounts of a matrix or major element, the aspect of selectivity is too restrictive to permit general applicability to different matrix-trace combinations. Although a few specific macro separation procedures have been studied using precipitation in conjunction with ion exchange, the basis was a difference in solubility due either to amphoteric behavior (*1, 5, 8, 9*) or to the formation of soluble complexes (*2*).

A new approach was investigated that would minimize the aspect of selectivity and still preserve a number of the advantages of column ion exchange. This was accomplished by the immobilization of the matrix on the column by precipitation, followed by the nonselective elution of as many elements as possible; before breakthrough of the matrix by dissolution of the precipitate. The applicability of the approach is governed by two main conditions. First, the matrix must be insoluble or only sparingly soluble in the eluent to prevent early breakthrough, and, second, the trace elements must have a very low distribution coefficient (preferably $D_v << 1$) in the eluting medium to permit a high yield of recovery in a small volume. This implies the use of an eluent of high ionic strength, in which case the sorption of many elements is greatly suppressed. The approach was tested in this study using matrix elements whose chlorides are insoluble in 12.2*M* HCl.

EXPERIMENTAL

Reagents and Tracers. All reagents used were of reagent grade. Dowex 50-X8, 100 to 200-mesh (J. T. Baker Co.) cation exchange resin was employed for column operations and was purified by passing large excesses of 6*M* and 2*M* HCl and washing thoroughly with distilled water until a negative acid test was obtained. Radioactive tracers Na^{22}, Rb^{86}, Ba^{133}, Co^{60}, Ag^{110}, Zn^{65}, Cd^{109}, and Sn^{113} were obtained from the Oak Ridge National Laboratory and Isoserve, Inc.

Apparatus. Eluate fractions were obtained using a Research Specialties Co. automatic fraction collector. Radioactive counting equipment consisted of a sodium iodide well-type scintillation crystal and Baird-Atomic scaler. An ORNL Model VI flame photometer employing a 0.5-meter Ebert monochromator was used for flame photometric measurements.

Procedure. The study of the recovery of trace elements from the various matrices was performed using the following procedure, each trace element being studied individually. Whenever feasible, radioactive tracers were employed; otherwise, flame photometry or precipitation of the eluted trace was used. Confirmation of the reliability of the radioactive studies was established by flame photometric analysis. The studies of the various matrix and trace elements involved the following sequence: sorption of the sample (matrix and trace) on the cation exchange resin, precipitation of the matrix on the resin, and elution of the trace elements.

SORPTION. Twelve milliequivalents of the respective matrix elements studied (Na^+, K^+, Ba^{+2}, Sr^{+2}, Ag^+) were sorbed at a flow rate of 0.5–1 ml. per minute on a 0.8-cm. diameter column containing 7 ml. of wet Dowex 50-X8 resin and then washed with 3 to 5 ml. of water to ensure complete sorption. The eluate from this operation—containing elements that are not sorbed on a cation exchange column—was collected and combined with the eluate obtained in the elution step below. The optimum resin volume was previously established by breakthrough experiments. The resin containing the sorbed matrix and trace elements was then suction dried for $^1/_2$ hour. In the study of Sr as a matrix element, the resin was additionally washed with methyl alcohol to remove residual gel water to decrease the solubility of $SrCl_2$ during subsequent precipitation.

PRECIPITATION. The dried resin containing the matrix and trace elements was transferred to a 1.1-cm. diameter column containing fresh resin previously equilibrated with 12.2*M* HCl. The level of HCl in this second column was approximately 5 ml. above the resin. Complete transfer was facilitated by subsequent washing of the first column with 1 ml. of 12.2*M* HCl. The volume of equilibrated resin employed varied with the matrix element being studied and will be described later. In the study with Ag both the column and eluent were maintained at ice bath temperature (~1° C.). At this point in the procedure the low solubility of the matrix metal chloride in 12.2*M* HCl resulted in precipitation in the resin network.

ELUTION. The system was allowed to settle before the trace elements were eluted from the precipitated matrix using 12.2*M* HCl at a flow rate of 0.3

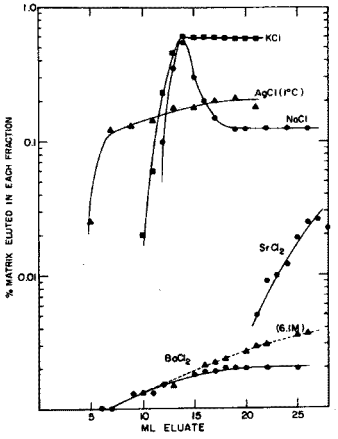

Figure 1. Elution behavior of insoluble chloride matrices

Amount of matrix: 12 meq.
Eluent: 12.2M HCl
Flow rate: 0.3–0.5 ml./minute

ml. per minute. Only when $BaCl_2$ was used as a matrix was it necessary to elute with 6.1*M* HCl after the initial precipitation with 12.2*M* HCl. The eluate containing those trace elements that were not initially sorbed on the resin was combined with the above eluate. In general 20 ml. of eluate was sufficient to recover the trace elements in greater than 90% yield with minimum accompaniment of matrix.

RESULTS AND DISCUSSION

Solubility of Matrix. An investigation of the solubility of various metal chlorides in 12.2*M* HCl was performed to ascertain which matrices would be applicable. Column behavior studies of the more insoluble chlorides using the procedure described in the experimental section revealed that breakthrough of the matrix could be sufficiently delayed in the case of $BaCl_2$, $SrCl_2$, NaCl, KCl, and AgCl to permit prior elution of trace elements (Figure 1). The volume of resin equilibrated with concentrated HCl required in the column to delay breakthrough was found to depend on the solubility of the respective chlorides, the more insoluble $BaCl_2$ and $SrCl_2$ requiring 3.9 ml. and the NaCl, KCl, and AgCl requiring 11.5 ml. of resin. Although all of these salts are relatively insoluble in 12.2*M* HCl, the residual water in the dried resin from the first column containing the sorbed sample when eluted with 12.2*M* HCl is displaced down the column causing some dilution of the acid, and therefore increasing solubility of the matrix chloride. Using a column of increased length served to delay breakthrough. An experiment to determine the effect of amount of matrix on its breakthrough revealed that doubling the amount of NaCl from 12 to 24 meq. (initially sorbed on 7 and 14 ml. of resin, respectively) resulted in breakthrough of NaCl at the same point but the amount coming through doubled.

Lowering the temperature of the column and eluent to 1° C. decreased the amount of breakthrough of AgCl about five-fold rendering it applicable to this approach. The decrease from room temperature to ~ 1° C. was not, however, sufficient to decrease the solubility of LiCl, RbCl, CsCl, $MgCl_2$, or $CaCl_2$. These salts broke through in sufficiently high amounts (1–10% per ml.) so as to prevent their easy applicability in preconcentration applications. A slight increase in the elution maximum for RbCl was observed as the lower temperature was used.

Trace Recovery. The study of the separation and preconcentration of trace elements by precipitation of the matrix on the cation exchange column was performed using 11 trace elements in NaCl matrix. The elution behavior of the various trace elements and matrix are shown in Figure 2, the arrows indicating the volume of eluate containing yields of 90% or higher of the various trace elements. Further elution always resulted in 100% yields but with the accompaniment of small amounts of the matrix due to its slight solubility in the additional volume of eluent. The amounts of trace studied in many cases varied from carrier-free isotopes to 10-mg. amounts with no apparent effect of concentration on the elution behavior.

Preconcentration of trace elements from $BaCl_2$ was studied using eight trace elements. In this case both 12.2*M* and 6.1*M* HCl were used as eluents, the latter being introduced after 10 ml. of the former had passed through the column. When only 12.2*M* HCl was used, long tailing of trace elements occurred, indicating partial trapping of these elements inside the resin gel because of the blocking of the gel network by the precipitated $BaCl_2$. Using 6.1*M* HCl this effect was less pronounced, so that diffusion of water and electrolytes through the resin was facilitated. The results of the elution of trace elements from $BaCl_2$ matrix are shown in Figure 3.

The generality of the approach to the

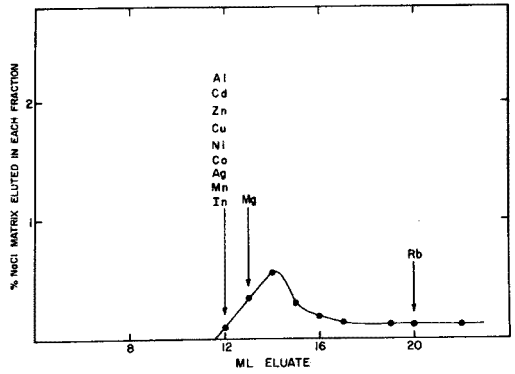

Figure 2. Separation of trace elements from NaCl matrix

Amount of matrix: 12 meq. (0.702 gram)
Eluent: 12.2M HCl
Flow rate: 0.3–0.5 ml./minute
Arrows indicate volume of eluent containing yields of 90% or higher of trace element

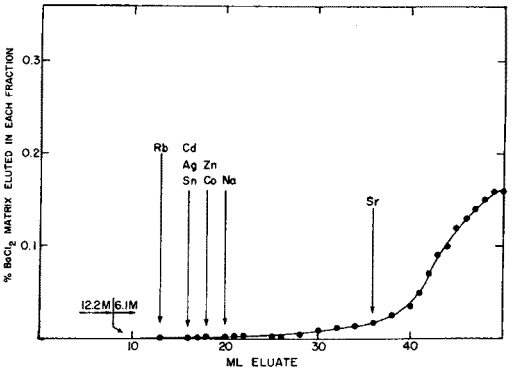

Figure 3. Separation of trace elements from $BaCl_2$ matrix

Amount of matrix: 12 meq. (1.466 grams $BaCl_2 \cdot 2H_2O$)
Eluent: 12.2M and 6.1M HCl
Flow rate: 0.3–0.5 ml./minute
Arrows indicate volume of eluate containing yields of 90% or higher of trace element

Table I. Estimated Volume Distribution Coefficients in 12M HCl (6)

D_v	Element
$\ll 1^a$	Cs, Be, Mg, V^{+4}, Mn, Co, Ni, Cu, Ag, Zn, Cd, Hg, Al, In, Sn, Pb, As, Sb^{+3}, Bi, $B(H_3BO_3)$, $N(HNO_3)$, $P(H_3PO_4)$, $S(H_2SO_4)$, Se, Te, Po, Br, I, Ru, Rh, Pd, Re, Os, Ir, Pt
<1	Li, Na, K, Rb, Pa, Cr^{+3}, Mo, W, U^{+6}
1–10	Ra, Y, R. E., Ti, V^{+5}, Nb, Cr^{+6}, Tl^{+3} Sr, Ba, Zr, Hf
10–100	Ca, Sc, Th^{+4}
>100	Ga, Au, Fe, Sb^{+5}

[a] Arbitrary classification where most values are estimated to be less than 0.3 based either on behavior up to 9*M* HCl or from observation in 12.2*M* HCl elutions.

separation and preconcentration of trace elements in $SrCl_2$ matrix was substantiated using Na and Co traces. Complete recovery of Co and 81% recovery of Na were effected before elution of the matrix occurred. A higher recovery of Na, matrix-free, could have been achieved with a longer column. Similarly, 93% of Co trace was recovered matrix-free from KCl matrix using the same procedure. At a reduced temperature of 1° C. it was possible to recover 97% Co trace from AgCl matrix in 16 ml. of eluate (~1.5% of matrix).

From these experiments it appears that the elution behavior of trace elements from the matrix precipitated on the cation column is governed mainly by their distribution coefficients. Those trace elements in NaCl which were obtained with a 90% yield or higher either matrix-free or with minor matrix accompaniment all have $D_v < 1$. An exception was Rb where possible interaction between trace and precipitated matrix slightly delayed the elution of Rb. Since no tailing occurred here, the effect may be caused mainly by weak physical adsorption of the trace on the precipitate.

The elution of elements possessing a somewhat higher distribution coefficient such as Li ($D_v \sim 1$) was delayed resulting in contamination with some matrix to a degree determined primarily by the distribution coefficient of the trace and the solubility of the matrix. In general, the lower the distribution coefficient of the trace and the less soluble the matrix, the higher the yield in a given volume and the higher is the preconcentration factor.

Since many elements form negatively charged chloride complexes in concentrated HCl as shown by their adsorbability on anion exchange resins (*3*), they will not be adsorbed significantly on a cation exchange resin under these conditions. This is also predicted on the basis of the mass action relationship. Notable exceptions are the strong adsorption of Fe(III), Ga(III), Sb(V), Th(IV), Sc(III), and Au(III) on strongly acidic cation exchange resins from concentrated HCl (*6*). The lighter rare earth elements and Ca, Sr, Ba, Y, Ti, Zr, Hf, and Ti show moderate adsorption ($D_v \sim 10$) under these conditions. On the basis of the volume distribution coefficients in 12*M* HCl summarized in Table I, it should be possible to predict the elution behavior of the elements.

To a first approximation, it is possible to predict the elution volume of a trace element from the relationship

$$D_v = V_{max} - i \qquad (1)$$

where D_v is the volume distribution coefficient of the element, V_{max} is the number of column volumes at which the element appears in maximum concentration, and i is the fractional interstitial volume. With a knowledge of the breakthrough behavior of the matrix and Equation 1 one can predict which trace elements can be obtained in high yield and what the preconcentration factor will be. According to Table I it should be possible to recover at least 30 trace elements from NaCl and at least 40 elements from $BaCl_2$ with high yields, matrix-free or with minor matrix contamination in a small volume.

Elements with $D_v > 1$ cannot be separated matrix-free or with only minor matrix contamination by this approach unless the matrix is extremely insoluble—e.g., $BaCl_2$.

Precipitate. In the method described it was considered advantageous to have both the matrix and the trace elements sorbed on the cation resin before precipitation was effected. Thus, when precipitation occurred the crystals of matrix formed over a large area in the network of the resin, permitting the efficient washing of the matrix and removal of adsorbed trace elements. Microscopic examination of the resin after precipitation revealed that the bulk of the precipitate existed inside the beads of the resin. The alkali and alkaline earth chlorides form fine crystalline precipitates in the column with a minimum of adsorption and occlusion of trace elements. The elution process provides efficient washing of the precipitate without appreciable solubility as would occur in a conventional gravimetric procedure. Also, the volume of eluate containing a high yield of the trace elements is much smaller than that obtained by washing of a precipitate by conventional means.

The effect of cross-linkage of the resin over the range of 4–12% on the elution of traces was examined using $SrCl_2$ as matrix and found not to be a factor. The resin mesh size was examined in connection with the precipitation of $BaCl_2$, however, and found to be important. A 100- to 200-mesh resin resulted in optimum behavior. A finer particle size resin (200- to 400-mesh) resulted in impractically long elution times, whereas a coarser resin (20- to 50-mesh) resulted in extreme broadening and tailing of the elution curve of the traces.

Analytical Applicability. This preconcentration approach has great potential for the analysis of high purity alkali and alkaline earth salts in the parts per billion range. The sensitivity of existing analytical techniques for impurities in these electronically important materials is greatly limited because of the effect of the matrix, either as an interference, as a diluent which limits the attainment of ultimate sensitivity, or because of interelement effects. The preconcentration of many elements in high yield from the matrix in a small volume of 12.2*M* HCl provides easy coupling with emission spectrometry, flame photometry, or other sensitive methods of estimation. The only reagent used in the procedure is concentrated HCl and only small volumes are employed so that the danger of contamination is greatly minimized. Transistor grade HCl of very high purity is commercially available. Finally, the small volume of eluate can be easily evaporated to permit completion of an analysis where necessary without loss or contamination.

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Solvent Extraction Equilibria of Certain 8-Quinolinols and Their Zinc(II) Chelates

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▶ Equilibrium distribution ratios have been determined for the extraction of zinc(II) with 8-quinolinol, 2-methyl-8-quinolinol, and 4-methyl-8-quinolinol into chloroform as a function of pH and reagent concentration at 25° C. Except in the case of 2-methyl-8-quinolinol, which involved a simple 1:2 chelate, the extractable complexes were 1:2 chelates to which a third molecule of reagent was coordinated. The overall formation constants of the zinc chelates in aqueous solution have been determined. The distribution coefficients of the chelates and chelate adducts are discussed in terms of structural influences. The analytical advantages of the use of 2-methyl-8-quinolinol in the extraction and subsequent determination of zinc(II) are outlined.

THE REACTION of bidentate chelating agents in aqueous media with metal ions whose coordination number is greater than twice the charge, results in the formation of chelates in which molecules of water occupy the additional coordination sites. In order to improve the extractability of these chelates some or all of the water molecules must be replaced by organic ligands, usually monodentate, called adducts (*1*). Thus, butyl Cellosolve (*3*) and butylamine (*10*) have been found to improve the extraction of the magnesium chelate of 8-quinolinol. Similarly, the extraction of the zinc chelate of 8-quinolinol was significantly improved through the formation of alcohol and amine adducts (*11*). In certain cases, chelating agents used in an extraction can also function as monodentate or chelating adducts. In view of the high coordinating tendency and the organophilic nature of most ligands, one would expect adduct formation in all such cases unless the additional coordination is sterically inhibited.

An experimental test of this hypothesis can be made with the extraction of zinc(II) with both 2-methyl and 4-methyl-8-quinolinol. Inasmuch as conflicting reports on the nature of the adduct formed in the extraction of zinc with 8-quinolinol have appeared in the literature (*4*, *7*), it was decided to reinvestigate this system also.

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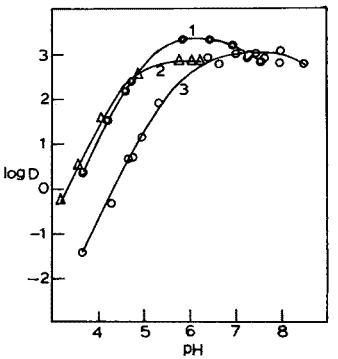

Figure 1. Distribution of zinc(II) chelates of 8-quinolinols between chloroform and water

1. 4-Methyl-8-quinolinol. $[HOx]_0 = 0.12M$
2. 8-Quinolinol. $[HOx]_0 = 0.17M$
3. 2-Methyl-8-quinolinol. $[HOx]_0 = 0.36M$

EXPERIMENTAL

Apparatus. An Eberbach Box Shaker in which 45-ml. cylindrical tubes, with plastic screw cap stoppers, could be accommodated was used to equilibrate the solutions at 25° ± 0.5° C.

Radioisotope counting was carried out with a Nuclear-Chicago Model DS-55 Well Type Scintillation Detector connected to a Model 192A Scalar, and a Model 1810 Radiation Analyzer.

A Beckman Model G pH meter with a glass and saturated calomel electrode pair was calibrated with Beckman buffer solutions at pH 4.00 and 7.00, and used for all pH measurements.

Materials. A.R. grade 8-quinolinol (Mallinckrodt), and 2-methyl-8-quinolinol (Eastman Kodak Co.) were recrystallized from absolute ethanol to give products having melting points at 72.5° to 73.5° C. and 74.5° C., respectively.

4-Methyl-8-quinolinol was synthesized from *o*-aminophenol and methylvinyl ketone as described by Phillips, Elbinger, and Merritt (*6*). The crude product was purified by vacuum distillation followed by two recrystallizations from absolute ethanol. The melting point of the purified product was 140° to 142° C. (lit. 141° C.).

Carrier free Zn^{65} radiotracer solutions (10^{-4} to $10^{-5}M$) were used in all the chelate extraction experiments. The solutions were buffered and the radioactivities were between 10^{-3} mc./ml. to 10^{-2} mc./ml.

Hydrochloric acid–potassium acid phthalate buffer solutions were used in the pH range 2–4; acetic acid–sodium acetate buffers in the pH range 4–6, and ammonia–ammonium chloride buffer solutions were used in the pH range 7–9. Sodium perchlorate was added to the buffers to maintain a constant ionic strength at 0.1.

All other chemicals were of A.R. grade and used without further purification.

Procedure. Ten milliliters of buffered Zn^{65} solution at a constant ionic strength (0.1) and 10 ml. of reagent solution (10^{-2} to $1.9M$) in chloroform, were equilibrated by shaking for 6 minutes, an adequate time for the attainment of equilibrium. The mixtures were then allowed to stand for 10 minutes. The pH value of the aqueous phase after extraction was taken as the equilibrium pH value. After phase separation, equal volume aliquots of both phases were pipetted out and counted separately.

RESULTS AND DISCUSSION

In general, the extraction of a simple chelate can be described by a plot of log D *vs.* pH, at constant reagent concentration in the organic phase, which consists essentially of two linear portions. Starting at a low pH, the log D increases with a slope of n (where n is the number of protons released on chelate formation) and then eventually reaches a constant, pH-independent, value determined by the distribution coefficient, K_{DC} of the chelate. At a higher value of the reagent concentration the entire curve shifts to the left—i.e., to a region of lower pH, without alteration of either the slope or the value of the maximum log D, which remains equal to log K_{DC}. When the extractable complex is an adduct rather than a simple chelate, the entire extraction curve will be affected by the adduct reagent concentration. In the event that the chelating agent is also involved in adduct formation, an increase in reagent concentration will cause the plateau portion of the extraction curve to shift to a higher log D, the initial linear portion of the curve to shift to a lower

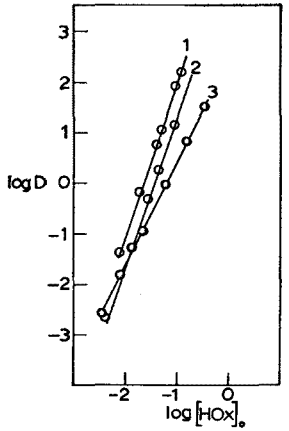

Figure 2. Distribution of zinc(II) chelates of 8-quinolinols between chloroform and water

1. 4-Methyl-8-quinolinol at pH 4.63
2. 8-Quinolinol at pH 4.56
3. 2-Methyl-8-quinolinol at pH 4.60

pH, but without changing its slope. In Figure 1 is shown the extraction curves (log D *vs.* pH) for the three reagents in the lower pH range. The slopes are each 2, which shows that in each of these extractions, two protons are released on the formation of the extractable complex.

From similar plots of log D *vs.* the logarithm of the reagent concentration, the slopes will show the number of reagent molecules incorporated in the extractable complex. Such plots were constructed for the extraction of zinc(II) with the 8-quinolinols as shown in Figure 2. The behavior of the 2-methyl-8-quinolinol extraction indicates that the extractable complex is the simple chelate since two reagent molecules per zinc ion are involved in the extraction. From the extraction curve shown in Figure 3 the value of K_{DC} for the 2-methyl-8-quinolinol chelate of zinc is obtained from the maximum value of D (Table I). Using this value, the overall formation constant ($K_1 \cdot K_2$) for this chelate in an aqueous medium may be calculated from the $pH_{1/2}$ value of the extraction curve (Table I). In the case of 8-quinolinol and the 4-methyl derivative, three reagent molecules are involved, which clearly indicate the importance of adduct formation in these extractions. The quantitative description of such extraction curves as well as the evaluation of the constants characterizing the reactions involved in the extraction are based on the following considerations.

Aqueous phase reactions:

Dissociation of the reagent

$$HOx \overset{K_a}{\rightleftharpoons} H^+ + Ox^- \quad (1)$$

Formation of the chelate

$$Zn^{+2} + Ox^- \overset{K_1}{\rightleftharpoons} ZnOx^+ \quad (2)$$

$$ZnOx^+ + Ox^- \overset{K_2}{\rightleftharpoons} ZnOx_2 \quad (3)$$

Formation of the adduct

$$ZnOx_2 + \mathbf{a}HOx \overset{K'}{\rightleftharpoons} ZnOx_2 \cdot \mathbf{a}HOx \quad (4)$$

Distribution equilibria:

$$K_{DR} = \frac{[HOx]_0}{[HOx]} \quad (5)$$

$$K_{DC} = \frac{[ZnOx_2]_0}{[ZnOx_2]} \quad (6)$$

$$K'_{DC} = \frac{[ZnOx_2 \cdot \mathbf{a}HOx]_0}{[ZnOx_2 \cdot \mathbf{a}HOx]} \quad (7)$$

The distribution ratio is given by:

$$D = \frac{[Zn]_0}{[Zn]} = \frac{[ZnOx_2]_0 + [ZnOx_2 \cdot \mathbf{a}HOx]_0}{[Zn^{+2}] + [ZnOx^+] + [ZnOx_2] + [ZnOx_2 \cdot \mathbf{a}HOx]} \quad (8)$$

Equation 8 may be modified when adduct formation predominates by incorporating the assumptions that the simple chelate, $ZnOx_2$, is not extracted to a significant extent and that, of the possible adduct complexes, $\mathbf{a} = 1$ to $\mathbf{a} = \mathbf{a}$, only the last is of importance. This latter assumption is quite reasonable since HOx is always present in large excess and the stepwise formation constants in a series of complexes with a monodentate ligand are usually closely spaced. The value of $\mathbf{a}$ can be determined from a plot of log D, for the zinc extraction, *vs.* log $[HOx]_0$. The slope of the resulting line is $(2 + \mathbf{a})$ since two reagent molecules are involved in the formation of the simple 1:2 chelate. As can be seen from Figure 2, the value of $\mathbf{a}$ for the 8-quinolinol and 4-methyl-8-quinolinol systems is unity and that for the 2-methyl-8-quinolinol system is zero—i.e., no adduct formation is involved in the extraction of the zinc chelate of 2-methyl-8-quinolinol.

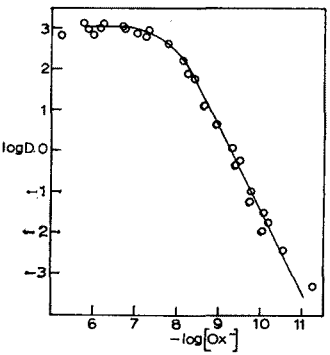

Figure 3. Distribution of zinc(II) chelate of 2-methyl-8-quinolinol at various values of pH and $[HOx]_0$

For the systems involving adduct formation, substitution of the appropriate equilibrium expressions in Equation 8 gives

$$D = \frac{K_1 K_2 K'_{DC} K' \cdot [Ox^-]^2 [HOx]_0}{K_{DR}\left\{1 + K_1[Ox^-] + K_1K_2[Ox^-]^2 + \frac{K_1K_2K'}{K_{DR}}[Ox^-]^2 \cdot [HOx]_0\right\}} \quad (9)$$

At the lower pH range, in which Zn^{+2} is the predominant species in the aqueous phase, Equation 9 may be simplified to

$$D = \frac{K_1 K_2 K'_{DC} K' [Ox^-]^2 [HOx]_0}{K_{DR}} \quad (10)$$

or

$$\log D - \log [HOx]_0 = \log \frac{K_1 K_2 K'_{DC} K'}{K_{DR}} + 2 \log [Ox^-] \quad (11)$$

According to Equation 11, a plot of (log D − log $[HOx]_0$) *vs.* log $[Ox^-]$ should give a straight line of slope 2 and intercept log $(K_1K_2K'_{DC}K')/K_{DR}$. The validity of Equation 11 in the description of the extraction of the 8-quinolinol and 4-methyl-8-quinolinol zinc(II) chelates may be seen from Figures 4 and 5.

Table I. Summary of Equilibrium Constants

	Species extracted	log K_{DC}	log $K'_{DC}K'$	log K_1K_2	log K_1K_2 (50% *v./v.*) aqueous dioxane
8-Quinolinol	$MR_2 \cdot HR$	...	6.22 ± 0.05	17.06 ± 0.20	18.86[a]
2-Methyl-8-quinolinol	MR_2	2.99 ± 0.07	...	15.68 ± 0.08	18.28[b]
4-Methyl-8-quinolinol	$MR_2 \cdot HR$	...	7.44 ± 0.03	18.11 ± 0.19	20.24[a]

[a] Johnston, W. D., Freiser, H., *Anal. Chim. Acta.* 11, 201 (1954).
[b] Takamoto, S., unpublished results, University of Arizona, Tucson, Ariz., 1964.

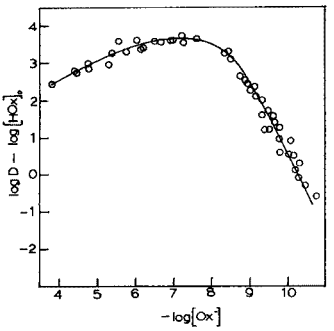

Figure 4. Distribution of zinc(II) chelate of 8-quinolinol between chloroform and water at various values of pH and $[HOx]_0$

At the higher pH range where the predominant metal containing species in the aqueous phase is either $ZnOx_2$ of $ZnOx_2 \cdot HOx$, Equation 9 may be simplified either to

$$\log D_{max} = \log [HOx]_0 + \log \frac{K'_{DC}K'}{K_{DR}} \quad (12)$$

or

$$\log D_{max} = \log K'_{DC} \quad (13)$$

respectively. If $ZnOx_2$ predominates in the aqueous phase then, according to Equation 12, the plot of ($\log D - \log [HOx]_0$) *vs.* $\log [Ox^-]$ should reach a constant maximum value at high $\log [Ox^-]$ values. If the adduct species, $ZnOx_2 \cdot HOx$, predominates in the aqueous phase, then such a plot would not give constant values according to Equation 13. Inasmuch as a plateau in these plots for 8-quinolinol and 4-methyl-8-quinolinol is not obtained at high $\log [Ox^-]$ values (Figures 4 and 5), it can be concluded that the adduct is not an important species in the aqueous phase. This results as much from the large water: 8-quinolinol concentration ratio in the aqueous phase as from the relative coordinating ability of water and 8-quinolinol as adduct reagents.

The values of the equilibrium constants of chelate formation and extraction are summarized in Table I. The value of $\log K'_{DC}K'$ for 8-quinolinol and the 4 - methyl - 8 - quinolinol were evaluated from $\log D_{max}$ shown in Figures 4 and 5 with the help of previously reported K_{DR} values (*2*), according to Equation 12. These values when substituted in Equation 11 permitted the calculation of the overall chelate formation constants by using the best straight line from the data in the appropriate parts of the extraction curves shown in Figures 4 and 5.

This study has revealed an important difference between the behavior of zinc(II) and 2-methyl-8-quinolinol from that of the other reagents. The reason for this difference, the extraction of the simple chelate, probably results from the steric hindrance to adduct formation presented by the substituent n the 2-position. This steric hindrance must extend to the hydration of the chelate as well since the results indicate that the extracted chelate is not hydrated. If the extracted chelate were hydrated, it would be expected that the 8-quinolinol, or certainly the 4-methyl-8-quinolinol, extractions at low reagent concentrations would have resembled those of the 2-methyl-8-quinolinol. Furthermore, the observed K_{DC} value of the zinc(II)-8-quinolinol chelate is only twenty-five times smaller than that observed for the corresponding copper(II) chelate (*2*) which is probably not hydrated.

Although K' and K'_{DC} cannot be evaluated separately it is possible to estimate an approximate maximum value for K'. Since, as mentioned above, the concentration of the adduct in the aqueous phase is small compared to that of the normal chelate, in both the 8-quinolinol and 4-methyl-8-quinolinol cases, we can assume a maximum ratio of these two species in either case as 1:1 which more than adequately allows for uncertainties introduced by the scatter in the experimental data. On this assumption the maximum value of K' for both 8-quinolinol and 4-methyl-8-quinolinol is $10^{2.6}$. This would mean that the minimum values for $\log K'_{DC}$ are 3.6 and 4.8 for the zinc chelate adducts of 8-quinolinol and 4-methyl-8-quinolinol, respectively. A reasonable value of K_{DC} for the nonhydrated 4-methyl-8-quinolinol chelate is $10^{3.0}$, the same as that for the 2-methyl-8-quinolinol chelate. Hence it may be concluded that adduct formation has increased the K_{DC} value by a factor of at least $10^{1.8}$. Based on the assumed similarity in the effect of a methyl substituent on the K_{DC} values of the copper(II)- and zinc(II)-8-quinolinol chelates, one can estimate a value of $\log K_{DC}$ for the nonhydrated zinc(II)-8-quinolinol chelate to be 1.0 unit lower than the 2-methyl analog (*2*). In this event the effect of adduct formation on the increase in K_{DC} value is a factor of $10^{1.6}$, in close agreement with the behavior of the 4-methyl-8-quinolinol.

The values of the overall formation constants obtained from the extraction curves are in good agreement with those obtained by potentiometric titration in 50% v./v. aqueous dioxane, allowing for the difference in the medium. The apparent discrepancy in the case of the formation constant of the 2-methyl-8-quinolinol–zinc(II) chelate did not disappear upon extensive redetermination of the extraction equilibria.

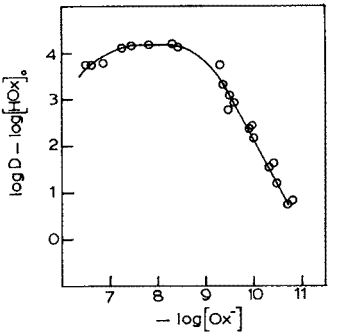

Figure 5. Distribution of zinc(II) chelate of 4-methyl-8-quinolinol between chloroform and water at various values of pH and $[HOx]_0$

Although the appreciation of the importance of reagent concentration in metal chelate extraction in general is not new (*5*), this factor is seen to assume even greater significance where adduct formation is involved. Thus the conflicting reports about the completeness of the extraction of zinc(II) with 8-quinolinol (*8*, *9*) can now be resolved.

From this work it may be concluded that the use of 2-methyl-8-quinolinol offers a distinct advantage in the extraction of zinc(II) for analytical application. It is possible to quantitatively extract zinc with this reagent at relatively low reagent concentrations, resulting in an increased flexibility with regard to methods of determination of zinc following its separation.

In extractions of other metals in the presence of zinc, either 8-quinolinol or its 4-methyl derivative may be used to better advantage than the 2-methyl derivative, if care is taken to keep the reagent concentration as low as possible.

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Determination of Tin in Hydrogen Peroxide Solutions by Atomic Absorption Spectrometry

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▷ **Atomic absorption spectrophotometry has been successfully applied to the determination of tin in hydrogen peroxide solutions. A sample diluted to contain 45% or less hydrogen peroxide is injected directly into an oxyhydrogen flame, and absorption of the tin 2863-A. line by the tin atoms in the flame is measured. Tin concentration is obtained by reference to a calibration curve prepared by injecting known concentrations of sodium stannate in hydrogen peroxide into the flame. The concentration of hydrogen peroxide is not critical. As little as 0.05 mg. per liter of tin in 90% hydrogen peroxide can be determined. The effects of other materials added to hydrogen peroxide solutions (phosphate, pyrophosphate, sodium nitrate) were established.**

HYDROGEN peroxide solutions containing 70 to 90% hydrogen peroxide undergo slow decomposition; therefore, for long-term storage, it is necessary to add stabilizers such as sodium stannate, sodium pyrophosphate, phosphoric acid, and sodium nitrate. The amounts added depend upon the intended use of the peroxide solution and range from less than 2.0 to 50 mg. per liter of tin, less than 0.1 to 40 mg. per liter of phosphorus, and about 100 to 400 mg. per liter of sodium nitrate. For proper performance and storage of the hydrogen peroxide, the concentration of stabilizers must be maintained over a narrow range. This report is concerned with the determination of tin. Solutions of sodium stannate in hydrogen peroxide are unstable and frequent testing is required.

The tin content of hydrogen peroxide is normally measured by decomposing the peroxide and measuring the tin content of the resulting aqueous solution by spectrophotometric or polarographic methods. The chief difficulty encountered in these methods is that stannic ions in hydrogen peroxide tend to form polymers, which are unreactive. It is necessary to treat the solution to decompose the polymers. One of the most effective treatments is to heat the solution to fumes of sulfuric acid. However, one is never sure that all of the tin polymers have been decomposed and the extra manipulations required plus the need for decomposing peroxide are time-consuming. Thus, use of atomic absorption spectrophotometry for the determination of tin in hydrogen peroxide has been investigated.

The author is unaware of any specific analytical application of atomic absorption to the determination of tin. Gatehouse and Willis (*3*) measured the limits of detection of many metal ions and report a limit of detection (amount of metal which gives an absorption of 1%) of 5 p.p.m. for tin. This limit of detection is too high for many formulations. The sensitivity of atomic absorption measurements can be increased by increasing the absorption pathlength. A long path can be obtained by directing the atomizer-burner into a long quartz tube and passing light to be absorbed axially through the tube (*2*). By use of such a device, the limit of detection (concentration which gives 1% absorption) of tin was lowered to 0.025 p.p.m. Conditions have been established for the determination of tin in hydrogen peroxide by diluting the peroxide, injecting it into a hydrogen-oxygen flame, and measuring the absorption of the tin 2863-A. line. Other materials added to hydrogen peroxide as stabilizers gave no interference.

EXPERIMENTAL

Apparatus. The apparatus is shown schematically in Figure 1. Modulated (60 cycle) light from a hollow cathode tube emitting the tin 2863-A. line is focused on the entrance of the absorption tube. The light goes through the tube and enters the monochromator (Jarrell-Ash, Ebert Model 8200 equipped with 100-micron entrance and exit slits), and 2863-A. tin line is detected by the photomultiplier (1P28). Output of the photomultiplier is amplified by an a.c. amplifier and displayed on a recorder.

Normally, sample is drawn into the flame by the Beckman atomizer-burner. With 45% hydrogen peroxide, the peroxide decomposed in the stainless steel capillary of the burner through which the peroxide flowed, and oxygen gas formed in decomposition caused an uneven aspiration. The sporadic operation led to a variation in the absorbance. The effect was greatly decreased, but not eliminated, by forcing the sample to the burner with a motor-driven syringe.

Absorbance, which is dependent upon the sample flow rate, is taken as the average of the recorded trace, and can be established with good accuracy. Maximum absorbance is observed between 2.5 and 5 ml. per minute.

A sample flow of 2.5 ml. per minute was used. To minimize decomposition of hydrogen peroxide, the syringe was all glass and connection to the burner was a Teflon needle (Hamilton Co., Inc., Whittier, Calif.). The burner was a Beckman large bore atomizer-burner (Beckman Instrument, Inc., Fullerton, Calif.).

Hydrogen and oxygen flow rates are controlled by the regulator unit used with Beckman flame photometers. The burner is positioned so the flame enters the quartz absorption tube (40 cm. long

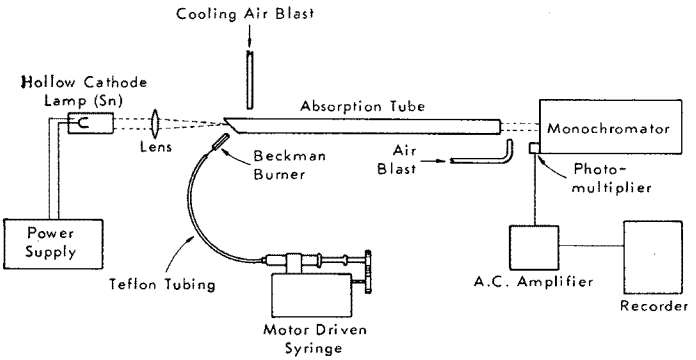

Figure 1. Atomic absorption apparatus with absorption tube

and 9 mm. in diameter). A vigorous air blast is directed against the tube as shown to prevent the flame from melting a hole in the tube. A second vigorous air blast, directed across the tube exit, blows the hot exit gases away from the monochromator and terminates the absorption path. Air outlets are 1/4-inch copper tubing, and the outlet at the tube exit has its end flattened to spread out the air blast. Air at 30 p.s.i. is supplied to these tubes.

Procedure. Apparatus Preparation. Turn on the hollow cathode power supply (60 c.p.s.) and adjust output to 5.0 ma. Turn on the hollow cathode lamp, a.c. amplifier, and recorder, and allow them to warm up for 1/2 hour before use. Apply 750 volts to the photomultiplier tube and align the apparatus so light from the hollow cathode lamp focuses on the quartz tube entrance and enters the monochromator.

Set the wavelength dial on the monochromator to 2863 A. and adjust until the recorder shows maximum transmittance. Adjust the amplifier gain to give a reading of 100 on the recorder.

Calibration. Prepare a standard tin solution containing 10.0 mg. per liter of tin by dissolving 22.5 mg. of sodium stannate ($Na_2SnO_3 \cdot 3H_2O$) in 1 liter of approximately 45% hydrogen peroxide solution. Use hydrogen peroxide free from tin. Tin solutions are unstable and should be discarded after 2 days.

Dilute the 10.0 mg. per liter tin standard with approximately 45% hydrogen peroxide to prepare 50-ml. portions of solutions containing 1.0, 0.5, and 0.2 mg. per liter of tin. Fill 10-ml. syringes with these solutions and fill one syringe with 45% tin-free hydrogen peroxide.

Remove the burner from the tube and turn on both the cooling air blast and the air blast at the tube exit. Turn on oxygen to the burner, then turn on the hydrogen and immediately light the burner.

Place a syringe in the syringe drive and attach it to the burner. Insert the burner into the absorption tube and adjust the amplifier gain to give a reading of 100 on the recorder. Turn on the syringe drive and record the absorption for about 10 seconds. Turn off the drive and, if necessary, readjust to 100. Again, turn on the drive for about 10 seconds. Repeat until consecutive readings agree to about 1% transmittance.

Remove the syringe, replace it with another, and determine the per cent transmittance. When all of the standards have been measured, convert transmittances to absorbances. Subtract the absorbance for the tin-free peroxide from the others and make a plot of absorbance *vs.* concentration of tin in milligrams per liter. If desired, the calibration curve can be extended. The author observed linearity up to 2 mg. per liter of tin. Calibration curves should be prepared with each batch of samples.

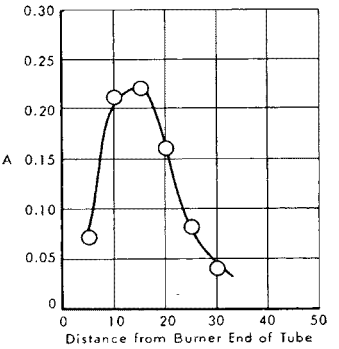

Figure 2. Distribution of tin atoms along absorption tube

Analysis of Sample. By suitable dilution with water or hydrogen peroxide solution, adjust the sample to contain 2 mg. per liter or less of tin and about 45% hydrogen peroxide.

Fill a syringe with the sample, inject it into the flame, measure the transmittance as described above, and determine the tin concentration in the sample solution from the calibration curve.

RESULTS AND DISCUSSION

Study of Variables. Optimization of Gas Flow Rates. Both acetylene-oxygen and hydrogen-oxygen mixtures were tried for production of tin atoms. The acetylene-oxygen combination was not satisfactory. Acetylene flames rich in oxygen were too hot and melted holes in the absorption tube. Flames rich in acetylene deposited soot in the tube, changing the effective pathlength (see section on Absorption Tube).

Optimum flow rates of hydrogen and oxygen were determined by measuring the absorbance of an aqueous tin solution at various combinations of hydrogen and oxygen flow rates. These tests gave the optimum flows for this apparatus, but at these flows the flame was hot enough to melt holes in the absorption tube despite the cooling air blast. The oxygen flow rate was, therefore, decreased, and the hydrogen flow rate maintained at optimum until the flame could be operated without melting the tube. Absorbance observed at these gas flows was 95% of optimum. An oxygen flow of 3 liters per minute and a hydrogen flow of 7.1 liters per minute were used. The best gas flows may be slightly different for other apparatus and should be established experimentally.

Absorption Tube. The diameter, length, and reflection from the inner walls of the absorption tube all affect the absorbance. The smaller the diameter, the higher will be the concentration of absorbing atoms and, hence, the higher the absorbance. However, Fuwa and Vallee (*2*) have shown that little is gained by decreasing the diameter below 1 cm. The optimum length of tube depends upon how far from the burner flame tin atoms can exist as free atoms.

Distribution of tin atoms within the absorption tube was examined by mounting a tube vertically and directing light from the hollow cathode source along the diameter of the tube. With the tube shifted vertically, absorbance at different distances from the burner could be measured. Because the absorption path was only 9 mm., it was necessary to use a concentrated (100 mg. per liter) tin solution to achieve significant absorbance. The distribution of tin atoms is shown in Figure 2. Concentration of tin atoms is highest about 15 cm. from the burner end of the tube and then drops off. The curve indicates there is little gain in absorbance to be realized by extending the tube length beyond 35 to 40 cm.

Light from the hollow cathode lamp undergoes multiple reflections from the inner surface of the tube, so the effective pathlength is longer than the tube length. A highly reflective inner surface such as clear fused quartz is therefore desirable. With use, the inner surface of the tube will gradually be coated. The tube is still usable in this condition, but sensitivity will be decreased. Coating of the walls is one reason for the need of frequent calibration.

Burner Position. The burner is placed so the flame can be directed into the tube and the burner top does not significantly obstruct the beam from the hollow cathode lamp. The inclination of the burner to the horizontal is important; for example, with the burner inclined at about 15°, 1 mg. per liter of tin gave an absorbance of 0.1. At about an inclination of 30°, the absorbance increased to 0.25. Highest absorbance was found with the burner tilted so a hot spot formed about 1 cm. from the tube end.

Concentration of Hydrogen Peroxide. The highest concentration of hydrogen peroxide in the samples was 90%. Because the handling of such concentrated peroxide is hazardous, samples are diluted to an arbitrary 45% hydrogen peroxide. The concentration of peroxide is not critical. Peroxide results in an absorbance about 10% higher than that observed with aqueous solutions, and the effect is essentially constant from 10 to 45% peroxide.

Interferences. Sodium pyrophosphate, phosphoric acid, and sodium nitrate are also added to hydrogen peroxide as stabilizers. The effects of these materials on the determination of tin are shown in Table I. Sodium phosphate was used instead of

Table I. Effect of Stabilizers on Determination of Tin by Atomic Absorption Spectrometry

Stabilizer added	Amount added to 0.6 mg. per liter of tin, in mg. per liter	Recovery of tin, %
$NaNO_3$	500	123
	250	98
Na_3PO_4	100 as P	50
	20 as P	91
$Na_4P_2O_7$	100 as P	75
	20 as P	91

phosphoric acid because phosphate ion was expected to be the interferent. Two concentration levels for each compound were tested. At the higher concentration interference was obtained. Sodium nitrate enhanced production of tin atoms. Both phosphate and pyrophosphate decreased the concentration of tin atoms, presumably by the formation of thermally stable tin phosphate and tin pyrophosphate. At lower concentration, sodium nitrate showed no interference and the phosphorus compounds gave results low by 9%. In most peroxide samples, the concentration of phosphorus compound is even lower than the lowest concentration given in Table I, so no significant interference is to be expected from phosphorus compounds.

CONCLUSIONS

The method was applied to a number of samples of hydrogen peroxide and comparison made with a spectrophotometric method (*1*) (Table II). Agreement was good except for sample E47 where atomic absorption gave a higher value. Because of the difficulties encountered with polymer formation, it is believed the atomic absorption result is the more correct. Data indicate a standard deviation for this method of 0.03 mg. per liter tin or 10% of the amount present, whichever is greater.

The method described is rapid and requires only that the hydrogen peroxide be diluted, a syringe be filled, the sample be injected in the flame, and the absorbance be measured. The spectrophotometric method, on the other hand, requires from 3 to 5 hours per determination depending upon how rapidly the hydrogen peroxide can be safely decomposed.

Table II. Comparison of Atomic Absorption Method with Spectrophotometric Method

Sample No., 90% H_2O_2	Tin, mg. per liter: Atomic absorption	Tin, mg. per liter: Spectrophotometric
E47	1.6	1.0
A146	0.08	0.13
EA64	0.44	0.43
A63	0.00	0.05
A96	0.08	0.08
A147	1.4	1.3

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Determination of Azide Ion by Hydrogen Ion Titration after Oxidation with Nitrite

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▷ **Measurement of the hydrogen ion consumed in the nitrite oxidation of azide is the basis for a simple and accurate method for determining azide ion in the range from 0.05 to 1.5 mmoles. The method is applicable to the direct determination of soluble azides, such as sodium azide, to the determination of silver azide after metathesis with sodium thiocyanate, and to the determination of lead azide after distillation of hydrazoic acid. Palladium azide requires chloride as a complexing agent in order to recover all of the hydrazoic acid by distillation. The precision is comparable to that of other weak acid–strong base titrations. Chloride, thiocyanate, nitrate, and perchlorate do not interfere.**

AZIDE ION has been analyzed by a variety of reactions. Macro methods, both gravimetric (*9*) and volumetric (*7, 11*) are based upon the low solubility of silver azide, and upon the quantitative oxidation of azide to nitrogen with cerate (*1*) permanganate (*16*), iodine (*6*) and nitrite (*13, 15*) as titrants. Semimicro methods make use of the red complex FeN_3^{+2} in a spectrophotometric determination (*14*) and of the Kjeldahl determination of nitrogen after thiosulfate reduction (*12*). A gas volumetric method involves the measurement of nitrogen liberated by cerate oxidation (*3*). These methods were developed for application to sodium azide and to primer components.

Silver precipitation methods usually give low results because of the appreciable solubility of silver azide. The various redox titrimetric methods use titrants which must be standardized periodically. The color of FeN_3^{+2} is unstable, varies with the pH, and is of no use in the presence of thiocyanate, a constituent of some primers. The Kjeldahl method is subject to positive errors; any ammonium ion or organic nitrogen present is counted as azide. The nitrogen volumetric method requires equipment and skills which may not be available for an occasional analysis of azide. A recent paper reported the analysis of palladium azide by a thermal decomposition technique in which the nitrogen evolved was measured (*2*). This method was not very satisfactory, as some samples were lost by explosion during analysis.

The method presented here was developed to overcome most of these difficulties and is based upon the stoichiometric consumption of two hydrogen ions for each azide ion oxidized by nitrite in a reaction which has been used in a different way (*5*). This simple approach does not appear to have been used before, though it offers some advantages. Large amounts of chloride, thiocyanate, nitrate, and perchlorate do not interfere under the conditions specified and the titrants, perchloric acid and sodium hydroxide, are stable. It is not necessary to standardize the unstable nitrite solution, as it is used in excess. As in some other methods, the azide must be in solution, and metal ions which hydrolyze at pH 8–9 must be absent; methods for meeting these conditions in the analyses of three insoluble azides are used and

discussed. The precision for the final titration is the same as that for other weak acid–strong base titrations.

EXPERIMENTAL

Materials. Solutions of sodium nitrite, 1.0*M* (fresh once a week), sodium thiocyanate, 1.0*M*, and sodium chloride, 2.0*M*, were prepared from reagent grade chemicals (Baker and Adamson). Carbonate-free, 0.1002*M* sodium hydroxide (Acculate) was checked against weighed amounts of N.B.S. primary standard potassium acid phthalate, using the phenolphthalein end point. Perchloric acid, 0.1067*M*, was obtained by dilution of the 70% acid (G. F. Smith Chemical Co.) and standardized against the sodium hydroxide, using phenolphthalein. One hundredth molar acid and base were prepared by dilution of the 0.1*M* solutions. Sodium azide (Eastman-Practical) was homogenized by grinding and tumbling; titration with cerate (*1*) indicated a purity of 99.2 ± 0.1%. A 0.1001*M* solution (later 0.1000*M*) made by weighing the azide, was also checked by cerate titration. Shiny, spectroscopically pure palladium metal was dissolved in red fuming nitric acid and heated to fumes with perchloric acid to displace the nitrate. The solution was diluted to give 0.1000*M* palladium perchlorate in about 0.2*M* acid.

Silver azide and lead azide samples were prepared by adding sodium azide solution to stoichiometric quantities of 0.1000*M* solutions of the respective metal nitrates (B. and A. reagent). The analytical procedures were tested on the resulting precipitates in the presence of the supernatant solutions because of the explosive nature of the dry metal azides. Palladium azide was similarly prepared from the palladium perchlorate solution and, in some cases, washed either with water to pH 4.0 or with 0.1*M* perchloric acid, by centrifugation and decantation. The precipitate was analyzed in the final wash solution, the palladium gravimetrically as the dimethylglyoxamate (*8*).

General Method. Add 3 drops of phenolphthalein indicator to 50 ml. of solution free of all metal ions hydrolyzing at pH 8–9, and containing 0.5–1.5 millimoles of azide. Adjust the initial pH of the solution to the phenolphthalein end point with the acid or base, if necessary. While stirring, add 20 ml. of 0.1*M* perchloric acid for every millimole of azide expected plus about 20% excess. Add 2.5 ml. of 1.0*M* sodium nitrite from a graduated pipet and allow the reaction to proceed with stirring for 5 to 10 seconds. Titrate with 0.1*M* sodium hydroxide, washing down the spray caused by gas evolution just before reaching the phenolphthalein end point. The titration should be completed without undue delay (3 to 4 minutes) to prevent loss of nitrous acid by decomposition. Five hundredths to 0.15 mmole of azide may be determined by using 0.01*M* acid and base if the solution is stirred for 3 minutes after the addition of 2.5 ml. of 1.0*M* sodium nitrate.

Silver Azide. Add 5 ml. of 2*M* sodium thiocyanate to the sample containing 0.05–1.5 mmoles of azide in 50 ml. of water and stir for 2 minutes. Proceed as described in the general method, titrating in the presence of the silver thiocyanate precipitate.

Lead Azide. Add 30 ml. of water and 1 ml. of 70% perchloric acid to the sample in a 50-ml. distilling flask. Stopper immediately and distill the hydrazoic acid (toxic) into 20 ml. of 0.1*M* or 0.01*M* sodium hydroxide, depending upon the amount of azide expected; take normal precautions to avoid excessive exposure to carbon dioxide in air. Recovery of hydrazoic acid is complete when 20 ml. of distillate has been collected. Proceed as described in the general method.

Palladium Azide. Add 5 ml. of 2.0*M* sodium chloride and 1 ml. of 70% perchloric acid to the sample in 30 ml. of water. Proceed as with lead azide.

DISCUSSION

For rapid and complete oxidation of azide ion, it is necessary to have excess acid at a pH of less than 3.0 before addition of sodium nitrite, a large excess of nitrite ion, and soluble azide. Nitrous acid is unstable in strongly acidic solutions, so it is better to add the sodium nitrite after acidification to avoid localized high acid concentrations. Hydrazoic acid is moderately volatile, boiling at 37° C.; however no losses were encountered when the initial volume was varied from 20 to 100 ml. or when the excess acid was varied from 0.1 to 3 mmoles, in 50 ml., while holding the sodium azide constant at 1.5 mmoles. In the case of silver azide an excess of 3 mmoles of acid cannot be tolerated. The thiocyanate, used for the metathesis of the sample, consumes nitrous acid to form nitrosylthiocyanate, which decomposes (*10*), leading to high results. The presence of 20% excess perchloric acid in the specified volume allows the azide–nitrite reaction to proceed without interference from the nitrosylthiocyanate side reaction.

The titration of a 1.5-mmole azide sample was followed potentiometrically. Upon the addition of sodium nitrite there was an immediate increase from the initial pH of 1.64, followed by a further increase to a constant pH of 2.85 after 5 to 10 seconds, indicating completion of the reaction. When all reactants except sodium nitrite were diluted 10-fold, a reaction time of about 3 minutes was noted, but when the sodium nitrite was also diluted 10-fold, the reaction was not complete within 3 minutes. The interrelated effects of azide, nitrite, and hydrogen ion concentrations are not known, but the titration of 0.01*M* azide appears to be about the limit of application of the method. The final titration is for nitrous acid, equivalent in amount to the unreacted hydrogen ion added; hence, the pH before adding standard perchloric acid must be adjusted to the phenolphthalein end point to avoid low results from excess acid or high results from excess base.

The problem of adapting the general method to heavy metal azides such as silver, lead, and palladium azides, is basically one of determining hydrogen ion in the presence of easily hydrolyzable metal ions. The procedure may be applied directly if the insoluble metal azide can be metathesized or complexed with an anion which yields a metal ion activity much lower than that of the metal hydroxide, and which does not undergo oxidation or reduction with nitrite or azide. Thiocyanate rapidly and completely replaces azide from silver azide in the concentration applied and the product of metathesis, silver thiocyanate, has a solubility product about 10^{-4} that of silver hydroxide. Chloride can be used to metathesize silver azide,

Table I. Statistical Summary

No. of samples	Millimoles of azide			Rel. std. dev., %
	Added	Av. found	Range	
		Sodium Azide		
24	1.502	1.504	1.502–1.508	0.1
10	0.5005	0.500	0.499–0.502	0.2
10	0.1502	0.1503	0.1496–0.1510	0.3
10	0.05005	0.0502	0.0499–0.0505	0.5
		Lead Azide		
5	1.502	1.499	1.495–1.502	0.2
5	0.5005	0.500	0.496–0.506	0.6
5	0.1502	0.1500	0.1497–0.1509	0.3
5	0.05005	0.0495	0.0486–0.0500	1.0
		Silver Azide		
5	1.500	1.500	1.499–1.500	0.1
5	0.5000	0.500	0.499–0.501	0.2
5	0.1500	0.1497	0.1489–0.1504	0.4
5	0.05000	0.0504	0.0497–0.0512	1.2

but the reddish-gray color, caused by light, interferes with detecting the phenolphthalein end point. If the proper conditions for metathesis or complexing cannot be obtained, the long-standing method of distillation of hydrazoic acid (*4*) may be used to separate an interfering metal ion such as lead. Large amounts of chloride, thiocyanate, nitrate, and perchlorate do not interfere in any of these procedures; in this respect they are superior to the direct acid titration after distillation of hydrazoic acid (*4*).

The results given in Table I show little difference in precision for the determinations of sodium, lead, and silver azides, though three somewhat different procedures are used.

Palladium and azide evidently form strong complexes, as the azide is quantitatively distilled from palladium only with great difficulty unless a large excess of another strong complexing anion, such as chloride, is present. Chloride complexing is not strong enough, however, to prevent hydrolysis of palladium ion at pH 8–9, and so the azide must still be separated by distillation. Samples were prepared in the distilling flask with a $Pd^{+2} : N_3^-$ ratio of exactly 1:2 and containing 16.81 mg. of azide. Distillation gave a recovery of about 5% when no chloride was added. When chloride was added as in the recommended procedure, 16.78 ± 0.16 mg. of azide was recovered.

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Wickbold Combustion and Spectrophotometric Analysis Procedure for Trace Amounts of Organic Chlorine in Viscous Polybutene Polymers

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▷ **A method has been developed for determining less than 10 p.p.m. of organic chlorine in viscous polybutene polymers. The polymer is diluted with a chlorine-free hydrocarbon and the organically bound chlorine is converted to hydrogen chloride in the oxyhydrogen flame of a modified Wickbold apparatus. The polymer-diluent solution is combusted at the rate of 5 to 10 grams per minute. A ferric thiocyanate spectrophotometric method is utilized for the chloride determination. Improvements in apparatus are presented.**

Methods have been published (*2*, *3*, *6*) for the analysis of organically bound chlorine in hydrocarbons, but no procedure has been directly applicable to the rapid, precise analysis of viscous polybutene-type polymers in the 0- to 10-p.p.m. range. Lamp combustion methods (*1*, *2*) are completely unsuitable because of fractionation of solvent and polymer at the wick. Previously published oxyhydrogen combustion methods (*3*, *6*) contain no data on polymeric materials and lack either the precision and accuracy desired, or have the disadvantages of an open system. Sodium biphenyl reduction methods (*2*, *5*) are time-consuming and require considerable manipulation, thereby increasing the possibility of contamination.

The Wickbold apparatus is particularly suited for trace chlorine analysis by virtue of good combustion characteristics, high sample introduction rate, and a system isolated from atmospheric contaminants. Sufficient heat is produced by the apparatus to vaporize the water of combustion obviating evaporation of the absorber solution. Elimination of the evaporation step decreases the possibility of contamination and reduces analysis time significantly.

The spectrophotometric procedure (*2*, *4*) selected for determining chloride content depends upon displacement of thiocyanate ion from mercuric thiocyanate by chloride ion in the presence of ferric ion with subsequent formation of the stable colored ferric thiocyanate complex. The color is proportional to the original chloride concentration (*4*).

EXPERIMENTAL

Equipment. Wickbold combustion apparatus is modified as follows: the glass stopcock valves for control of oxygen and hydrogen to the burner are replaced with metal needle valves; the vacuum adjustment is by-passed altogether (Figure 1); 18/9 semiball joints are installed at the connection between the quartz combustion chamber and the glass absorber. These modifications can be effected by the supplier Englehard Industries, Inc., Hillside, N. J.

Two rotary vacuum pumps with a free air capacity of 1.3 cubic feet per minute and maximum vacuum of 27 inches of mercury are used. A suitable pump is manufactured by Central Scientific Co., Chicago, Ill. (Catalog No. 93971).

Water Scavenging System. Water vapor and gaseous combustion products exit the combustion apparatus via the spray trap (Figure 1). Water is condensed by the cooling bath and is aspirated from the system by the water-driven filter pump connected to the water separator. Gaseous products are removed by the vacuum pumps.

Reagents. Water used in the analysis of chlorine or chloride is de-

ionized or distilled water. All chemicals are analytical reagent grade unless otherwise specified.

Purified iso-octane, ASTM Knock-motor grade, is percolated through a 150- by 25-mm. i.d. glass column packed with 200-mesh silica gel.

Procedure. Dissolve up to 100 grams of polymer, depending upon chloride content, in a weighed quantity of purified iso-octane so that the resulting solution may be aspirated into the burner at the rate of 5 to 10 grams per minute. (For example: 2 to 1 weight ratio of 40 SSU at 210° F. polybutene to iso-octane; equal weights of 300 SSU at 210° F. polybutene and isooctane; 1 to 3 weight ratio of 20,000 SSU at 210° F. polybutene to iso-octane.) Activate the vacuum pumps, cooling water supplies and filter pump. Charge the absorber with 30 ml. of a 3% hydrogen peroxide solution and connect the vacuum line to the apparatus. Oxygen supply pressure of 30 p.s.i.g. and hydrogen supply pressure of 10 p.s.i.g. are recommended. Open oxygen and hydrogen valves slightly and ignite the burner. Open the stopcock which connects the absorber and combustion tube permitting air flow through the system; immediately insert the burner.

Increase oxygen and hydrogen flow to the burner to obtain a flame length of approximately 5 inches. Reduce hydrogen flow until the flame is approximately 1 inch long. Introduce the sample to the burner and adjust oxygen and hydrogen flow to the burner for a blue flame covering the entire horizontal length of the combustion tube. A smaller, more intense flame should extend 2 inches from the burner tip surrounding the sample solution being introduced into the system.

Under proper operating conditions the mercury manometer will indicate a differential pressure of approximately 340 mm. of mercury while a sample is being combusted. After the sample solution is combusted, burn three 2-gram portions of purified iso-octane to remove residual polymer from the burner.

When combustion is completed, turn off the hydrogen supply valve first to prevent backfire in the burner. After the flame has been extinguished, turn off the oxygen supply valve. Close the absorber valve and remove the burner. Release vacuum to the absorber and collect the absorbent. Rinse the spray trap and absorber with four successive 5-ml. portions of water and add the washings to the absorbent. Total solution volume should be no more than 60 ml. An iso-octane blank should be burned in conjunction with each series of samples, or at least once per day.

Chloride Determination. Pipet exactly 2 ml. of 0.25*M* ferric ammonium sulfate solution in 9*M* nitric acid and 2 ml. of a saturated mercuric thiocyanate solution in ethyl alcohol into a 25-ml. flask. Dilute to volume with an aliquot of absorbent from the sample combustion and water, if necessary. Mix well. Treat the burning blank in the same manner. Prepare a reagent blank, diluting to volume with water. Allow the solutions 10 minutes for color development and measure the absorbance of the sample and isooctane blank at 460 mμ in 40-mm. cells.

Prepare the calibration curve with a standard sodium chloride solution containing 0.01 mg. of chloride per ml. Dilution, color development, and absorbance measurement are as outlined above. Plot absorbance *vs.* chloride for the 0- to 0.1-mg. range.

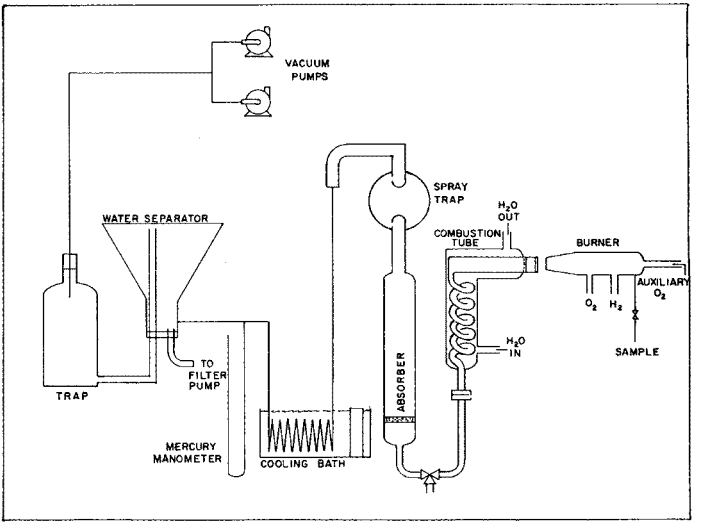

Figure 1. Arrangement of equipment

Table I. Chlorine Recovery from Standard Polybutene–Iso-octane Solutions

Compound	P.P.M. Added	Found, mean	Std. dev.	Mean error
1-Chloronaphthalene	2.7	2.6	0.1	0.1
1-Chlorobutane	4.5	4.2	0.1	0.3
1-Chloronaphthalene	6.8	6.4	0.1	0.4
1-Chlorobutane	7.0	6.6	0.1	0.4
1-Chloronaphthalene	10.0	9.6	0.1	0.4

DISCUSSION

Standard solutions were prepared containing 1-chlorobutane and 1-chloronaphthalene as sources of organic chlorine. The diluent was a mixture of equal weights of polybutene with a viscosity of 60 SSU at 210° F. and iso-octane. Purity of the chlorine-containing compounds was confirmed by combusting weighed amounts in iso-octane. Theoretical chloride recovery was obtained by titration of the resulting absorbent solutions with 0.1*N* silver nitrate.

The results in Table I were obtained by burning between 50 and 100 ml. of

Table II. Precision Comparison for Polybutenes of Different Viscosities

Polymer	Found, p.p.m.	Deviation from mean
POLYVIS 06 SH[a] 60 SSU at 210° F.	3.1	+0.2
	3.0	+0.1
	2.8	−0.1
	2.7	−0.2
	3.1	+0.2
	Mean 2.9 p.p.m. Std. dev., 0.2 p.p.m.	
POLYVIS 3 SH[a] 300 SSU at 210° F.	5.7	−0.1
	5.9	+0.1
	5.8	...
	5.9	+0.1
	5.7	−0.1
	Mean, 5.8 p.p.m. Std. dev., 0.1 p.p.m.	
POLYVIS 10 SH[a] 1,000 SSU at 210° F.	8.7	+0.2
	8.4	−0.1
	8.4	−0.1
	8.5	...
	8.3	−0.2
	Mean, 8.5 p.p.m. Std. dev., 0.1 p.p.m.	

[a] Cosden Oil & Chemical Co., Box 1311, Big Spring, Tex., trade name for polybutene polymers.

standard blend solution. For chlorine content of less than 6 p.p.m., the total absorbent and wash volume was kept below 50 ml. All values have been corrected for chlorine content of the isooctane.

Precision of the method is independent of polymer viscosity as indicated by Table II. Polybutene polymers with viscosities to 20,000 SSU at 210° F. have been successfully analyzed by this method and all viscosity grades combust cleanly with no tendency toward carbon formation under correct operating conditions. Inorganic chloride, if present, may be removed by water extraction and analyzed separately.

Water or a dilute alkaline solution may be used as absorbent instead of the 3% peroxide solution, if desired. However, this laboratory prefers the peroxide solution because both trace sulfur and chloride analyses are performed on aliquots of the same absorbent. The absorbent solution must be clear and water white on completion of combustion. Haze or color caused by incompletely combusted hydrocarbons will produce erroneous apparent chloride values.

Prior to the introduction of these modifications, safe operation of the Wickbold apparatus was an impossibility. A great deal of the explosion hazard associated with the apparatus is caused by gas leakage at the burner supply stopcocks. Replacement with conventional metal valves virtually eliminates this fault.

The taper joint on the standard equipment is prone to self-destruction because of the difference in coefficients of expansion of glass and quartz; installation of the semiball joint removes this problem. The modified apparatus has been in constant use in this laboratory for 1 year without incident.

A combination of higher gas supply pressures and doubled vacuum pump capacity has increased the sample combustion rate twofold.

The water scavenging system permits the use of inexpensive, high capacity vacuum pumps.

Effluent water vapor from the spray trap has been collected on several occasions and subsequent analysis of the condensed vapor has shown no detectable chloride, eliminating the necessity of water build-up in the absorber during combustion.

Fifteen complete analyses may be completed in an 8-hour day. It would be possible to decrease analysis time by combusting a smaller quantity of sample and adopting the more sensitive null-point method of Malmstadt and Winefordner (*6*) for the chloride determination.

This procedure should be applicable to the analysis of other viscous hydrocarbon-soluble polymers.

ACKNOWLEDGMENT

The author thanks Joe Snyder and Birt Allison for their helpful suggestions.

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Spectrophotometric Determination of Pentaborane with Pyridine

Application to Air Analysis

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▷ A new spectrophotometric method for the determination of pentaborane, based on the formation of a colored pyridine complex, and its application to atmospheric analysis, is described in this report. Using toluene as the solvent, Beer's Law is followed through the concentration range of 2 to 12 μg. per ml., and at 400 mμ the carbon solution of the complex showed an absorptivity value of 123. A trapping system was designed which permits dynamic air sampling at rates as high as 15 liters per minute with over 95% efficiency. Using a 30-liter air sample, the method would be suitable for pentaborane concentrations as low as 0.1 p.p.m., provided the same trapping efficiency is obtained at this low concentration.

DEVELOPMENT of boron hydrides as industrial chemicals and their use in rocket technology has led to the development of several methods for the detection of trace amounts of these toxic materials as air contaminants. Reagents which have been proposed for the colorimetric determination of decaborane are quinoline (*3*), *N,N*-diethylnicotinamide (*2*), dipyridylethylene (*7*), and phosphomolybdic acid (*5*). A spot test for estimating low concentrations of boron-hydride vapors in air, using a silver amine complex, was described by Etherington and McCarthy (*1*), and an air-monitoring device for boron hydrides, using triphenyltetrazolium chloride (TTC), was described by Kuhns and coworkers (*6*). Also the quantitative estimation of pentaborane, based on the same reagent, was reported by W. H. Hill and coworkers (*4*). Contained in Hill's paper was the observation that a yellow color appeared after the addition of pentaborane to pyridine, which was used as the solvent medium in the described method.

This pyridine–pentaborane reaction was investigated as the basis of an analytical procedure for the determination of pentaborane in air. Pentaborane and pyridine associate in a hydrocarbon solvent to form a soluble yellow-colored adduct, and the absorbance of this adduct is proportional to the pentaborane concentration. The procedure as described provides a simple and sensitive method for the determination of pentaborane in solution or in the atmosphere.

EXPERIMENTAL

Color Reaction Apparatus. A conventional all-glass vacuum-manifold system fitted with mechanical and mercury-diffusion pumps was used to transfer the pentaborane. A Beckman DK-2 ratio-recording spectrophotometer was used for the absorbance measurements.

Reagents. Stock pentaborane solution (1%). The cylinder containing the solution of pentaborane (99%-

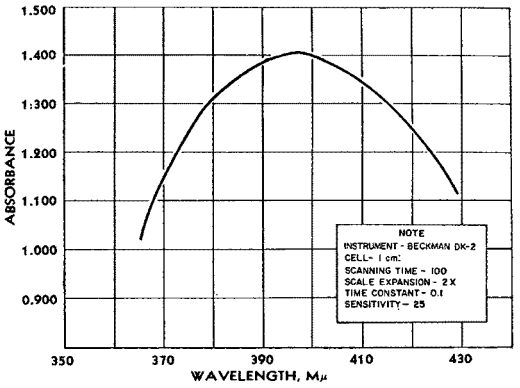

Figure 1. Pentaborane–pyridine in toluene absorbance–wavelength scan

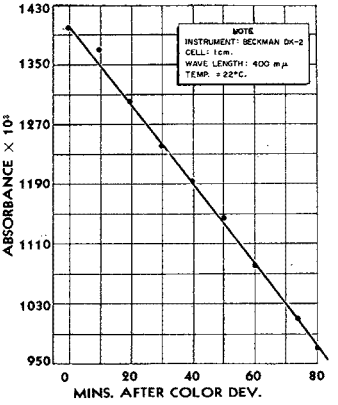

Figure 2. Decomposition rate of pentaborane–pyridine complex in toluene

pure: Olin Mathieson Co.) and a weighed glass ampoule containing 10 grams of toluene were connected to the vacuum system. The toluene (Baker's Analyzed Reagent) was previously dried over barium oxide and freeze-degassed on the vacuum line. The ampoule was cooled in liquid nitrogen, and the system was evacuated, tested, and corrected for any leakage. The cylinder valve and ampoule stopcock were opened to allow the pentaborane to migrate and condense in the ampoule. After 30 seconds the cylinder valve and ampoule stopcock were closed. The gain in weight of the ampoule represents the pentaborane collected. A working solution of pentaborane was prepared by diluting approximately 1 gram of the 1% solution to 100 ml. with toluene. Transfer of the stock solution was made using a hypodermic syringe, and the exact amount transferred was determined by weighing the receiving flask.

Calibration Procedure. Measured increments of the working pentaborane solution are delivered into 50-ml. volumetric flasks containing 30 to 40 ml. of toluene. Add 1.0 ml. of pyridine, make to mark with toluene, and mix. Read the absorbance in a 1-cm. cell at 400 mμ 15 minutes after color development.

Atmospheric Analysis Apparatus and Sampling Procedure. The trap used to remove the pentaborane from a moving air stream consists of a U tube, 1 inch in diameter, and 20 inches in total length, which is packed with $^1/_8$-in. glass helices, and contains 20 ml. of toluene. The tube and contents are cooled in a dry-ice alcohol bath (−78° C.) for the trapping operation. Air may be moved through the trap at a rate as high as 15 liters per minute using either a pump or, for field operation, a large evacuated tank. This flowrate can be maintained for a maximum time of 2 minutes before the toluene warms sufficiently to decrease the efficiency of the trap. After the air has been aspirated through the trap, the contents are made to a known volume with toluene, and a suitable aliquot is removed for analysis.

RESULTS AND DISCUSSION

Color Reaction. A wavelength scan of the complex in toluene (Figure 1) shows a broad absorption band with a maximum in the region 395 to 400 mμ. Beer's law is followed through the concentration range of 2 to 12 μg. of pentaborane per ml., with a sensitivity corresponding to an absorptivity value of 123.

The yellow color first formed faded slowly, indicating a subsequent reaction involving the pyridine complex. As shown in Figure 2, the absorbance of a pentaborane–pyridine solution in toluene containing originally 11 μg. of pentaborane per ml. decreased linearly to 77% of its original value after one hour. The effect of water was examined as a possible cause for this fading. A pentaborane standard solution was prepared from undried toluene (300 p.p.m. of water) and pyridine. The absorbance of this solution decreased to 73% of its original value after 1 hour. In the stability test represented in Figure 2, the toluene and pyridine were dried and distilled from barium oxide, and contained less than 8 p.p.m. of water (Karl Fischer method). This would indicate that water in the reagents is not responsible for the observed color instability.

Another possible explanation would be the reaction of dissolved oxygen with the pentaborane or its complex. Oxygen is quite soluble in many organic liquids, and no effort was made to deoxygenate the toluene or pyridine, except in the preparation of the pentaborane stock solution. The problem merits further investigation along this line.

Atmospheric Sampling and Analysis. The efficiency of the trap was measured by passing a nitrogen stream containing pentaborane through two such traps connected in series. The gas was allowed to flow for 2 minutes at 15 liters per minute at the ambient temperature to simulate conditions of actual use. The pentaborane was introduced into the nitrogen by diverting a portion of the nitrogen through a bubbler containing a 0.4% solution (weight-volume) of pentaborane in *n*-decane. Analyses of the contents of both traps showed the first trap contained 99.4, 97.8, and 98.8% (in three successive runs) of the total amount of pentaborane recovered. From the analysis of the first trap and the volume of nitrogen measured with a flowmeter, it was calculated that the nitrogen stream contained 200 parts per million by volume (p.p.m.) of pentaborane.

Nitrogen rather than air was used in the above experiment to prevent oxidation of the pentaborane during its passage through the bubbler solution and into the cold trap. Since the pentaborane will actually be present in air, however, it was necessary to show hat it would not be destroyed by air when concentrated in toluene at −78° C.

This was shown to be the case. A standard pentaborane–toluene solution containing 2.1 mg. of pentaborane was introduced into the trap cooled at −78° C. Thirty liters of air were then aspirated through the trap at the rate of 15 liters per minute. The pentaborane recovered, as measured by the pyridine spectrophotometric method, was 96.0% of the amount taken.

This method would be suitable for concentrations as low as 0.1 p.p.m. of pentaborane in air using a 30-liter air sample, provided the trapping efficiency remained at 96%. At this concentration, using a 10-cm. path cell for absorbance measurements and

developing the color in the undiluted solution in the trap, an absorbance value of 0.080 would be obtained.

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Study of the Pi Complexes of 2,4,7-Trinitrofluorenone with Phenols, Aromatic Hydrocarbons, and Aromatic Amines

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▷ In contrast to tetracyanoethylene (TCNE), which is a π complexing agent with some selectivity for methyl substituted benzenes and phenols, 2,4,7-trinitro-9-fluorenone (TNF) complexes more strongly with aromatic molecules having at least three fused rings—e.g., phenanthrene, pyrene, perylene, etc. TNF and TCNE are compared as to their complexation of various π bases. Selectivity in complexing π bases appears to be gained by using a π acid of the same dimensions. To make TNF complexing more selective, a new mild nitrating reagent of nitric acid–acetic anhydride in triethyl phosphate is utilized. Also useful are 0.1M perchloric acid in triethyl phosphate, acid-catalyzed acetylation, and TCNE (Diels-Alder reaction). Plots for the spectrophotometric determination of small and large rings are obtained which do not deviate appreciably from Beer's law. TNF obeys the same equilibrium constant expression as TCNE, and absorbances of solutions of known concentrations can be calculated. Solubilities, precipitation effects, solvent effects, temperature effects, and acid–base–salt effects are reported. The TNF–pyrene precipitate appears to obey a solubility product expression over a limited concentration range. The interference of molecules like phenanthrene, but not 2-naphthol, on the complexation of pyrene–TNF appears to be predictable.

IN INORGANIC analysis, some selectivity in complexometric titrations has been achieved by substitution of all-nitrogen type chelons, such as triethylenetetramine, for EDTA as titrant. The principle involved is that of selecting a chelating agent which coordinates more readily with a restricted set of ions because of the properties of the ligand.

In organic analysis, some selectivity has been observed in the utilization of tetracyanoethylene (TCNE), a π complexing agent which is especially effective for π complexing substituted benzenes (*16*) as compared to naphthalene and higher homologs. For instance, the stability constant, K, for the TCNE–hexamethylbenzene complex is 263 compared to a K of 11.7 for the TCNE–naphthalene complex and a K of 29.5 for the TCNE–pyrene complex (*9*). The principle involved seems to be that a π acid complexes more strongly with a π base of comparable size.

It is desirable to investigate the analytical properties of other π acids to discover some with a selectivity for larger aromatic rings than benzene. For example, the tetracyanoquinodimethane (TCNQ)–pyrene complex has a K of 78.4 compared to a K of 14.5 for the TCNQ–hexamethylbenzene complex (*8*). Unfortunately, TCNQ is not nearly as soluble as TCNE in chlorinated solvents.

2,4,7-Trinitro-9-fluorenone (TNF), another large π acid, is as soluble or more soluble than TCNE in many chlorinated solvents, and is also commercially available. Klemm and Sprague (*5*) have shown TNF to have some selectivity in that it complexes 2-substituted naphthalenes more strongly than 1-substituted naphthalenes because of greater overlap of π orbitals.

TNF is a strong π acid, and its complexes have been studied from an organic (*1, 5, 10, 11*), physical (*6*), and qualitative analytical (*4*) viewpoints. TNF complexes have also been analyzed by nonaqueous titration (*2*). TNF has additional advantages over TCNE in that it is not hydrolyzed by water and does not react with anthracene and other Diels-Alder active dienes. The work reported shows that it has an increasing selectivity for complexing aromatic systems as the number of fused benzene rings is increased from three to four to five.

Sensitivity of TCNE and TNF. TCNE and TNF both form 1 : 1 complexes with π bases. The formation constant, or stability constant, expression for analytical situations where the π acid is at concentrations appreciably higher than the aromatic π base is (*16*):

$$K = \frac{(C)}{\{(B) - (C)\}\{[T] - [C]\}} \quad (1)$$

in which (C) is the molarity of the complex at equilibrium, (B) is the analytical or initial molarity of the π base, $[T]$ is the analytical or initial mole fraction of TCNE or TNF, and $[C]$ is the mole fraction of the complex at equilibrium.

The $[C]$ term is usually negligible compared to the $[T]$ term. Neglecting the $[C]$ term, rearranging Equation 1, and (assuming 1-cm. cells) substituting A/ϵ for (C) gives:

$$(B) = \frac{A\{1 + K[T]\}}{\epsilon K[T]} \quad (2)$$

Given a constant lower limit of absorbance, A, Equation 2 predicts that (B) will be decreased by increases in ϵ, K, and $[T]$. (The term $K[T]$ is usually small compared to one. A relatively large value would be 0.54 for pyrene in 0.11M TNF). TNF is definitely the more sensitive reagent for pyrene if Equation 2 is used to compare the two practical reagents, 0.11M TNF in methylene chloride and 0.05M TCNE in methylene chloride.

EXPERIMENTAL

Apparatus. The transistor regulated model Bausch and Lomb Spectronic 20 Colorimeter with 11.7-mm. test tubes and 11.6-mm. square cells, as well as the Beckman Model DB spectrophotometer were used for spectrophotometric measurements.

The Temp-Blok Module Heater (module No. 2076) was used for the temperature stability studies. The Farrand spectrophotofluorometer was used for studying the fluorescence of the pyrene–TNF complex.

Reagents. 2,4,7-Trinitro-9-fluorenone (TNF), obtained from the Eastman Kodak Co., was recrystallized from 3 : 1 nitric acid–water (*6*), and dried over phosphorus pentoxide. Recrystallization of TNF from organic solvents is not always satisfactory since frequently a colored TNF–π base complex precipitated with the first crystals of TNF. A better method is that of purification from 3:1 nitric acid–water. This apparently nitrates any mono- or dinitrofluorenone, but does not form 2,4,5,7-tetranitrofluorenone. The latter results only when TNF is treated with fuming nitric acid–sulfuric acid (*13*).

2,3,5,6-Tetrachlorobenzoquinone was obtained from Matheson, Coleman & Bell Co. 2,3-Dichloro-5,6-dicyanobenzoquinone was obtained from Arapahoe Chemicals, Inc. Tetracyanothiophene was kindly supplied by the Central Research Dept. of E. I. du Pont de Nemours & Co. All were used as received.

Triethyl phosphate was Matheson, Coleman & Bell practical grade and was not purified further. Aromatic hydrocarbons, phenols, and amines were Eastman White Label grade or the equivalent in most cases.

The 0.1*M* perchloric acid was prepared by mixing 4.3 ml. of 72% perchloric acid in 200 ml. of triethyl phosphate with 10 ml. of acetic anhydride and diluting to 500 ml. with triethyl phosphate.

The 2*M* acetylating reagent was prepared from 0.47 ml. of 72% perchloric acid, 30 ml. of triethyl phosphate, and 10 ml. of acetic anhydride.

The 1.6*M* and 0.2*M* nitric acid reagents were prepared by cooling mixtures of 0.5 ml. of concentrated nitric acid in 1.5 ml. and 36.5 ml. of triethyl phosphate, respectively, and then adding 3 ml. of acetic anhydride to each. The nitric acid–acetic anhydride reagent of Malins, Wekell, and Houle (*7*) was also prepared.

Procedure. The tests of Equation 4 as well as the determination of the stability constants were performed on the Spectronic 20 using the square cells. In the determination of the *K*'s (*9*) of TNF–pyrene, TNF–2-naphthol, and tetracyanothiophene–pyrene, final π acid concentrations were $1.5 \times 10^{-4}\,M$, $1.0 \times 10^{-3}\,M$, and $5 \times 10^{-4}\,M$, respectively. Mole fractions of pyrene ranged from 0.02 to 0.05; mole fractions of 2-naphthol ranged from 0.035 to 0.05. Blanks were used to correct for the side band absorption of pyrene at 520 and 480 mμ.

Solvent effects were determined by measuring the absorbance of solutions containing an excess (0.02*M*) of pyrene over TNF (0.002*M*) to avoid precipitation in some solvents.

Temperature effects were investigated by reading the initial absorbance of about 3 ml. of solution in an 11.7-mm. Spectronic 20 test tube, inserting the tube into the Module heater for 30 or 60 minutes, cooling and reading the absorbance again. Solutions of TNF used to set 100% *T* were not so treated.

Adherence to Beer's law was investigated by always setting 100% *T* with a solution of TNF in the appropriate solvent. Because of the broad absorption spectrum of TNF, it is necessary to purify it carefully and choose somewhat arbitrary wavelengths for measurement of its π complexes. The absorption spectrum at 350 to 410 and 450 to 520 mμ of a 0.11*M* solution of unpurified TNF varied as much as 0.15 absorbance unit from that of purified TNF.

The use of 0.1*M* perchloric acid in triethyl phosphate to avoid amine interference was investigated by making up a standard solution of pyrene in the 0.1*M* perchloric acid and always diluting to volume with this solvent. In contrast, only 0.3 ml. of the acetylating reagent was added to 5 ml. of methylene chloride solutions.

The use of the nitric acid–acetic anhydride reagents to reduce interferences was investigated by adding 0.2 ml. of the reagent to about 4 ml. of a methylene chloride solution of pyrene and the interference. After the appropriate time, 0.1 ml. of methanol was added followed by solid TNF. The solution was diluted to 5 ml. with methylene chloride, and the absorbance was read.

Table I. Comparison of Complexes of Pyrene and Various π Acids in CH_2Cl_2 Solvent

π Acid and *K* of its pyrene complex		*M* of π acid in CH_2Cl_2	$5 \times 10^{-3}M$ pyrene + π acid, *A* (wavelength, mμ)
Dichlorodicyanobenzoquinone	>80	0.08	~2 (540)
Trinitrofluorenone	73	0.15	1.4 (520)
Tetracyanoethylene	29.5[a]	0.10	0.8 (720)
Tetracyanothiophene	29	0.10	0.48 (480)
Tetrachlorobenzoquinone	23.3[a]	0.01	0.12 (610)

[a] Determined by Merrifield and Phillips (*9*).

RESULTS AND DISCUSSION

Acid Strengths. Since an object of this study is to find π complexing agents with a selectivity for larger aromatic rings, the data in Table I have been collected to give a comparison of the strengths of various π acids toward pyrene in methylene chloride. The TNF–pyrene complex is obviously a relatively strong complex. Since the molar absorptivities of complexes in Table I are all of the order of 10^3, the sensitivity of these reagents for pyrene will depend on *K* and on the [*T*] term in Equation 2. For actual comparison, the absorbances of solutions of pyrene saturated with the respective π acid are given in Table I. This comparison overrates TCNE because 0.1*M* TCNE must be prepared by heating, making it impractical to use with dilute solutions of π bases.

Although dichlorodicyanobenzoquinone is more sensitive for pyrene than TNF, the former also has a more appreciable absorption spectrum. This makes the setting of 100% *T* with the π acid solution alone more subject to error, etc.

Choice of Wavelengths. The use of TNF as a complexing agent greatly depends on an appreciation of the spectra of TNF alone and of its complexes with molecules such as pyrene and 2,6-dimethylphenol, as shown in Figure 1. TCNE differs from TNF in that it is colorless and absorbs in the ultraviolet region with a peak at 265 mμ.

An inspection of Figure 1 leaves no doubt that measurements are only practical at wavelengths at or longer than 450 mμ. Of interest is the fact that molecules containing one or two rings show absorption spectra similar to that of 2,6-dimethylphenol: a sharp peak near 450 mμ and a moderate tailing off. The shape of absorption spectra of molecules containing three or more fused aromatic rings is somewhat similar to that of pyrene: one or more (410 to 520 mμ) broad maxima and very gradual tailing. In these cases, the greater overlap of π orbitals possible is apparently responsible. Spectrophotometric determination of pyrene and similar molecules is thus more selective at 520 mμ.

The spectra of the complexes of carbazole, fluorene, and dibenzothiophene (Figure 2) are presented because of the structural similarity of these π bases to TNF, all molecules having a central five-membered ring fused to two benzene rings. There are some differences in the spectra, particularly in

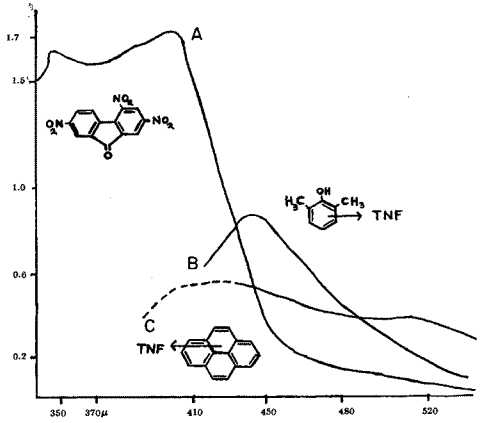

Figure 1. Absorption spectra of trinitrofluorenone (TNF) and its π complexes in $C_2H_4Cl_2$

Curve A. 0.15M recrystallized TNF
Curve B. 0.025M 2,6-dimethylphenol–0.15M TNF
Curve C. 0.001M pyrene–0.11M TNF
Both curves B and C were recorded by setting 100% T with a solution of the corresponding concentration of TNF. The dotted portion of curve C is an extrapolation from more dilute solutions

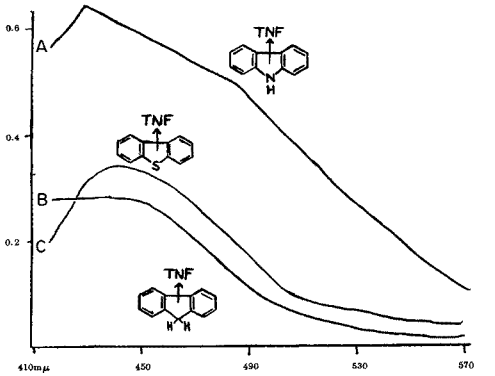

Figure 2. Absorption spectra of TNF π complexes of three similar molecules in CH_2Cl_2

Curve A. 0.003M carbazole–0.03M TNF
Curve B. 0.002M dibenzothiophene–0.02M TNF
Curve C. 0.005M fluorene–0.03M TNF
All curves were recorded by setting 100% T with a solution of the corresponding concentration of TNF

the case of carbazole. This difference suggests that TNF may be somewhat more sensitive a reagent for aromatic amines such as carbazole than for the corresponding aromatic hydrocarbon.

As shown in parentheses in Table II, the longest wavelength absorption peaks of TNF complexes of π bases having an increasing number of fused aromatic rings, are not as well separated as those of TCNE. The TCNE–pyrene and TCNE–perylene complexes have peaks located in the near infrared region in contrast to the TNF complexes.

Lower Limits of Detection. The data in Table II compare the experimentally determined lower limits of detection (A = 0.10) by TCNE and TNF of aromatic species consecutively increasing in size by one ring.

TCNE obviously has the greater sensitivity for substituted benzene rings such as 2,6-dimethylphenol and durene. Its sensitivity is somewhat lower and is relatively constant for molecules with two (2-naphthol) to five (perylene) fused aromatic rings.

The sensitivity of TNF for benzene and naphthalene rings is not high, but its sensitivity continues to increase as the number of fused aromatic rings increases. Thus TNF shows a certain selectivity for three or more aromatic rings as compared to benzene or naphthalene rings. This is probably because of the increase in π orbital overlap as the size of the π base increases. An examination of models reveals that maximum overlap of π orbitals is probably not yet attained with TNF and perylene, but might be attained with TNF and an aromatic containing 6 or 7 (coronene) rings. It seems probable that the detection limit for such aromatics would be lower than that for perylene. It is also apparent that TNF is a more selective π acid when the π base is large enough to overlap the nitro groups as well as the ring system of TNF.

Some of the TCNE detection limits in Table II have already been calculated from Equation 2 (*16*). Using Equation 2, a K of 73 and an ϵ of 10^3 for pyrene–TNF, a detection limit (A = 0.10) of $2.3 \times 10^{-4}M$ was calculated for pyrene. Somewhat lower limits than those in Table II would be found on prism spectrophotometers where the molar absorptivities are some 10% higher than on the Spectronic 20.

Solvent Effects. Table III gives the solubilities of TNF in various solvents and the effect of solvent on absorbance, and presumably K, of the pyrene–TNF π complex. The effect of solvent on complexation of pyrene by TNF is somewhat different

Table II. Comparison of Lower Limits of Detection of π Bases by TCNE and TNF

A = 0.10, b = 1.17 cm., CH_2Cl_2 solvent

Compound	Detected by 0.11M TNF, M (wavelength)	Detected by 0.05M TCNE, M (wavelength)
2,6-Dimethylphenol	3.0×10^{-3} (450 mμ)	8×10^{-4} (520 mμ)
Durene	2.5×10^{-3} (440 mμ)	3×10^{-4} (480 mμ)
2-Naphthol	2×10^{-3} (450 mμ)	1.4×10^{-3} (580 mμ)
Phenanthrene	4×10^{-4} (450 mμ)	1×10^{-3} (520 mμ)
Pyrene	2×10^{-4} (520 mμ)	1×10^{-3} (724 mμ)
Perylene	5×10^{-5} (620 mμ)	1×10^{-3} (890 mμ)

Table III. Solubilities of TNF and Effect of Solvent on TNF Complexation

0.002M TNF, 0.02M pyrene, (b = 11.7 mm.)

Solvent	Solubility	$A_{520\ m\mu}$	$A_{450\ m\mu}$
CCl_4	<0.005M	... (pptn.)	...
$CHCl_3$	>0.04M	0.43	0.65
$CHBr_3$	0.05M	0.35	0.57
CH_2Cl_2	>0.15M	0.27	0.41
$CHCl_2CHCl_2$	<0.02M	0.32	0.53
CH_2ClCH_2Cl	0.13M	0.20	0.26
HOAc	0.03M	... (pptn.)	...
EtOAc	0.07M	... (pptn.)	...
$(EtO)_3PO$	0.12M	0.14	0.21
CH_3NO_2	0.41M	0.30	0.43
CH_3CN	0.12M	... (pptn.)	...
$(CH_3)_2CO$	0.14M	0.20	0.28
$(CH_3)_2SO$	0.5M	0.18	0.33
CH_3OH	>0.02M	... (pptn.)	...

from that on complexation of durene by TCNE. In the latter case, it appears that solvent hydrogen bonding to the aromatic π electron system competes favorably with complexation by TCNE (*16*).

Thus the absorbance of the TCNE–durene complex is predictably higher in bromoform than in chloroform, but the reverse is true for the TNF–pyrene complex. It may be that in the complex there is a solvent molecule(s) hydrogen bonded to the ring and that the chlorine or bromine atoms of the solvent provide some steric hindrance to TNF complexing. The larger size of bromine would explain why bromoform is a poorer solvent for complexation than chloroform.

Dissolution of TNF does not appear to depend on hydrogen bonding alone since it has limited solubility in acetic acid, ethyl acetate, and methanol, all solvents which readily dissolve TCNE largely because of hydrogen bonding.

Nitromethane, methylene chloride, and triethyl phosphate appear to be the most suitable solvents for analytical work. The latter is useful for utilizing acid-catalyzed acetylation and protonation by perchloric acid. Precipitation of the pyrene–TNF complex resulted in many solvents; this effect was investigated further.

Precipitation. Many phenols and aromatic hydrocarbons form insoluble complexes (*10, 11*); this phenomenon has been utilized for analytical purposes (*2, 4*). Precipitation occasionally limited the upper range of concentration in the investigation of adherence to Beer's law discussed below.

The precipitation of the pyrene–TNF complex was briefly investigated to see whether a solubility product expression would be valid for a 1:1 precipitate. The data in Table IV demonstrate this may be true over a limited concentration range. As long as the TNF concentration was higher than, or about the same as that of pyrene, a somewhat constant "K_{sp}" value was obtained in methylene chloride. When the concentration of pyrene was appreciably greater than that of TNF, no precipitate was formed at the predicted concentrations.

A similar but more limited investigation in chloroform revealed that the K_{sp} became progressively larger as the concentration of pyrene increased and that of TNF decreased.

Acid, Base, and Salt Effects. Bases, but not acids, tend to decompose both TCNE (*16*) and TNF. Only one experiment was made on the effect of acid on a TNF complex because of the insolubility of many complexes in acetic acid. The 0.1*M* perchloric acid reagent in triethyl phosphate did lower the absorbance of the TNF–pyrene complex by some 25% at both 450 and 520 mμ. Because this reagent contained acetic acid from the reaction of acetic anhydride and water, it is not possible to state that this effect arises entirely from perchloric acid.

Salts also effect the absorbance of TNF complexes. An experiment involving 0.3*M* sodium perchlorate revealed that this salt increased the absorbance of the TNF–pyrene complex by some 10% at both 450 and 520 mμ.

Temperature Effects. Gordon and Huraux (*4*) reported that the colors of TNF complexes of substituted anilines and substituted phenols disappear when the complexes are heated on filter paper 5 minutes at 110° C. However, in solution at 80° or 115° C. no such decoloration is found, as shown in Table V. Pyridine apparently causes some decomposition of TNF at 115° C., and some decomposition of TNF appears to occur at 115° C. when it is heated alone in solution.

Similar differences in reactivity have been noted with TCNE (*16*) where the colors of TCNE complexes disappear with heating on paper but not in solution. Evidently the chemistry of the complexes on paper is different than that in solution. At any rate, no preferential destruction of the color of selected complexes to permit measurement of other complexes, seems possible.

Agreement with Beer's law. Table VI lists various π complex systems which do not deviate significantly from Beer's law from concentrations of π base at which the absorbance is 0.10 to the stated upper limits. All experiments involved using a high concentration of TNF relative to that of the π base.

Deviations from Beer's law at high concentrations of π base may be the result of a significant $[C]$ term in the following equation:

$$\epsilon = \frac{A}{(B)} \frac{1 + [T] - [C]}{K\{[T] - [C]\}} \qquad (3)$$

(This equation is derived from Equation 1 by substituting A/ϵ for (C), assuming 1-cm. cells, and rearranging.)

It has been pointed out that neglecting the $[C]$ term in Equation 1 will cause an error in the determination of K (*3, 18*). The same should hold true for agreement with Beer's law. The instrumental value of ϵ should be constant over a concentration range only if the right side of Equation 3 is sensibly constant over this range. One way of measuring this is to calculate

Table IV. Precipitation of Pyrene–TNF Complex

TNF, *M*	Pyrene, *M*	Precipitation	"K_{sp}"
	CH_2Cl_2 solvent, 22° C.		
0.10	2×10^{-3}	Slight	2×10^{-4}
0.09	2×10^{-3}	None	
...	...		
0.035	5×10^{-3}	Slight	2×10^{-4}
0.031	5×10^{-3}	None	
...	...		
1.5×10^{-2}	2×10^{-2}	Slight	3×10^{-4}
1.2×10^{-2}	2×10^{-2}	None	
...	...		
1.1×10^{-3}	2 to 8×10^{-1}	None	...
	$CHCl_3$ solvent, 22° C.		
1.7×10^{-2}	4×10^{-3}	Slight	7×10^{-5}
1.5×10^{-2}	4×10^{-3}	None	
...	...		
1.5×10^{-2}	8×10^{-3}	Slight	1×10^{-4}
1.0×10^{-2}	8×10^{-3}	None	
...	...		
1.0×10^{-2}	2×10^{-2}	Slight	2×10^{-4}
8.0×10^{-3}	2×10^{-2}	None	

Table V. Effect of Temperature on TNF Complexes

0.11*M* TNF, 520 mμ, b = 11.7 mm.

	Absorbance CH_2ClCH_2Cl		Absorbance $(EtO)_3PO$	
π Base, *M*	Initial	60 min., 80° C.	Initial	60 min., 115° C.
None	...	...	0.05	0.08
None[a]	...	...	0.37	0.47
Aniline, $1 \times 10^{-2}M$	0.45	1.2	...	...
Pyridine, $2 \times 10^{-2}M$[a]	0.09	0.11	0.05	1.05
2,6-Dimethylphenol, $5 \times 10^{-2}M$	0.140	0.140	0.33	0.41
Pyrene, $1 \times 10^{-3}M$	0.38	0.37	0.28	0.38

[a] Absorbance measured at 440 mμ.

Table VI. Agreement with Beer's Law

520 mμ, b = 11.7 mm.

Compound	Concentration range[a]	TNF, final M	Solvent
Carbazole	4 to 32 × $10^{-4}M$	0.11	CH_2Cl_2
Dibenzothiophene	1.6 to 8 × $10^{-4}M$[b]	0.30	CH_3NO_2
2,6-Dimethylphenol	3 to 20 × $10^{-3}M$[b]	0.10	$(EtO)_3PO$
Diphenylamine	1 to 8 × $10^{-3}M$	0.11	CH_2Cl_2
Durene	5 to 37.5 × $10^{-3}M$	0.11	CH_2Cl_2
2-Naphthol	2 to 12 × $10^{-3}M$	0.11	CH_2Cl_2
Pyrene	2 to 15 × $10^{-4}M$	0.11	CH_2Cl_2
Pyrene	0.3 to 10 × $10^{-4}M$[b]	0.11	CH_2Cl_2

[a] The lower figure quoted corresponds to A = 0.10.
[b] 450 mμ.

Table VII. Complexation of a Stronger π Base in Weaker π Bases

0.11M TNF, CH_2Cl_2, b = 11.6 mm.

(Weaker base)/(Pyrene)	Pyrene, M	Weaker base	$A_{520\ m\mu}$	Rel. error, %
...	3 × 10^{-4}	None	0.106	...
0.6	3 × 10^{-4}	2-Naphthol	0.119	12
1.4	3 × 10^{-4}	Phenanthrene	0.117	10.5
...	6 × 10^{-4}	None	0.243	...
0.6	6 × 10^{-4}	2-Naphthol	0.265	9
1.4	6 × 10^{-4}	Phenanthrene	0.267	10
...	9 × 10^{-4}	None	0.389	...
0.6	9 × 10^{-4}	2-Naphthol	0.403	3.5
1.4	9 × 10^{-4}	Phenanthrene	0.425	9.5
1.0	9 × 10^{-4}	Chrysene	0.68	74
1.0	9 × 10^{-4}	Anthracene	0.76	95
1.0	9 × 10^{-4}	Carbazole	0.59	51

the right hand side of Equation 3 for the highest and lowest concentrations of the range and then compare their relative difference with instrumental error. This relative difference for pyrene between the two points A = 0.10 and 0.70 given in Table VI is about 0.5 p.p.h., compared to a relative error in concentration ($\Delta c/c$.) of 1.6 p.p.h. resulting from instrumental reading error at A = 0.70. (This relative error was calculated by assuming an instrumental reading error of 0.5% T.)

The plot of the pyrene–TNF complex at 450 mμ did not deviate significantly from Beer's law but did not pass through the intercept. Since in this case, as for all systems listed in Table III, 100% T was set with a solution of TNF alone at the final concentration listed, the higher absorbance of TNF at 450 mμ (than at 520) is probably responsible. The plot of the 2-naphthol–TNF complex also did not pass through the intercept.

Since Gordon and Huraux (*4*) noted fluorescence of many TNF complexes, the activation wavelength for the TNF–pyrene complex was investigated. This complex was found to be activated for fluorescence in the 310- to 360-mμ region. Since absorbance measurements are made at 450 or 520 mμ, no activation to fluoresce is to be expected because the optical system of the Spectronic 20 focuses light on the sample only after the light has been dispersed by the grating.

INTERFERENCES AND SELECTIVITY

Of the many approaches to removing interferences that are possible with TCNE (*16*), some could not be evaluated readily because of solubility problems. Acetic acid and acetic anhydride were not investigated for this reason. The effect of water was also not investigated as was done for TCNE because there is no hydrolysis of TNF. The approaches investigated are treated individually below.

Strength of π Bases. Some aromatic hydrocarbons, phenols, and aromatic amines may be determined in the presence of others by virtue of being much stronger π bases. Obviously, large amounts of benzene, halogenated aromatics, and nitroaromatics can be tolerated in the determination of stronger π bases such as durene (*16*) or pyrene.

If it is assumed that there is no interaction between two different π complexes, it is possible to use Equation 2 to predict interferences. Suppose that a strong π base, B_1 is to be determined in the presence of a weak π base, B_2. Writing a ratio of Equation 2 for B_2 and Equation 2 for B_1 permits one to predict the relative concentration of B_2 that will cause a given error in absorbance (A_2/A_1):

$$\frac{(B_2)}{(B_1)} = \frac{A_2\{1 + K_2[T]\}\epsilon_1 K_1}{A_1\{1 + K_1[T]\}\epsilon_2 K_2} \qquad (4)$$

Equation 4 predicts that in the determination of B_1, the error caused by the weaker π base, B_2, is constant if the ratio $(B_2)/(B_1)$ is constant. This means the error is independent of the actual concentrations. This prediction was tested by measuring pyrene in 2-naphthol and in phenanthrene as shown in Table VII.

To use Equation 4, K for the 2-naphthol–TNF complex was measured and found to be about 9; ε at 520 mμ was found to be about the same as ε at 520 mμ for the pyrene–TNF complex. A value of 0.0073 was used for $[T]$. The solution to Equation 4 predicts that a relative error of 10% (A_2/A_1 = 0.10) will occur at a 2-naphthol/pyrene ratio of 0.6/1. As seen in Table VII, the relative error is somethat higher than 10% at low concentrations but is much lower than 10% at higher concentrations.

Two explanations seem plausible: one is that there is an interaction between the two pi complexes, and the other is that the hydroxyl group of 2-naphthol is exerting some unpredictable influence. It seems likely that at higher concentrations 2-naphthol can hydrogen bond to itself to a greater extent. Certainly if this hydrogen bond involves the π electron system of 2-naphthol, this would reduce π complexation of 2-naphthol by TNF and would reduce the relative error.

As a further test, K for the phenanthrene–TNF complex was measured and found to be about 13; ε at 520 mμ was found to be about one fourth of ε at 520 mμ for the pyrene–TNF complex. The value of 0.0073 was again used for $[T]$ in solving Equation 4. The solution predicts that a relative error of 10% (A_2/A_1 = 0.10) will occur in the measurement of TNF–pyrene at 520 mμ at a phenanthrene/pyrene ratio of 1.4 to 1.

As seen in Table VII, the relative error in absorbance is sensibly constant for the measurement of various concentration levels of 1.4 to 1 ratios of phenanthrene to pyrene. The relative error in absorbance decreases only very slightly with an increase in concentration. Equation 4 appears to hold for a mixture of phenanthrene and pyrene with TNF, and it may possibly hold for other mixtures of aromatic hydrocarbons.

Phenanthrene and 2-naphthol are both fairly weak π bases compared to pyrene and might not be expected to cause appreciable error. As seen from

Table VIII. 0.1M Perchloric Acid/-(EtO)$_3$PO as Solvent for Selective Complexation

0.08M TNF, 0.0006M pyrene, b = 11.7 mm.

π Base, M	$A_{520\ m\mu}$	$A_{450\ m\mu}$
None	0.21	0.22
β-Naphthylamine, 0.003M	0.21	0.22
β-Naphthylamine, 0.006M	0.22	0.25
Pyridine, 0.006M	0.235	0.24
Triethylamine, 0.05M	0.21	0.22
Carbazole, 0.001M	0.33	0.75
Diphenylamine, 0.001M	0.26	0.27

Table VII, anthracene, chrysene, and carbazole, π bases of strengths comparable to pyrene, interfere seriously in the complexation of pyrene.

Perchloric Acid. Perchloric acid was the first of a number of chemical reagents investigated for the reduction of interferences. Table VIII indicates that 0.1M perchloric acid in triethyl phosphate as solvent materially reduces the interference of amines in the complexation of pyrene. Perchloric acid in acetic acid (*16*) could not be used because the pyrene–TNF complex precipitates in that solvent.

Apparently protonation reduces the π basicity of amines with a pK_b (H_2O) of at least 10 but not the π basicity of more weakly basic amines such as carbazole or diphenylamine.

Acid-Catalyzed Acetylation. The substitution of an electron-withdrawing group like the acetyl group on a phenol or aromatic amine markedly reduces the π basicity of these compounds (*16*). This is accomplished by uncatalyzed acetylation of amines or acid-catalyzed acetylation of amines, phenols, and mercaptans.

Instead of employing a dilute 0.06M acetylating reagent in ethyl acetate as solvent (*16*), a small volume of a 2M acetylating reagent (*15*) was added to a methylene chloride solution of TNF complexes. Triethyl phosphate was used as the solvent since the pyrene–TNF complex precipitates in ethyl acetate.

Table IX illustrates the usefulness of this acetylating reagent in reducing the interference of phenols and amines. Once again the interference of carbazole cannot be reduced. The acetylation of aryl mercaptans was not investigated, but it seems likely that this would reduce their interference. Dodecyl mercaptan did not appear to interfere with the complexation of pyrene at concentrations up to 0.01M.

It seems probable that acetic anhydride could be used in small amounts in triethyl phosphate as solvent to reduce the interference of amines in the complexation of phenols or aromatic hydrocarbons.

Table IX. Acid-Catalyzed Acetylation at Room Temperature for Selective Complexation

0.0006M pyrene, 0.11M TNF, CH_2Cl_2, 0.3 ml of 2M Ac_2O/(EtO)$_3$PO

Interference, M	$A_{520\ m\mu}$ Initial	$A_{520\ m\mu}$ 30 min.	$A_{450\ m\mu}$ Initial	$A_{450\ m\mu}$ 30 min.
None	0.23	...	0.29	...
2,6-Dimethylphenol, 0.004M	0.25	0.23	0.40	0.31
2-Naphthol, 0.003M	0.47	0.26	0.82	0.46
Carbazole, 0.001M	0.58	0.58	0.96	0.96
2-Naphthalamine, 0.001M	0.72	0.35	1.00	0.49

Diels-Alder Reaction. Neither of the above reagents reacts at more than one atom of the large molecules investigated and therefore does not appreciably reduce the π basicity of carbazole, 2-naphthylamine, etc. [Acetylation of resorcinol, for instance, apparently reduces its π basicity more than that of p-methoxyphenol (*16*).] A better reagent would be one which reacts at more than one atom of a molecule to reduce its π basicity either by attaching some electron-withdrawing substituent or by attaching a substituent which will offer steric hindrance to complexation. A Diels-Alder dienophile would be ideal in that it would do both.

Such a dienophile is TCNE which, in contrast to TNF, reacts rapidly in Diels-Alder fashion with such dienes as cyclopentadiene, anthracene, naphthacene (tetracene), etc. (*12*). This permits the addition of micro amounts of TCNE to mixtures of aromatic hydrocarbons to react selectively with dienes such as anthracene. The resulting adduct is much too weak a π base to complex with a macro amount of TNF. Aromatics which are not dienes, such as pyrene, can then be determined spectrophotometrically, as shown in Table X.

Although the interference of anthracene is readily removed, benz(α)anthracene appears to react slowly and incompletely at this concentration with TCNE. It reacts quantitatively at semimicro levels (*12*). Naphthacene appears to react quantatively with TCNE; the absorbance of the final solution is somewhat lower than that of TNF–pyrene alone. Some variation in the purity of the TNF may be partly responsible.

Table X. Diels-Alder Reactions Using TCNE for Selective Complexation

Room temperature, 0.11M TNF, 5 × 10^{-4}M pyrene, CH_2Cl_2 (Purity of TNF varies) 5 ml. total volume

0.0005M diene	$A_{520\ m\mu}$
None (blank)	0.31
Anthracene	0.91
Anthracene + 5 mg. TCNE: 5 min.	0.335
Anthracene + 5 mg. TCNE: 10 min.	0.325
Benz(α)anthracene	0.51
Benz(α)anthracene + 5 mg. TCNE: 5 min.	0.53
Benz(α)anthracene + 5 mg. TCNE: 5 hr.	0.43
Naphthacene	0.48
Naphthacene + 5 mg. TCNE: 5 min.	0.26
Naphthacene + 5 mg. TCNE: 10 min.	0.265

Nitric Acid–Acetic Anhydride. The 2.3M nitric acid–acetic anhydride (no solvent) reagent of Malins, Wekell, and Houle (*7*) was investigated because nitration will introduce more than one electron-withdrawing substituent on a ring and tend to reduce π basicity more than perchloric acid or acetic anhydride. Nitric acid can also reduce π basicity by oxidation, but this frequently produces colored products. This reagent

Table XI. Nitric Acid–Acetic Anhydride Reagent for Selective Complexation

Room temperature, 0.2 ml. reagent/5 ml CH_2Cl_2, 0.0006M pyrene, 0.11M TNF

Interference, M	HNO_3 reagent	$A_{520\ m\mu}$ Initial	$A_{520\ m\mu}$ After reaction (time)
None	...	0.24	...
2-Naphthol, 0.003M	1.6M	0.47	0.48 (10 min.)
Carbazole, 0.001M	1.6M	0.58	0.45 (40 min.)
Dibenzothiophene, 0.001M	1.6M	0.31	0.28 (40 min.)
Phenyl sulfide, 0.02M	2.3M	0.43	0.20 (0.5 min.)[a]
2-Naphthylamine, 0.001M	0.2M	0.72	0.38 (5 min.)

[a] To reduce oxidation of pyrene, 0.05 ml. of triethyl phosphate was added immediately after the nitric acid reagent. Not less than 30 seconds later, 0.1 ml. of methanol was added.

presumably nitrates by acid-catalyzed formation of the nitronium ion:

$$H^+ + HO\text{-}NO_2 + Ac_2O \rightarrow NO_2^+ + 2HOAc \quad (5)$$

To control the nitration to avoid production of yellow nitrated pyrene compounds (*14*), triethyl phosphate solvent was used to prepare 1.6*M* and 0.2*M* nitric acid reagents. Turbak (*19*) has found that 1:1 complexes of triethyl phosphate and sulfur trioxide will not attack aromatic rings but will react with other functional groups. The 1.6*M* reagent (1.5:1 triethyl phosphate–nitric acid) did attack carbazole but not pyrene as shown in Table XI. It would appear as though the phosphoryl oxygen of triethyl phosphate controls the reactivity of nitric acid because reagents containing 0.5:1 or 1:1 triethyl phosphate–nitric acid did react rapidly with pyrene. The 0.2*M* reagent was mild enough to reduce the interference of 2-naphthylamine, as shown in Table XI, without producing the excessive colored oxidation products encountered with the more concentrated reagents.

To eliminate slow side reactions of nitric acid, excess methanol was added to react with the nitric acid and thus quench the reaction (*7*):

$$NO_2^+ + MeOH - MeONO_2 + H^+ \quad (6)$$

This was critical in the oxidation of phenyl sulfide with the 2.3*M* reagent to avoid appreciable nitration of pyrene.

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Isolation and Identification of Alcohols in Cold-Pressed Valencia Orange Oil by Liquid-Liquid Extraction and Gas Chromatography

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▷ **A procedure for the qualitative analysis of alcohols in cold-pressed Valencia orange oil is presented. The method utilizes the partitioning of the oil between carbon tetrachloride and propylene glycol. Water is added to the propylene glycol layer and the essential oil alcohols are extracted with ether. The alcohols are further purified by column chromatography, separated by gas chromatography, and identified by infrared and mass spectrometry. Nineteen alcohols were isolated from Valencia cold-pressed orange oil and identified as *n*-octanol; *n*-decanol; linalool; citronellol; α-terpineol; *n*-nonanol; *trans*-carveol; geraniol; nerol; heptanol; undecanol; dodecanol; elemol; *cis*- and *trans*-2,8-*p*-menthadiene-1-ol; *cis*-carveol; 1-*p*-methene-9-ol; 1,8-*p*-menthadiene-9-ol; and 8-*p*-methene-1,2-diol. The first nine alcohols have been reported to be in orange oil or essence by others. The remaining 10 have not been reported to be constituents of orange oil, and the last four alcohols of these 10 have not been reported in natural products.**

VARIOUS INVESTIGATORS attempted to determine the alcohols present in citrus essential oils or essence directly from mixtures either by column chromatography (*7, 8*), by column chromatography followed by gas chromatography on total terpenoids (*2*), or by subtractive analyses of the whole oil in conjunction with gas chromatography (*15*). Recently, Attaway *et al.* (*1*) described a procedure in which alcohols were isolated from orange essence oil through removal of the carbonyls by Girard-T reagent (*13*) followed by solvent gradient elution through columns of either activated alumina or silicic acid. Frilette, Mower, and Ruben (*4*) have subsequently shown that the conditions under which the Girard-T procedure is performed are sufficient to promote dehydration of some tertiary alcohols.

The present paper describes a procedure for isolation of the alcohols from cold-pressed orange essential oil using the nonaqueous extraction procedure of Suffis and Dean (*12*) with some modifications. Nonalcoholic materials which resulted from incomplete partitioning were removed from the alcohol fraction by column chromatography. The alcohols were subsequently separated by gas chromatography and identified spectrometrically.

The partitioning of citrus oils between carbon tetrachloride and propylene glycol is particularly effective because the major portion of the oil is nonalcoholic and expeditiously removed by the carbon tetrachloride. The alcohols are isolated from the oil by preferential solubility in propylene glycol, eliminating the danger of artifact formation.

The extractive procedure is relatively fast and only a relatively small amount of oil is needed to obtain a sufficient quantity of material for analysis by gas chromatography. This procedure makes monitoring of alcohols possible when studying the changes which take place in flavor under various conditions of processing and storage.

EXPERIMENTAL

Apparatus. Column chromatography was accomplished in a $^5/_8$- × 18-inch column containing basic alumina. The hydrocarbons and carbonyls were separated from the crude alcoholic extract, which had been placed on the column, by elution with a 50/50 solution of *n*-hexane and ethyl ether. The alcohols remaining on the column were desorbed with absolute ethanol.

The alcohols were separated by gas chromatography in an F & M Model 500 gas chromatograph containing a $^1/_4$-inch o.d. by 20-foot aluminum tube packed with 17% Carbowax-30M on acid-washed Chromosorb-G. The oven temperature was programmed from 150° to 220° C. at 1.1° C. per minute with a helium flow rate of 54 ml. per minute. Fractions were collected directly onto micro salt plates (*5*) for infrared analysis and mass spectra were obtained on the same material following infrared analysis. Larger quantities of material were collected when necessary in small vials immersed in a vapor bath of liquid nitrogen.

Mass spectra were obtained using a Bendix Model 12-100 whose source was operated at 70 e.v. and recorded on an EAI X-Y Variplotter.

Infrared spectra were obtained using a Perkin-Elmer Model 137 Infracord spectrometer and, when necessary, critical absorption assignments were determined on a Beckman IR-7 spectrometer.

Procedure. The alcohols were enriched by an adaption of the carbon tetrachloride–propylene glycol partition method of Suffis and Dean (*12*). One liter each of orange oil and carbon tetrachloride and 500 ml. of propylene glycol were vigorously shaken in a 4-liter separatory funnel for 20 minutes. The two layers were separated and the propylene glycol portion was centrifuged to remove insoluble materials and residual carbon tetrachloride. One liter of a saturated aqueous solution of sodium chloride was added to the glycol and the resulting solution was extracted with four 150-ml. portions of ethyl ether. The combined ether extracts were washed with three 500-ml. portions of water and dried over anhydrous sodium sulfate. The ether was removed under reduced pressure to yield 11.0 grams of residue.

The alcohol fraction was further purified by column chromatography. A 3.5-gram portion of the residue was placed on a basic alumina column and eluted with a 100-ml. solution of *n*-hexane and ethyl ether to remove the nonalcoholic materials. The alcohols were stripped from the column with 100 ml. of absolute ethanol to yield 1.5 grams of residue upon removal of the solvent under reduced pressure.

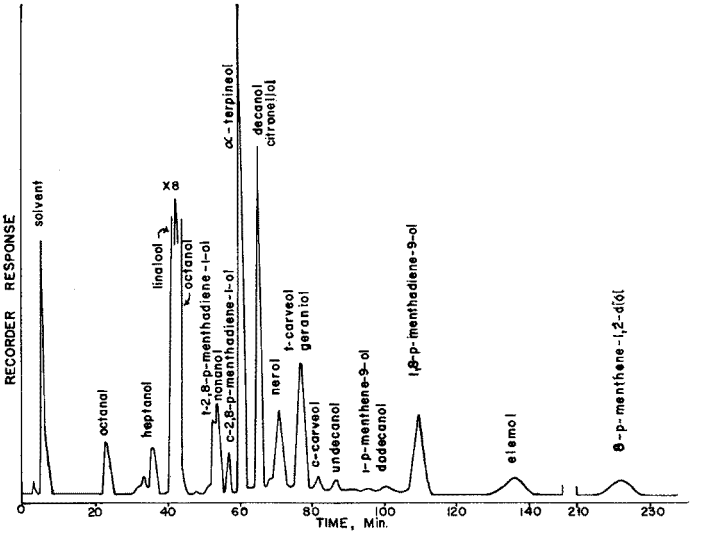

Figure 1. Chromatogram of 35-μl. sample of alcohol fraction

The alcohols were separated by gas chromatography and the materials represented by the peaks were collected and analyzed. When two alcohols are represented by a single peak in the chromatograms, such as linalool–octanol and *trans*-carveol–geraniol, the material represented by each side of the peak was collected to yield each component sufficiently pure for identification by infrared and mass spectrometric analyses.

RESULTS AND DISCUSSION

Combination of the liquid-liquid extraction procedure and column chromatography of the whole essential oil simplified the gas chromatographic separation of the alcohols by removal of other functional group components. The chromatogram shown in Figure 1 was obtained from a 35-μl. sample of the alcoholic fraction and the names of 19 compounds are indicated thereon.

The alcohols *n*-octanol, *n*-nonanol, *n*-decanol, citronellol, linalool, and α-terpineol, which have previously been identified as constituents of orange oil (*1*, *8*) are shown to be present by comparison of infrared spectra.

Geraniol, nerol, and *trans*-carveol, which have been tentatively identified to be in orange oil by other workers (*1*, *2*, *8*), are now confirmed as a result of separation and purification by gas chromatography and comparison of their infrared and mass spectrometric properties with published data (*14*).

The remaining 10 alcohols (*n*-heptanol; *n*-undecanol; *n*-dodecanol; *cis*- and *trans*-2,8-*p*-menthadiene-1-ol; elemol; *cis*-carveol; 1-*p*-menthene-9-ol; 1,8-*p*-menthadiene-9-ol; and 8-*p*-menthene-1,2-diol) are reported here to be constituents of Florida cold-pressed Valencia orange oil for the first time. The last four alcohols have not been found before in natural products.

The three aliphatic alcohols, *n*-heptanol, undecanol, and dodecanol, were identified by comparison of their respective infrared and mass spectra and gas chromatographic retention data with that obtained on materials of known structure.

The infrared spectra of *trans*- and *cis*-2,8-*p*-menthadiene-1-ol show a terminal double bond absorption at 890 and 1640 cm.$^{-1}$, and a disubstituted double bond absorption at 735 cm.$^{-1}$ for the *trans* isomer and 745 cm.$^{-1}$ for the *cis* isomer. Their molecular weights were determined to be 152 by mass spectrometry, indicating a monocyclic terpene alcohol containing two double bonds. The hydroxyl group was established to be in the one position by catalytic reduction with platinum oxide and hydrogen at 70 p.s.i. to yield 1-*p*-menthol. The tentative structures were confirmed by direct comparison with infrared spectra kindly provided by Naves and Grampoloff and described by them (*9*).

The structure of elemol, a sesquiterpene alcohol, was indicated by the nature of its mass spectrometric cracking pattern. The mass spectrum showed the loss of water by the appearance of the molecular ion at *m/e* 222 and a peak at 204. The cracking pat-

tern of the remaining spectrum was characteristic of elemene (*6*). In addition, the infrared spectrum of elemol was identical to that published by Pliva *et al.* (*11*).

The identity of *cis*-carveol was indicated by the similarity of its infrared spectrum to that of *trans*-carveol. In addition, the mass spectrum of the uncharacterized alcohol is all but identical to that of *trans*-carveol. The infrared and mass spectra and gas chromatographic retention time of *cis*-carveol, obtained by the reduction of carvone with lithium aluminum hydride, were identical to the material in question. The possibility that *cis*-carveol resulted from the isomerization of *trans*-carveol during gas chromatographic analysis was ruled out because each gave only a single peak during the purification procedure.

The structure of 1-*p*-menthene-9-ol was proved by infrared and mass spectrometry. The infrared spectrum of 1-*p*-menthene-9-ol showed an absorption at 802 $cm.^{-1}$, indicating a trisubstituted double bond. Its molecular weight, determined by mass spectrometry, is 154 and, upon reduction with PtO_2 and hydrogen at 70 p.s.i., increased to 156, indicating a monocyclic terpene alcohol with one double bond. The infrared spectrum of the completely reduced alcohol was identical to that of 9-menthol. The infrared spectrum of the unknown terpene alcohol was identical to the spectrum obtained on an authentic sample of 1-*p*-menthene-9-ol kindly provided by Brown (*3*).

The identity of 1,8-*p*-menthadiene-9-ol was established by comparison with 1-*p*-menthene-9-ol following reduction of the terminal double bond of the former, infrared absorption at 900 and 1648 $cm.^{-1}$, with Pt black and hydrogen at 70 p.s.i. The molecular weight of 152 for the diene, 154 for the monoolefin after reduction of the terminal double bond, and 156 for the totally reduced derivative, as a result of reduction with PtO_2 and hydrogen at 70 p.s.i., were determined by mass spectrometry. The infrared spectrum of the totally reduced derivative is identical to that of 9-*p*-menthol.

The identity of the material represented by the last peak in Figure 1 was shown to be 8-*p*-menthene-1,2-diol. Information on the structure was indicated by the appearance of three key *m/e* values in its mass spectrum; 170 represents the molecular ion; 152, the loss of a mol cule of water; and 134, the loss of a second molecule of water. Infrared analyses showed the presence of a terminal double bond by absorption at 1640 and 918 $cm.^{-1}$ The data indicated the compound to be a terpene diol with a terminal double bond. The mass and infrared spectra and gas chromatographic retention time of 8-*p*-menthene-1,2-diol, obtained by the hydration of limonene oxide (*10*), were identical to that obtained from the orange oil.

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Gas Chromatographic Determination of Free Formic and Acetic Acids in Cigarette Smoke

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▷ **Free formic and acetic acids and their salts in cigarette smoke may be quantitatively determined in the presence of formates and acetates after adsorbing the acids on a strong base anion exchange resin in the fluoride form. The compounds are eluted and methylated in a single step with an anhydrous methanol–hydrochloric acid solution. The methyl esters are subsequently determined by gas chromatography. This method is applicable to problems requiring the analysis of free formic and acetic acids in the presence of their esters.**

DETERMINATION of free formic and acetic acids in complex mixtures containing formates and acetates has long been a problem. Most methods reported for the analysis of formic and acetic acids require alkali which hydrolyzes the esters of these acids. Formates and acetates are easily hydrolyzed even when passed through a strong base anion exchange resin in the OH^- form. The method described here is for the separation of free formic and acetic acids in cigarette smoke extracts, without hydrolyzing the esters, by adsorption onto a strong base anion exchange resin in the fluoride form, followed by simultaneous methylation and elution from the resin. The resulting methyl esters are separated and quantitatively determined by gas chromatography.

EXPERIMENTAL

Reagents. A strong base anion exchange resin, Rexyn 202 ($Cl\text{-}SO_4$) from Fisher Scientific Co. is used.

Anhydrous methanol–hydrochloric acid solution. Anhydrous hydrochloric acid (The Matheson Co., East Rutherford, N. J.) is bubbled into anhydrous methanol (J. T. Baker Chemical Co., Phillipsburg, N. J.) so that the solution contains 7 to 10% HCl. The concentration of hydrochloric acid is checked by titration of an aliquot with 0.1*N* NaOH to the methyl red end point.

Potassium fluoride solution. Reagent grade potassium fluoride from Fisher Scientific Co. is used to prepare a 10% aqueous solution.

One milliliter of a solution containing 2.5 mg. per milliliter of formic acid (Fisher Scientific Co.) and 5.0 mg. per milliliter of acetic acid (Baker and Adamson Chemical Co.) is used for recovery studies. The exact concentrations of the acids are determined by titration with 0.1*N* NaOH to the methyl red end point.

Methyl formate and methyl acetate standards, 0.1, 0.2, 0.4, 0.8, 1.0, and 2.0 μg. per microliter of pure methyl formate (Eastman Kodak) and methyl acetate (Fisher Scientific Co.) dissolved in methanol are used as gas chromatographic standards. The purity of the esters should be checked.

Chromosorb P, 60- to 80-mesh (Johns Manville, New York, N. Y.) containing 20% Carbowax 20M (Union Carbide Corp., Boundbrook, N. J.) is used as the stationary phase.

Apparatus. An F & M Model 500 gas chromatograph (F & M Scientific Corp., Avondale, Pa.) modified with a D-204-TWH detector (Loenco, Inc., Altadena, Calif.) and 1-mv. recorder (Minneapolis-Honeywell Co., Philadelphia, Pa.) is used. A Phipps and Bird automatic smoking machine (Phipps and Bird, Inc., Richmond, Va.) (*4*) is used for smoke collection.

Pretreatment of Resin. Rexyn 202 (10 grams) is stirred with 50 ml. of 10% potassium fluoride solution. The mixture is allowed to stand for one hour with occasional stirring. The supernatant liquid is then discarded and the resin is washed 5 or 6 times with distilled water or until the liquid is fluoride free. The presence of fluoride can be detected by reacting the supernatant liquid with a barium chloride solution and noting a precipitate of barium fluoride.

Procedure. Cigarettes are smoked on the automatic smoking machine under standard conditions (*4*) (35-ml. puffs of 2-second duration at 1-minute intervals) to a 30-mm. butt length. The particulate matter is collected on a Cambridge filter pad and any acids in the gas phase are collected in a bubbler trap containing 35 ml. of water. Five cigarettes are smoked in succession, the Cambridge filter pad and holder are replaced with a fresh filter assembly, and 5 more cigarettes are smoked. The filter pads containing the particulate matter are kept in a small stoppered test tube. The trapped material from 20 cigarettes (4 filter pads and 2 water traps) is combined in a Waring Blendor jar. The traps and test tubes are thoroughly rinsed with water and the washings are added to the blender jar. The sample is macerated for 30 seconds in the blender. The slurry is vacuum filtered through Whatman No. 41 filter paper, and the disintegrated pads are macerated again in the blender with 150 ml. of distilled water. The slurry is vacuum filtered and the two filtrates are combined.

Column Chromatography. Ten grams of Rexyn 202 (F^-) are washed with water into a 50-ml. buret containing a small wad of glass wool. After the resin has settled, the water level is lowered to 1 inch from the top of the resin. A 500-ml. separatory flask and a siphon tube are sealed onto the buret with rubber tubing. The filtrate is transferred to the separatory funnel, and by adjusting the stopcock and the liquid level above the resin bed the flow rate is limited to 5 ml. per minute.

The resin is then washed successively with 100 ml. of water, 100 ml. of 1:1 methanol–H_2O solution and, finally, with 100 ml. of anhydrous methanol. The resin is washed with methanol immediately before elution to ensure a low resin blank.

For elution and methylation, the siphon tube is removed and the liquid level is lowered to the top of the resin bed. The acids are eluted with HCl–methanol solution flowing at a rate of 2 ml. per minute. The first 5 ml. of eluate are discarded and the next 35 ml. are collected.

Gas Chromatography. An F & M Scientific Corp. Model 500 programmed temperature chromatographic unit fitted with a Loenco D-204-TWH thermal conductivity detector is used. A 4-foot by 1/4-inch o.d. column containing Carbowax 20M as the stationary phase (7 grams, 20% Carbowax on 60/80 mesh Chromosorb P) (*5*) is used. The helium flow rate is 100 ml. per minute, the column is kept at 50° C., the injection port temperature is 200° C., the detector temperature is 225° C., and the bridge current is 90 ma. Fifty microliters of sample or standard are injected.

Quantitative Analysis of Acids. Since the standard curves of methyl formate and acetate are linear from 0.1 to 2.0 μg. per microliter, only one standard solution of the acids (0.2 μg. per microliter) is run daily. The column is preloaded each day with two 50-μl. injections of the standard solution to re-equilibrate the column. Samples are then chromatographed at regular intervals of approximately 20 minutes. A resin–HCl impurity having the same retention time as methyl formate has been observed (Figure 1). Therefore, the peak height of a resin blank treated the same way as a sample is subtracted from the peak height of the sample. The net peak height is used for calculations.

RESULTS AND DISCUSSION

Several different trapping systems were tried for the collection of whole smoke, including a trap packed with ion exchange resin, a bubbler trap containing distilled water, a bubbler trap containing water and cellulose powder. The most efficient trapping system proved to be a Cambridge filter pad in a Lucite holder (*6*) in series with a bubbler trap containing distilled water. This system has the added advantage that the total particulate matter and the formic and acetic acids can be determined simultaneously. Separate analyses of the filter pads and water indicated that all the formic acid is trapped on the pad, but 8% of the acetic acid is in the water trap. Serial extraction of the Cambridge filter pads, first with water from the bubbler trap, then with distilled water, ensures complete removal of the acids from the filter pads (Table 1).

Originally, Rexyn 202, a strong base ion exchange resin, was used in the hydroxyl form and in a batch-type operation, as described by Robb and Westbrook (*5*) and Hornstein *et al* (*3*). The resin in the hydroxyl form hydrolyzed formates and acetates, such as triacetin, ethyl formate, ethyl acetate, benzyl acetate, and phenyl ethyl acetate. About 70% of the acetate and formate moiety was recovered as the free acids.

Table I. Recovery of Known Formic and Acetic Acids

	% Recovered	
	HCOOH	CH_3COOH
From clean Cambridge filter pads	98	102
From Cambridge filter pads and smoke	105	100
From smoke extracts	101	102
From water trap	95	97

A mixture of these compounds added to smoke extract was also hydrolyzed by the resin in the OH^- form. Rexyn 202 (F^-) did not hydrolyze these esters in solution nor when they were added to smoke extract. The resin in the fluoride form also quantitatively removes the formate and acetate ions from solution containing sodium and ammonium salts of the acids. Because of the buffering capacity of cigarette smoke, some of the formic and acetic acids may be present as salts.

Hydrolysis with sodium hydroxide of the effluent from the resin in the fluoride form can be used to determine the amount of esterified formic and acetic acids. Rexyn 202 (OH^-) quantitatively adsorbs the anions, and the acids are completely recovered in the elution and methylation step. Rexyn 203 (OH^-), a weak base anion exchange resin, did not hydrolyze the esters, but neither did it quantitatively trap the acids. Rexyn 202 (F^-) form did not quantitatively remove the free acids when used batchwise, but did so when used in a column.

The elution and methylation of the acids from the ion exchange column can be readily accomplished in a single step by using 7 to 10% anhydrous hydrochloric acid in methanol. Hydrochloric acid concentration below 7% broadens the elution peak and a larger fraction is required for complete collection.

A study of the methylation rate showed that both acids are completely methylated by the time they are eluted off the Rexyn 202 (F^-) column. Formic acid was 90% methylated when eluted off Rexyn 202 (OH^-) column and was completely methylated within 24 hours. The acetic acid was completely methylated by the time it was eluted.

The Loe detector has improved the gas chromatographic sensitivity fourfold over the sensitivity obtained with the standard F & M W1 detector even though it is used at lower filament current (90 ma.). With this detector we can conveniently determine the formic and acetic acid present in the smoke from 20 cigarettes.

Peak heights *vs.* concentrations of standard solutions of methyl formate and methyl acetate in methanol over a range of 0.1 to 2.0 μg. per microliter give a linear plot. It is necessary, however, to preload the column each day with the standard ester solution before making any measurements of peak height. The variation of the peak height of a single standard solution from day to day and within a day is very small, if the column has been preloaded and if injections are made at regular intervals of about 20 minutes.

Table II. Comparison of Results

	μg. in smoke/cigt. HCOOH	CH_3COOH
Bradford *et al.* (*1*)		
All-bright cigarette	410	2496[a]
All-burley cigarette	252	2303[a]
Buyske *et al.* (*2*)		
All-bright cigarette	424	1032
All-burley cigarette	356	846
By this procedure		
All-bright cigarette	179	437
All-burley cigarette	93	235

[a] Total volatile acids as acetic acid.

Table III. Comparison of Resin Forms

Eluted and methylated on	μg in smoke/cigt. of blended tobacco HCOOH	CH_3COOH
1 Rexyn 202 (OH^-)	213	771
2 Resyn 202 (F^-)	61	161
3 Effluent passed through Rexyn 202 (OH^-)	157	868
4 Total (2 plus 3)	218	1029

Table IV. Cigarette Smoke Delivery

Cigt. brands	μg./cigt. HCOOH	CH_3COOH
A	61	161
B	50	137
C	48	158
D	51	153
E	55	138
F	58	149
G	60	117
H	62	154
I	68	252
J	79	202
K	77	198
L	94	322
M	78	125

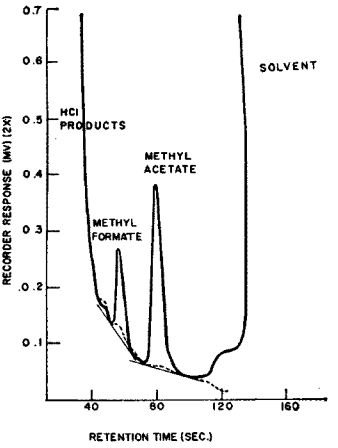

Figure 1. Gas chromatogram of methylated smoke components

— Smoke solution
--- Blank solution

The chromatogram of a typical smoke sample is shown in Figure 1. Hydrogen chloride and its reaction products with the resin appear first, followed by methyl formate at about 55 seconds and methyl acetate at about 78 seconds. The methanol solvent peak appears at about 140 seconds and is not completely eluted for 15 to 20 minutes. A small peak from the reagent blank solution which has the same retention time as the methyl formate peak must be subtracted from the sample peak height. Other peaks from the blank solution do not interfere. The peak height from the blank is higher if the resin is not washed with methanol immediately before elution with HCl–methanol.

Recovery studies were made by adding known quantities of aqueous solutions of formic and acetic acids to distilled water, to filter pads containing smoke particulate matter, and to the water traps before smoking. Recoveries of 95 to 105% of each acid were usually obtained, as shown in Table I.

The relative standard deviation of the method for an individual determination of the acids in cigarette smoke is ±18% for formic acid and ±14% for acetic acid at the 95% confidence level (2σ). This includes sample variation and smoking variation as well as analytical error.

Buyske, Wilder, and Hobbs (*2*), and Bradford *et al* (*1*), reported formic and acetic acid values for all-burley and all-bright tobacco cigarettes (Table II). Most authors extracted the acids with sodium hydroxide. Using Rexyn 202 (OH^-) gave comparable results, while using it in the F^- form gave lower values (Table III). The sum of the acids obtained by passing the F^- form resin effluent through the OH^- form resin also gave comparable values; however, it appears that the extent of hydrolysis has changed.

Table IV gives results of some commercially available cigarettes analyzed by this procedure.

The experiments that have been described show that this procedure quantitatively determines the amount of free formic and acetic acids in cigarette smoke and does not cause any hydrolysis of formic and acetic acid esters. This method should therefore be applicable to problems requiring the analysis of free formic and acetic acids in the presence of esters.

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Correction

Resorufin Butyrate and Indoxyl Acetate as Fluorogenic Substrates for Cholinesterase

In this article by George G. Guilbault and David N. Kramer [ANAL CHEM. **37**, 120 (1965)], the caption for Figure 1 on page 121 should read as follows:

Figure 1. Excitation and emission curves for resorufin fluorescence
A. Excitation curve: emission wavelength 580 mμ
B. Emission curve: excitation wavelength 540 mμ

Quantitative Gas Chromatography of Amino Acids

Preparation of *n*-Butyl *N*-Trifluoroacetyl Esters

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▶ **A procedure was developed for preparing *n*-butyl *N*-trifluoroacetyl esters of amino acids for use in analysis by gas liquid chromatography. This derivative was found to have advantages over others investigated. Single chromatographic peaks were obtained for all of the common protein amino acids except tryptophan and arginine. Tryptophan gave two peaks but could be converted into a single derivative by longer acylation. Reproducibility of response was found to be good for derivatives carried through the entire chemical and chromatographic procedure, and no problems were indicated in the analysis of mixtures. Under anhydrous conditions the derivatives were stable with respect to time, and yield of derivative was found to be above 96% for each of six representative amino acids.**

Because of its speed, accuracy, and sensitivity, gas chromatography offers advantages over other chromatographic methods which have been employed for the determination of amino acids. However, the development of satisfactory gas chromatographic procedures has been rather slow as a result of the fact that amino acids are not sufficiently volatile to permit direct analysis and must thus be converted into volatile derivatives prior to gas chromatography. The present study was undertaken to evaluate the problems involved, and reaction conditions required, in quantitatively converting amino acids into volatile derivatives suitable for analysis by gas liquid chromatography.

Since 1956, a number of derivatives have been investigated for possible use in the gas chromatographic determination of amino acids. Hunter, Dimick, and Corse (*8*) used oxidation with ninhydrin to prepare volatile aldehydes from several aliphatic amino acids, and the procedure was developed by Zlatkis, Oró, and Kimball (*24*) into a fully automated method for the analysis of seven amino acids. Other approaches have included decarboxylation to give volatile amines (*2*), conversion to methyl α-hydroxy esters (*12, 20*), and conversion to methyl α-chloro esters (*13*). In 1957, Bayer, Reuther, and Born (*1*) reported that the methyl esters of a number of aliphatic amino acids prepared by the Fischer method could be separated by gas chromatography. Saroff, Karmen, and Healy (*18*) successfully chromatographed the ester hydrochlorides of 14 amino acids by adding ammonia to the carrier gas, and Nicholls, Makisumi, and Saroff (*14*) explored the possibility of chromatographing the acid salts of amino acid methyl esters by operating the flash heater at a temperature sufficiently high to cause dissociation to the free ester.

One of the first to recognize the advantages of *N*-substituted esters of amino acids as derivatives for gas chromatography was Youngs (*23*), who in 1959 reported that chromatographic peaks had been obtained for the *n*-butyl *N*-acetyl esters of glycine, alanine, valine, leucine, isoleucine, and proline. Johnson, Scott, and Meister (*9, 10*) investigated the preparation and gas chromatographic separation of the *n*-amyl *N*-acetyl esters. Chromatographic peaks were obtained for the derivatives of 36 amino acids including 18 of the common protein amino acids, but difficulties were experienced with tryptophan, histidine, cystine, and arginine. A significant aspect of the work was the use of columns containing small percentages of liquid phase at relatively low temperatures, and the separations achieved were generally good. Graff, Wein, and Winitz (*6*) considered the *n*-propyl *N*-acetyl esters to be the best amino acid derivatives for gas chromatography because of the ease with which they could be separated, but an examination of the properties of a number of derivatives led Blau and Darbre (*3*) to favor the *n*-amyl *N*-trifluoroacetyl esters. Zomzely, Marco, and Emery (*25*) reported that the *n*-butyl *N*-trifluoroacetyl esters of 22 naturally occurring amino acids could be prepared and that they could be chromatographed on a single column by means of temperature programming. Chromatographic separation of the derivatives was fairly complete, but a quantitative study of the procedure used for derivative preparation was not made. Pisano, Vanden Heuvel, and Horning (*15*) investigated the gas chromatographic behavior of the phenylthiohydantoins and methyl 2,4-dinitrophenyl esters, and the latter derivatives were also studied by Landowne and Lipsky (*11*), who obtained high sensitivity by employing an electron capture detector. Rühlmann and Giesecke (*16*) separated a mixture of trimethylsilyl *N*-trimethylsilyl amino acid esters, but the derivatives were not found to be sufficiently stable to be utilized for quantitative analysis (*5*).

The methyl *N*-trifluoroacetyl esters have been investigated by a number of workers including Weygand *et al.* (*22*), Saroff and Karmen (*17*), Wagner and Winkler (*21*), and Hagen and Black (*7*). Cruickshank and Sheehan (*4*) chromatographed all of the common protein amino acids and ornithine after conversion to their methyl *N*-trifluoroacetyl esters, but a detailed study was not made of the quantitative aspects of derivative preparation.

Since most of the functional groups likely to be encountered in any amino acid analysis are also found in the protein amino acids, the present study was limited chiefly to those amino acids which are commonly found in proteins. Emphasis was placed on quantitative and reproducible derivative preparation because it was recognized that a high yield of derivative was an essential prerequisite for an accurate gas chromatographic method for amino acids.

EXPERIMENTAL

Apparatus. A Barber-Colman Model 10 gas chromatograph having a 20-mc. Sr^{90} argon ionization detector (5-ml. internal volume) was used in early phases of the work. Samples were introduced through the sample injection system of an attached capillary column conversion kit, but the included sample splitter was removed. Argon was used as the carrier gas.

Also employed was an F & M Model 300 linear programmed temperature gas chromatograph equipped with an F & M Model 1609 flame ionization attachment. The instrument

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was used without modification, but the column oven and detector module of an F & M Model 400 biomedical gas chromatograph was installed for the final passes of the work. Cylinders packed with silica gel and Linde molecular sieve, type 5A, were placed in the hydrogen and air lines to remove water and hydrocarbons. Nitrogen was used as the carrier gas.

During the course of the investigation, it was frequently necessary to heat samples, with magnetic stirring, in a constant-temperature oil bath. Sample flasks containing magnetic stirring bars were placed in an aluminum pan, and the contents were stirred with a Labline Multi-Magnestir (Labline, Inc.) while mineral oil was circulated in the pan and maintained at a constant temperature by means of an Aminco constant-temperature circulating bath (American Instrument Co.). This arrangement made it possible to heat and stir six samples simultaneously.

Samples were introduced for gas chromatography by means of a Hamilton 701N 10.0-μl. syringe, and an Ott compensating polar planimeter calibrated in square inches and accurate to 0.01 square inch was used for the measurement of peak areas. Unless otherwise indicated, a CaLab Model C rotary evaporator (California Laboratory Equipment Co.) was used for all vacuum distillations.

Reagents. All amino acids except cysteine were purchased from Nutritional Biochemicals Corp. and Mann Research Laboratories. Amino acids obtained from Nutritional Biochemicals Corp. had been tested by available recognized techniques to assure highest purity, and those from Mann Research Laboratories were "Mann assayed" chromatographically pure chemicals. Cysteine was obtained from California Corporation for Biochemical Research and was "A grade," which was the highest purity obtainable from this source. Amino acids used in the study were either of the L- or DL-configuration, and no differences were observed between the chromatographic behaviors of derivatives prepared from L- and DL-amino acids.

Anhydrous methanol was a "Fisher certified reagent" obtained from Fisher Scientific Co. To ensure that it was anhydrous, it was dried by treatment with magnesium turnings prior to use. 1-Butanol was a "Baker analyzed reagent" obtained from J. T. Baker Chemical Co., and trifluoroacetic anhydride was an "Eastman grade" chemical produced by Distillation Products Industries. Hydrogen chloride used as esterification and interesterification catalyst was purchased as a compressed gas from The Matheson Co., Inc., and was 99.0% minimum purity.

Procedure. Analytical Preparation of *n*-Butyl *N*-Trifluoroacetyl Esters. The amino acid or mixture (<60 mg.) was placed in a 125-ml. flat-bottom flask, and 10 ml. of anhydrous methanol containing 1.20 ± 0.10 meq. per ml. of anhydrous HCl were added. The flask was then stoppered with a ground-glass stopper; the solution was stirred on a magnetic stirrer for 30 minutes at room temperature; and the methanol was removed by vacuum distillation at 60° ± 1° C. Ten milliliter of 1-butanol containing 1.20 ± 0.10 meq. per ml. of anhydrous HCl were added; the solution was heated for 180 minutes with magnetic stirring in an oil bath at 90° ± 3° C., and the butanol was removed by vacuum distillation at 60° ± 1° C.

n-Butyl ester hydrochloride(s) was (were) then trifluoroacetylated by adding 5.00 ml. of methylene chloride and 0.50 ml. of trifluoroacetic anhydride and stirring for 120 minutes at room temperature on a magnetic stirrer. The trifluoroacetic anhydride and solvent were removed by vacuum distillation at room temperature, and the *n*-butyl *N*-trifluoroacetyl ester(s) was (were) dissolved in anhydrous chloroform prior to gas chromatography. Preparation of derivatives by this procedure required over 5 hours, but since only about 10 minutes of the analyst's time was needed per sample, a number of samples (six with the apparatus employed) could be carried through the procedure simultaneously.

Preparation of Pure *n*-Butyl *N*-Trifluoroacetyl Esters. Pure *n*-butyl *N*-trifluoroacetyl esters of valine, isoleucine, methionine, glutamic acid, tyrosine, and lysine were synthesized for use as reference standards. One (1.000) gram of amino acid and 200 ml. of 1-butanol containing 2.00 ± 0.10 meq. per ml. of anhydrous HCl were placed in a 250-ml. flat-bottom flask, and the solution was heated in an oil bath at 90° ± 3° C. for 180 minutes with magnetic stirring. After removal of the butanol by vacuum distillation at 60° ± 1° C., 50 ml. of 1*M* aqueous Na_2CO_3 were added and the solution was extracted with two 25-ml. portions of methylene chloride (or until extraction of the amino acid ester was complete in the case of tyrosine) in a 250-ml. separatory funnel. The combined methylene chloride extracts were then extracted with 50 ml. of distilled water, placed in a 125-ml. flat-bottom flask, and evaporated to dryness by vacuum distillation at room temperature. Twenty-five additional milliliters of methylene chloride were added, and evaporation was repeated to remove remaining traces of water by azeotropic distillation.

The residue was dissolved in a solution of 25 ml. of *n*-hexane containing 1.0 ml. of anhydrous diethyl ether, and the solution was saturated with anhydrous HCl. The solvent was then removed by vacuum distillation at room temperature; 25 ml. of *n*-hexane were added and the solution was allowed to stand for 15 hours at −30° C. If the *n*-butyl ester hydrochloride crystallized, the hexane was removed by filtration, and if crystallization did not occur, the solvent was removed by vacuum distillation at room temperature.

The ester hydrochloride was then trifluoroacetylated in a 125-ml. flat-bottom flask by adding 10 ml. of methylene chloride and 3.00 ml. of trifluoroacetic anhydride and stirring for 180 minutes at room temperature on a magnetic stirrer. The anhydride and solvent were removed by vacuum distillation at room temperature, and the *n*-butyl *N*-trifluoroacetyl ester was purified by vacuum distillation. A 10-ml. heart-shaped Claissen flask was employed to purify the derivatives of valine, isoleucine, methionine, and glutamic acid. For tyrosine and lysine, a special molecular distillation apparatus was required (*19*).

Yield of Derivative. Ten milligrams of amino acid were placed in a 125-ml. flat-bottom flask, and *n*-butyl *N*-trifluoroacetyl ester was prepared by the analytical procedure. Approximately the same number of moles of pure *n*-butyl *N*-trifluoroacetyl ester was weighed and placed in another flask, and each derivative (analytical and pure) was dissolved in 2.000 ml. of a 10.0-ml. chloroform solution containing the *n*-butyl *N*-trifluoroacetyl ester prepared from 50.0 mg. of glutamic or aspartic acid. Each solution was then analyzed by gas chromatography under the conditions indicated for Figure 4, and per cent conversion of amino acid to derivative was computed by comparing the peak area obtained for the derivative prepared by the analytical procedure with that obtained for the pure derivative. The butyl trifluoroacetyl ester of glutamic or aspartic acid added to each sample was employed as an internal standard to correct for variations in injected sample volume, solution volume, and instrumental response.

RESULTS AND DISCUSSION

Selection of Derivative. Procedures investigated in preliminary experiments included oxidation to volatile aldehydes with ninhydrin, reduction to amino alcohols with lithium aluminum hydride, preparation of the methyl esters, and preparation of the *n*-butyl *N*-acetyl esters. Chromatographic peaks were obtained for the *n*-butyl *N*-acetyl esters of all of the common protein amino acids except histidine, arginine, and cystine, and the conclusion was reached that the *N*-acyl esters were ideal derivatives for the gas chromatography of amino acids. By employing the proper reagents and reaction conditions it should be possible to esterify all carboxyl groups and to acylate all amino, hydroxy, phenolic, sulfhydryl, imidazole, and guanido groups, thereby masking the polarity of all groups which would cause difficulty in gas chromatographic separations.

Experiments were conducted to evaluate the problems involved in separating the *n*-butyl *N*-acetyl esters for which chromatographic peaks were obtained, and, as shown by Figure 1, a good separation was achieved within 11 minutes for the derivatives of alanine, valine, glycine, isoleucine, and leucine, which are the first five components to be eluted from most columns. A complete separation was not attempted

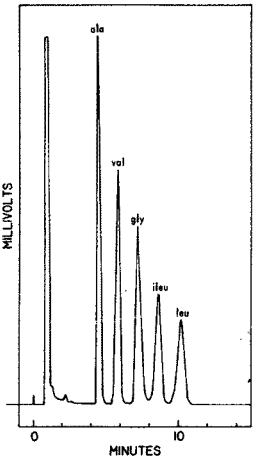


Figure 1. Separation of five *n*-butyl *N*-acetyl amino acid esters (Barber-Colman Model 10)

Column: 250- × 0.47-cm. i.d. stainless steel packed with 0.25% (w./w.) Carbowax 1500 on 30- to 60-mesh acid-washed Chromosorb W. Flow rate: 46 ml. per minute argon. Column temp.: 150° C. Flash-heater temp.: 302° C.

at this time since it was recognized that such a study should be delayed until peaks had been obtained for those amino acids which had given negative results. It was apparent, however, that the desired separations could be attained for any *N*-acyl ester which was sufficiently volatile and sufficiently nonpolar to permit gas chromatography.

In order that their chromatographic behaviors could be compared, the methyl *N*-trifluoroacetyl, methyl *N*-acetyl, *n*-butyl *N*-trifluoroacetyl, and *n*-butyl *N*-acetyl esters of each of the amino acids listed in Table I were prepared and chromatographed. The amino acids were selected to give derivatives which would represent a wide range of volatilities, and the derivatives prepared were chosen to give extremes of volatilities. The temperature of the chromatographic column was programmed as indicated, and the temperature at which each derivative emerged from the column (retention temperature) was recorded. Two different chromatographic columns were employed because the range of volatilities was too great to permit chromatography on a single column.

Table I shows that the trifluoroacetyl esters are more volatile than the corresponding acetyl esters and that the methyl esters are more volatile than the *n*-butyl esters. Table I also reveals that difficulties are involved in the gas chromatography of the acetyl esters of those amino acids which yield the least volatile *N*-acyl esters. The *n*-butyl acetyl ester prepared from lysine tailed badly and was eluted from the chromatographic column at a high temperature, and the methyl acetyl ester was not eluted under the conditions employed. The evidence clearly indicated that the trifluoroacetyl esters were better derivatives than the acetyl esters.

However, the results did not permit a choice between the methyl and *n*-butyl trifluoroacetyl esters. The methyl trifluoroacetyl esters of valine, phenylalanine, and glutamic acid had retention temperatures considerably lower than those for the corresponding *n*-butyl trifluoroacetyl esters, but the methyl and *n*-butyl trifluoroacetyl esters of lysine were eluted at approximately the same temperature. The conclusion was reached that the difficulties involved in the gas chromatographic separation of the methyl or *n*-butyl trifluoroacetyl esters would be approximately equal, and the chromatographic behavior of the ethyl, propyl, and amyl trifluoroacetyl esters would be expected to be similar to that of the methyl and butyl trifluoroacetyl derivatives.

Another important consideration in selecting a trifluoroacetyl ester for gas chromatography is volatility. If volatility is too great, the esters cannot be readily concentrated following trifluoroacetylation, and the analysis of samples containing small amounts of amino acids presents considerable difficulty. It is therefore important to select a trifluoroacetyl ester which can be readily concentrated without volatility losses.

For a comparison of their relative volatilities, the derivatives listed in Table II were prepared from 10.0-mg. quantities of amino acid, chromatographed without removal of the acylation solvent (1.000 ml. of trifluoroacetic anhydride dissolved in 4.000 ml. of methylene chloride), evaporated just to dryness in a rotary evaporator, dissolved in 5.000 ml. of methylene chloride, and then rechromatographed. Because of the accuracy required, 10.0 mg. of glutamic acid hydrochloride were included with the amino acids from which the *n*-butyl *N*-trifluoroacetyl esters were prepared so that the *n*-butyl *N*-trifluoroacetyl ester served as an internal standard.

Table II shows that serious losses were involved in concentrating the methyl trifluoroacetyl ester of valine, and similar losses were observed for other methyl trifluoroacetyl esters. No such difficulties were involved, however, with the *n*-butyl trifluoroacetyl esters, and recoveries of 99, 100, and 97% were obtained for valine, alanine, and glycine, respectively, which would be expected to yield the most volatile derivatives. The *n*-butyl *N*-trifluoroacetyl esters were

Table I. Retention Temperatures of Four *N*-Acyl Esters Prepared from Each of Four Amino Acids

	Retention temperature of derivative,[a] °C.				
	Methyl *N*-trifluoro-acetyl	Methyl *N*-acetyl	*n*-Butyl *N*-trifluoroacetyl		*n*-Butyl *N*-acetyl
Amino acid	A[b]	A[b]	A[b]	B[c]	B[c]
Valine	56	65	109	71	110
Phenylalanine	133	141	167	130	156
Glutamic acid	123	137	180	144	170
Lysine	200	[d]	209	173	216 (tailed)

[a] Five microliters of a 2.00-ml. $CHCl_3$ solution containing derivative prepared from 10.0 mg. of amino acid were injected directly on the chromatographic column without the use of a flash heater.
[b] Instrument: F & M Model 400. Column: 100- × 0.3-cm. i.d. borosilicate glass packed with 2.00% (w./w.) neopentylglycol succinate on 80- to 100-mesh acid-washed Chromosorb W. Column temp.: 41° C. for 3.0 minutes, then programmed at 3.3° C. per minute to 218° C., then isothermal for 15 minutes. Other conditions as described for Figure 4.
[c] Conditions of chromatography as described for Figure 4.
[d] Not eluted under the chromatographic conditions employed.

Table II. Volatilities of Methyl and *n*-Butyl *N*-Trifluoroacetyl Esters of Amino Acids

	Peak area, sq. in.		
Derivative	Before evaporation	After evaporation[a]	Recovery, %
Methyl *N*-trifluoroacetyl valine	0.495[b]	0.316[b]	64
n-Butyl *N*-trifluoroacetyl valine	1.255	1.243[c]	99
n-Butyl *N*-trifluoroacetyl alanine	1.71	1.708[c]	100
n-Butyl *N*-trifluoroacetyl glycine	1.37	1.327[c]	97

[a] At room temperature (26° C.) and about 4 mm. of mercury.
[b] Average of four independent determinations.
[c] Corrected with internal standard.

therefore selected for subsequent study because they represented a satisfactory compromise between volatility and ease of chromatographic separation.

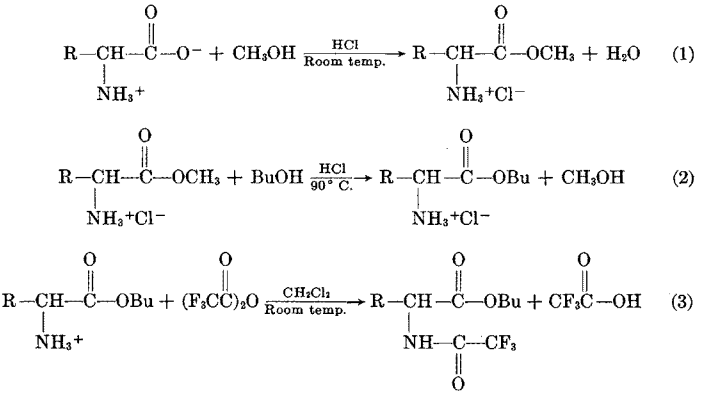
Stability of *n*-Butyl *N*-Trifluoroacetyl Esters. In early experiments with the *n*-butyl *N*-trifluoroacetyl esters, extraneous peaks were often encountered which had not been observed for the corresponding *n*-butyl *N*-acetyl esters. These peaks were found to be the result of decomposition of derivative in the metal flash heater of the chromatographic apparatus and could be reduced in size by lowering the flash-heater temperature. Figure 2 shows chromatograms obtained by injecting 5.00 μl. of a 2.00-ml. chloroform solution of the *n*-butyl *N*-trifluoroacetyl ester prepared from 10.0 mg. of threonine. By lowering the temperature of the flash heater from 223° C. to 142° C., the size of the major extraneous peak was considerably reduced. Problems due to thermal instability were completely avoided by eliminating the flash heater, and no extraneous peaks due to thermal decomposition were observed with any of the derivatives when samples were injected directly on the chromatographic column without the use of a flash heater.

Stability with respect to time was also found to be good. As shown by Table III, recovery, as determined by peak area, was found to be essentially quantitative for derivatives which had been allowed to stand for 90 hours or longer, and no difficulties due to instability were indicated.

When the *n*-butyl *N*-trifluoroacetyl ester of tyrosine, serine, threonine, or hydroxyproline was allowed to stand prior to chromatography, a second peak was often observed which had a longer retention time than the peak initially obtained. The second peak could be made to disappear by reacylation and was apparently due to the monoacyl ester produced by hydrolysis of the trifluoroacetylated phenolic or hydroxy group. Problems due to hydrolysis could be avoided by storing the derivatives in a solvent containing a small amount of trifluoroacetic anhydride.

Preparation of the *n*-Butyl *N*-Trifluoroacetyl Esters. Reaction conditions required to prepare the *n*-butyl *N*-trifluoroacetyl esters were studied, and a procedure for their quantitative preparation was evolved. Esterification presented problems because of the insolubility of cystine and the basic amino acids in butanol. Among the procedures tried were direct esterification with HCl, HBr, and *p*-toluenesulfonic acid as catalysts; direct esterification in a polar solvent; and interesterification with HCl, H_2SO_4, Dowex 50, BCl_3, and BF_3 as catalysts.

The methyl esters, which are more soluble in butanol than the free acids, were easily prepared as a result of the high polarity of methanol, and good results were obtained by methyl ester formation followed by interesterification. The *n*-butyl esters were prepared by esterification in methanol (Equation 1) at room temperature followed by interesterification in 1-butanol (Equation 2) at 90° C. with anhydrous HCl used as a catalyst in both cases; the *n*-butyl ester hydrochlorides were then trifluoroacetylated (Equation 3) at room temperature in a methylene chloride solution of trifluoroacetic anhydride. For cysteine it was necessary to conduct the esterification and interesterification under a nitrogen atmosphere to prevent oxidation.



The time required for interesterification was determined by observing the time required to cause disappearance of the peaks corresponding to the methyl *N*-trifluoroacetyl esters, and a temperature of 90° C. was selected because this was the lowest temperature at which interesterification could be accomplished within 3 hours. The reaction of HCl with butanol to yield butyl chloride and water was already significant at 90° C., and thus a temperature above 90° C. was not employed. The reaction was much slower at 80° C. and almost insignificant at 70° C., but interesterification was not complete at these temperatures.

Because the phenolic group is difficult to acylate under acidic conditions, tyrosine was selected for a study of the time required for trifluoroacetylation. The ratio of the peak area obtained for the *n*-butyl *N,O*-ditrifluoroacetyl ester prepared from 10.0 mg. of tyrosine divided by the peak area of dibutyl suberate used as an internal standard is plotted as a function of trifluoroacetylation time in Figure 3. Trifluoroacetylation was essentially complete after 1 hour, and the conclusion was reached that the *n*-butyl ester hydrochlorides of all of the common protein

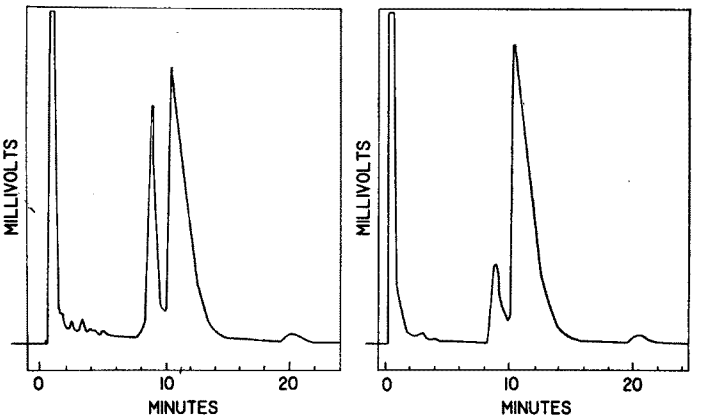


Figure 2. Thermal decomposition of the *n*-butyl *N*-trifluoroacetyl ester of threonine as influenced by flash-heater temperature (F & M Model 1609)

Column: 100- × 0.39-cm. i.d. stainless steel packed with 1.00% (w./w.) neopentylglycol succinate on 60- to 80-mesh Gas-Chrom A. Flow rate: 37 ml. per minute N_2. Column temp.: 93° C. Flash-heater temp.: 223° C. left, 142° C. right

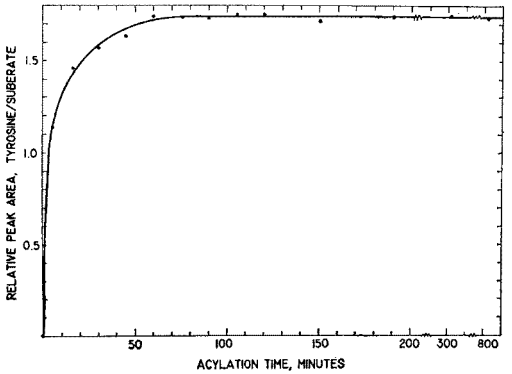


Figure 3. Relative peak area of tyrosine as a function of trifluoroacetylation time

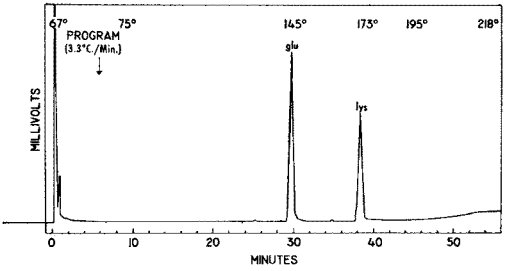


Figure 4. Chromatogram of the *n*-butyl *N*-trifluoroacetyl ester prepared from lysine with glutamic acid as an internal standard (F and M Model 400)

Column: 100- × 0.3-cm. i.d. borosilicate glass packed with 1.00% (w./w.) neopentylglycol succinate on 60- to 80-mesh Gas-Chrom A. Flow rate: 38 ml. per minute N_2. Column temp.: 67° C. for 6.0 minutes, then programmed at 3.3° C. per minute to 218° C. Amplifier range: 100. Sensitivity: 1/128 max. Sample size: 5.0 μl. of a 2.00-ml. $CHCl_3$ solution containing derivative prepared from 10.0 mg. of each amino acid

amino acids, with the exception of refractory ones such as arginine and tryptophan, could be quantitatively trifluoroacetylated by allowing 2 hours for acylation.

By employing the chromatographic conditions described for Figure 4, which is a reproduction of the chromatogram obtained for the lysine derivative, single chromatographic peaks were obtained for all of the common protein amino acids except tryptophan and arginine, and the retention temperatures are recorded in Table IV. Tryptophan gave two peaks apparently because the acylation conditions were sufficiently vigorous to give some diacyl derivative, and the peak having a retention temperature of 176° C. was considered to represent the ditrifluoroacetyl ester. When the acylation was continued for 12 additional hours, the peak having a retention temperature of 203° C. almost disappeared and the second peak became quite large. Under the acylation conditions employed a minimum of 1 hour was required for the quantitative trifluoroacetylation of tyrosine; thus acylation time could not be reduced sufficiently to give a single peak (monoacyl) for tryptophan.

The *n*-Butyl *N*-Trifluoroacetyl Esters as Derivatives for the Analysis of Amino Acids. Relative molar response, with glutamic acid arbitrarily assigned a value of 1.00, was determined independently for each of the 19 amino acids for which peaks were obtained, and, as shown by the last three columns of Table IV, reproducibility of response for amino acids carried through the entire chemical

Table III. Stability of *n*-Butyl *N*-Trifluoroacetyl Amino Acid Esters[a]

Components in sample	Time standing	Recovery,[b] %
Valine	13 hr., 45 min.	100
Phenylalanine		102
Glutamic acid		101
Lysine		103
Glutamic acid	13 hr., 14 min.	99
Valine	15 hr., 55 min.	100
Phenylalanine		103
Glutamic acid		101
Lysine		98
Valine	92 hr., 55 min.	106
Phenylalanine		103
Glutamic acid		105
Lysine		103
Glutamic acid	87 hr., 26 min.	101
Valine	91 hr., 30 min.	100
Phenylalanine		102
Glutamic acid		99
Lysine		99

[a] Each sample was a 2.00-ml. $CHCl_3$ solution containing derivative prepared from 10.0 mg. of each amino acid indicated, and 10.0 mg. of succinic acid was included so that dibutyl succinate served as an internal standard.

[b] Per cent recovery was determined by comparing the peak area obtained after standing with that obtained immediately after derivative preparation.

Table IV. Retention Temperatures and Relative Molar Responses of *n*-Butyl *N*-Trifluoroacetyl Esters[a]

Amino acid	Retention Temp.,[c] °C.	Retention Time, min.	Relative molar response[b] by flame ionization A	B	Av.
Alanine	68	6.3	0.536	0.514	0.53
Valine	70	6.9	0.692	0.664	0.68
Isoleucine	78	9.3	0.786	0.801	0.79
Glycine	83	10.8	0.428	0.433	0.43
Threonine	86	11.8	0.615	0.633	0.62
Leucine	87	12.1	0.764	0.790	0.78
Proline	97	15.1	0.701	0.740	0.72
Serine	98	15.4	0.531	0.548	0.54
Cysteine	115	20.5	0.523	0.501	0.51
Hydroxyproline	120	22.1	0.755	0.766	0.76
Methionine	126	23.9	0.685	0.707	0.70
Aspartic acid	130	25.1	0.940	0.898	0.92
Phenylalanine	130	25.1	1.127	1.114	1.12
Glutamic acid	145	29.6			1.00[d]
Tyrosine	152	31.8	1.014	1.029	1.02
Lysine	173	38.1	0.886	0.830	0.86
Histidine	197	45.4	0.572	0.553	0.56
Tryptophan	176, 203	39.0, 47.2			1.12[e]
Cystine	211	49.6	0.415	0.410	0.41

[a] Five (5.0) μl. of 2.00-ml. $CHCl_3$ solutions each containing derivatives prepared from 10.0 mg. of an amino acid and 10.0 mg. of glutamic acid were injected directly on the chromatographic column without the use of a flash heater. Each value is an independent observation.

[b] Amino acid molar response = area per mole of amino acid. Relative Molar Response $= \frac{\text{Amino Acid Molar Response}}{\text{Glutamic Acid Molar Response}}$.

[c] Conditions of chromatography as described for Figure 4.

[d] Arbitrarily set at unity.

[e] Two peaks were obtained and the relative molar response was computed from the sum of the two areas.

and chromatographic procedure was found to be good.

Also, a preliminary experiment suggested that no problems were involved in the analysis of mixtures. A mixture containing 10.0 mg. of each of six different amino acids was carried through the entire procedure, and the relative molar response was determined for each component of the mixture. Table V shows that the values obtained were essentially the same as those obtained when amino acids were carried through the procedure individually. The components of the mixture were selected so that many different functional groups were represented, and, therefore, no problems due to interactions are expected in the analysis of mixtures.

The most important single factor affecting the accuracy of a gas chromatographic method for the determination of amino acids is the yield of derivative. A low yield would probably result in poor precision and would severely limit the usefulness of the method for quantitative analysis. To assess the accuracy to be expected in an actual analysis, it was therefore necessary to determine the yield of derivative for representative amino acids, and pure reference standards were synthesized for this purpose.

Physical constants determined for the *n*-butyl ester hydrochlorides and *n*-butyl *N*-trifluoroacetyl esters of those amino acids from which reference standards were prepared are summarized in Table VI. The boiling-point or melting-point range obtained for each *n*-butyl *N*-trifluoroacetyl ester prepared for use as a reference standard served as a criterion of purity, and purity was also checked by gas chromatography. Each derivative gave a peak having the correct retention temperature, and no extraneous peaks were observed. All evidence indicated high purity.

The results of carbon, hydrogen, nitrogen, and fluorine analyses of the derivatives prepared for use as reference standards are summarized in Table VII. As expected, glutamic acid was found to be converted into the dibutyl ester, and tyrosine and lysine gave the ditrifluoroacetyl derivatives. It had been anticipated that methionine would be converted into its sulfoxide during preparation of its *N*-acyl ester, and a preliminary experiment showed that the *n*-butyl *N*-trifluoroacetyl ester prepared from methionine sulfoxide had the same retention time as the derivative prepared from methionine. Elemental analyses revealed, however, that the sulfur was not oxidized during derivative preparation. The results indicated that in the analytical procedure all carboxyl groups are esterified and all amino, phenolic, hydroxy, sulfhydryl, and imidazole groups are trifluoroacetylated.

Per cent conversions of six amino acids to their *n*-butyl *N*-trifluoroacetyl esters are recorded in Table VIII. Good results were obtained, and the yield was found to be above 96% in each case. The amino acids were selected so that most of the functional groups present in the protein amino acids were represented, and it therefore follows that amino acids can be analyzed with good accuracy by gas chromatography of their *n*-butyl *N*-trifluoroacetyl esters. Further investigations of the method by Stalling, Gehrke, and Shahrokhi (*19*) have shown that quantitative results were obtained for the other protein

Table V. Relative Molar Responses and Recoveries for Amino Acids in Mixture

Component	Relative molar response: Mixture $(X)^a$	Relative molar response: Amino acid $(Y)^b$	Recovery,[c] %
Leucine	0.773	0.777	99
Serine	0.533	0.540	99
Methionine	0.718	0.696	103
Glutamic acid	1.00[d]	1.00[d]	100
Tyrosine	0.985	1.022	96
Lysine	0.714	0.715	100

[a] Chromatographic conditions were as described for Figure 4, and relative molar responses were computed as indicated in Table IV.
[b] From Table IV.
[c] % Recovery $= \frac{X}{Y}100$.
[d] Arbitrarily set at unity.

Table VIII. Per Cent Conversions of Amino Acids to Their *n*-Butyl *N*-Trifluoroacetyl Esters

Amino acid	Yield of derivative, %: A	B	Av.
Valine	100.2	96.8	99
Isoleucine	96.2	96.4	96
Methionine	99.0	96.2	98
Glutamic acid	95.8	98.0	97
Tyrosine (*19*)	102.3	97.2	100
Lysine (*19*)	98.8	98.7	99

Table VI. Physical Constants of *n*-Butyl Ester Hydrochlorides and *n*-Butyl *N*-Trifluoroacetyl Esters

Amino acid	*n*-Butyl ester HCl, m.p., °C.	*n*-Butyl *N*-trifluoroacetyl ester: B.P., °C./mm. Hg	n_D^{25}	M.P., °C.
Valine	59.2–60.0	98.0–99.0/43	1.4110	
Isoleucine	Liq.	94.8–95.3/1.7	1.4158	
Methionine	57.6–59.0	126.0–129.0/18	1.4477	
Glutamic acid	62.7–63.2	159.2–161.0/13	1.4278	
Tyrosine (*19*)	161.8–164.0	70–83[a]/ca. 10^{-3}		96.9–98.0
Lysine (*19*)	Liq.	85–90[a]/ca. 10^{-3}		86.0–87.3

[a] These derivatives were purified by molecular distillation, and the temperature given is the temperature of the oil bath.

Table VII. Elemental Analyses of *n*-Butyl *N*-Trifluoroacetyl Esters of Amino Acids

Amino acid	Empirical formula	Molecular weight	Calculated, %: C	H	N	F	Found,[a] %: C	H	N	F
Valine	$C_{11}H_{18}NO_2F_3$	269.3	49.07	6.74	5.20	21.17	48.82	6.70	5.48[b]	20.97
Isoleucine	$C_{12}H_{20}NO_2F_3$	283.3	50.88	7.12	4.94	20.12	50.86	6.93	4.88[b]	19.88
Methionine	$C_{11}H_{18}NO_2F_3S$	301.3[c]	43.84[c]	6.02	4.65	18.92	44.11[d]	6.04[d]	4.56[d]	19.98[d]
Glutamic acid	$C_{15}H_{24}NO_5F_3$	355.4[e]	50.70	6.81	3.94	16.04	50.75	6.73	4.02[b]	16.12
Tyrosine (*19*)	$C_{17}H_{17}NO_5F_6$	429.3[f]	47.55	3.99	3.26	26.55	47.64	3.94	3.23[d]	26.27
Lysine (*19*)	$C_{14}H_{20}N_2O_4F_6$	394.3[f]	42.64	5.11	7.10	28.91	42.86	5.30	7.13[d]	28.83

[a] All values represent single determinations unless otherwise indicated.
[b] Average of three independent determinations.
[c] Calculated for the methylsulfide and not the sulfoxide.
[d] Average of two independent determinations.
[e] Calculated for the dibutyl ester.
[f] Calculated for the ditrifluoroacetyl ester.

amino acids with the exception of tryptophan and arginine. Tryptophan can probably be analyzed by establishing a response factor for each of the two derivatives obtained, but the chemistry of arginine will need to be investigated in greater detail.

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Study of the Photoionization Detector for Gas Chromatography

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▶ **A study has been made of the properties of a photoionization detector for gas chromatography. The source of ionization is a beam of high energy photons generated in a glow discharge in an inert atmosphere at reduced pressures. The ultraviolet radiation is of such energy that photoionization of the sample molecules occurs without any accompanying ionization of the carrier gas. The main advantage of this detector over other types of ionization detectors is its inherent selectivity based on differences in ionization potentials among the chemical types in the sample. The detector was constructed of a cell made of Teflon and Pt tubing and electrical leads. In general, as ionization potential decreases, response increases. No response was found for the fixed gases CO_2, SO_2, or H_2O. The halogenated compounds disturb the discharge. The apparent ionization efficiency of the device, which has a noise level of 10^{-12} amp. and a background current of 5×10^{-10} amp., is about 10^{-4}. The linear dynamic range is 10^5. The minimum detectable quantity of propane is 2×10^{-10} gram.**

THE OPERATION of the photoionization detector is based on the specific ionization of some ionizable gas or vapor in the presence of an inert carrier gas by irradiation of the mixture with photons of the appropriate energy. A reduced pressure glow discharge in one of the rare gases, N_2, or H_2, can be used to supply ultraviolet radiation of energy greater than the ionization potential of most organic compounds, but less than that of the common carrier gases.

The application of such a device seems to have been contemplated first by Robinson and Brubaker (*12*), but a practical version of the detector was first described by Lovelock (*7*). Recently, a preliminary study of the characteristics of a photoionization detector has been discussed by Roesler (*13*).

Spectrometry in the vacuum ultraviolet has become a field of considerable interest to molecular and atomic spectroscopists. Much valuable information about the highly excited states and electronic structures of molecules is available from this region of the spectrum (*9*). It has been shown by Watanabe (*16*) that photoionization measurements in the vacuum ultraviolet provide a powerful technique for the determination of ionization potentials (*8*). Subsequent work has been carried out using a mass spectrometer in conjunction with a vacuum ultraviolet monochromator–ion source for the determination of photoionization efficiences and cross sections. These are of interest in studying the upper energy states of molecules (*14*).

Photoionization occurs when an irradiated molecule absorbs a quantum of the appropriate energy and undergoes an electronic transition to an ionized state. The ion current resulting from photoionization sets in very sharply as the energy of the incident photons is increased. For compounds of distinct absorption spectra in the vacuum ultraviolet and favorable transition probabilities, even minimum energy quanta—i.e., those of the threshhold energy—give rise to an ion pair. For example, for aromatic hydrocarbons, as the energy of incident photons is increased, the ionization yield shows a sharp leveling off at the ionization potential (adiabatic ionization potentials are obtained with photoionization). With paraffins, however, the break in the curve is less sharp, which is consistent with the diffuse nature of their absorption spectra in the vacuum ultraviolet (*10*).

Photoionization–mass spectrometric studies on polyatomic organic compounds have shown that the ionization and absorption cross sections for the parent ion increase sharply at the ionization threshhold, pass through a maximum, and fall off as the incident photon energy is increased. However, fragment ions often are formed which have higher appearance potentials than the parent ion and cross sections extending to higher energies. Thus an ionization current may be obtained over a wide energy span.

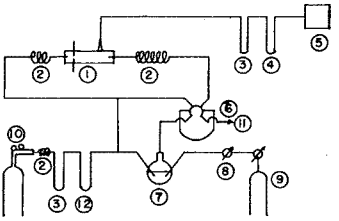

Figure 1. Schematic diagram of apparatus

1 Photoionization detector cell
2 Capillary restrictors
3 Dry ice–acetone traps
4 Hg manometer
5 Vacuum pump
6 Six-way gas sampling valve
7 Microbubbler
8 Needle valve
9 Sample source
10 Carrier and diluent gas source
11 To vent
12 Molecular sieve column

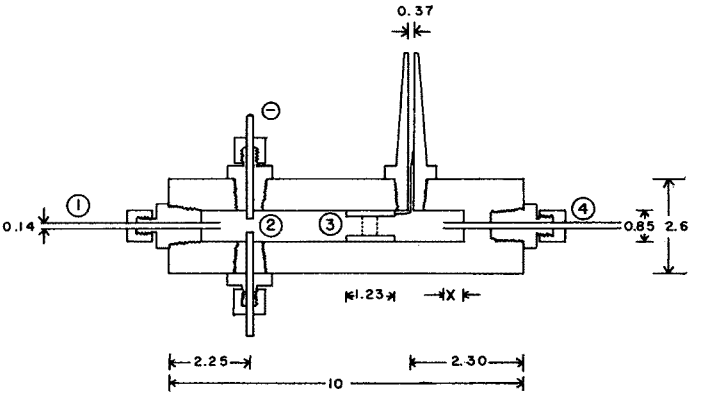

Figure 2. Schematic diagram of photoionization detector cell (not to scale)

1 Discharge gas inlet
2 Discharge electrodes; gap = 0.12 cm.
3 Collector anode containing two Pt screens; grounded through vacuum port
4 Collector electrode and sample inlet tube
X = Distance cathode protrudes
All dimensions given are in cm.

The simple photoionization detector, in which the total output of the glow discharge ultraviolet source irradiates the sample end of the cell, will thus produce an ionization current for nearly all ionizable compounds, even though the incident photons may have energy considerably above the ionization potential of the sample molecules.

With this simple detector, where no attempt is made to separate the photon energies produced, it is desirable to have a simple emission spectrum. This is accomplished by using a D.C. discharge of a few milliamperes, operated in Ar, He, Kr, N_2, or H_2, at a few millimeters Hg pressure. It is expected that only the most intense lines will be available for interaction with the sample entering the detector. Impurities in the supply gases in addition to those introduced through small leaks in the apparatus will absorb or filter out the most energetic and the low intensity lines. All these lines arise from the neutral atoms, except the continuum in He which originates from the He_2 molecule formed in the discharge (*15*). Comparison of the ionization potentials of these gases with the energy supplied to the discharge indicates that the highest multiple charged ions that will be obtained in the photoionization detector glow discharge are Ar(II), Kr(III), and N(II). This is consistent with the mass spectrometric results of Knewstubb and Tickner (*3–5*), who studied ions in glow discharges set up under conditions comparable to those used in this work.

The presence of lines of these energies places definite limitations on the response of the detector. The use of a Kr discharge should make the detector insensitive to compounds of ionization potential greater than 10.64 e.v.—i.e., some inorganic gases, C_1–C_4 saturated hydrocarbons, etc. On the other hand, photons generated in He discharges are able in principle to ionize all compounds, assuming small energy and intensity losses in tranversing the detector tube and favorable ionization cross sections and transition probabilities.

EXPERIMENTAL

Construction and Design. Several preliminary experiments with trial models of the photoionization detector were carried out. These results indicated that detectors constructed of soft glass with Pyroceram cement were mechanically unsatisfactory; in one experiment, the heat produced by an accidental arcing of the discharge irreparably melted the end of the device. Further, movement and positioning of the electrodes was difficult, although the Pyroceram cement is soluble in hot 1:1 HNO_3. The use of Teflon TFE-fluorocarbon resin (DuPont), however, simplified the problem of making and adjusting electrical and gas lead connections to the device. One-eighth-inch pipe $^1/_{16}$-inch tubing Swagelok unions are well adapted to this purpose. Further, Teflon has the advantage of filtering out ultraviolet radiation which is harmful to the operator's eyes over extended periods of time. However, it is not possible to see the shape and configuration of the glow discharge except in a darkened room.

It was further found that the greater the distance from the discharge to the collector, the lower is the background signal in the absence of ionizable vapor. This signal was reduced from 10^{-8} amp. to 10^{-10} amp. by lengthening this distance from 4 to 7 cm.

In addition to maintaining maximum distance between the discharge and the collector, a grounded shield containing two fine-mesh Pt screens supported in a small brass cylinder was necessary to prevent interactions between the discharge and the ion collector. Without the screens, pronounced space charge effects were obtained at high collecting voltages (25 volts). These effects were evidenced by M-shaped peaks for large samples, excessive noise, and unusally high background signals. Further, removal of the ground lead from the cylinder anode had no effect under these conditions. The two grounded grids, however, entirely eliminated these problems.

Experiments such as these led to the final version of the detector studied here. Figure 1 gives a schematic diagram. As shown in Figure 2, entering at the extremes of the cell are the leads for the discharge and sample gases. These leads were 0.14-cm. o.d. Pt tubing, connected to the apparatus using $^1/_{16}$-inch Swagelok fittings with silicone rubber O-ring compression seals. These leads also served as electrodes for the discharge and ion collector, respectively. The collector anode was a brass cylinder, 1.23 cm., 0.52-cm. i.d. which fit snugly in the cell and which was grounded through the vacuum connection.

The 500-volt D.C. power supply was a Microtek Instruments Model HCP-500 thryatron tube current-regulated hollow cathode power supply. The positive terminal was grounded. Ionization currents were measured with a Keithley Model 610A electrometer amplifier used in the negative feedback (fast) mode of operation. In experiments requiring a recorder, the 1-ma. fullscale signal from the electrometer was fed into a Texas Instruments Servo-Riter recorder across a 1.02-ohm resistor. A.C. line power was voltage-stabilized.

The discharge was set up between two 0.14-cm. o.d. Pt rods, separated by a 0.12-cm. gap. Although the discharge

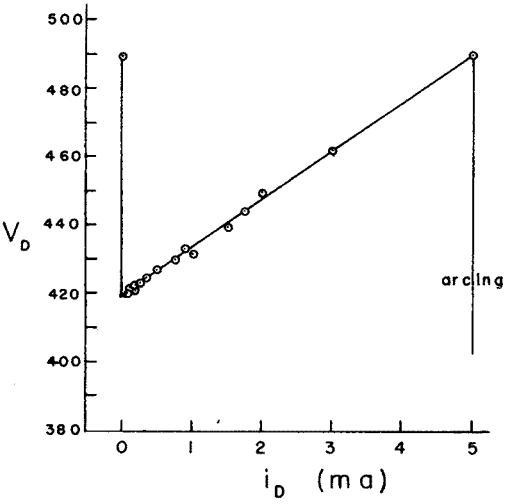

Figure 3. Discharge current as function of discharge voltage in He

was usually self-initiating, a Tesla coil was occasionally required to strike the discharge, especially at higher pressures. When the lead supplying the gas to the discharge was grounded, the discharge could be moved with the aid of the Tesla coil to cover the whole end of the cell. The lead was located 1.65 cm. from the discharge electrodes and was perpendicular to the midpoint of the gap. This resulted in a more stable discharge and a lower background current.

Power was supplied to the electrodes from the power supply through a 2-watt, 2.5-megohm potentiometer which allowed continuous adjustment of the discharge voltage up to 500 volts.

After extended periods of operation (several hundred hours) under conditions of high discharge currents, sputtering of Pt black from the discharge cathode necessitated removal of the electrodes and thorough cleaning with a small wire brush. Faster cleaning was accomplished in a solution of concentrated HNO_3 in a sonic cleaner.

The collector electrode was polarized negatively with respect to ground by the use of five Eveready 7.5-volt industrial "C" batteries in series. The batteries were connected in a guard ring circuit and shielded by wrapping them individually with the following materials: first, aluminum foil, connected to the positive terminal of the battery; second, sheeting of Teflon to cover completely the guard ring; and third, aluminum foil, connected to ground. Without this shielding, current leakage from the surface of the batteries and A.C. pickup produced signals of the order of 10^{-7} amp.; after shielding in this manner, the current from the batteries was reduced to less than 10^{-13} amp., with negligible A.C. pickup even at the highest sensitivity ranges of the electrometer.

Belden 8240 RG58/U shielded cable was used for all electrical connections. Since the photoionization current collector electrode also served as the sample inlet tube, connection to the gas sampling valve was made through a piece of Teflon. Care was taken to keep the electrical leads as short as possible, to avoid ground loops, and to shield the apparatus from sources of A.C. pickup and static electricity.

Calibration and Flow System. A method is required for the reproducible introduction of small, accurately known amounts of sample vapor. The several dynamic methods available for calibration (*6*) are not readily adapted to reduced pressure operation. A microbubbler system similar to that described by Riley (*11*) and a gas sampling valve was used in this work.

A 200-ml., 3-neck, round-bottom flask containing 75 ml. of concentrated H_2SO_4 was used. Nondetectable diluent gas and sample vapor (usually propane) were bubbled into the H_2SO_4 from opposite sides of the flask through fine glass jets. The gases mixed in the chamber and were flushed out the middle neck into one side of a 6-way Perkin-Elmer gas sampling valve. Concentrated H_2SO_4 was used because none of the common carrier gases or simple saturated hydrocarbons are appreciably soluble in it. Further, traces of water vapor and olefins are removed from the gas streams.

To determine the quantity of propane in the diluent gas, the volume, V, per bubble of propane was determined by counting several times the number of bubbles required to displace 50.00 ml. of water from a 50-ml. buret. With the jet used here, $V = 0.045$ ml./bubble at S.T.P. The volume of the gas sampling loop on the gas sampling valve, which consisted of a short piece of capillary tubing containing a volume-reducing coaxial Pt wire, was 20 μl. This value was determined from the weight of Hg required to fill it under actual conditions; good agreement was obtained with the volume calculated from the dimensions of the loop. In practice, it is most convenient to measure the time, t_2, required for 10 bubbles to emerge from the jet. Further, the diluent gas plus propane flow rate is most easily measured with a soap bubble flow meter where t_1 is the time required for a bubble to rise 10 ml. After correcting the measured diluent gas plus propane flow rate to S.T.P., calculating the fraction of propane in the mixture, and applying the ideal gas equation, it is readily calculated that the weight of propane introduced to the ionization chamber in 20 μl. is $1.75 \times 10^{-6}\ t_1/t_2$ gram. t_1/t_2 ratios smaller than 0.01 are easily achieved by proper variations of the flow rates. This is entirely adequate for the sensitivity of this detector. This quantity could be reduced further by reducing the sample volume.

For samples soluble in H_2SO_4, a microsyringe was used to inject vapor samples.

The flow system supplying gases for the discharge, for the bubbler, and for carrier gases to the detector, is shown schematically in Figure 1. He, Ar, and N_2 were passed through a dry ice–acetone trap and a molecular sieve column to remove water and other impurities. The organic gases used were Matheson Instrument grade and were dispensed from lecture bottles through two needle valves.

RESULTS AND DISCUSSION

Discharge Parameters. As noted above, the glow discharge was set up in He, Ar, N_2 across two Pt electrodes. A typical plot of discharge current, i_D, as a function of discharge voltage, V_D, is presented in Figure 3. In general, much lower currents and higher voltages were required in He to produce and sustain the discharge than in Ar or N_2; the largest currents were necessary in Ar. The plot is shaped like a backwards N. A high voltage is required to strike the discharge. Upon starting, an arc may be formed which can be turned off by varying the potentiometer, reducing the V_D. As the voltage is increased again, the current rises nearly linearly until the arc is initiated. Arcing occurred in He at about 5 ma.; approximately 20 ma. were required in Ar. Arcing produced much sputtering of the electrodes, background currents of the order of 10^{-7} amp., and rapidly burned out the potentiometer in the circuit.

Cell pressure had a definite effect on the voltage required to initiate the discharge. Figure 4 reveals a minimum in this curve with increasing pressure in millimeters Hg of N_2. Similar behavior is reported in Goldstein's review (*2*) of gaseous electronics.

Ideally, it is desired to have a pure source of photons. With the simple photoionization detector, however, the

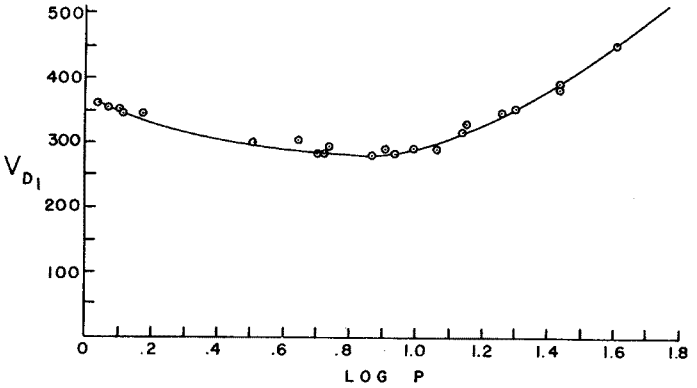

Figure 4. Pressure dependence of voltage required to initiate discharge in N_2

Units of pressure are mm. Hg

proximity of the glow discharge to the collector electrode produces some interaction. The background current is produced from several sources: (1) photionization of traces of impurities present in the chamber; (2) photoelectric current from the collector electrode; and (3) ionization of impurities by bombardment with high energy electrons from the discharge. Cleanup of the gases used and prevention of leaks will reduce the current arising from (1) and (2); inclusion of the dry ice–acetone trap reduced the background current by a factor of about 1.5. The use of fine-mesh Pt screens in the collector anode, as noted above, reduced this current by a factor of about 10. As seen below (Figure 5), minimizing the exposed area of the collector electrode decreases the photoelectric current. By setting up the discharge perpendicular to the axis of the detector tube, directional properties of electrons in the discharge are eliminated which reduces the current resulting from electron impact.

Response of Photoionization Detector to Propane. Effect of Discharge Current and Cell Pressure. The effect of discharge current, i_D, and Ar cell pressure on response of the detectorto 3.00×10^{-7} gram of propane is displayed in Figure 6. An important feature of these curves is the sudden increase in response at some low i_D. This is apparently due to the application of sufficient energy of discharge to ionize Ar^+ to Ar^{+2}. The second ionization potential of Ar is 27.62 e.v. At a cell pressure of 3 mm., an i_D = 1.2 ma. corresponds to a discharge voltage of 230 volts, which for an electrode gap of 0.12. cm. is equivalent to 27.6 e.v., which coincides very well with the second ionization potential. Arcing occurs before Ar^{+3} can be formed. For He discharges, no such jump in the curve is noted; in N_2, one jump is found at an i_D corresponding to an energy of about 30 e.v. (the second ionization potential of N is 29.593 e.v.).

Response decreases with increasing cell pressure. This can be accounted for in two ways: first, higher pressures will allow less radiation to reach the sample; second, recombination of ions is expected to occur to a larger extent as the pressure is increased (*1*).

Effect of Collector Voltage. A normal current-voltage relationship is obtained with the photoionization detector, as shown in Figure 7. At the lowest cell pressure studied, 3 mm. Hg, any probe potential greater than about 5 volts may be used. At higher pressures, the linear region is attained at higher voltages, probably due to recombination effects. In general, 17 volts was used in this work.

Collector Cathode Position. The extension of the collector cathode had a marked effect on the response of the photoionization detector. Figure 5 shows the effect of cathode position, x, at two different pressures and at several different probe potentials. The center of the vacuum hole (i.d. = 0.37 cm.) was located 0.33 cm. from the end of the tube (x = 0). It appears that as x increases to about 0.1 cm., sufficient time

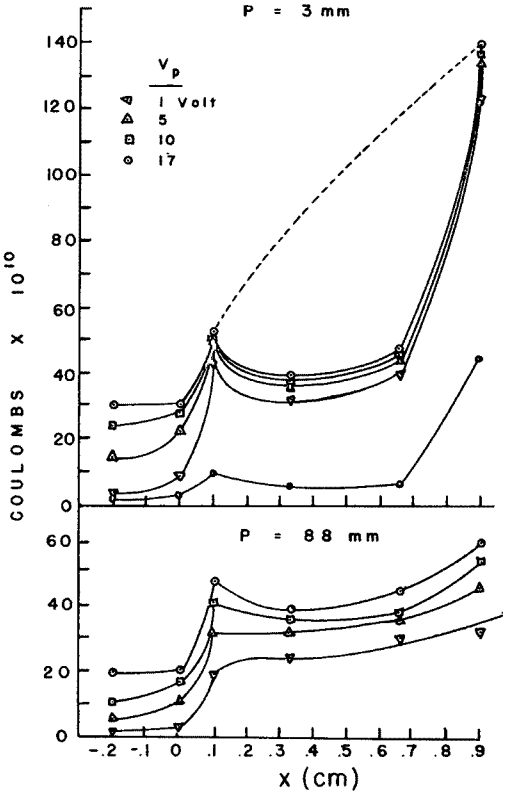

Figure 5. Effect of collector position on response of photoionization detector

Conditions: Ar discharge; i_D = 1.0 ma.; V_p = 17 volts; sample weight = 1.00×10^{-6} gram propane

X is defined by Figure 2

Dark circles are for background current at V_p = 17 volts

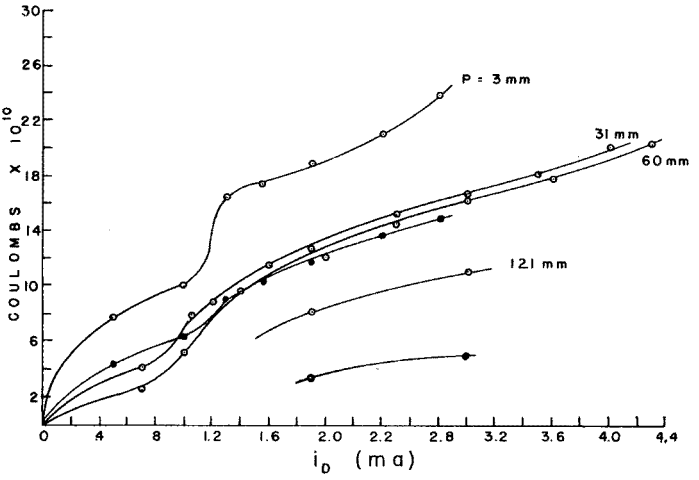

Figure 6. Effect of discharge current on response of photoionization detector

Conditions: Ar discharge; collecting voltage = 17 volts; cathode protrudes 0.33 cm.; sample weight = 3.00×10^{-7} gram propane
Dark circles are for background current at 3 mm. and 121 mm. Hg

is allowed for the sample to interact with the photons before it is removed by the vacuum. Between this distance and about 0.7 cm., however, most of the sample is gone before it can be measured. Beyond this, more efficient ionization and ion collection is realized. The increased collector surface area serves mainly to increase the background current and noise level. This behavior was reproducible.

Had the vacuum line been attached closer to the discharge end of the detector, a response curve similar to that shown by the dotted line would probably result.

It is interesting to note that as the collector is withdrawn into the Teflon body, ionization continues to occur. This indicates that some ionization is occurring inside the entrance tube, which was located coaxially with respect to the cell.

Effect of Flow Rate to Discharge. Only a small flow of gas is required to sustain the discharge. For this reason, a long capillary flow restrictor was used to supply gas to the discharge. Because the gas is pulled into a vacuum, its flow rate is not easily measured under operating conditions. The effect of Ar tank pressure, which is proportional to flow rate, was briefly studied at a constant cell pressure of 3 mm. Hg. The results are presented in Figure 8. As the flow increases, the discharge current rises slightly; the background current and response to 4.6 $\times 10^{-7}$ gram of propane increases sharply, passing through a fairly broad maximum. The flow rate measured under atmospheric conditions at the maximum was 0.5 cc per minute. This flow rate was used in most experiments.

Effect of Ambient Temperature Changes. This study was conducted at room temperature, nominally 27° C. The stability, sensitivity, and noise level were unaffected by small changes in ambient temperature and pressure. Operation of the detector at high discharge currents did produce significant local heating. Under normal operating conditions (roughly 2 ma. in Ar, 1.5 in N_2, and 0.5 in He), no excessive heating was noted. The outside of the detector remained at ambient temperature; the metal fitting through which the discharge electrode passed was only warm (about 40° C).

Linearity. Figure 9 shows the response of the detector to different quantities of propane from photons generated in Ar, He, and N_2 discharges. The diluent gas in each case was the same as the discharge gas. As seen in the figure, response is highest for the He discharge and lowest for the N_2 discharge. It is apparent that ionization cross sections and transition probabilities of propane are highest for the photons generated in the He discharge, and lowest for those of N_2. As could be anticipated, and as will be seen below, this does not necessarily apply to all compounds.

The linear portion of the curve extends to about 4×10^{-5} gram. Larger

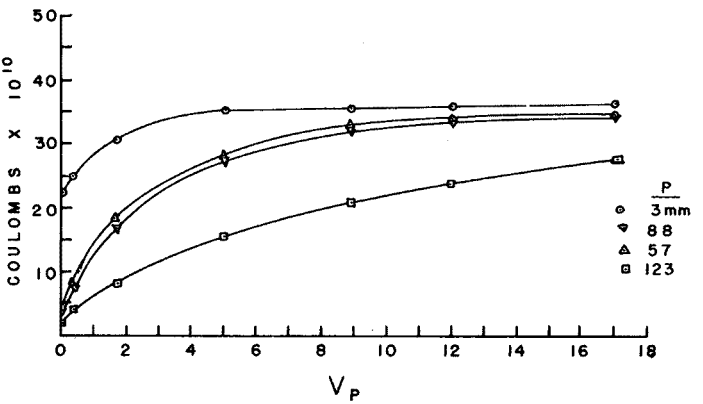

Figure 7. Current-voltage relationship for photoionization detector

Conditions: Ar discharge; i_D = 1.8 ma.; P = 3 mm. Hg.; cathode protrudes 0.1 cm.; sample weight = $1.00 \times 10_D$ gram propane

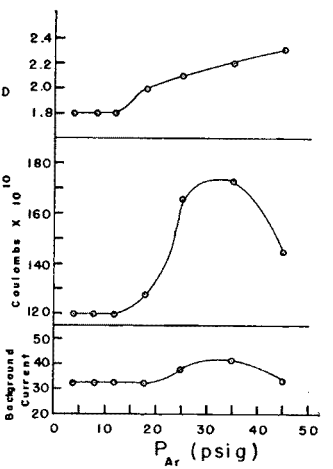

Figure 8. Effect of discharge gas flow rate on discharge current, background current, and response of detector

Conditions: Ar discharge; cathode protrudes 0.57 cm.; V_p = 17 volts; one screen in anode; i_D = 1.8 ma.; sample weight = 4.59×10^{-7} gram propane

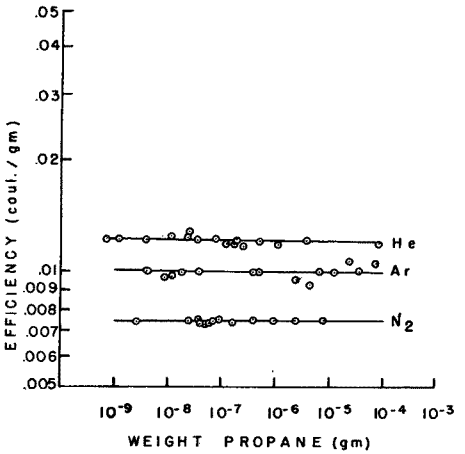

Figure 9. Efficiency of photoionization detector using He, Ar, and N_2 discharges

Conditions: V_p = 17 volts; P = 3 mm.; i_D = 0.5 ma. (He), 1.8 ma. (Ar), 1.5 ma. (N_2); cathode protrudes 0.05 cm.

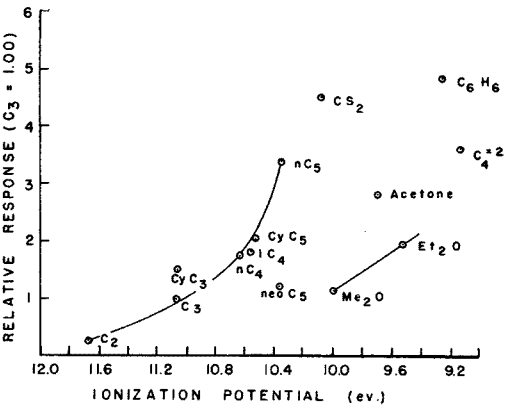

Figure 10. Effect of sample ionization potential on relative response (propane = 1.00)

Conditions: Ar discharge

quantites of sample altered the properties of the discharge by diffusing into it. This produced spurious results, accompanied by an increase in the discharge current, and effects similar to those caused by space charges. An external ultraviolet source would eliminate this problem. The random noise level of the detector was of the order of 10^{-12} amp. Based on the ionization efficiency of the device (see Figure 8), that quantity of propane producting a signal twice the noise level is about 2×10^{-10} gram. This provides a linear dynamic range (*6*) of about 10^5, which is comparable to the Argon detector. The apparent ionization efficiency (*6*) of the detector under optimum conditions is about 10^{-4}, midway between that of the hydrogen flame ionization detector and the argon detector (*6*).

Response of Photoionization Detector to Different Compounds. The operating parameters of the photoionization detector were studied using propane as the test sample, as recommended by Lovelock (*6*). In addition, the response to several other compounds was determined. As noted above, compounds of ionization potential greater than the available photon energy cannot be detected. In general, this conclusion was verified. The maximum energy available from Ar is 11.83 e.v.; from He, 21.22 e.v.; from N_2, 11.30 e.v.

The response to different compounds relative to propane = 1.00 is listed in Table I. A plot of some of these relative responses is presented in Figure 10. In general, as ionization potential decreases, response of the detector increases. With some notable exceptions, as the incident energy increases, response increases.

As expected, no response is obtained for methane using Ar or N_2 discharges; a low response is obtained for He. Walker and Back (*15*) attribute He-produced photionization of CH_4 to the resonance He 584 A. line, to the He_2 600–900 A. continuum, and to ionization by collisions with He metastable atoms produced by the resonance line. They were unable to separate the three effects. Although in principle the photons from the He discharge are capable of ionizing any molecule or atom, no response was noted for H_2O, SO_2, CO_2, air, H_2, etc. This anomaly shows the need for further study of the response of the detector.

Strongly electron-attaching compounds produced spurious results by disturbing the discharge. With the N_2 and He discharges, the chloromethanes (except CH_3Cl), Freon-12, hexafluoroacetone, and, to some extent, H_2S, CS_2, and Me_2O, caused either a large increase in the discharge current, or a large increase immediately followed by extinguishment of the discharge. As the sample was pumped out of the chamber, the current either dropped back, or restarted itself and rose, to its equilibrium value.

Although water-saturated air is reported to be entirely satisfactory for a

Table I. Response of the Photoionization Detector to Various Molecules

Compound	Ionization potential	Discharge medium and carrier gas: Ar	He	N_2
Methane	12.98	0	0.41	0
Ethane	11.65	0.26	...	...
Propane	11.07	1.00	1.00	1.00
n-butane	10.63	1.74	2.50	1.38
isobutane	10.56	1.78	2.76	0.97
Cyclopropane	11.06	1.50	2.60	0.56
Neopentane	10.37	1.20	2.95	3.66
Cyclopentane	10.52	2.02	...	...
n-pentane	10.34	3.37	...	...
Benzene	9.25	4.80	...	1.52
cis-Butene-2	9.13	3.57	5.88	2.17
Acetylene	11.41	...	0.12	0
Acetone	9.69	2.78	6.95	2.10
Dimethyl ether	10.00	1.11	...	...
Diethyl ether	9.53	1.91	...	...
Methyl chloride	11.28	1.13	...	...
CH_2Cl_2	11.35	2.72?	...	...
$CHCl_3$	11.42	2.32?	...	...
CCl_4	11.45	1.90?	...	...
NH_3	10.15	0?	...	...
CS_2	10.08	4.47	...	...
H_2O	12.59	0	...	...
CO_2	13.79	0	0	0
SO_2	12.34	0	0	0
Fixed and inert gases		0	0	0

discharge medium (7), the admission of small amounts of water vapor to the detector produced results similar to those encountered with electron-attaching compounds.

The lack of response noted for NH_3 may not be due to insensitivity of the detector to it, but rather to its never reaching the detector because of reaction with the brass fittings and union that were used in the gas line carrying the sample vapors. The response to paraffins falls on a curve which rises sharply from butane to pentane. It is expected that the curve will level out for higher members of the series. Qualitatively, the generalizations about ionization potentials noted above apply to the response of the photionization detector. Isobutane has a slightly higher response than *n*-butane. The detector's sensitivity is neopentane < cyclopentane < *n*-pentane. Butene-2 produces a much larger response than the saturated butanes.

Comparison of the results with the three discharge gases reveals certain anomalies. In He, abnormally large response is found for acetone and butene -2. In N_2, neopentane gives an unusually large signal. Further study of the response of the detector should account for or correct these results.

CONCLUSIONS

The photoionization detector is a quite versatile device, with good sensitivity and linearity, and with potential for extreme selectivity. The operating and constructional parameters are not critical.

Future studies should be concerned with investigation of an external source and vacuum monochromator, utilizing LiF or CaF_2 windows. Several advantages to this arrangement are anticipated. First, the problems associated with the use of a glow discharge in the detector would be eliminated—the sample could not interact with the photon source, the source-generated background signal would be eliminated, and a more intense energy could be applied to the sample. Second, the potential extreme selectivity of the device could be realized by using the monochromator. Third, the detector would also be of use as an instrument for making precise physical measurements. Fourth, by the inclusion of a photocell in the chamber, the detector could be used as a nondestructive far ultraviolet monitor for aromatic hydrocarbons.

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Semiquantitative Determination of Impurities in Bisphenol A by Circular Paper Chromatography

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▶ A semiquantitative method for the determination of the principal impurities in commercial bisphenol A utilizes reversed-phase circular paper chromatography and is especially useful in analyzing samples containing minor amounts of impurities. As little as 0.03% of an individual impurity can be detected in bisphenol A by this method. The components are separated on circular filter paper impregnated with tricresyl phosphate, using an aqueous solution of trisodium phosphate as the eluent. The chromatogram is sprayed with a diazonium salt solution to develop color. The concentration of each impurity in an unknown can be calculated by determining its respective extinction point and using the previously established sensitivity value.

THE principal impurities normally associated with commercial bisphenol A have been reported (*1,4*) as Dianin's compound (4-*p*-hydroxyphenyl - 2,2,4 - trimethylchroman), the 2,4′ isomer [2-(*o*-hydroxyphenyl)-2 - (*p* - hydroxyphenyl)propane], and a trisphenol [2,4-bis(α,α-dimethyl-4-hydroxybenzyl)phenol. Work in this laboratory has confirmed these findings and, additionally, has revealed the presence in trace amounts of several other impurities.

In certain reactions, the presence of any impurity in bisphenol A is objectionable; in other cases, the amounts of individual impurities present are of concern. Of the methods generally available for identification and measurement of impurities, the most useful, in this case, have been found to be gas liquid and paper chromatography. Tominaga has reported on the direct analysis of bisphenol A using gas liquid chromatographic analysis (*6*). Gill has also reported on a quantitative gas liquid chromatographic method after acetylation of all reactive hydroxyl groups in the bisphenol A sample (*3*). Paper chromatographic methods have been reported by Anderson, Carter, and Landua (*1*), who used a dual chromatographic scheme to separate and measure impurities and by Challa and Hermans (*2*), who employed a single one-dimensional chromatographic method. Whereas Anderson, Carter, and Landua (*1*) and Challa and Hermans (*2*) require preconcentration of impurities when present in low concentration, work in this laboratory has resulted in a simple analytical procedure using reversed-

Table I. Physical Properties of Principal Components of Commercial Bisphenol A

Compounds	Trivial name	Melting point, °C.	Boiling point at 0.25 mm., °C.
4-*p*-Hydroxyphenyl-2,2,4-trimethylchroman	Dianin's compound, codimer	156	165–170
2-(*o*-Hydroxyphenyl)-2-(*p*-hydroxyphenyl)propane	2,4′-Bisphenol A	108.5	170
2,2-Bis(*p*-hydroxyphenyl)-propane	4,4′-Bisphenol A	157	175
2,4-Bis(α,α-dimethyl 4-hydroxybenzyl) phenol	Trisphenol I	193	240–245

phase paper chromatography, which is particularly effective for estimating individual phenolic impurities in concentrations as low as 0.1% or less.

GENERAL PROCEDURE

This method employs circular filter paper, impregnated with tricresyl phosphate, and an aqueous solution of trisodium phosphate as the eluting agent. The completed chromatogram is sprayed with a diazonium salt solution to develop color. The various phenolic derivatives are separated effectively by this system and appear as concentric rings of distinctive color and R_f value.

This well-known qualitative technique has been converted into a semiquantitative method by the following rather simple and straightforward method. The sensitivity of the chromatographic procedure to each of the principal impurities was established by chromatogramming successively more dilute solutions of each compound until its characteristic band could no longer be observed. By this means, the minimum amount of each impurity which could be detected was established. Unknowns were analyzed by a similar procedure using successively more dilute solutions until the extinction point was bracketed for each impurity. The concentration of each impurity in the original sample could then be calculated using the previously determined sensitivity value for that particular impurity.

This surprisingly simple procedure is satisfactorily reproducible and sensitive when carried out under specifically defined conditions.

EXPERIMENTAL

Apparatus. Whatman No. 1, 24.0-cm. circular filter paper, conditioned at 50% relative humidity, was employed in all cases. Using a specially prepared die, a wick 3 mm. × 4 cm. was cut from the center of the paper. To support the paper during elution, two glass plates (9 × 9 × 1/4 inch), the lower with a center hole to allow passage of the wick, were used. Small Petri dishes were employed as a reservoir for the eluting solvent. A glass aspirator was used to spray the developed chromatograms.

Reagents. Chemicals required were tricresyl phosphate, 0.125*M* aqueous trisodium phosphate solution, benzene, methanol, and *p*-nitrobenzenediazonium fluoborate (Eastman P-7078). The compounds used for reference were 4,4′-bisphenol A, 2,4′-bisphenol A, trisphenol I, and Dianin's compound. The latter were isolated from commercial bisphenol A by fractional crystallization and distillation, purity being established by paper chromatographic examination, infrared examination, and melting point determination. Properties of the pure compounds are shown in Table I.

Procedure. The circular filter paper, with a 3 mm. × 4 cm. wick cut at the center, was impregnated with tricresyl phosphate by immersion in a 9.1% (by volume) solution of this reagent in benzene for 5 seconds. It was then air-dried, taking care that the concentration of tricresyl phosphate was uniform throughout the paper. Two microliters of a methanolic solution of the sample was spotted 5 mm. below the junction of the paper and the wick by means of a suitable pipet. The paper was then placed between two glass plates, the lower one having a center hole. The wick was allowed to protrude through the opening into the eluting solvent (0.125*M* Na_3PO_4).

The chromatogram was removed from the plates when the solvent boundary extended exactly 100 mm. from the center of the paper. After air drying, the chromatogram was developed with a saturated methanolic solution of *p*-nitrobenzenediazonium fluoborate, applied as a spray. The most satisfactory elutions were obtained when the chromatograms were prepared in a constant temperature-humidity (25° C. and 50% R.H.) chamber.

The sensitivity of the procedure to the various impurities was determined by chromatogramming successively smaller amounts—i.e., more dilute solutions—of the known compounds until the respective bands disappeared. Below a 4% concentration of a given impurity in 4,4′-bisphenol A, the sensitivity of the analysis was found to be unaffected by the total concentration in bisphenol A and equal to the sensitivity determined for the impurity alone. The extinction points (minimum detectable amount in grams) for the major impurities under such conditions were: Dianin's compound, 8×10^{-8}; trisphenol I, 4.8×10^{-8}; 2,4′-bisphenol A, 6.4×10^{-8}.

Unknowns were analyzed by this same procedure, the sample size being progressively reduced (by diluting the principal solution) until the extinction point had been closely bracketed. The sensitivity values were used, along with the "unknown" sample concentration at the extinction point, to calculate impurity concentrations in the original sample. For greater convenience,

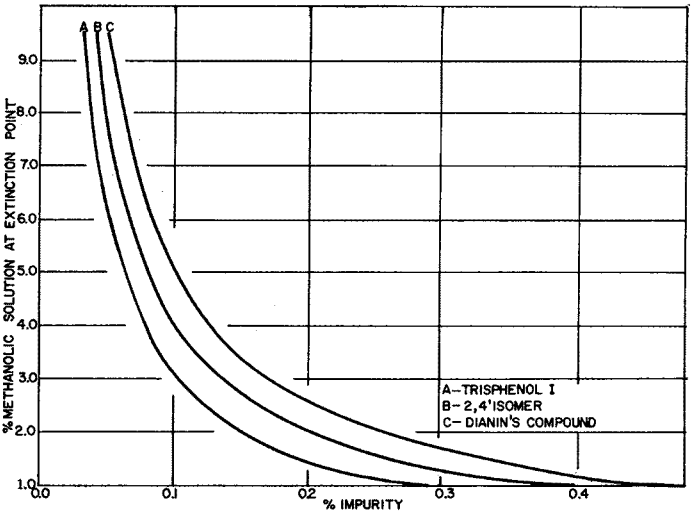
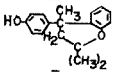
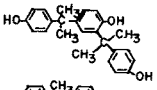
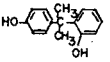
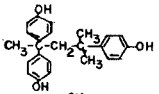
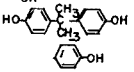


Figure 1. Correlation of sample concentration with impurity levels in bisphenol A as determined by semiquantitative paper chromatographic analysis

Table II. Phenolic Compounds Present in Commercial Bisphenol A

Identity or probable identity	Structure	R_f	Color of band[a]
Unknown		0.03	Purple
Dianin's compound		0.04	Red
Unknown		0.07	Lavender
Unknown[b]		0.08	Green
Trisphenol I		0.13	Red
2,4'-Bisphenol A		0.18	Purple
Trisphenol II		0.33	Pink
4,4'-Bisphenol A		0.65	Red
Phenol		0.78	Pink

[a] After development with *p*-nitrobenzenediazonium fluoborate.
[b] Preliminary data indicate this is 2,2' isomer of bisphenol A.

curves correlating composition with sample concentrations at the extinction point were prepared. These plots are reproduced in Figure 1.

RESULTS AND DISCUSSION

Nine components have been detected in commercial bisphenol A by the circular paper chromatographic method. The R_f values and colors of the individual bands (developed with *p*-nitrobenzenediazonium fluoborate) along with the corresponding structures, where known, are shown in Table II.

Because the individual impurities in bisphenol A rarely exceed 4%, attention was concentrated on a procedure for detecting impurities at or below this concentration. Particular emphasis was placed on the detection of the principal impurities associated with bisphenol A when present in less than 1% concentration.

It is obvious that, in using the bracketing procedure described, the accuracy of a given series of analyses depends to some extent on how closely one desires to bracket the extinction point. In general, it was found that the precision shown in Table III could be obtained easily without an involved or extensive bracketing procedure.

Data for a series of repeat analyses of synthetic mixtures by an experienced operator are shown in Tables IV and V. Repeatability of the procedure is indicated in Table VI, which shows the results of repeat analyses of an authentic bisphenol A sample.

Table III. Precision of Analyses for Principal Impurities at Various Concentrations

Concentration range	Precision
<0.1	±0.03
0.2–0.5	±0.05
0.5–1.0	±0.1
1–5	±0.2

Table IV. Repeated Analyses of a Synthetic Bisphenol A Mixture

Weight, %	2,4' isomer	Trisphenol I	Dianin's
Actual	1.0	0.8	0.2
Found			
1	>0.94 <1.14	>0.71 <0.86	>0.18 <0.22
2	>0.94 <1.07	>0.71 <0.80	>0.18 <0.22
3	>0.94 <1.14	>0.71 <0.86	>0.18 <0.22

Table V. Repeated Analyses of Synthetic Bisphenol A Mixtures Containing One Impurity

Weight, %	2,4' isomer	Trisphenol I
Actual	4	...
Found	>3.8 <4.2	...
	>3.8 <4.2	
	>3.8 <4.2	
Actual		2
Found	...	>2 <2.2
		>2 <2.2
		>2 <2.2

Table VI. Repeated Analyses of an Authentic Bisphenol A Sample

Found, wt. %		
2,4' isomer	Trisphenol I	Dianin's
0.72–0.88	0.38–0.42	0.1–0.2
0.72–0.88	0.38–0.42	0.1–0.15
0.72–0.88	0.38–0.42	...
0.76–0.84	0.35–0.45	0.1–0.2
0.76–0.84	0.35–0.45	...

This chromatographic method was particularly effective in measuring trace amounts of impurities in bisphenol A, as little as 0.03% of a given impurity being detectable with a total sample size of only 160 μg. Even lower concentrations could be detected with a larger sample.

Because of interference bands at about $R_f = 0.78$ arising from unknown impurities in the paper and trace amounts of cresol (formed by saponification of tricresyl phosphate) it is not possible to determine phenol by this method. However, other procedures, such as the Koppeschaar method (*5*), are available for the quantitative determination of small amounts of phenol.

ACKNOWLEDGMENT

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Aromatic Hydrocarbons Produced during Combustion of Simple Aliphatic Fuels

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▷ **The combustion of simple aliphatic fuels such as methane and propane at atmospheric pressure results in the formation of a wide array of products. Previous work has been concerned with arene-type products. Current work has shown the relative production of benzene, toluene, ethylbenzene, as well as other simple alkyl substituted derivatives of benzene. The practical aspects include an index of relative abundance of the latter type of compounds that might be found in polluted atmospheres as well as indicating a method for predicting the relative contribution of automobile exhaust to atmospheric pollution.**

THIS PAPER is an extension of previous work concerned with the combustion of simple aliphatic fuels at atmospheric pressure and the separation, identification, and quantitative analysis of combustion products (*5*). The products of current interest include benzene and the simple alkyl substituted derivatives of benzene. The fuels include methane, propane, isobutylene, and acetylene.

Combustion and Sample Collection. The combustion and recovery is performed within a complete glass system. A diffusion type burner is coupled to tank air and fuel through pressure regulators and rotameters. Complete combustion infers the use of both primary and secondary air and that combustion is predominantly occurring at the stoichiometric end of the combustion spectrum. Incomplete combustion as indicated by a smoky yellow flame occurs predominantly at the pyrolysis end of the combustion spectrum and is accomplished by using only secondary air (*5*). A typical set of combustion data for each of the four fuels is given in Table I together with the corresponding recovery weights of the compounds of interest. Particulate collection occurs in a tared glass thimble, causing a pressure buildup in the combustion chamber

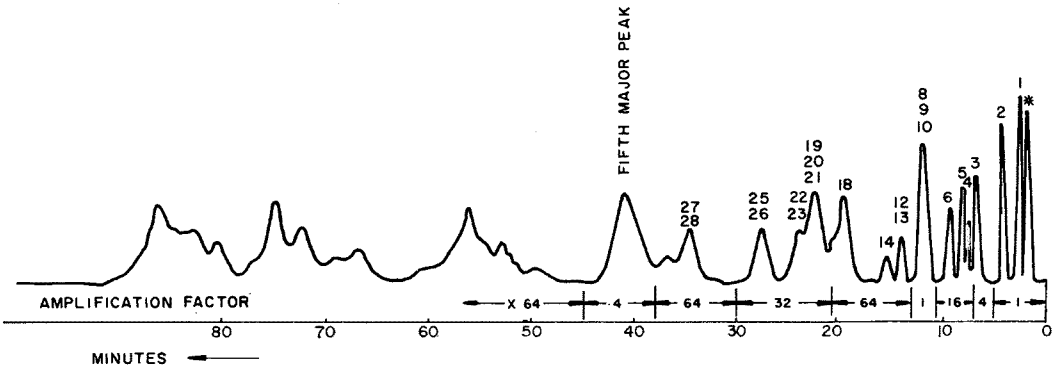

Figure 1. Chromatogram of concentrated composite sample exemplifying array of compounds produced

Fuel: Propane—Incomplete combustion
Column: 5% Di-isodecylphthalate, 5% Benton-34, N_2-30 ml./min. H_2-20 ml./min., 95° C.
Note: Retention times approximately one half normal.
* Solvent peak

Table I. Experimental Data Related to Combustion Studies

Fuel	Combustion	Weight of fuel (grams)	I Air (l./min.)	II Air (l./min.)	Duration of run (min.)	Weight of combustion products[a] (mg.) B	T	E	DB	TB	*p*	*m*	*o*	S
Methane	Complete	16.9	0.25	6.6	30	105	2.19	0.03	1.96	11.0	...	...	...	262
	Incomplete	14.2	0	6.7	25	171	3.27	0.03	2.36	8.8	...	...	...	362
Propane	Complete	18.8	0.65	5.6	26	139	10.6	1.58	10.3	7.7	0.1	0.2	0.4	382
	Incomplete	22.1	0	5.7	25	199	16.1	2.61	16.8	14.7	0.2	0.5	0.5	553
Iso-butylene	Complete	10.4	0.84	6.8	10	149	17.9	0.84	8.6	8.15	0.2	0.4	0.2	909
	Incomplete	9.47	0	6.8	9	176	21.8	1.17	11.1	11.9	0.3	0.8	0.6	911
Acetylene	Complete	4.88	1.1	6.8	6									
		4.63	1.1	6.9	7	...	...	...	0.07[b]	0.42[b]	...	...	...	3404[b]
	Incomplete	6.41	0	6.8	8	54	1.67	0.05	2.18	12.0	...	...	...	1422

[a] B—Benzene, T—Toluene, E—Ethylbenzene, DB—Styrene, TB—Phenylacetylene, *p*—*p*-Xylene, *m*—*m*-Xylene, *o*—*o*-Xylene, S—soot.
[b] Weight of combustion products for complete combustion of acetylene based on summation of two runs.

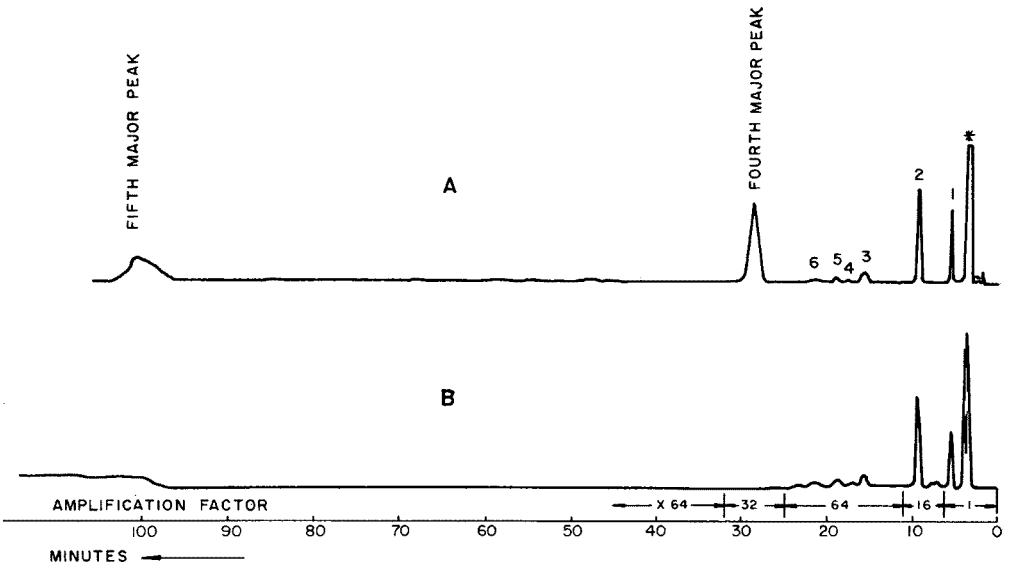

Figure 2. *A.* Typical chromatogram of combustion sample
B. Aliquot of same sample after ozonolysis

Column: 5% Di-isodecylphthalate, 5% Benton-34, N_2-15 ml./min. H_2-20 ml./min., 91° C.
* Solvent peak

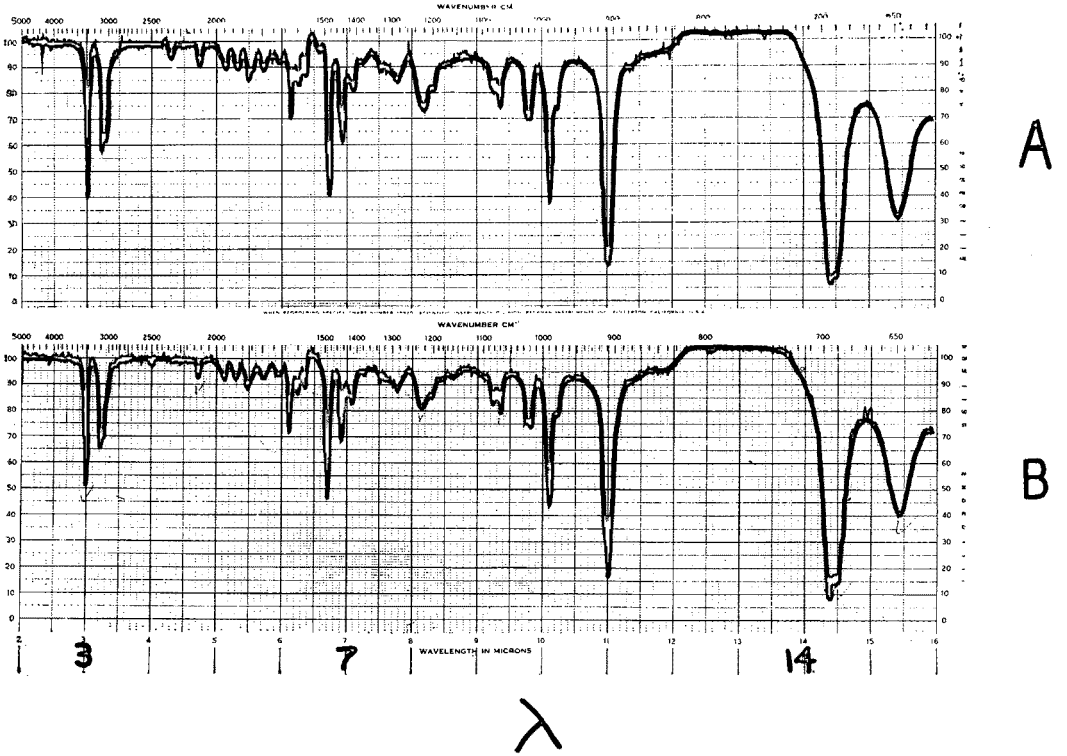

Figure 3. Infrared spectra in CCl_4 of:

(*A*) Prepared composite sample of styrene and phenyl-acetylene. (1:1—0.05 ml./ml.)
(*B*) Chromatographed fraction corresponding to fourth major peak. (Incomplete combustion of propane)

which must be overcome by an exhaust pump. Each run in the data is of maximum possible duration as determined by the capacity of the exhaust pump to maintain a pressure of one atmosphere in the combustion chamber. Water which is one of the major products is collected by means of a series of four condensers maintained at 2° C.

A series of in-line freeze out traps utilizing dry ice–acetone is used for the collection of the more volatile organic components. Samples are prepared by washing the freeze out traps or by extracting the various trapped fractions with methylene chloride. Suitable aliquots are subsequently injected directly into gas chromatography columns. The material of current interest is found in the freeze out traps with a negligible amount being extractable from the aqueous phase. There is nothing apparently contained in the extract of the particulate fraction. Working with known quantities of benzene vapor through the collection system for determining collection efficiency indicates that more than 80 per cent of the most volatile component, benzene, is caught in the freeze out trap.

Chromatography. Details and programming of the various chromatographic techniques are included in Table II. Chromatographed compounds in the table are numerically keyed to the chromatogram. The initial chromatographic resolution of combustion samples was accomplished with System 1 which utilizes a Benton-34 column and a hydrogen flame detector. Resolution of larger quantities of the same samples was accomplished using System 2 which also utilizes a Benton-34 column in a preparative chromatography unit with a thermal conductivity detector. Disc integration was used for quantitative analysis.

A chromatogram of a concentrated composite sample is shown in Figure 1 to exemplify the wide array of combustion products present in minute quantities. A more typical chromatogram is shown in Figure 2*A*.

The first three major chromatogram peaks indicate the presence of benzene, toluene, and ethylbenzene. Preparative gas chromatography was used to obtain sufficient quantities of the resolved material to make positive identification by means of infrared and ultraviolet spectrophotometry. The fourth major peak was initially thought to be a composite of styrene, phenylacetylene, and propylbenzene. Infrared spectrophotometry as shown in Figure 3 indicated the presence of styrene and phenyl acetylene but propylbenzene was completely absent. Material corresponding to the fourth major peak as resolved by the preparative chromatography unit was introduced into System 3 utilizing a Carbowax column which is capable of resolving propylbenzene, styrene, and phenylacetylene. The result shown indicates the presence of only styrene and phenylacetylene.

A further verification of the complete absence of propylbenzene was made by chromatographing ozonized aliquots of the combustion samples. Chromatogram peaks for benzene, toluene, and ethylbenzene persist after ozonolysis but the fourth peak completely disappears as shown in Figure 2*B*. Details of the ozonolysis technique are included in Table II.

There are three minor chromatogram peaks falling between the ethylbenzene and the styrene-phenylacetylene peaks. These have been identified as *ortho*, *meta*, and *para* xylenes using ultraviolet spectroscopy. There are also several minor peaks following the styrene–phenylacetylene peak occurring approximately at 44, 47, 53, 58, and 67 minutes after injection. The peaks probably are derived from compounds with carbon number between seven and ten. A fifth relatively major peak occurs at 99 minutes. Based on retention time, relative boiling points, spectroscopy, and ozonolysis the following general conclusions have been made. The peak corresponds to a mixture of simple, aromatic polyalkyl substituted compounds with some unsaturation in the alkyl groups. Work is continuing on the identification of all minor substituents.

Table II. Operational Data on Chromatography and Ozonolysis

	Compound	Retention time, min. System 1	System 2	System 3
	Methylene chloride[a]	3.6	2.6	
	AROMATIC			
1	Benzene	5.5	4.4	4.5
2	Toluene	9.0	8.4	7.4
3	Ethylbenzene	16.2	14.0	11.8
4	*p*-Xylene	17.4	15.1	
5	*m*-Xylene	19.2	15.1	
6	*o*-Xylene	21.6	16.6	14.8
7	Isopropylbenzene[b]	22.0	19.0	
8	Propylbenzene	28.3	24.8	17
9	Styrene	28.3	24.8	21
10	Phenylacetylene	28.3	24.8	37
11	*p*-Ethyltoluene[b]	30.0	25.5	
12	*m*-Ethyltoluene[b]	33.2	28.2	18.3
13	*Tert*-butylbenzene[b]	33.5	28.6	
14	*o*-Ethyltoluene[b]	36.5	30.9	
15	Isobutylbenzene[b]	37.5	31.6	
16	*Sec.* butylbenzene[b]	37.0	31.9	
17	1,3,5-Trimethylbenzene[b]	41.0	34.1	
18	1,2,4-Trimethylbenzene[b]	45.2	38.1	
19	1,2,3-Trimethylbenzene[b]	52.2	44.2	
20	*p*-Diethylbenzene[b]	53.0	45.6	
21	*m*-Diethylbenzene[b]	54.0	46.0	
22	4-Phenyl-1-butene[b]	54.3	46.6	
23	Butylbenzene[b]	56.0	47.7	
24	*o*-Diethylbenzene[b]	60.2	50.6	
25	1,1-Dimethylpropylbenzene[b]	63.9	55.0	
26	1-Phenyl-2-butene[b]	67.3	56.7	
27	1-Phenyl-1-propene[b]	83.5	68.3	
28	Isoamylbenzene[b]	84.8	72.0	
29	*n*-Amylbenzene[b]	...	92.0	
	ALIPHATIC			
	Isooctane	3.4	...	
	Octane	6.3	...	
	Nonane	11.0	10.0	
	Decane	22.5	18.3	

[a] See Figures 1, 2, 5. Methylene chloride is a solvent.
[b] Compounds tentatively identified, correspond to numbers in figures.

System 1. Wilkens Instrument & Research, Inc., HiFi Model 600. Column: 5% di-isodecylphthalate–5% Benton-34 on 80/100-mesh Chromosorb W, 12-foot × 1/8-inch o.d., 15 ml. of N_2 per minute, 91° C. Detector: hydrogen flame, 20 ml. of H_2 per minute, 250 ml. of air per minute. Reference: (*3*).

System 2. Wilkens Instrument & Research, Inc., Autoprep Model A 700. Column: 5% di-isodecylphthalate–5% Benton-34 on 80/100-mesh Chromosorb W, 12-foot × 3/8-inch o.d., 200 ml. of He per minute, 91° C., isothermal. Detector: thermal conductivity, temp. 132° C. Recovery efficiency: (e.g., styrene). Using glass wool, CCl_4 scrubber–dry ice acetone trap. 83% at concn. of 10^{-3} cc./cc.; 60% at concn. of 10^{-4} cc./cc.

System 3. Wilkens Instrument & Research, Inc., HiFi Model 600. Column: 10% carbowax 1540 on 60/80-mesh Firebrick C-22, 13-foot × 1/8-inch o.d., 29.5 ml. of N_2 per minute, 95° C. Detector: Hydrogen flame, 21 ml. of H_2 per minute, 250 ml. of air per minute.

Ozonolysis. Welsbach Corp. Ozonator T-23 (2.4 grams/hr.). Applied voltage: 80 volts. Pressure: 4 p.s.i. Air flow: <0.01 c.f.m. Time: 2 minutes in CCl for styrene (10^{-4} cc./cc.) (Listed for example only—must be uniquely determined for each sample). Reference: (*4*).

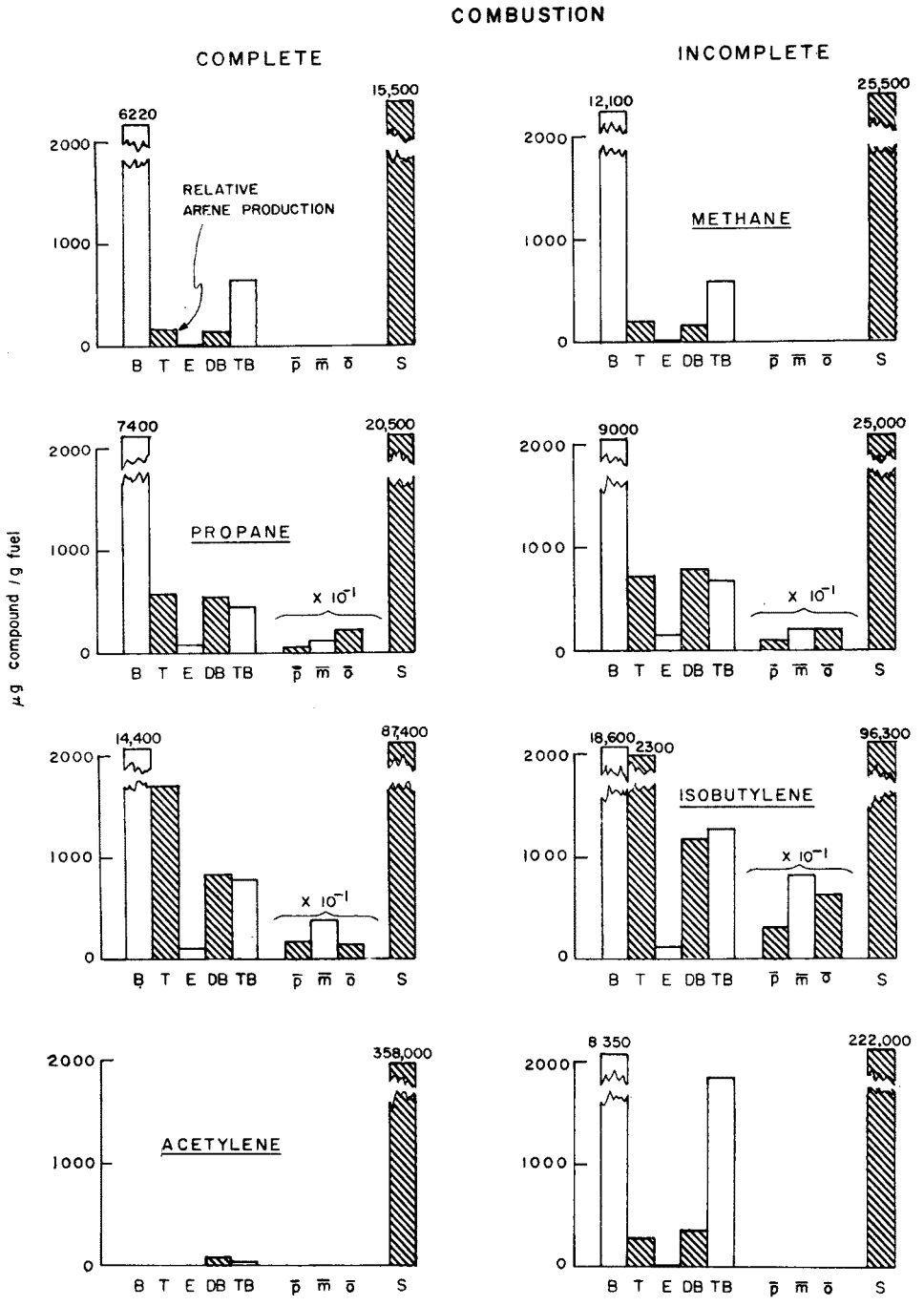

Figure 4. Comparative yields of products normalized to 1 gram of fuel

B—Benzene; T—Toluene; E—Ethylbenzene; DB—Styrene; TB—Phenylacetylene; *o*—o-Xylene; *p*—*p*-Xylene; *m*—*m*-Xylene; S—Soot

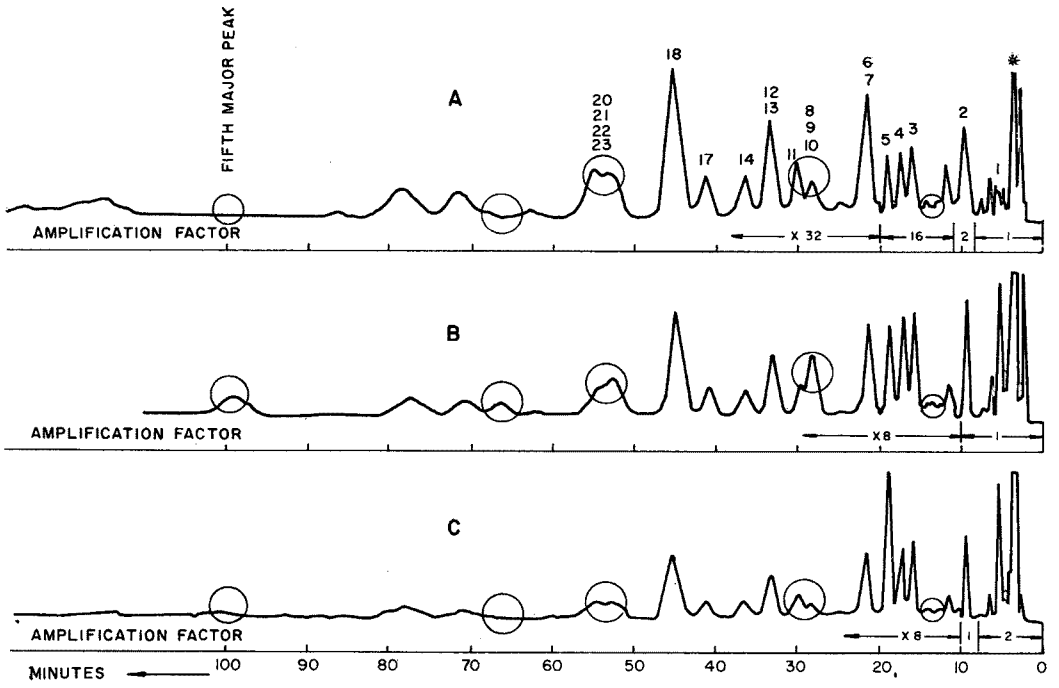

Figure 5. A. Chromatography of gasoline (regular grade)
B. Chromatography from internal combustion source using gasoline as fuel (idling)
C. Aliquot from same source after ozonolysis

Column: 5% Di-isodecylphthalate, 5% Benton-34, N_2-15 ml./min. H_2-20 ml./min., 91° C.
Note: Compounds modified by ozonolysis encircled. (2 minutes O_3—2 ml.)
* Solvent peak, i.e., methylene chloride

DISCUSSION

Aside from finding which and how much of the simple aromatic hydrocarbons are produced during combustion at atmospheric pressure, an evaluation as to relative abundance of each compound has been made which might be used to give some insight into the composition of polluted atmospheric samples. A graphical presentation of the yields from the combustion data is made in Figure 4 on which the following conclusions are based. The data is normalized as to yield of individual compounds per gram of fuel.

Benzene is generally produced in quantities one order of magnitude greater than the methyl substituted derivative, toluene. Ethylbenzene is generally produced in quantities one order of magnitude less than the methyl substituted derivative. It is not possible to detect the propyl derivative by the techniques used. Comparing normalized data from previously published work (*5*) concerned with the production of arene-type hydrocarbons indicates that arenes, pyrene in particular, always are produced in quantities falling between the yield of toluene and ethylbenzene.

The yield of dimethyl substituted benzenes—i.e., the xylenes—is again one order of magnitude less than toluene. Figure 4 indicates recoveries of xylenes for only two of the four fuels and these have been plotted in an exaggerated manner because only minute amounts of product are involved which makes quantitative work difficult. The relative abundance of styrene and phenylacetylene compared to each other and other compounds, for example, toluene, is quite variable, being unique for each fuel and type of combustion. The presence of relatively large amounts of these unsaturated compounds in general interesting to note.

Also included in Figure 4 are normalized yields of soot. In general for saturated fuels the carbon production is double or triple the benzene production. For unsaturated fuels the relative carbon production is many times again greater. Speculation as to meaning with respect to reaction mechanisms and responsible free radical production can be made, but no discussion is included for lack of more complete information.

A note should be included on the use of acetylene as a fuel. The soot production is tremendous compared to the other fuels with the normalized yield being greater for complete rather than incomplete combustion. This is probably due to a complete lack of premix, low gas velocities, and insufficient turbulence at the combustion source. The elevated temperature associated with complete combustion merely accelerate the soot production occurring at the cooler flame front. As previously mentioned, the soot production limits the duration of the run. With acetylene the runs were very short, resulting in very small recovery yields of the other products. This is the only explanation being offered for the anomalous lack of benzene production observed during complete combustion but this, in turn, does not explain the presence of styrene and phenylacetylene.

A very interesting and possible practical application of this study results when a comparison is made to internal combustion sources. Published data indicate the presence of propylbenzene in automobile exhaust (*1*, *2*). Using the herein described chromatographic techniques, gasoline itself was found to contain propyl

benzene but not styrene or phenylacetylene. The chromatogram of a combustion sample from an internal combustion engine as shown in Figure 5 also indicates a composite fourth major peak. Chromatographing an ozonized aliquot results in a great reduction in the peak area of the fourth major peak. If propylbenzene is not produced in measurable quantities during combustion, there is an indication that the relative concentration of propylbenzene in atmospheric samples may indicate the relative contribution of internal combustion sources to the atmosphere. Work is being continued on this over-all aspect to determine the complete significance.

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Nuclear Magnetic Resonance Spectra-Structure Correlations for Chlorinated 2,2-Difluoropropanes

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▶ The nuclear magnetic resonance spectra of a series of terminal chlorinated 2,2-difluoropropanes have been studied. Proton functional group chemical shifts are correlated with the sum of electronegativities of the nonskeletal atoms and are found to change predictably with varying nonadjacent substituent. The F^{19} spectra, while first-order and related to the proton spectra, show no correlatable shift property. Protonfluorine coupling constants do vary with molecular composition and are related to the proton-to-fluorine dihedral angle in a manner analogous to the dependency others have established for fluoroethanes.

THE terminal chlorination of 2,2-difluoropropane has resulted in a series of compounds similar to those recently discussed (*12*). These novel compounds have been identified by nuclear magnetic resonance spectrometry through the use of a correlation diagram also similar to those recently published (*12*). F^{19} resonance patterns and proton-fluorine couplings have been valuable adjuncts in assigning structures to these molecules.

EXPERIMENTAL

Proton resonance spectra were obtained on a Varian Model A60 spectrometer and are of 10% by liquid volume solutions of solute in carbon tetrachloride. A few drops of tetramethylsilane were placed in each sample tube for internal reference. Resonance shifts were recorded to the nearest 0.3 cycle and converted to chemical shifts in parts per million by the usual method (*10*).

Fluorine resonance spectra of all samples were obtained at 56.4 megacycles on a Varian Model 4300-B high-resolution spectrometer equipped with a field homogeneity control unit. The materials were scanned as 10% by liquid volume solutions in carbon tetrachloride and, when possible, as pure liquids; in either case, a small amount of fluorotrichloromethane was added to each sample tube for internal fluorine resonance reference (*6*). Chemical shifts and coupling constants were determined by the usual side-band modulation technique using a Hewlett-Packard Model 200-CDR audio-oscillator and measuring the side bands with a Hewlett-Packard Model 524-D electronic counter. The various samples exhibit a different degree of shift on dilution with carbon tetrachloride; the 10% solution shifts are considered equivalent to infinite dilution shifts at the reported accuracy.

RESULTS AND DISCUSSION

Proton Spectra. Qualitative analysis of products produced in the terminal chlorination of 2,2-difluoropropane has been facilitated by the development of a correlation between proton chemical shift and propane substituent electronegativity (*9*) found to exist in analogous materials (*12*). Figure 1 shows the correlations produced from the compounds listed in Table I. These graphs differ from the previously discussed correlations (*12*) in that all the variations are linear not only among the molecular series but also within the end groups. While the proton spectra of some molecules (*3*) show very fine structure, second order effects (*10*), the F^{19} resonance patterns (at the resolution used) were simple, first-order spectra; therefore, the second-order splittings were ignored in the preparation of the proton correlations.

Fluorine Spectra. F^{19} spectra-structure correlations have been discussed by several authors (*1, 4, 5, 11*), and these discussions have shown that the F^{19} chemical shift is related to the molecular environment. For these molecules, a linear relationship between chemical shift and propane substituent electronegativity (*9*) does not exist. However, in general, the F^{19} resonance shifts to higher fields with increasing substituent electronegativity; such a higher field shift is exactly opposite to the proton shift. The resonance positions given in Table I are the algebraic mean of the individual line positions and the spectra are simple, first-order patterns.

Coupling Constants. Proton-fluorine coupling constants have also been included in Table I. These values were derived primarily from the F^{19} spectra and agree to 0.1 cycle with the main splittings observed in the proton spectra. In Figure 2, the observed constants are plotted against carbon substituent electronegativity in a manner analogous to the chemical shifts. Such a correlation allows the prediction of coupling constants for the two unavailable members of this series (7.0 and 13.3 c.p.s. for $CHCl_2CF_2CH_2Cl$ and 12.4 c.p.s. for $CH_2ClCF_2CH_2Cl$).

Gutowsky (*7*) and Karplus (*8*) have discussed the dependency of coupling constant on dihedral angle between coupled atoms for proton-proton and proton-fluorine couplings in ethanic and ethylenic compounds. Anet (*2*)

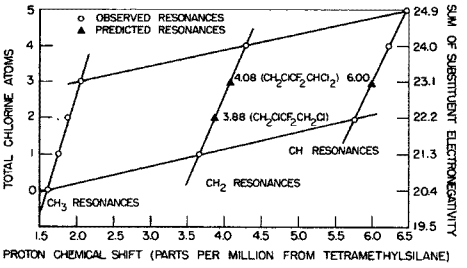

Figure 1. Variation of proton chemical shift in $CH_xCl_yCF_2CH_mCl_n$

$x + y = 3 = m + n$

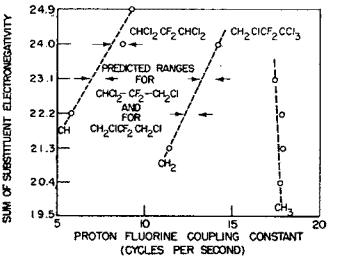

Figure 2. Variation in H-F coupling in $CH_xCl_yCF_2CH_mCl_n$

$x + y = 3 = m + n$

has extended the proton-proton dependency to include ring systems, while Elleman, Brown, and Williams (*5*) have substantiated the proton-fluorine results with ranges for H-F coupling constants for many fluorocarbons. However, an angular dependency has not been explicitly demonstrated for the H-F case as it has been for the H-H couplings. The present study offers an opportunity for investigating such an angular dependency in some saturated fluoropropanes.

When a molecular model of 2,2-difluoropropane is viewed along one carbon to carbon bond, it is seen that the three methyl protons in the staggered configuration are all equivalent with respect to the two fluorine atoms. Similarly viewing the methylene protons of the monochloro compound shows the most favorable position to be protons opposed to fluorines (*cis*), while the methine proton of the dichloroderivative would most likely be gauche to both fluorine atoms. Figure 3 shows the dependency obtained when the above assumptions of molecular geometry are plotted against coupling constant. The methyl group is assumed to be in the staggered position, with the coupling constant derived from the nondigauche protons. In Figure 3 the digauche dihedral angle has been chosen as the origin. Table II summarizes the assumptions used in preparing Figure 3 as well as the dihedral angles derived from the coupling constants of the higher molecular weight members of this series. Also included in Table II are the coupling constants predicted from Figure 2 for the unavailable molecules and their dihedral angles predicted from Figure 3. The data presented graphically in Figure 3 agree with the ranges calculated by Karplus (*8*) for *cis* and *trans* H-F coupling constants.

Table I. Observed Chemical Shifts and Coupling Constants for Halogenated Propanes

Compound	Sum of electronegativities of substituents[a]	Proton chemical shift[b]			Fluorine chemical shift[c]	Coupling constants[d]	
		Methyl	Methylene	Methine		Fluorine to methyl	Fluorine to nonmethyl
$CH_3CF_2CH_3$	20.4	1.61	...	...	85.04	17.76	...
$CH_3CF_2CH_2Cl$	21.3	1.76	3.66	...	94.90	17.92	11.41
$CH_3CF_2CHCl_2$	22.2	1.88	...	5.77	97.97	17.84	5.85
$CH_3CF_2CCl_3$	23.1	2.07	...	...	99.95	17.42	...
$CH_2ClCF_2CCl_3$	24.0	...	4.30	...	110.60	...	14.20
$CHCl_2CF_2CHCl_2$	24.0	...	...	6.24	117.44	...	8.74
$CHCl_2CF_2CCl_3$	24.9	...	...	6.47	106.49	...	9.23

[a] Pauling's electronegativities; F = 3.9; Cl = 3.0; H = 2.1.
[b] Chemical shifts in parts per million to lower field from tetramethylsilane internal standard.
[c] Chemical shifts in parts per million to higher field from fluorotrichloromethane internal standard.
[d] Coupling constants in cycles per second; values obtained from dilute solution measurements.

Table II. Coupling Constants and Dihedral Angles for Halogenated Propanes

Compound	Coupling constants[a]		Dihedral H·C·C·F angle[b]
	Fluorine to methyl	Fluorine to nonmethyl	
$CH_3CF_2CH_3$	17.76[c]	...	120°[d]
$CH_3CF_2CH_2Cl$	17.92[c]	11.41	60°[d]
$CH_3CF_2CHCl_2$	17.84[c]	5.85	0°[d]
$CH_3CF_2CCl_3$	17.42[c]	...	...
$CH_2ClCF_2CCl_3$	...	14.20	84[e]
$CHCl_2CF_2CHCl_2$	...	8.74	32[e]
$CHCl_2CF_2CCl_3$	...	9.23	36[e]
$CH_2ClCF_2CH_2Cl$	...	12.4[e]	68[e]
$CH_2ClCF_2CHCl_2$	...	13.3; 7.0[e]	76, 14[e]

[a] Coupling constants in cycles per second.
[b] Dihedral angle measured from digauche configuration.
[c] Average to 17.7 c.p.s. for 120° configuration.
[d] Assumed from inspection of models.
[e] Predicted from Figures 3 and 4.

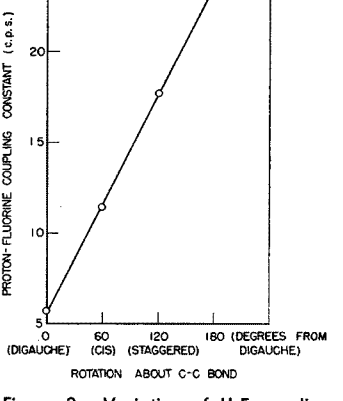

Figure 3. Variation of H-F coupling with dihedral angle

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Refractive Indices of Sucrose-Water Solutions in the Range from 24 to 53% Sucrose

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▶ **The presence of a dip in the refractive index curves currently proposed for official acceptance by the International Commission for Uniform Methods of Sugar Analysis suggested some inconsistencies calling for resolution. Measurements were made of refractive index for sucrose-water solutions between 22 and 59% sucrose, covering the range in question. Results are tabulated. The new values appear to produce a consistent and smooth curve when compared with Landt-Schönrock data between 0 and 25% sucrose and Snyder and Charles data above 50% sucrose, but they deviate from the International scale values, giving refractive index higher by 14×10^{-5} unit near 40% sucrose. The calculation of a consistent five-place sucrose refractive index table now appears possible.**

In 1936 the International Commission for Uniform Methods of Sugar Analysis (*6*) adopted officially the International scale of refractive indices. This scale was a composite of results of at least three separate investigations. Below 24% solids Landt (*7*) had shown good agreement between his results and Schönrock results of 1933 (apparently unpublished). Therefore, the official scale was carried to five decimal places in this region, using the Schönrock data as listed by Landt (*7*). Above 71%, data of Main (*8*) were used. Between 24 and 66%, Schönrock data of 1911 (*11*) were used, with a straight line interpolation from 66 to 71%. Because of discrepancies and uncertainties, the table carried only 4 places in refractive index (R.I.) above 24% solids.

Subsequent investigations, in particular those of Snyder (*12*) and Charles (*2*), indicated significantly higher refractive indices than those of the International scale of 1936 in the commercially important range above 50% sucrose. Hill and Orchard (*4*) presented a statistical appraisal which showed the Snyder and Charles results in good agreement for the concentration range of 53 to 82%.

Still later Hill and Orchard (*5*) and Charles (*3*) discussed the problem of relating the new data in the upper concentration range to the International scale values for lower concentrations to produce a smooth and continuous variation. The Hill and Orchard (*5*) mathematical smoothings and the Charles graphical smoothing (*3*) are in substantial agreement. Following a suggestion of Van Hook (*13*), Charles (*3*) prepared a plot of $(N - N_0)/C$ which showed a dip in what otherwise might be a smooth curve joining the Landt data in the range of 0 to 24% solids (*6*) with the Charles-Snyder data above 53% solids (*4*). To verify if such a dip was real, a further series of determinations was made and is the subject of this paper.

PROCEDURE

Solutions were prepared in ground glass-stoppered Erlenmeyer-shape weighing bottles. The sugar used was a high purity commercial sucrose, confectioner's sanding. Weights of the crystalline sugar were corrected for 0.060% internal moisture as determined by Onna (*9*) as well as for 0.003% external moisture as determined by drying of air-equilibrated sugar at 70° C. under vacuum. Total impurities in the sugar, aside from moisture, were of the order of 0.01%.

Refractive indices were read on a Bausch and Lomb precision sugar refractometer (Catalog No. 33-45-91, serial No. XD7176, prism series 719). Readings made on the arbitrary linear scale were corrected to 20° C. Measurement techniques and temperature corrections were as discussed by Charles and Meads (*14*). Corrections were applied based on a concurrent series of distilled water readings. An additional correction was based on readings of a triangular test plate certified by the National Bureau of Standards to have a refractive index of 1.46632. The scale error at this point averaged +0.014 scale unit, equivalent to 0.000041 unit of refractive index or 0.018% sucrose. The corrections were assumed linear in scale units between the water reading and the glass plate reading at 1.46632 R.I.

RESULTS AND DISCUSSION

Table I shows per cent sucrose by weight in air and corresponding refractive index determined experimentally. The third column lists values of the function $(N - N_0)/C$ as suggested by Van Hook (*13*) and discussed in a previous paper (*3*). Values of C were computed from Table 113 of Bates (*1*). The refractive index of water, N_0, was taken to be 1.33299 as in the Bates table.

Because $N - N_0/C$ is so nearly constant, a graph of this function against C serves to magnify the effects of small differences in refractive index. Figure 1 illustrates that the new data deviate significantly from the values of the 1936 scale. Further, as shown by the dashed curve, the new data bridge the gap more smoothly between the five-place Landt figures (*6*) and the Snyder-Charles data (*4*).

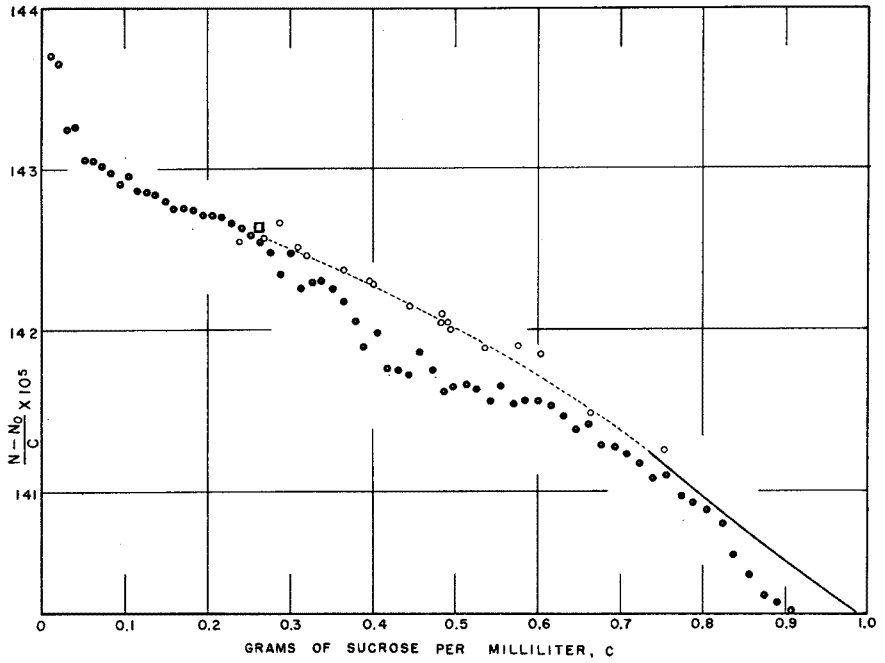

Figure 1. Refractive indices for sucrose solutions

O. 1936 International scale
—O—. This paper
□ Rosenhauer
——. Orchard-Hill smoothing of Charles-Snyder data
N. Refractive index corresponding to concentration C, grams of sucrose per 100 ml.
No Refractive index for water (C = 0)

Table I. Refractive Indices of Sucrose Solutions for 20° C. and the Sodium D Lines

% Sucrose calculated from weights in air	N	$(N - N_0/C) \times 10^5$
21.805	1.36684	142.55
23.882	1.37039	142.57
25.563	1.37333	142.66
27.448	1.37660	142.50
28.119	1.37778	142.47
31.803	1.38441	142.37
34.496	1.38938	142.30
34.557	1.38949	142.28
37.822	1.39564	142.14
40.697	1.40123	142.10
40.724	1.40126	142.05
41.335	1.40247	142.05
41.481	1.40274	142.01
44.470	1.40869	141.89
47.159	1.41424	141.91
49.047	1.41814	141.80
53.144	1.42676	141.49
58.875	1.43938	141.19

As the value of $N - N_0$ approaches 0, the ratio $(N - N_0)/C$ approaches indeterminacy. The deviation of the points below 5% from the upper portion of the curve represents a slight inconsistency, no more than 1×10^{-5} in R.I., between the refractive indices measured for dilute sugar solutions and that assumed for water.

Rosenhauer (*10*) has reported several recent determinations at 23.7% sucrose (the normal concentration for sucrose polarizations) using the potentially very accurate minimum deviation method; a hollow prism with quartz glass windows contains the solution to be measured. The square in Figure 1 shows his data to be in close agreement with the Landt data (*6*) and with a smoothing of the present data.

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Condensation Pressure Analyzer and Its Application to Continuous Uranium Hexafluoride Determination

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▶ **An automatic instrument continuously determines the first condensable component in a gas system by measuring the dewpoint or condensation pressure at a fixed temperature. A pressure control valve actuated by a condensation detector maintains condensation pressure equilibrium. The instrument is applicable to corrosive systems and to mixtures of condensable gases; its pneumatic output signal is suitable, without modification, for automatic system control. One model provides a continuous and specific measurement of uranium hexafluoride in a plant stream with a relative standard deviation of ±0.12%.**

WITH INCREASED handling of uranium hexafluoride, the need exists for simple low cost instruments to monitor and control its concentration in gas streams. Only expensive mass spectrometer analyzers have been able accurately to monitor uranium hexafluoride in the presence of fluorocarbons, hydrogen fluoride, oxygen, and nitrogen. Other instruments such as the Acoustic Gas Analyzer (*1*) have been applied, but they are dependent on gas density variations and are not specific.

This report describes an inexpensive analyzer for determining uranium hexafluoride in complex gas streams, even in the presence of appreciable amounts of fluorocarbons. The design basis, a description of the development model, and the application of an automatic plant stream analyzer are presented.

DESIGN PRINCIPLES

From Dalton's law of partial pressures, the partial pressure of a component of an ideal gas mixture is directly proportional to its molar concentration; therefore,

$$\text{per cent molar concentration} = \frac{\text{partial pressure}}{\text{total pressure}} \times 100 \quad (1)$$

Where the partial pressure exerted by the analytically desired component is maintained constant by varying the total pressure, the total pressure responds reciprocally to concentration to provide an analysis. One means of instrumentally setting the partial pressure of a condensable component at a constant value is to select the partial pressure equal to the vapor pressure at a constant temperature.

The basic design of the Condensation Pressure Analyzer, illustrated in Figure 1, consists of five components: the control valve that adjusts total gas pressure to cause the partial pressure of the analytically desired component to seek its condensation pressure; the element which senses that the partial pressure has exceeded or become less than the condensation pressure; the element to feed back the response from the sensing element to the control valve; the flow limiter to limit the evacuation rate of the sample gas, so that it can attain pressures sufficient for condensation while permitting flows adequate for acceptable response; and the meter to continuously measure the total pressure as the analytical signal.

As the sensing element, a condensation detector is employed which utilizes the variations in the pressure drop in a flowing system caused by condensation within a cool restriction. For some chemical systems, the sensing device used to detect the degree of condensation could be a type other than the cooled constriction—e.g., a fogged mirror type using photometric measurement or an electrical conductivity system responding to the presence of a liquid phase.

LABORATORY MODEL ANALYZER

Description. The laboratory model, Figure 2, consists of the pressure control valve (*PCV*), the differential pressure (ΔP) transmitter, the constant temperature capillary, the pressure measuring system, and the flow restricting exit valve.

The transmitters (*2*) convert the measured pressure signals of the corrosive gas to amplified air pressure signals. The signal from the absolute pressure transmitter (Taylor-Model 206 RA) is recorded as total gas pressure. The pressure P_2 downstream of the cool capillary was more indicative of condensation pressure than the upstream pressure, and therefore was selected for the analytical response. The output air pressure signal from the ΔP transmitter (Taylor-Model 206 RD) is the control signal to the top of the inlet diaphragm-operated control valve (Hoke - Part No. 1148); regulated air pressure is applied to the bottom of the diaphragm to fix the differential

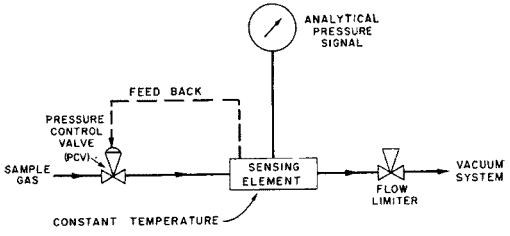

Figure 1. Condensation pressure analyzer

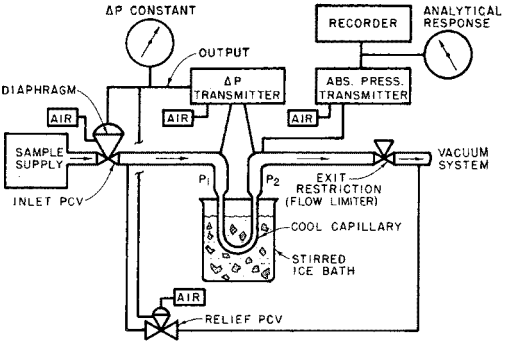

Figure 2. Laboratory model condensation pressure analyzer

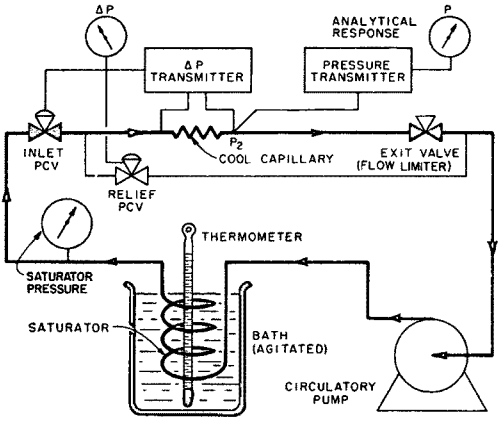

Figure 3. Circulatory method of calibration

pressure at a control value, small compared to the total pressure.

To prevent a complete and prolonged plugging of the capillary restriction after a rapid increase in concentration, a bypass controlled by a relief pressure control valve was installed as shown in Figure 2. The relief valve setting is such that the valve opens when the differential pressure across the capillary becomes abnormally high. In practice the need for this bypass was marginal since it was rarely activated.

The detector capillary necessarily is colder than the rest of the system and for best operation only the center portion is cooled to prohibit condensation before or after the capillary. Copper and nickel capillaries from 2 to 4 inches long with internal diameters of 0.030 to 0.060 inch proved satisfactory. The smaller diameter and shorter capillaries are more sensitive and, therefore, were selected for studies at low concentrations.

In tests with uranium hexafluoride, a wet ice bath was conveniently used to provide a constant temperature of 0° C. The vapor pressure of uranium hexafluoride at 0° C. is 17.57 mm. of Hg (*3*).

All components expected to come in contact with uranium hexafluoride or fluorine were constructed of resistant metals such as copper, nickel, and Monel. All joints were silver soldered, and Fluorothene plastic valve seats were used.

Operation. The analyzer automatically adjusts the total pressure to maintain the partial pressure of the analytically desired component at its condensation pressure as follows. Sample gas passes through the system at a flow rate established by the pressure P_2 and the resistance of the exit restriction. The exit restriction had previously been adjusted with an air flow so that the differential pressure developed at the open cool capillary is less than the control differential pressure, for example, 2 mm. of Hg when a control value of 6 mm. of Hg was used. Initially, the inlet control valve is fully open and the analyzer pressure increases, approaching the sample supply pressure. If uranium hexafluoride content is within the concentration range of the instrument, condensation of uranium hexafluoride partially plugs the cool capillary, causing the differential pressure across the capillary to rise above the control point and the inlet control valve to close. The system pressure then gradually decreases, and when the pressure drops below that required for condensation, evaporation occurs and the capillary deposit decreases, causing the differential pressure to be reduced and the control valve to open again. System pressure then increases and the cycle is repeated.

The cyclic operation is observed only at low flow rates. With sufficient flow, an equilibrium is reached (with the capillary partially plugged) and the cycling effect is negligible. The output signal is a smooth line on a pressure recorder chart and follows changes in concentration without overshoot or cycling.

Calibration. Two methods were used for preparing and handling standard gas samples. In one method, known mixtures of uranium hexafluoride and dry air were passed through the analyzer and exhausted through a chemical trap. In the second method, illustrated in Figure 3, the sample gas was circulated by means of a bellows-sealed reciprocating pump through the analyzer and a saturator containing solid uranium hexafluoride. The temperature and pressure in the saturator were measured, and from an established vapor pressure temperature curve (*3*), the uranium hexafluoride concentrations were calculated. This circulatory method was more convenient since the concentration could easily be changed by varying the pressure or temperature of the saturator.

Calibration of the instrument was accomplished by passing known concentrations of uranium hexafluoride in air through the analyzer and recording the equilibrium condensation pressures measured at P_2. To maintain suitable flows it was necessary to adjust the exit valve setting for different concentration levels. Table I includes the data obtained in the range of 2.5 to 55 mole %. Pressure was measured with a 0- to 1000-mm. Hg transmitter at 2.5% uranium hexafluoride and a 0- to 100-mm. Hg transmitter at the higher concentrations. For the known concentrations and measured total pressures, the calculated partial pressures of uranium hexafluoride listed in the third column of Table I are slightly higher than the value reported by Oliver, Milton, and Grisard (*3*); the small differences were not affected by further immersion of the cold capillary into the cold bath, indicating that the detector was at thermal equilibrium. If it is assumed that the condensate plug formed an orifice, the partial recovery of pressure following the orifice might explain the positive pressure bias since the probe was remotely located, while the true condensation pressure would be exerted directly on the condensate. A calibration curve was prepared using the average value of 17.89 mm. of Hg for the empirical partial pressure of uranium hexafluoride.

Precision. Using a fixed exit valve setting, eight determinations were made with a stream containing 2.45% uranium hexafluoride. Each of these

Table I. Calibration Data for Laboratory Model

Mole % UF_6 in air	Pressure response, P_2, mm. of Hg (abs.)	Calculated[a] partial pressure of UF_6, mm. of Hg (abs.)
2.45	719.0	17.62
21.3	82.5	17.57
21.9	82.5	18.07
22.1	81.5	18.01
23.2	77.5	18.00
23.4	76.5	17.90
23.6	76	17.94
39.8	44.5	17.71
54.6	33.0	18.02
55.4	32.5	18.01
	Av. =	17.89 mm. of Hg
Vapor pressure pure UF_6 at 0° C. (*3*)		17.57 mm. of Hg

[a] Partial pressure = $\frac{(\text{Mole \% } UF_6) \times P_2}{100}$

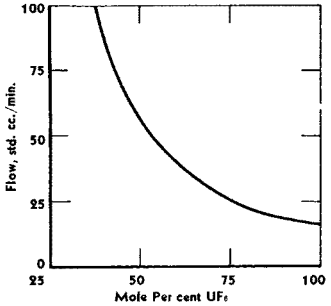

Figure 4. Flow requirement of field model

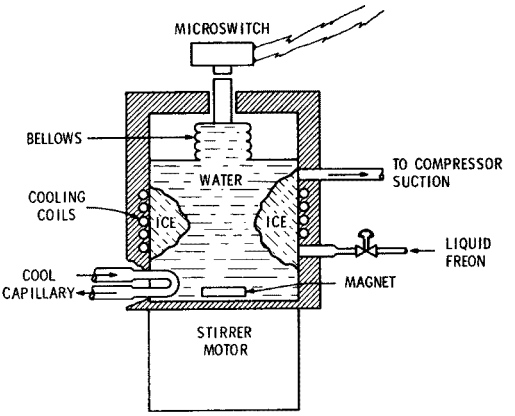

Figure 5. Automatic ice bath

measurements was made after upsetting the pressure equilibrium conditions instrumentally and/or by introducing temperature variations between determinations. For the eight replicate determinations a standard deviation of ±0.004% (absolute) or 0.16% (relative) was obtained, which is approximately equivalent to the limit of readability of the pressure gauge.

Accuracy. To evaluate the accuracy of the instrument for fluorination tower monitoring, known mixtures of uranium hexafluoride and fluorine, in the range of 25 to 60% uranium hexafluoride, were analyzed using the calibration curve established with uranium hexafluoride–air mixtures. No significant bias was found; the average bias of +0.11% relative was well within the accuracy of the pressure measuring system.

PLANT STREAM ANALYZER

Description. A field model analyzer was developed and tested to monitor uranium hexafluoride between 40 and 100 mole % in a plant stream containing fluorocarbons, hydrogen fluoride, and inert gases. The sample supply pressure was approximately 100 mm. of Hg (absolute).

The design of the field model was basically the same as that of the laboratory instrument except for modifications in the exit constriction, the cold bath, and the system for handling the analytical pressure signal.

Exit Constriction. To eliminate an adjustment variable, a fixed capillary tube was used in place of the manually adjusted valve for the exit restriction. Flows ranging from 16 to 100 standard cc. per minute (plotted *vs.* uranium hexafluoride concentration in Figure 4) were obtained using a capillary 12 inches long with an internal diameter of 0.051 inch; these variations in flow proved relatively unimportant.

Automatic Ice Water Bath. An automatic ice bath, Figure 5, was devised. In an insulated sealed chamber completely filled with water, a bellows-microswitch arrangement responds to the volume changes associated with the freezing of water and melting of ice and automatically controls the cooler to maintain an ice water system. The amount of ice is adjusted by the vertical position of the microswitch. A magnetic stirrer keeps the hermetically sealed sensing element in thermal equilibrium with the bath. The simple and rugged system is especially convenient for application to a continuous analyzer. For other applications where the heat load is small, for example a thermocouple reference standard, agitation may not be necessary except for extreme accuracy; for such small loads, thermoelectric cooling would be adequate.

Relatively large analytical errors would be introduced by small changes in the temperature of the condensation detector; a fluctuation of ± 0.1° C. at 0° causes an error of ± 0.8% of the analytical value. The automatic ice bath provides a constant temperature which fluctuates less than 0.025° C. Since the equilibrium temperature obtained is a fundamental fixed point, no reference compensation is necessary.

Signal Handling. A Sorteberg pneumatic force bridge (*4*) is applied to the analytical response to give a linear indication rather than a reciprocal measure of uranium hexafluoride concentration. The pneumatic output may be applied directly to control systems.

Calibration. The measured analytical pressure response to 100% uranium hexafluoride was 17.0 mm. of Hg absolute. This lower value, as compared to 17.89 mm. of Hg for the average partial pressure calculated for the laboratory model, may be due to the greater pressure drop within the cool capillary downstream of the condensate as a result of higher volumetric flows used in the field model analyzer. The calibration curve, Figure 6, was prepared by using a single standard sample, and substituting 17.0 mm. of Hg for the effective partial pressure in Equation 1.

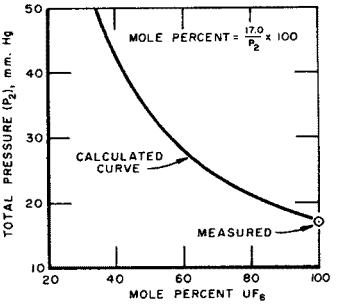

Figure 6. Calibration curve for field model

Performance. A standard deviation of ±0.12% (relative) was determined with 10 measurements at 100% concentration. Using the calculated curve (Figure 6) over the range 40 to 100% uranium hexafluoride, the standard deviation of agreement between the analyzer and prepared standards was ±0.66% (relative), a portion of which is attributed to inaccuracies in sample preparation.

The field model has operated for more than three years with over 99% on-stream efficiency and little maintenance; no difficulties have resulted from the corrosive characteristics of the gas stream. The analyzer has a response time of less than 1 minute and no effects of impurities have been noted even when the stream contained relatively large concentrations of fluoro-

carbons; for example, perfluorodimethylcyclohexane, which in its pure form is more condensable than uranium hexafluoride, gives no interference when its partial pressure is below its condensation pressure.

ACKNOWLEDGMENT

The authors thank the Instrument Engineering Department of the Oak Ridge Gaseous Diffusion Plant for permission to mention their application of the Sorteberg pneumatic force bridge to the plant stream analyzer.

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Determination of Diphenylhydantoin by Ultraviolet Spectrophotometry

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▷ A method for determining diphenylhydantoin permits analysis for that substance in blood in the presence of other drugs without preliminary separation by extraction. In the procedure, hydrolysis of the hydantoin ring in strong alkali is followed by a Hofmann degradation of the resulting amide to yield a steam-distillable product. Hydrolysis and degradation proceed spontaneously, permitting immediate steam distillation of the product which, in contrast to diphenylhydantoin, has a high molar absorptivity in the ultraviolet region. It has a well defined maximum at 257 mμ and a minimum at 228 mμ. The method is rapid and, for forensic toxicologic purposes, is specific for diphenylhydantoin. It is sufficiently sensitive for the determination of diphenylhydantoin in therapeutic concentration in the blood.

DIPHENYLHYDANTOIN and phenobarbital interfere with each other in spectrophotometric and colorimetric analytical procedures. Frequent combined therapeutic use of the two drugs has posed a considerable problem in the development of methods for determining concentrations of diphenylhydantoin in blood. In 1941 Kozelka and Hine (*6*) introduced a titrimetric technique for measuring milligram quantities of the drug; the technique failed as a micromethod. Plaa and Hine (*8*) described a spectrophotometric method capable of determining diphenylhydantoin in samples of blood containing phenobarbital also, but only after separation of the two drugs by a tedious operation based on differences in their partition between blood and a cyclohexane-butanol mixture. Separation by their method was incomplete. Dill and associates (*2*) developed a method for analysis of diphenylhydantoin in which the drug was extracted into an organic solvent, which was then evaporated. Subsequent steps included nitration of the residue, reduction with stannous chloride to form an aromatic amine, and finally diazotization and coupling with the Bratton-Marshall reagent as used in the colorimetric test for sulfonamides. An elaborate extraction procedure was necessary to prevent interference by phenobarbital when that drug was present in the sample.

Svensmark and Kristensen (*11*) recently described a more precise and rapid method for determining diphenylhydantoin in the presence of phenobarbital. Their method, which required less serum than the earlier procedures, consisted of extracting the drugs from acidified serum, separating them by partition between chloroform and a borate buffer of pH 8.8, and then determining each drug spectrophotometrically. As in the previous methods, separation was incomplete.

The procedures which have been developed for determining diphenylhydantoin are all time consuming and, as micromethods, they have no more than fair specificity and sensitivity. Lack of a well defined ultraviolet absorption spectrum for diphenylhydantoin makes its direct determination in low concentration difficult. Other hydantoins, particularly the mono-5-phenyl derivatives, and acidic drugs including the barbiturates, interfere with procedures in current use.

This report describes a rapid, sensitive, more specific method for the determination of diphenylhydantoin. The method does not require separation of diphenylhydantoin from other hydantoins or from barbiturates or other drugs. In the determination, hydrolysis of the hydantoin ring in strong alkali is followed by a Hofmann degradation of the resulting amide to yield a steam distillable product. In contrast to diphenylhydantoin, this product has a well defined ultraviolet absorption spectrum and a high molar absorptivity.

EXPERIMENTAL

Apparatus. A Beckman DK-2A ratio-recording spectrophotometer with linear presentation, settings, and operation routine was used for the ultraviolet absorption measurements. The sample path length was 10 mm. throughout.

Procedure. Ten-milliliter amounts of whole oxalated blood or serum are placed in a 250-ml. separatory funnel to which 2 ml. of 0.5*N* HCl and 100 ml. of chloroform are added. This mixture is shaken vigorously for five minutes, after which the organic and aqueous phases are allowed to separate. The lower chloroform layer is transferred from the separatory funnel and is filtered through Whatman No. 541 filter paper into a graduated cylinder having a ground glass joint. The volume of chloroform recovered is recorded. Complete recovery of the chloroform should not be attempted, but a correction for the lost chloroform must be included in the final calculations. Ten milliliters of 0.45*N* NaOH is added to the filtered chloroform. This mixture is shaken for five minutes. After the chloroform and aqueous layers have separated, the aqueous layer is carefully removed and centrifuged for 10 minutes at 2000 r.p.m.

Five milliliters of the aqueous layer are transferred to a 1000-ml. round-bottom flask to which a steam distillation assembly can be connected. The remaining sodium hydroxide extract can be used for the determination of barbiturates. One-hundred milliliters of 10*N* NaOH and 0.5 ml. of pure bro-

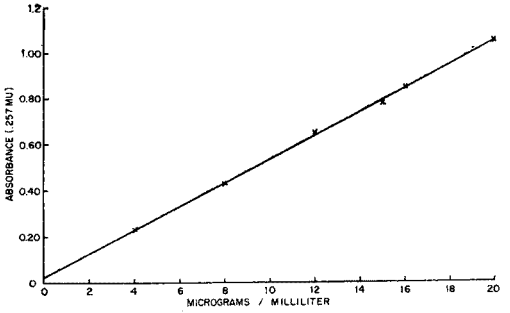

Figure 1. Standard curve of steam distilled diphenylhydantoin reaction product, concentrations expressed as micrograms of diphenylhydantoin per milliliter of water

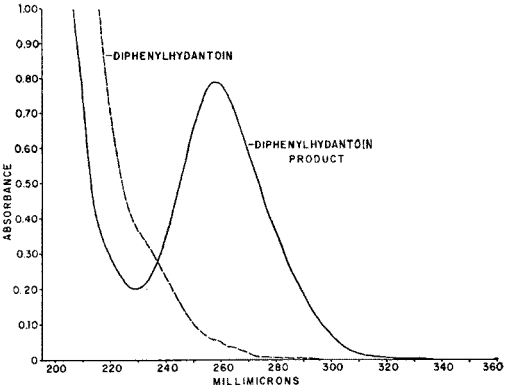

Figure 2. Ultraviolet absorption spectrum of diphenylhydantoin 15 μg. per ml. of water, and of the steam distilled diphenylhydantoin reaction product derived from a sample of equivalent concentration

mine are added to the reaction flask. The bromine should impart a yellow color to the contents of the flask. If the color disappears immediately after the addition of the bromine, slightly more of the halogen (no more than 0.5 ml.) is required. It is imperative that the color exist during the entire period of steam distillation, but excessive amounts of bromine make the ultraviolet absorption curve of the reaction product less well-defined. Distillation is initiated by passing steam into the intact distillation assembly. The distillate should appear at a rate of 5 to 10 ml. per minute. Fifty milliliters of distillate are collected and read against a blank at 257 mμ. The blank should be a distillate obtained by subjecting 10 ml. of blood containing no diphenylhydantoin to the procedure outlined above.

If the steam distillate contains less than 5 μg./ml. of diphenylhydantoin reaction product, as it usually does when the original sample contained therapeutic amounts of the drug, the following concentration procedure should be accomplished: Fifty milliliters of distillate are extracted by vigorous shaking with 10 ml. of carbon tetrachloride (spectro grade). The diphenylhydantoin reaction product is preferentially soluble in the organic phase of the mixture. After the phases have separated, 8 ml. of the carbon tetrachloride are placed in a 125-ml. flask, which is then attached to a rotary vacuum evaporator. The solvent is evaporated by vacuum while the flask rotates at room temperature, with no heat applied. The vacuum is released as soon as the carbon tetrachloride is completely removed. The residue is dissolved in 2, 4, or 8 ml. of water, depending on the absorbance at 257 mμ previously observed for the unextracted distillate.

The diphenylhydantoin content of the sample is calculated from a standard curve prepared from aqueous solutions in appropriate concentrations carried in identical fashion through the procedures which have been outlined, including the concentration technique for solutions containing only small amounts of drug.

Materials and Methods for Infrared Spectral Characterization of Diphenylhydantoin Reaction Product. A Beckman IR-4 double beam infrared spectrophotometer was used with routine instrument settings. The diphenylhydantoin reaction product was purified for infrared analysis by extraction of an appropriate steam distillate with carbon tetrachloride. The solvent was transferred to a rotary vacuum evaporator, evaporated, and the residue was suspended in anhydrous potassium bromide.

RESULTS AND DISCUSSION

Table I summarizes the recovery of diphenylhydantoin which had been added to whole blood in known amounts. Ultraviolet absorption by the diphenylhydantoin reaction product adheres to the Beer-Lambert law over a wide range, as indicated both by the recoveries in Table I and by the plots of absorbance in Figure 1. Linearity extends at least over the range 0 to 20 μg./ml.

When 10-mm. cuvettes are used in the determination, the slope of the line in Figure 1 is 0.053 absorbance unit per μg. of diphenylhydantoin. This represents an increase in sensitivity of approximately eight-fold over the 0.0065 absorbance unit per μg. obtained with the ultraviolet method of Svensmark and Kristensen (*11*).

Table I. Recovery of Diphenylhydantoin Added to Whole Blood

Concn. of diphenylhydantoin, μg./ml.	No. of detns.	Recovery μg./ml., (Mean ± std. dev.)	Mean, %
200.0	10	180.7 ± 6.4	90.4
100.0	10	90.2 ± 3.7	90.2
50.0	12	47.0 ± 3.5	94.0
25.0	10	21.6 ± 0.7	86.4[a]
10.0	10	9.2 ± 0.6	92.0[a]
5.0	12	4.6 ± 0.3	92.0[a]
2.5	10	2.2 ± 0.1	88.0[a]
Av. recovery			90.4

[a] Distillate concentrated through carbon tetrachloride extraction.

Table II. Recovery of Diphenylhydantoin and Phenobarbital Added to Whole Blood

Concn. μg./ml.			Recovery			
			Diphenylhydantoin		Phenobarbital	
Diphenylhydantoin	Phenobarbital	No. of detns.	μg./ml. (Mean ± std. dev.)	Mean, %	μg./ml. (Mean ± std. dev.)	Mean, %
100.0	100.0	6	95.3 ± 4.3	95.3	91.9 ± 0.9	91.9
50.0	50.0	6	46.9 ± 3.0	93.8	43.9 ± 0.4	87.8
25.0	25.0	4	21.6 ± 0.2	86.4[a]	23.1 ± 0.5	92.4
10.0	10.0	6	9.0 ± 0.2	90.0[a]	9.6 ± 0.3	96.0
5.0	5.0	4	4.4 ± 0.2	88.0[a]	4.9 ± 0.3	98.0
2.5	2.5	4	2.3 ± 0.1	92.0[a]	2.4 ± 0.2	98.0
Av. recovery				90.9		93.7

[a] Distillate concentrated through carbon tetrachloride extraction.

Figure 2 displays the ultraviolet absorption spectrum of diphenylhydantoin and of its steam distilled reaction product. The absorption curve of the product is well defined and exhibits an absorption maximum at 257 mμ and a minimum at 228 mμ. The peak of high absorbancy at 257 mμ accounts for the increased sensitivity of the present determination over those methods which rely on spectrophotometric analysis of unconverted diphenylhydantoin.

Table II summarizes the recovery of diphenylhydantoin and phenobarbital from whole blood to which the drugs had been added in equivalent amounts. Phenobarbital content was determined by the method of Goldbaum (*3*). That phenobarbital fails to interfere with the determination of diphenylhydantoin by the techniques described is apparent from a comparison of the recovery values in Tables I and II. Under the conditions of the method, phenobarbital forms no steam distillable product in amounts significant to the determination (Figure 3).

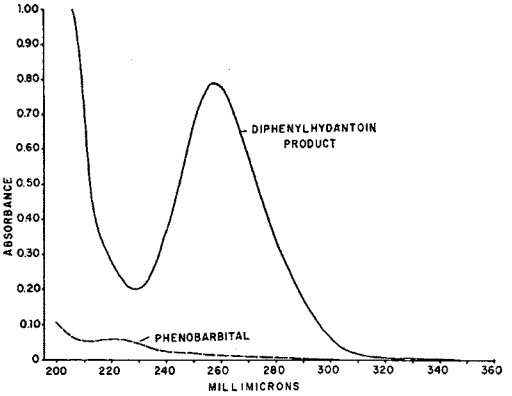

Figure 3. Ultraviolet absorption spectrum of steam distilled reaction products of diphenylhydantoin and of phenobarbital, each derived from aqueous solutions containing 15 μg. of drug per ml.

Other drugs which might be given to patients concomitantly with diphenylhydantoin were investigated for interference. None produced a steam distillable product with significant absorbance at 257 mμ (Table III).

Recovery of diphenylhydantoin by the method presented (90%, Tables I and II) compares favorably with that of methods described earlier: Plaa and Hine 78% (*8*), Svensmark, Schiller, and Buchthal 72.3% (*12*), and Svensmark and Kristensen 77% (*11*).

Infrared spectra of diphenylhydantoin (Figure 4*A*) and of its steam distilled reaction product (Figure 4*B*) show several distinct differences, of which the most striking are the loss in the product of infrared absorption bands at 3200 to 3300 cm.$^{-1}$ and at 1720 to 1780 cm.$^{-1}$. The first of these bands is considered to be due to the secondary amide (NH stretching) group in the diphenylhydantoin molecule, and the second to the amide I band (carbonyl absorption) characteristic of secondary amides in four- or five-membered rings (*1, 5, 7, 9, 14*). As might be expected, these amide groups and their absorption bands were eliminated in the reactions which produced the steam distillable compound. The strong absorption band which appeared at 1662 cm.$^{-1}$ in the reaction product (Figure 4*B*) is in the approximate region reported for the stretching vibrations of carbonyl groups with two aryl groups directly attached (*4, 13*). The absorption band which appeared at 1580 cm.$^{-1}$ in the reaction product is in the range of the band which Randall *et al* (*9*) regard as a positive indication of conjugation of a

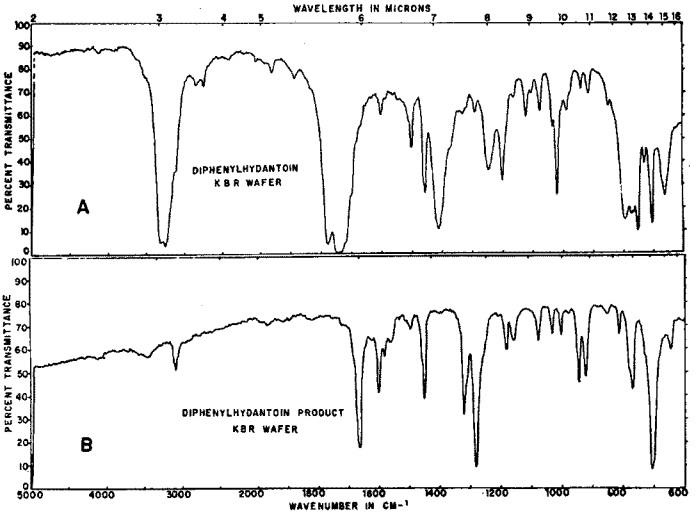

Figure 4. Infrared absorption spectra

A. Diphenylhydantoin, 1 mg. in 400 mg. potassium bromide
B. Steam-distilled diphenylhydantoin reaction product, 1 mg. in 400 mg. of potassium bromide

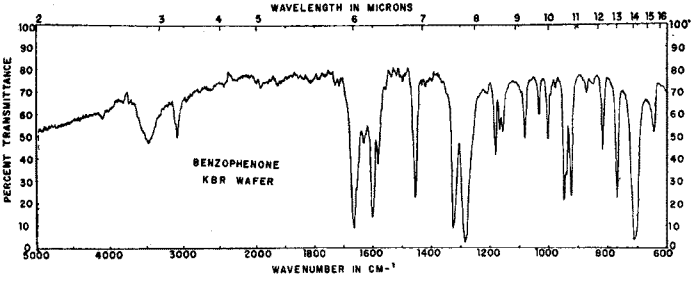

Figure 5. Infrared absorption spectrum of benzophenone, 1 mg. in 400 mg. of potassium bromide

Table III. Compounds Investigated for Interference with the Determination of Diphenylhydantoin[a]

Compound		Absorbance of steam distillate[b]
Trade name	Chemical name	
Dilantin[c]	5,5-Diphenylhydantoin	1.080
Blank		0.025
Mesantoin[d]	3-Methyl-5-ethyl-5-phenylhydantoin	0.035
Phenurone[e]	Phenacetylurea	0.032
Tridione[e]	3,5,5-Trimethyl-2,4-oxazoladinedione	0.025
Milantin[c]	*N*-Methyl-2-phenylsuccinamide	0.025
Peganone[e]	3-Ethyl-5-phenylhydantoin	0.025
Phenobarbital	5-Ethyl-5-phenylbarbituric acid	0.025
Veronal	5,5-Diethylbarbituric acid	0.025
Alurate[f]	5-Allyl-5-isopropylbarbituric acid	0.025
Amobarbital[g]	5-Ethyl-5-isoamylbarbituric acid	0.027
Deltoin[d]	1-Methyl-5-phenyl-5-ethylhydantoin	0.025
Aspirin	Acetylsalicylic acid	0.035
	Hydantoin	0.025

[a] Each compound was determined from aqueous solution in a concentration of 20 μg./ml. Each value is the average of three determinations.
[b] Read at 257 mμ.
[c] Parke, Davis and Company, Detroit, Mich.
[d] Sandoz Pharmaceuticals, Hanover, N. J.
[e] Abbott Laboratories, North Chicago, Ill.
[f] Roche Laboratories, Nutley, N. J.
[g] Eli Lilly and Company, Indianapolis, Ind.

double bond with an aromatic ring. Rasmussen, Tunnicliff, and Brattain (*10*) have observed that contemporary absorption bands at 1600 cm.$^{-1}$ and at 1585 cm.$^{-1}$, as in Figure 4*B*, indicate the presence of a benzoyl group.

These observations, and also comparisons of the ultraviolet and infrared spectra of the diphenylhydantoin reaction product (Figures 2 and 4*B*) with those of benzophenone (Figures 5 and 6) suggest that the reaction product has a chemical structure which agrees with that of benzophenone. Steps leading to formation of the diphenylhydantoin reaction product may be thought to include hydrolysis of the hydantoin ring to an amide, degradation of the amide to an amine by a Hofmann hypobromite reaction, and hydrolysis of the amine to benzophenone under the conditions of the steam distillation. Comparison of the ultraviolet absorption curves of diphenylhydantoin and its reaction product indicates that approximately 80% of the diphenylhydantoin is converted to benzophenone.

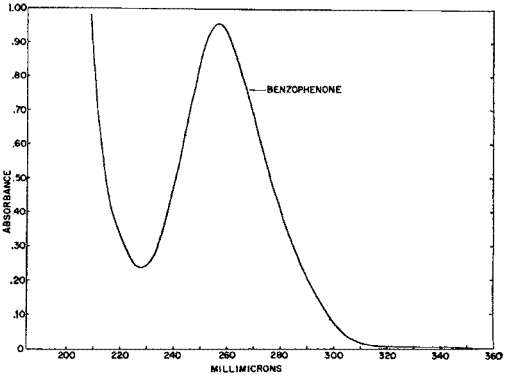

Figure 6. Ultraviolet absorption spectrum of benzophenone, 10 μg. per ml. of water

ACKNOWLEDGMENT

The authors are indebted to L. P. Bauman for technical assistance.

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Corrections

In the item entitled Spectrometry Nomenclature [ANAL. CHEM. **36,** 2558 (1964)] there is an error in column 1 under the definition of Angstrom. The final sentence should read "For practical purposes it is considered equal to 10^{-8} cm."

Pore-Size Distribution by a Rapid, Continuous Flow Method

In this article by R. M. Cahen *et al.* [ANAL. CHEM. **37,** 133-7 (1965)] in the Abstract and on page 136, line six, the pressures 4.000 and 5.000 mm. of Hg should be 4,000 and 5,000 (four thousand and five thousand) mm. of Hg.

Gas Analysis by X-Ray Fluorescence Emission Spectrometry

SIR: The analysis of solids and liquids by the x-ray fluorescent method is now widespread, and successes of the liquid method for quantitative work have been repeatedly demonstrated. An obvious extension of the technique is to gases, including the vapors of volatile liquids. The experiment described here demonstrated the feasibility of x-ray fluorescent gas analysis.

The analyses were performed on a General Electric XRD-3 x-ray generator and spectrometer, equipped with a reflecting quartz crystal cut on the 013 planes and a scintillation detector. Water cooling of the sample case was eliminated so that the case would heat sufficiently to completely volatilize the methyl iodide and ethyl bromide used in the analysis.

Because this experiment was purely exploratory, no efforts were made to construct a refined sample cell. The cell consisted of the glass body described by Pish and Huffman (*1*) covered with 0.002-inch Mylar film. A small rubber balloon fitted over the neck of the cell served as a reservoir for the volatile halides and as an expansion chamber. The included air was not detrimental, causing only a reduction in the counting rate.

A bromide–iodide system was used as the gas because of the availability of pure organic halides. The particular choice of ethyl bromide and methyl iodide was made on the basis of their boiling points, (ethyl bromide, b.p. 38°–40° C., methyl iodide, b.p. 42°–44° C.). Samples were prepared simply by metering the liquids from micropipets into the rubber balloon, which was then collapsed and slipped over the neck of the cell. Care was taken that no liquid spilled directly into the cell. The liquid was shielded from x-rays by the thick top of the sample drawer. Counting was started immediately, 1-minute counts being taken, first on IKα, then on the BrKα. The counting rates rose at first as the liquids volatilized and diffused into the sample chamber, reached a simultaneous maximum—typically 1800 counts per minute for each component of a 50–50 mixture—then simultaneously decreased as the vapors diffused from the cell assembly. Probable counting errors ranged from 2 to 5%. A correction was made for background counts, which were low and nearly uniform over the compositions counted. The ratios of counts of the IKα peak to counts of the BrKα peak at the maximum counting rates were used to construct the working curve.

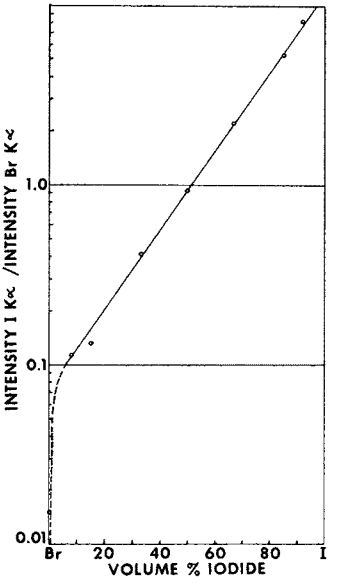

Figure 1. Intensity ratio of iodide and bromide Kα radiations as a function of the volume fraction of iodide

A semilogarthmic plot (Figure 1) of the working curve is nearly linear over a wide range of compositions. The rapid changes of slope at the ends of the curve are to be expected from the nature of the plot, which is essentially a plot of mole fraction M *vs.* the function log $(I)_I/(I)_{Br}$, which is equal to log $KM/1-M$, where K is a constant and $(I)_{Br}$, $(I)_I$ are the intensities of x-ray emission from each element.

X-ray fluorescent gas analysis could easily be extended to systems of more than two components. The internal standard need not necessarily be a gas. Possible applications would include vapor phase equilibria (in conjunction with fluorescent liquid analysis), vapor pressure determinations on corrosive or radioactive systems, and analysis of pure compounds containing more than one detectable atom.

ACKNOWLEDGMENT

Appreciation is extended to Mrs. A. A. Huffman for assistance during the experiment.

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Analytical Oxidation of Americium with Sodium Perxenate

SIR: I wish to report a successful application of sodium perxenate, Na_4XeO_6, to the analytical oxidation of Am(III) to Am(VI). This work may be the first report of a practical use of this compound.

Since the first discoveries that xenon would react with other elements (*2, 3*), much research effort has been put forth in this new field of the noble gas compounds. One of these compounds, sodium perxenate, appears to be potentially useful as an analytical reagent.

Sodium perxenate was first prepared by Malm, Holt, and Bane (*5*), who found the compound to be a stable solid under ordinary conditions. Later studies by Appelman and Malm (*1*) revealed that the compound had a high oxidation potential of about 3 volts in acidic solutions. However, they also found that the reaction Xe(VIII) → Xe(VI) was almost instantaneous below pH 7. In view of these properties sodium perxenate appeared to be a convenient, stable analytical reagent for methods requiring a readily available and powerful oxidant.

Commercially prepared sodium perxenate was studied as an oxidant in the separation of americium in tracer quantities from curium by means of calcium fluoride (*4*). Originally, in this separation, americium(III) was oxidized to the (VI) state with silver catalyzed persulfate. Following the oxidation, the solution was passed through a column of calcium fluoride, which retained the fluoride-insoluble trivalent actinides and lanthanides but allowed the fluoride-soluble Am(VI) [and Pu(VI)] to pass through the column. The silver catalyzed persulfate oxidation required about 30 minutes at elevated temperature. When solid sodium perxenate in the presence of silver(I) was used, oxidation was complete in less than 30 seconds at room temperature, thus reducing the time required for the separation.

EXPERIMENTAL

Reagent. At the author's request, the sodium perxenate was prepared by Peninsular ChemResearch, Inc., Gainesville, Fla., according to the method of Malm, Holt, and Bane (*5*). The material was a fine, slightly off-white powder. Analysis of the material showed a weight loss of 9.1% on drying at 125° C. for 16 hours. On a dry basis, the compound had 95.3% of its theoretical oxidizing capacity (as Na_4XeO_6) and contained ess than 0.1 wt. % fluoride (as NaF). The only other observed impurity was sodium carbonate.

Table I. Influence of Silver(I) on the Oxidation of Americium with Na_4XeO_6

	Americium oxidized, %	
	Silver(I) present	Silver(I) absent
	95.2	91.2
	96.2	85.0
	94.2	92.8
	96.2	88.5
	93.7	94.3
	96.2	96.2
	95.2	86.2
Av.	95.3	90.6
Rel. std. dev.:	1.0% ($n = 7$)	4.6% ($n = 7$)

Separation of Americium from Curium. Use the previously described procedure (*4*) with the following modifications: In Pretreatment C under Sample Preparation following the wash of the precipitate with 3 ml. of water, dissolve the precipitate in 4 drops of 1*M* nitric acid. Do not dilute. Repeat Pretreatment C if necessary. Then to the solution from Pretreatment C, add 1 drop of 0.1% silver nitrate and, if necessary, enough water to give a solution volume between 0.3 and 0.5 ml. Add about 5 mg. of solid sodium perxenate and immediately mix well. Dilute the solution with water to approximately 1.5 ml. and transfer to the calcium fluoride column. Wash the column with three 1-ml. portions of fresh 0.001*M* ammonium persulfate, and continue as in the previously described procedure (*4*).

DISCUSSION AND RESULTS

Sodium perxenate alone will quickly oxidize tracer amounts of Am(III) to Am(VI) in acidic solution and in the presence of lanthanum(III). However, because of the high oxidation potential of the Am(VI)–Am(III) couple, tracer quantities are difficult to keep oxidized unless stabilized or kept in a strongly oxidizing medium. Table I shows the influence of silver(I) on the oxidation. In this comparison, solutions containing 1.05×10^5 d.p.m. (disintegrations per minute) Am^{241} were oxidized with sodium perxenate in the presence or absence of silver(I). Instead of using the calcium fluoride column, Am(VI) was determined by alpha counting after removal of any remaining Am(III) by coprecipitation with lanthanum fluoride, a technique similar to Moore's method (*6*).

Moore (*6*) found a similar effect of silver(I) in his study of the persulfate oxidation of americium. The role of the silver ion in the perxenate oxidation is thought to be that of a holding oxidant. When sodium perxenate is added to an acidic solution containing silver(I), the amber color of argentic ion is immediately seen, remains for some time, and gradually fades. Since sodium perxenate is such a powerful oxidant, it probably oxidizes both americium and silver and almost instantaneously decomposes, leaving argentic ion, which serves as a holding oxidant for Am(VI).

The determination of americium was made in five synthetic samples with the sodium perxenate–calcium fluoride procedure. Each sample contained 1.05×10^5 d.p.m. of americium, 1.13×10^6 d.p.m. of curium, and 0.5 mg. of La (III). The average americium recovery was 98.4% with a relative standard deviation of 2.1%. Curium impurity averaged less than 0.5% by alpha counting. These results are quite similar to those obtained in the silver-catalyzed persulfate oxidation–calcium fluoride procedure (*4*).

ACKNOWLEDGMENT

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Influence of Electrometer Noise on Limit of Detectability in Atomic Absorption and Atomic Emission Flame Spectrometry

SIR: In papers on limit of detectability in atomic emission (*4*) and atomic absorption (*5*) flame spectrometry, the noise signal was defined as the root-mean-square fluctuation in the background anodic current of the phototube. However, in some cases the electrometer noise must be considered, as well as the noises previously (*3–5*) considered. The electrometer noise is primarily caused by five sources: shot noise, thermal agitation noise, flicker noise, power supply hum, and microphonic hum (*1*). Each of these types of noise have been considered by Cannon (*1*). In literature concerning commercial electrometers (*2*) and in measurements of electrometer noise in these laboratories, electrometer noise is most conveniently listed as a certain fraction of the input signal of the electrometer. In this manuscript, it is also more convenient to refer electrometer noise to the input (*2*). The total noise signal and the signal caused by the sample are also conveniently referred to the input of the electrometer. The influence of electrometer noise on the limit of detectability and optimum slit widths in atomic emission and atomic absorption flame spectrometery will be considered.

In atomic emission flame spectrometry, the total noise signal introduced into the electrometer input is given by

$$\overline{\Delta i_T} = (\overline{\Delta i_p}^2 + \overline{\Delta i_c}^2 + \overline{\Delta i_e}^2 \Delta f)^{1/2} \quad (1)$$

where $\overline{\Delta i_p}$ is the root-mean-square fluctuation current caused by noise in the phototube, $\overline{\Delta i_c}$ is the root-mean-square fluctuation current caused by flicker in the flame source, and $\overline{\Delta i_e}$ is the root-mean-square fluctuation current per second$^{-1/2}$ in the electrometer. Because these noises are independent, they will add quadratically as indicated above. The electrometer noise is assumed to be white as previously indicated for other types of noise (*4*), and thus Δf, the frequency response band width in seconds^{-1}, of the detector-readout system must be included. The value of $\overline{\Delta i_e}$ can be simply measured, and so no expression for it is necessary. The value of N_m, the minimum detectable number of atoms per cubic centimeter of flame gases, differs from the previous N_m (*4*) only in that an additional noise term, $\overline{\Delta i_e}^2 \Delta f$ must also be included within the square root.

$$N_m = \frac{3.8 \times 10^{34} B(T) e^{E_u/kT}}{\nu_o g_u A_t L T_f W H (A/F^2)} \times \left\{ 2e_c B M \Delta f [i_d + \gamma T_f W H (A/F^2)\, I_c s] + [\gamma T_f W H (A/F^2) \xi I_c s]^2 \Delta f + \overline{\Delta i_e}^2 \Delta f \right\}^{1/2} \quad (2)$$

All terms have been previously defined (*4*). The exact equation for W_o, the optimum slit width, differs only by a term $\overline{\Delta i_e}^2$—i.e.,

$$[\gamma T_f H (A/F^2) \xi I_c R_d]^2 W_o^4 + [\gamma T_f H (A/F^2) \xi I_c]^2 R_d s_c W_o^3 - e_c B M \gamma T_f H (A/F^2) I_c s_c W_o - (2 e_c B M i_d + \overline{\Delta i_e}^2) = 0 \quad (3)$$

Now if $s_c \ll R_d W$, then W_o is given by

$$W_o = \left\{ \frac{2 e_c B M i_d + \overline{\Delta i_e}^2}{[\gamma T_f H (A/F^2) \xi I_c R_d]^2} \right\}^{1/4} \quad (4)$$

To a good approximation (*1, 2*) the electrometer noise varies linearly with the anode current of the electrometer tube raised to a power which should be near unity and will probably be between 1 and $^1/_2$. Thus the electrometer noise should also vary approximately linearly with the photodetector output current raised to the same power. Therefore when the electrometer sensitivity is high, such as at the limit of detectability—e.g., 10^{-9} ampere full-scale when the flame background is low—the electrometer noise terms in Equations 2, 3, and 4 should be negligible. Therefore the equations for N_m and W_o reduce to those previously given (*4*). However, if the electrometer noise term is significant, then Equations 2, 3, and 4 must be used to obtain accurate values of N_m and W_o. In the above discussion and the discussion which follows, it is assumed that the recorder-readout system has a negligible noise compared to other noise sources. This assumption will certainly be valid for the majority of good quality recorders.

In atomic absorption flame spectrometry, the total noise signal introduced into the electrometer input is given by

$$\overline{\Delta i_T} = (\overline{\Delta i_p}^2 + \overline{\Delta i_c}^2 + \overline{\Delta i^\circ}^2 + \overline{\Delta i_e}^2 \Delta f)^{1/2} \quad (5)$$

where $\overline{\Delta i^\circ}$ is the root-mean-square fluctuation current caused by the fluctuations in the intensity of the incident radiation. For this case, the value of N_m, the minimum detectable number of atoms per cubic centimeter of flame gases, differs from the previous value of N_m (*5*) only in that an additional electrometer noise term must be included with the phototube shot noise.

$$N_m = \frac{53.5 \Delta \nu_D B(T)\, (\Delta f)^{1/2}}{\rho L \lambda_o^2 g_u A_t \delta} \times \left\{ \frac{2BMe_c \gamma T_f W H (A/F^2) I^\circ + \overline{\Delta i_e}^2}{[\gamma T_f W H (A/F^2)\, I^\circ]^2} + \chi^2 + \left(\frac{\xi I_c s}{I^\circ} \right)^2 \right\}^{1/2} \quad (6)$$

The symbols above and below have been defined previously (*5*). Now if the flame background is low and $s_c \ll R_d W$, then the optimum slit width, W_o, is given by

$$\left(\frac{\xi I_c R_d}{I^\circ} \right)^2 W_o^4 - \frac{BMe_c W_o}{\gamma T_f H (A/F^2) I^\circ} - \frac{\overline{\Delta i_e}^2}{[\gamma T_f H (A/F^2) I^\circ]^2} = 0 \quad (7)$$

which differs (by the final term) from the equation for W_o previously given (*5*). The electrometer noise should always be considerably greater than the shot noise because the incident radiation is generally quite intense, and so W_o is given by

$$W_o = \left\{ \frac{\overline{\Delta i_e}}{\xi I_c R_d \gamma T_f H (A/F^2)} \right\}^{1/2} \quad (8)$$

If the electrometer noise is small compared to the photodetector shot noise term, then W_o is given by the equation previously derived (*5*).

$$W_o = \left\{ \frac{BMe_c I^\circ}{[\gamma T_f H (A/F^2)]\, (\xi I_c R_d)^2} \right\}^{1/3} \quad (9)$$

In atomic absorption flame spectrometry, the source intensity is generally sufficiently large that the resultant anodic current of the photodetector is quite large—e.g., 10^{-6} ampere. Therefore the electrometer noise, in most practical cases, should be large com-

pared to the other noise terms in Equation 6 and so the optimum slit width will then be more accurately expressed by Equation 8 than by Equation 9. If the electrometer noise is the major source of noise, then N_m will be more simply given by

$$N_m \cong \frac{53.5\Delta\nu_D B(T)\ (\Delta f)^{1/2}\overline{\Delta i_e}}{\rho L\lambda_o{}^2 g_u A_{ij}\delta[\gamma T_f WH(A/F^2)I^\circ]} \quad (10)$$

For any given atomic absorption spectral line of a certain atom and for any given source–flame cell–monochromator–detector–electrometer combination, the limit of detectability should be essentially constant. An increase in slit width, W, or slit height, H, or intensity, I°, results in a proportional increase in the intensity of radiation reaching the detector. This results in a proportional increase in the electrometer current setting for full-scale deflection and a slightly less than proportional increase in electrometer noise—i.e., the electrometer noise (*1*, *2*) will increase linearly with the anode current of the electrometer tube raised to some power which will probably be between $^1/_2$ and 1. Therefore, an increase in slit width or height or an increase in I° with no resultant change in emission line half-width should give little change in the values of N_m and W_o.

Whatever the situation, the analyst must at least be aware of the electrometer noise. In atomic emission flame spectrometery, the electrometer noise will rarely be the significant noise, whereas in atomic absorption flame spectrometery, the total noise signal will in many instances be primarily a result of electrometer noise.

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Spectrophotometric Determination of Iron, Nickel, Copper, and Cobalt in Tungsten and Tungsten Alloys

SIR: Iron, nickel, and copper in tungsten and tungsten alloys have previously been determined spectrophotometrically by somewhat lengthy extraction procedures using bathophenanthroline (*3*), diethyldithiocarbamate (*5*), and neocuproine (*2*), respectively, as the colorimetric reagents. No method has been proposed for the spectrophotometric determination of cobalt in tungsten or tungsten alloys.

In the present work iron, nickel, copper, and cobalt in tungsten and tungsten alloys are determined rapidly by spectrophotometric procedures by taking aliquots of a hydrofluoric–nitric acid solution that has been buffered to a pH of approximately 6 by the addition of ammonium tartrate and sodium borate. No subsequent adjustment of pH is necessary for the spectrophotometric determination of the iron, copper, or cobalt.

EXPERIMENTAL

Reagents. Sodium Borate Solution (4.5%). Dissolve 90 grams of sodium borate ($Na_2B_4O_7$, anhydrous fused powder) in about 1800 ml. of hot water, cool, and dilute to 2 liters.

Blank Solution. Transfer 5 ml. of hydrofluoric acid and 4 ml. of nitric acid to a platinum dish and evaporate to a volume of about 4 to 7 ml. on the hot plate (the purpose of the heating is to attain similar conditions as in the actual method). Add about 30 ml. of water, wash into a 250-ml. volumetric flask containing 50 ml. of ammonium tartrate solution (20%), add 90 ml. of sodium borate solution (4.5%), cool, and dilute to the mark.

Preparation of Calibration Curves. IRON. Transfer 50 ml. of blank solution to six 100-ml. volumetric flasks. Use one solution as a blank. Add 0.5-, 1.0-, 2.0-, 3.0-, and 3.5-ml. portions of standard iron solution (1 ml. = 0.10 mg. of Fe). Dilute to about 75 ml. and add 1 ml. of hydroxylamine hydrochloride solution (10%) and 5 ml. of *o*-phenanthroline solution (0.2%). Dilute to about 90 ml., heat in a water bath at 60° to 70° C. for 30 minutes, cool, and dilute to the mark. Measure the transmittance at 510 mμ with a spectrophotometer (1-cm. cell) that has been set to 100% transmittance with the reagent blank. Plot milligrams of iron against per cent transmittance.

NICKEL (CURVE NO. 1). Transfer 50 ml. of blank solution to six 100-ml. volumetric flasks. Use one solution as a blank. Add 1.0-, 3.0-, 4.0-, 5.0-, and 6.0-ml. portions of standard nickel solution (1 ml. = 0.10 mg. of Ni). Add 5 ml. of bromine water. Add ammonium hydroxide until the bromine color is bleached, and then add 5 ml. of excess ammonium hydroxide. Add 5 ml. of alcoholic dimethylglyoxime solution (1%). Add the bromine water, ammonium hydroxide, and dimethylglyoxime within a period of 2 minutes. Dilute to the mark and within 15 ± 2 minutes measure the transmittance at 540 mμ with a spectrophotometer that has been set to 100% transmittance with the reagent blank. Plot milligrams of nickel against per cent transmittance.

NICKEL (CURVE NO. 2). Proceed as for curve No. 1 up to and including the addition of the bromine water. Add 10 ml. of ammonium hydroxide and 5 ml. of alcoholic dimethylglyoxime solution (1%), allow to stand for 1 minute, and add 10 ml. of sodium hydroxide solution (25%). Dilute to 100 ml., allow to stand for 5 minutes or more, and measure the transmittance as for curve No. 1.

COPPER. Transfer 50-ml. portions of blank solution to five 100-ml. separatory funnels that have been rinsed with 95% ethyl alcohol to remove water from the stems. Add 2.0-, 5.0-, 7.5-, and 10.0-ml. portions of standard copper solution (1 ml. = 0.01 mg. of Cu). Add 5 ml. of hydroxylamine hydrochloride solution (10%), 10 ml. of neocuproine solution (0.1% in ethanol), and 10 ml. of chloroform. Shake for 30 seconds, allow the layers to separate, and drain off the chloroform layers into 25-ml. volumetric flasks containing 3 ml. of 95% ethyl alcohol. Repeat the extraction with 5 ml. of chloroform. Dilute to the mark with 95% ethyl alcohol and measure the transmittance at 455 mμ with a spectrophotometer that has been set to 100% transmittance with the reagent blank. Plot milligrams of copper against per cent transmittance.

COBALT. Transfer 10-ml. portions of blank solution to seven 150-ml. beakers. Use one solution as a blank. Add 1.0-, 2.0-, 3.0-, 4.0-, 5.0-, and 6.0-ml. portions of standard cobalt solution (1 ml. = 0.01 ml. of Co). Add 2.0 ml. of nitroso-R salt solution (1%), cover with watch glasses, heat to boiling, and boil moderately for 60 seconds. Remove from the hot plate and add 2.0 ml. of hydrochloric acid. Return to the hot plate and heat just to boiling. Cool to room temperature, wash into 25-ml. volumetric flasks, and dilute to the mark. Measure the transmittance at 510 mμ with a spectrophotometer

Table I. Results (%) for Iron, Nickel, Copper, and Cobalt in Samples of Tungsten and Tungsten Alloys

Sample	Fe	Ni	Cu	Co
1	0.0010	0.004	0.0000	0.0002
(tungsten	0.0015	0.004	0.0000	0.0002
metal)	0.0010	0.004	0.0000	0.0000
	0.0015			
	Av. 0.0013	0.004	0.0000	0.0001
2[a]	5.08	4.91	0.0000	0.51
	5.18	4.91	0.0000	0.51
	5.18	4.78	0.0000	0.53
		4.78		0.51
	Av. 5.15	4.85	0.0000	0.52
3[b]	1.08	6.75	2.20	0.010
	1.00	6.75	2.00	0.011
	1.08	6.92	2.10	0.011
		6.75	2.10	0.010
	Av. 1.05	6.79	2.10	0.011
4[c]	5.15	4.63	0.0035	0.53
	5.01	4.63	0.0035	0.53
	5.15	4.51	0.0040	0.54
		4.51	0.0040	0.54
	Av. 5.10	4.57	0.0038	0.54
5[d]				11.64
				11.92
				11.88
				11.84
	Av.			11.82
6[e]				11.76
				11.68
				11.80
				11.76
	Av.			11.75

[a] Contains (%) 5.13 Fe (titr.); 4.83 Ni (grav.); 0.52 Co (potent.).
[b] Contains (%) 1.03 Fe (titr.); 6.76 Ni (grav.); 2.16 Cu (elect.).
[c] Contains (%) 5.13 Fe (titr.); 4.55 Ni (grav.); 0.54 Co (potent.).
[d] Contains (%) 11.77 Co (potent.).
[e] Contains (%) 11.68 Co (potent.).

that has been set to 100% transmittance with the reagent blank. Plot milligrams of cobalt against per cent transmittance.

If desired, 10 ml. of 20% ammonium tartrate solution (diluted to about 50 ml.) may be used in place of the blank solution in preparing the curves for the iron, nickel, and copper. The blank solution must be used in preparing the curve for cobalt.

Procedures. For the determination of less than 0.09% iron, 0.15% nickel, 0.03% copper, and 0.04% cobalt weigh a 2-gram sample into a platinum dish, add 5 ml. of hydrofluoric acid and 4 ml. of nitric acid, and warm to dissolve (away from direct heat). Also, heat a blank in the same manner. If prolonged heating is necessary add more hydrofluoric and nitric acids. The final volume should be about 4 to 7 ml. Add 30 ml. of water and wash into a 250-ml. volumetric flask containing 50 ml. of ammonium tartrate solution (20%). Add 90 ml. of sodium borate solution (4.5%), dilute to about 220 ml., cool to room temperature, and dilute to the mark.

IRON. Pipet a 50-ml. aliquot into a 100-ml. volumetric flask. Add 1 ml. of hydroxylamine hydrochloride solution (10%) and proceed as in the preparation of the calibration curve. Calculate the per cent iron by referring to the calibration curve.

NICKEL. Pipet a 50-ml. aliquot into a 100-ml. volumetric flask. Add 5 ml. of bromine water and proceed as in the preparation of calibration curve No. 1. Calculate the per cent nickel by referring to the calibration curve.

COPPER. Pipet a 50-ml. aliquot into a 100-ml. separatory funnel. Add 5 ml. of hydroxylamine hydrochloride solution (10%) and proceed as in the preparation of the calibration curve. Calculate the per cent copper by referring to the calibration curve.

COBALT. Pipet a 20-ml. aliquot into a 150-ml. beaker. Add 2.0 ml. of nitroso-R salt solution (1%), develop the color, and dilute to 25 ml. in a volumetric flask as in the preparation of the calibration curve. Filter a portion of the solution through a dry Whatman No. 42 filter paper into a 50-ml. beaker, discarding the first few milliliters. Measure the transmittance at 510 mμ on a portion of the filtrate and calculate the per cent cobalt by referring to the calibration curve.

For tungsten-iron, tungsten-nickel, tungsten-copper, and tungsten-cobalt alloys proceed as above but use a 1-gram sample and dilute to 500 ml. in a volumetric flask. Pipet a 25-ml. aliquot into a 250-ml. volumetric flask (1-liter volumetric flask for cobalt higher than 8%) and dilute to the mark. For the determination of iron, nickel, and copper, pipet aliquots containing preferably 0.15 to 0.3 mg. of iron, 0.3 to 0.5 mg. of nickel, and 0.06 to 0.10 mg. of copper; dilute to about 50 ml.; and proceed as above. Use curve No. 2 for nickel. For cobalt, pipet an aliquot containing preferably 0.03 to 0.06 mg. of cobalt (the aliquot should be 10 ml. or less), add 10 ml. of blank solution to act as a buffer, and proceed as above. If a small size aliquot is used for the cobalt determination, the tungsten remains in solution and the filtration is unnecessary.

DISCUSSION AND RESULTS

In the spectrophotometric method for iron the maximum amounts of nickel, copper, and cobalt that may be present in the aliquot without causing interference are 0.8 mg. of nickel, 1.6 mg. of copper, and 0.8 mg. of cobalt. More than these amounts cause low results.

The usual technique of determining nickel spectrophotometrically by adding bromine water, ammonium hydroxide, and dimethylglyoxime (*1*) gave satisfactory results for small amounts of nickel but variable results for large amounts of nickel where the stability of the color is all-important. Satisfactory results were obtained for larger amounts of nickel by adding sodium hydroxide to stabilize the color (*4*);

Table II. Recovery of Iron, Nickel, Copper, and Cobalt

Added, mg.	Recovered, mg.
Fe	
0.010[a]	0.012
0.050	0.053
0.100	0.098
0.200	0.205
0.300	0.302
Ni (NH_4OH Method)	
0.010[a]	0.012
0.100	0.102
0.200	0.200
0.400	0.397
0.600	0.590
Ni (NH_4OH–NaOH Method)	
0.100[a,b]	0.097
0.200	0.200
0.400	0.406
0.600	0.598
Cu	
0.005[a]	0.004
0.010	0.008
0.050	0.051
0.070	0.070
0.100	0.097
Co	
0.005[c]	0.005
0.010	0.011
0.030	0.031
0.040	0.040
0.060	0.061

[a] Added to 50-ml. aliquots of pure tungsten solution.
[b] This method designed for larger amounts of nickel; no data given for less than 0.1 mg. of nickel.
[c] Added to 20-ml. aliquots of pure tungsten solution.

however, erratic results were obtained for trace amounts using this technique. Therefore, two procedures for the determination of nickel are recommended; the ammonium hydroxide method for low percentages and the ammonium hydroxide–sodium hydroxide method for higher percentages.

In the spectrophotometric determination of nickel by the ammonium hydroxide method the maximum amounts of iron, copper, and cobalt that may be present in the aliquot are 20 mg. of iron, 0.2 mg. of copper, and 1.5 mg. of cobalt. In the ammonium hydroxide–sodium hydroxide method the maximum permissible amounts are 15 mg. of iron, 0.2 mg. of copper, and 1.5 mg. of cobalt. More than these amounts cause erratic results.

There are no interferences with the neocuproine method for copper (*2*).

In the cobalt method, on adding the hydrochloric acid to large size aliquots and boiling to destroy the heavy metal complexes of nitroso-R salt, some tungsten precipitates and must be filtered off. Because color is developed prior to the precipitation of the tungsten, this precipitation causes no error.

The maximum permissible amounts of iron, nickel, or copper that may be present in the aliquot in which the cobalt color is developed are 15 mg. of iron, 2 mg. of nickel, and 3 mg. of copper. More than these amounts cause low results.

The results obtained for iron, nickel, copper, and cobalt in samples of tungsten and tungsten alloys are shown in Table I. The results by the spectrophotometric methods checked the results by classical methods where the range permitted the use of both techniques. The recoveries obtained on adding standard iron, nickel, copper, and cobalt solutions to tungsten metal and carrying the samples through the procedures were satisfactory (Table II).

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Rapid Removal of Transuranium Elements from Aqueous Solutions Prior to the Determination of Total Lanthanide Fission Products

SIR: The radiochemical determination of total lanthanide fission products in solutions containing high levels of the very radiotoxic transuranium alpha emitters presents a difficult problem to the radiochemist. It is desirable to remove the bulk of the alpha radioactivity before performing conventional radiochemical determinations and nuclear studies of the lanthanide fission products. Such a step is required because of the potential hazard involved in handling large amounts of alpha radioactivity directly. In addition, at this installation it is necessary to reduce the alpha content of transuranium solutions before transportation to another laboratory for the determination of the lanthanide fission products.

Because of its speed and simplicity a recent amine extraction technique (*1*, *5*) may be used for the removal of transuranium elements preferentially. However, some revision of this method for the multiple batch actinide–lanthanide group separation is necessary. Excess hydrochloric acid must be maintained at all times in the aqueous phase to prevent high losses of lanthanide elements and precipitation of various metal ions. Also, because the lanthanide fission products exhibit slightly different extractability (*5*), a yield correction based on a single carrier is not representative of the entire group. Use of a mixed rare earth carrier containing lanthanum, cerium, europium, and yttrium has been found quite satisfactory. The decontaminated aqueous solution may then be analyzed for total lanthanide fission products by one of several conventional procedures (*2*, *3*, *6*) with the application of a yield correction.

EXPERIMENTAL

Reagents. 30% (w./v.) Alamine 336-S–xylene. Dissolve 300 grams of Alamine 336-S in 1 liter of reagent grade xylene. Pretreat the solvent by mixing well for 3 minutes with an equal volume portion of 1*M* hydrochloric acid solution. Centrifuge the organic phase for several minutes and decant it into a glass bottle. Alamine 336-S is available from General Mills, Inc., Chemical Division, Kankakee, Ill.

Mixed lanthanide carrier. Dissolve the appropriate amounts of the oxides or chlorides of lanthanum, cerium, europium, and yttrium to give 5 mg./ml. of each metal in 0.1*M* hydrochloric acid solution.

11.6*M* lithium chloride–0.2*M* hydrochloric acid solution.

Procedure. Dilute the sample solution as much as is practical with 0.1*M* hydrochloric acid solution. A 1000-fold or greater dilution of transuranium solutions is often possible.

Pipet a suitable aliquot of the sample dilution into a 50-ml. beaker. Pipet 1 ml. of the mixed lanthanide carrier into the beaker. Evaporate just to dryness on a hot plate. Add 2 ml. of 0.1*M* hydrochloric acid solution. Evaporate just to dryness. Add 2 ml. of 0.1*M* hydrochloric acid solution and again evaporate just to dryness.

Add 10 ml. of 11.6*M* lithium chloride–0.2*M* hydrochloric acid reagent, warm gently, and transfer to a 50-ml. heavy duty glass centrifuge tube. Add 10 ml. of 30% Alamine 336-S–xylene and extract for 3 minutes. High speed motor stirrers equipped with glass paddles are excellent for performing the extraction. Centrifuge in a clinical centrifuge for 1 minute. Draw off the organic phase by vacuum and discard. Adjust the aqueous phase to about 0.2*M* by adding 0.16 ml. of 12*M* hydrochloric acid solution with a 0.2-ml. graduated pipet.

Add 10 ml. of 30% Alamine 336-S–xylene and extract again for 3 minutes. Centrifuge for 1 minute and draw off and discard the organic phase. If more extractions are required, repeat with fresh 10-ml. portions of 30% Alamine 336-S–xylene. Do not add additional hydrochloric acid, however, after the second and third extractions. Wash the sides of the centrifuge tube with about 10 ml. of distilled water and centrifuge for 1 minute. Draw off and discard the organic phase, being careful to lose a minimum of the aqueous phase.

Precipitate the mixed lanthanide hydroxides by adding 2 ml. of 6*M* ammonium hydroxide. Centrifuge for 3 minutes and decant the supernatant solution. Wash the precipitate by stirring well with about 35 ml. of distilled water. Centrifuge for several minutes and discard the supernatant solution.

Dissolve the mixed lanthanide hydroxides with about 10 drops of either concentrated hydrochloric or nitric acid. Analyze the decontaminated solution for total lanthanide fission products by one of the conventional procedures (*2*, *3*, *6*) involving a yield correction.

Table I. Recovery and Decontamination of Lanthanide Fission Products from Transuranium Elements

No. of extractions	Transuranium α radioactivity added, d.p.m.	Total lanthanide fission product yield, %	Transuranium α radioactivity found in lanthanide product, %
2	1.6×10^7	83.1	1.46
		81.6	1.69
3	1.6×10^7	71.8	0.17
4	1.1×10^9	50.0	0.007
		61.3	0.01
		73.7	0.02

RESULTS AND DISCUSSION

The preferential extraction of transuranium elements by tertiary amines is highly dependent on the concentration of hydrochloric acid, lithium chloride, and amine (*1*, *5*). Removal of these heavy elements must necessarily be a compromise with rare earth yield. Preliminary studies indicated best results were possible using the system 11.6*M* lithium chloride–0.2*M* hydrochloric acid–30% Alamine 336-S–xylene. The amine is pretreated with 1*M* hydrochloric acid solution to form the amine hydrochloride.

Typical data (Table I) obtained using the procedure described above show that a high degree of decontamination of lanthanide fission products from transuranium elements may be achieved in a rapid and simple manner. To determine the lanthanide yields the mixed lanthanide hydroxide was first precipitated to eliminate the lithium which interferes in the final lanthanide oxalate precipitation. The transuranium alpha emitters used for testing consisted of ^{239}Pu (39.4%), ^{241}Am (19.9%), ^{244}Cm (39.3%), and ^{242}Cm (1.4%). High levels of Bk, Cf, and heavier elements were not available for testing, but it is known that they extract considerably better than curium. The number of extractions necessary depends on the amount of alpha radioactivity which can be tolerated in the subsequent analysis. At this installation, transuranium alpha radioactivity in the approximate range 10^6 to 10^7 d.p.m. may be used in a conventional chemical hood. Two extractions are often adequate. An incidental advantage in the method is that the anionic chloride complexes of many fission products and associated elements (*1*, *4*) extract essentially quantitatively with the transuranium elements. Among these are zirconium, niobium, ruthenium, silver, molybdenum, technetium, zinc, iron, cobalt, copper, mercury, nickel, lead, titanium, manganese, palladium, cadmium, tin, antimony, thorium, protactinium, and uranium. Subsequent lanthanide chemistry may thus be simplified. The method is readily adaptable to glove box or hot cell techniques.

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Voltammetric Determination of the Monomethylether of Hydroquinone with a Carbon–Ceresine Wax Paste Electrode

SIR: The carbon paste electrode was developed by Adams and Olson to find a new electrode material better suited for anodic voltammetry than solid electrodes (*3*, *4*). Other authors have used this electrode to determine trace quantities of metals in water (*1*), and to study the electrochemical behavior of organic compounds in water (*2*). Attempts to use the paste electrode in nonaqueous media have been unsuccessful. Organic solvents dissolve enough of the pasting liquid to cause the paste to flake which continuously changes the effective electrode area.

It occurred to us that a paste preparation with melted Ceresine wax might produce an electrode with characteristics of the paste electrode of Adams and Olson, but usable in nonaqueous media. This report describes a specific application of a carbon–Ceresine wax paste electrode to the determination of the monomethylether of hydroquinone (MEHQ) in methyl methacrylate monomer (MMA).

EXPERIMENTAL

The carbon-wax electrode (CWE) was prepared by mixing powdered graphite (Acheson Grade No. 38) with melted Ceresine wax in a beaker. This was done by weighing a given quantity of graphite on a trip balance in a small beaker. Ceresine wax was weighed into a 2-ounce glass jar, and melted on a hot plate with a minimum of heat. The graphite was slowly poured into the melted wax and the mixture was stirred for about 10 to 15 minutes with a glass rod. The hot paste was tamped into a 2- to 3-inch tube (Du Pont Teflon) of about $^1/_4$-inch i.d. to an approximate depth of $^1/_4$ inch. Excess paste was removed from the tip of the tube with a Kimwipe and the paste was allowed to cool and solidify. Electrical contact was made to the paste by filling the tube with mercury. The electrode was connected to a conventional polarograph through a platinum wire placed into the mercury.

All experiments were done in 80% alcohol with 0.1*N* lithium chloride and 0.05*M* potassium acid phthalate as the supporting electrolyte. The reference electrode was 1*N* calomel (NCE). The cell was thermostated at 25° ± 0.1° C. Either a Leeds & Northrup Electro-chemograph Type E or a Sargent Model XXI was used to record all voltammograms. All scans were started from 0 volt.

RESULTS AND DISCUSSION

The CWE was fabricated with different weight ratios of carbon to wax. This was done to determine the effect of electrode composition on the peak current intensity. The methyl ether of hydroquinone (MEHQ) was used as the electroactive species. The data in Table I show that both the peak cur-

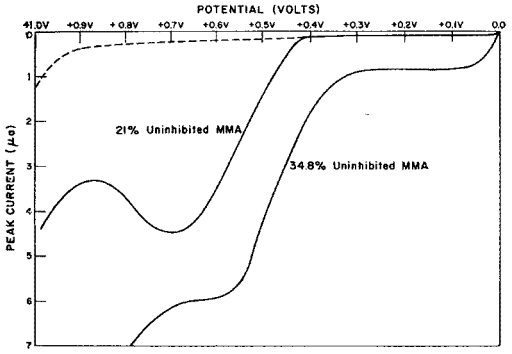

Figure 1. Effect of monomer concentration on voltammogram of MEHQ

rent intensity (i_p) and residual current (i_r) increase as the ratio of carbon to wax increases. This would be expected on the basis that an increase in carbon content should increase the effective electrode area. We chose a carbon to wax ratio of 1.3 for the remainder of the experiments because this electrode is easier to fabricate.

The peak current-concentration relation was studied by adding aliquots of a solution of MEHQ to a solution of MMA in 80% alcohol containing the supporting electrolyte. Voltammograms of the solution were obtained after each addition of MEHQ and the peak current (i_p) was plotted as a function of MEHQ concentration. The data in Table II show that a linear relation is obtained between i_p and MEHQ concentration, and that the peak potential (E_p) is independent of MEHQ concentration.

Some compounds interact with solid electrode surfaces. To determine if the carbon-wax electrode would be affected by monomers such as the acrylics, the peak current of MEHQ was measured in the presence of varying concentrations of uninhibited MMA. The data in Table III show that i_p increases with increasing monomer concentration. However, the residual current or "background current" also increases with increasing monomer concentration. The net effect of the increases in both currents causes them to merge so that the peak current is less distinctly resolved from the background (Figure 1).

Table I. Effect of Carbon-to-Wax Ratio on Current Intensity

0.161 mmole MEHQ/liter; scan rate, v = 1.3 mv./second; E_p = +0.75 volt *vs.* NCE

Weight ratio, carbon-to-wax	i_p[a], μa.	i_r, μa.
0.8	1.34	0.34
1.0	1.98	0.44
1.3	2.40	0.40
1.7	2.42	0.96
2.0	2.40	0.80

[a] Corrected for residual current.

Table II. Peak Current–Concentration Relation

Scan rate, v = 3.3 mv./second; 11.7% MMA in cell; cell resistance, 4020 to 4050 ohms

MEHQ, m*M*	i_p[a] μa.	E_p (volts) *vs.* NCE[b]	i_p/C
0	(0.15)	+0.74	...
0.081	1.24	+0.75	15.3
0.161	2.54	+0.74	15.8
0.242	3.84	+0.75	15.9
0.323	5.26	+0.74	16.3
0.484	7.76	+0.74	16.0
0.645	10.70	+0.74	16.6
0.807	12.20	+0.74	15.1
			Av. = 15.9
			σ = ±5%

[a] Corrected for residual current.
[b] Corrected for cell resistance.

Table III. Effect of Monomer on Peak Current of MEHQ

Scan rate, v = 3.3 mv./second; MEHQ, 0.262 m*M*

% MMA in cell	i_p[a] μa.	E_p (volts) *vs.* NCE[b]	Cell resistance, Ω
0	4.25	+0.73	3,180
6.3	4.18	+0.70	3,400
11.7	4.26	+0.70	3,400
21.0	4.42	+0.68	3,700
34.8	5.95	+0.57	4,350

[a] Corrected for residual current.
[b] Corrected for cell resistance.

We chose a range of monomer concentrations in the cell of 1 to 21% for the analyses because in this range i_p is distinctly separated from the residual current.

One major disadvantage of solid electrodes is that they usually must be reproducibly treated before and/or after each analysis. Platinum electrodes are sometimes dipped into nitric acid to remove oxides, and the tips of wax-impregnated graphite rods are sandpapered or cut off after each analysis. Improper or nonreproducible treatments may cause serious errors to arise in the analyses of organic compounds. The time involved in treating these electrodes can vary from 1 to 30 minutes or longer; however, in the hands of experienced analysts reproducible results are obtained.

The carbon-wax electrode can be used repeatedly without any pretreatment for the oxidation of MEHQ. A new electrode surface can be prepared by simply wiping the tip of the electrode with a Kimwipe, and new electrodes can be fabricated in a matter of minutes. The reproducibility of the carbon-wax electrode used without any pretreatment in the oxidation of 0.306 mmole MEHQ/liter (five determinations) is about 2 to 3% (2σ). Similar results are obtained when new electrodes are made for each analysis.

ACKNOWLEDGMENT

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Studies of Recovery by Foam Fractionation on 1-Naphthylamine

SIR: The technique of foam fractionation for the separation of substances has been known for a long time (*4*). Foam separation takes advantage of the surface activity of certain solutes at a gas liquid interface. When a solution is foamed, the active components collect at the surface or foam layer, which can then be removed and broken to give a rich liquid product. An excellent review of the whole field can be found in an article by Rubin and Gaden (*7*).

Initially, only surface active substances which formed stable foams were separated by foam fractionation, and the applications were therefore somewhat limited. More recently it has been found that even nonsurface-active compounds can be separated by this technique. For example, metal ions have been separated by adding to the solution a foaming agent which can complex the metal ions and carry them into the foam (*8*). Karger and Rogers (*3*) have separated organic compounds which do not form stable foams by themselves. They showed that in the case of an ionic solute, the component could be concentrated most effectively by using an ionic foaming agent of opposite charge.

In this paper, a study has been made of the recovery of an ionic organic solute, protonated 1-naphthylamine, which does not form a stable foam. An oppositely charged surfactant, sodium lauryl sulfate, was used to produce the foam and carry the organic solute into the foam column. A new and simplified method has been developed to increase recovery.

Foam fractionation is a particularly good method for recovery problems of ionic, nonsurface-active solutes due to the fact that the technique becomes more effective at low concentrations as seen from the Gibbs adsorption equation (*7*). In other words, quantitative removal and accumulation of solutes in the foam should be easily achieved.

Lemlich and Lavi (*5*) have shown that the enrichment of surfactant increases considerably with the increase of external reflux. Total reflux, in which the foam is broken and returned as liquid to the top of the foam column, has been tested by Schnepf and Kevorkian (*9*) and also by Brunner and Lemlich (*1*); in both cases considerably higher enrichments were obtained. Rogers and Olver (*6*) have pointed out that the increased enrichment of a solute in the foam may be due not only to reflux but also to the drainage of bulk liquid from the foam. In these experiments the conditions have been designed to increase both drainage and reflux and thus recovery.

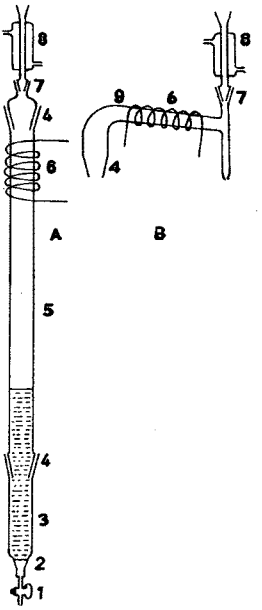

Figure 1.
A. Apparatus for foam fractionation
B. Apparatus for foam collection

1. Two-way stopcock
2. Porous glass frit, coarse, 15 mm., Kimax, 28280
3. Funnel foam column section, 36 mm. × 20 mm.
4. 40/50 standard tapered joints.
5. Foam column, proper, 36 mm. × 90 mm.
6. Heating tape, Briskeat ½" × 4', 192 watts
7. 19/22 standard tapered joints
8. Reflux condenser, Metroware, ME-517-83
9. Recovery tube, 36 mm. × 27 mm., 75° bend

EXPERIMENTAL

Figure 1 shows the apparatus used in this work. In each run, 300 ml. of solution were pipetted into the column. Nitrogen gas was passed through a saturator (to prevent spurious evaporation effects) and entered the solution through a coarse porous glass frit. The flow was adjusted to 30 ml. per minute by means of a calibrated rotameter. A heating tape (Briskeat ½" × 4', 192 watts) controlled by a variac was wound near the top of the column, and the temperature in the column was maintained at about 105° C. The foam rose to the top and broke in the heated section, the liquid flowing down as reflux. A small condenser was fitted at the top of the column to prevent any vapors from escaping. Reflux time began at the moment foam reached the heated section. After the reflux period, the heater was switched off, and the condenser was removed from the top of the column and replaced by the collector. The collector was also heated by a similar heating tape and fitted with a condenser to prevent any vapors from escaping. The gas flow was increased to 60–70 ml. per minute, and 3 ml. of the collapsed foam were collected in a graduated cylinder. The solutions used in the experiments were $2 \times 10^{-3}M$ sodium lauryl sulfate and $10^{-4}M$ 1-naphthylamine adjusted to pH 2 with HCl. Sodium lauryl sulfate was recrystallized from a water acetone mixture, 1-naphthylamine from toluene, and both were dried in a vacuum desiccator.

The concentration of 1-naphthylamine in the foamate was determined spectrophotometrically after the 3 ml. of the collected liquid were diluted to the required volume with HCl at pH 2. The spectrophotometer used was a Hitachi Perkin-Elmer Model 139. The wavelength for maximum absorbance was 277.5 mμ and the extinction coefficient 5.8×10^3. It was determined that sodium lauryl sulfate did not interfere with the analysis at this wavelength.

The amount of sodium lauryl sulfate collected in the 3 ml. was determined as sulfate by the wet oxidation method of Du Bose and Holland (*2*). The surface tension determinations were made with a Fisher Model 19 du Noüy Tensiometer.

RESULTS AND DISCUSSION

When gas is passed through a solution of a surface active agent, a foam is produced which can then travel up the column. The foam consists of films of bulk liquid and surface active species adsorbed at the gas liquid interface (*7*). Bulk liquid drains countercurrent to the rising foam, thus thinning the film at the top of the foam. This drainage is a factor in the concentration of the surface active agent at the top.

The thinning of the film can eventually lead to the breakage of the bubbles at the top. When this breakage occurs, the surface active agent can then be adsorbed at the gas liquid interface of the rising layers of bubbles. Interchange can occur between the more surface active and the less surface active species to produce a concentration of the most surface active agent

at the top of the foam column. This phenomenon is called internal reflux. It should be noted that drainage can also cause interchange of surface active species, and thus reflux, due to the fact that the bulk liquid does contain some of the surface active species.

To produce high recovery in foam fractionation, conditions should be devised to increase drainage and reflux. This increase can best be made by breaking the foam artificially at the top of the column either thermally or mechanically; however, thermal breakage is often more convenient. Essentially the principle involved is to prevent foam from rising out of the column by breakage at the top during the reflux period. After this total reflux period the breaker must be removed so that foam can go out of the column and be collected. In thermal breakage, this removal can easily be achieved by switching off the heater whereas in mechanical breakage removal may not be so easy. Also, in many types of mechanical breakage there is a possibility of trappage of foam or liquid in the breaker. However, when components are thermally unstable at the foam breakage temperature, the mechanical breaker is preferable.

The concentration of the surface active agent, sodium lauryl sulfate ($2 \times 10^{-3}M$), was at the point just prior to the critical micelle concentration as measured on the du Noüy tensiometer. This concentration results in the greatest foam stability. If higher concentrations are used, micelles would form which would adversely affect recovery and foam stability. If lower concentrations of surfactant are used, the foam column is less stable and less reproducible and it may become necessary to add surfactant during the run in order to maintain the foam column. In these studies the concern is not removal of foaming agent but only using it to remove solute and produce an enlarged gas-liquid interface.

For the recovery measure of $\frac{\text{wt. collected}}{\text{wt. original}} \times 100$, the results with thermal breakage are shown in Figure 2. It can be immediately seen that after a reflux period of one hour, recovery is complete in the 3 ml. of the collected liquid. This result shows the high recovery possibilities of ionic solutes at low concentrations by foam fractionation when drainage and reflux are emphasized. It can be seen that the 1-naphthylamine represents only 14 p.p.m. in the solution. Recent experiments with dyes have shown that high recovery can be accomplished with 10^{-5}–$10^{-6}M$ concentrations (1.4–0.14 p.p.m.) of solute. Thus the $10^{-4}M$ concentration certainly does not represent a lower limit. In these experiments the collected product contains both the surfactant and the solute. If the goal is to obtain the pure solute, it may be done by a relatively easy extraction or the use of an ion exchanger to remove the surfactant.

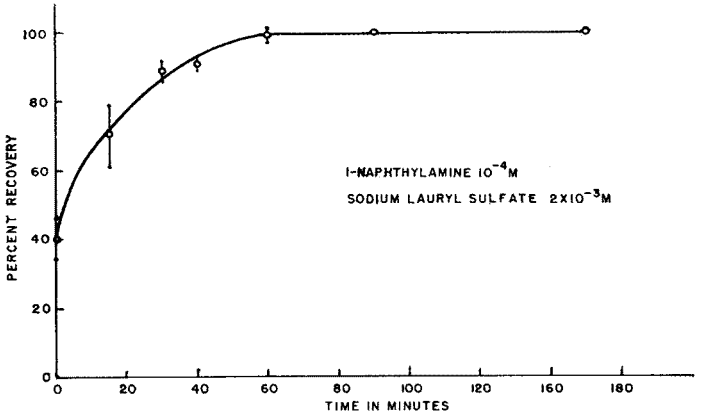

Figure 2. Recovery of 1-naphthylamine as a function of reflux time

At zero reflux time, about 40% of the solute is recovered. This 40% recovery represents initial adsorption, internal reflux, and drainage since the foam takes about 15 minutes to reach the top of the heated section of the column. Figure 2 shows that the results are more scattered at low reflux times. The cause of this scattering may be, for the most part, the rapid change in solute concentration during early reflux. When recovery is complete, the system reaches a time invariant situation for the 1-naphthylamine. This situation is not necessarily a steady state, for nearly all the solute is at the top of the foam and thus no more solute is being adsorbed in the foam layer from the solution. To have a true steady state it would be necessary to have a balancing of addition and removal of solute in the bulk solution. Schnepf *et al.* (*8*) have broken the foam and recycled it continuously into the bulk solution until no change occurred in the system. From a theoretical standpoint it is helpful to produce such a steady state, but if one wishes to recover components completely it does not seem necessary to recycle.

During the longer reflux periods a solid was observed at the top of the foam column because of the high concentration. This solid may be either the salt 1-naphthylamine hydrochloride or the surfactant–solute complex; both species are stable at the temperature of the heated section of the column (105° C). It is possible to skim off the solid; however, a more efficient and reproducible method is described in the experiments.

To test whether 3 ml. were necessary to collect all the 1-naphthylamine, runs were made with a reflux period of one hour in which 1-ml. fractions were collected in succession up to 5 ml. The results indicated very poor reproducibility in the 1st, 2nd, and 3rd ml. because of the carry over of solid and the dissolved 1-naphthylamine could not be maintained at the same rate each time. However, it was found that in a total volume of 3 ml., essentially all the material was collected.

Analysis of the sodium lauryl sulfate in the collected volume was also made in a few cases. During a one-hour reflux period, roughly 10% recovery of the surfactant could be made in the 3 ml. There was not a significant difference between the cases in which $10^{-4}M$ 1-naphthylamine was present and those in which it was not present. To produce a higher recovery of the surfactant, it would be necessary to collect a much larger volume of foam because of the higher concentration of the surfactant. Thus the technique of thermal breakage is an aid in recovery and concentration not only for solutes, but also for the foaming agents themselves.

In their production of a steady state, Schnepf *et al.* (*8*) have defined an enrichment ratio as: concentration in collected foam/concentration in the remaining bulk solution. With this measure the enrichment ratio goes from 68 at zero reflux to infinity at complete recovery in the experiments of this paper. When there is complete recovery, the enrichment ratio is not a good measure of the concentrating effect, as has been previously noted by Brunner and Lemlich (*1*). However, if a concentration ratio defined as con-

centration of collected foam/concentration of the original solution is used for the 1-naphthylamine, some measure of the concentrating effect can be obtained. With this concentration ratio, the results in this work go from 40 at zero reflux to 100 at complete recovery. If a volume smaller than 3 ml. is collected, the concentration ratio would be higher.

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Ultraviolet Spectrophotometric Determination of Trace Quantities of Phosgene in Gases

SIR: A spectrophotometric method for the determination of phosgene in gases has previously been described (*1*). This method depends upon the absorption of 1,3-diphenylurea formed when phosgene is allowed to react with aniline in aqueous solution. It is possible, by incorporation of an extraction step, to increase the sensitivity fold. Aside from a color reaction of phosgene with γ-(nitrobenzyl)pyridine, described by Lamouroux (*2*), the modified method is the most sensitive spectrophotometric one yet available for traces of phosgene.

APPARATUS AND REAGENTS

A Cary recording spectrophotometer, Model 11MS, with matched 1-cm. silica cells, was used for absorbance measurements. A manually operated spectrophotometer may be used, if enough points are plotted.

The 1,3-diphenylurea was a recrystallized product, melting point 235.5–7° C. Freshly distilled aniline was used to prepare solutions in water containing 2 mg. of aniline per ml. Phosgene (99.5 mole %) was obtained from the Matheson Co. The 1-pentanol was Eastman practical grade. The chlorine, nitric oxide, and carbon monoxide were commercial grade gases. All other reagents were of analytical quality.

CALIBRATION

Prepare a solution of 100 mg. of 1,3-diphenylurea in 100 ml. of methanol. Dilute a 10-ml. aliquot to 1000 ml. with water. Add a 1-ml. aliquot of the aqueous solution to a separatory funnel containing 25 ml. of the aniline solution. Add 1 ml. of concentrated sulfuric acid and approximately 9 ml. of a 1:1 mixture of 1-pentanol and *n*-hexane. Shake the separatory funnel for 3 minutes, allow the layers to separate, and make the organic layer to volume in a 10-ml. volumetric flask by washing the separatory funnel with a small volume of the solvent mixture. Scan the spectrum of a portion of this solution in the ultraviolet from 290 to 215 mμ, using the hexane-pentanol mixture as a reference solution. Draw a base line tangent to the curve at approximately 280 mμ and 220 mμ. Read the absorbance at 257 mμ and divide the diphenylurea concentration by the absorbance to calculate a coefficient *C*. This should have a value of about 68.5 μg. per 10 ml. per absorbance unit when a 1-cm. light path is used.

Bubble the gas under investigation through 25 to 50 ml. of the aqueous aniline solution at such a rate that not more than 2 mg. of phosgene are passed per minute (*1*). Transfer the solution to a 125-ml. separatory funnel; add 1 ml. of concentrated sulfuric acid and about 9 ml. of hexane-pentanol solvent mixture. Extract and make to a 10-ml. volume. If necessary, take an appropriate aliquot and dilute to volume with the solvent mixture. Scan the spectrum of a portion of this solution in a 1-cm. absorption cell from 290 to 215 mμ. Determine the net absorbance at 257 mμ as above. Call this quantity *A*.

Milligrams of phosgene in 10 ml. of solution = $A \times C \times 0.466$. The factor 0.466 represents the molecular weight ratio of phosgene to diphenylurea.

RESULTS AND DISCUSSION

To test the method, small quantities of phosgene were weighed in sealed capillary tubes. These tubes were broken under *n*-hexane in which phosgene is very soluble. The resulting solution contained 18.4 μg. of phosgene per ml. The phosgene content was initially 17.7 μg. per ml. by the extraction method. This decreased to 15.6 μg. per ml. in 3 days, after which it remained constant for a period of several weeks. This initial change in concentration was probably caused by reaction of the phosgene with solvent impurities.

The limit of detection of phosgene per 10 ml. of solution is approximately 1 μg. In air, 0.01 p.p.m. (1 p.p.m. = 4.05 μg. per liter of air) can be determined by blowing about 30 liters of air through the aniline solution and then using the extraction procedure.

Two different techniques were used to allow the phosgene to react with aniline in the aqueous solution. First, portions of the standard solutions were vaporized and aspirated through the aniline solution. In a second approach portions of the standard solutions were shaken with the aniline solutions. The results are summarized in Table I.

Although the results are quantitative in only a few instances, they show better than 90% recovery in most cases. This is sufficient for practical applications. Difficulties encountered in handling phosgene solutions quantitatively and in assuring complete contact of phosgene with aniline account for the low results. They are not caused by the extraction which is shown in Table II to remove 1,3-diphenylurea quantitatively.

The pH of the aniline solution may change when combustion products or vent gases are bubbled through it. The effect of pH on the reaction of phosgene with aqueous aniline was investigated by shaking 1.00 ml. of a *n*-hexane solution containing 15.6 μg. of phosgene with 50 ml. of the aqueous

Table I. Determination of Phosgene

Aspirated samples		Shaken samples	
Phosgene taken, μg.	Phosgene found, μg.	Phosgene taken, μg.	Phosgene found, μg.
6.2	5.8	1.3	1.0
6.2	5.9	3.1	2.8
7.7	6.9	9.4	9.1
7.7	7.1	13.2	13.2
		26.4	26.3

Table II. Extraction of Diphenylurea from Aqueous Acidified Aniline Solution with 50:50 n-Pentanol–n-hexane

1,3-Diphenylurea taken, μg.	1,3-Diphenylurea found, μg.
0.00	0.05
6.0	5.9
13.7	13.3
13.7	13.7
13.7	13.7
27.4	27.7

aniline solution and carrying this through the procedure. The results are shown in Table III. The initial pH of the aniline solution was 7.4. Higher pH values were obtained by adding ammonium hydroxide and lower ones by adding hydrochloric acid. The incomplete reaction at pH 9 and above is caused by hydroxyl ion concentration and not by a reaction between aniline, phosgene, and ammonia to form phenylurea or between phosgene and ammonia to form urea. This was shown by using other bases to obtain the same recovery at the same pH values, and by examining the reaction products for phenylurea.

Nitric oxide, if present in large quantities, will react with aniline to form a yellow-orange compound which interferes. Free chlorine will oxidize aniline to form a brown tar. These materials, however, are seldom present in concentrations high enough to interfere in practice.

Large excesses of carbon monoxide (10^6) have no effect on the reaction. Samples of vent gases from gas burners produced aniline solutions of a pH from 4 to 8. They did not contain enough nitric oxide or chlorine to cause interference.

Materials which are extracted into the hexane-pentanol solution and interfere by absorbing ultraviolet light can often be eliminated by extracting the aniline solution with *n*-hexane before it is acidified with sulfuric acid. Diphenylurea is not appreciably soluble in *n*-hexane and remains in the aqueous layer. Such interferences are seldom encountered in combustion products, however.

Table III. Effect of pH of Aniline Solution on Recovery of Phosgene

pH	Recovery, %[a]
0.5	0
1.97	9.3
4.04	79.4
4.95	98.6
6.07	102.0
7.03	100.4
8.06	92.0
9.01	63.4
10.42	12.4

[a] 15.6 μg. of phosgene; 50 ml. of aqueous aniline solution (2 μg./ml.).

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Use of Highly Acid Supporting Electrolytes in Polarography

Observed Changes in Polarographic Waves of Selenium(IV) upon Standing

SIR: The polarographic characteristics of selenium(IV) in a number of electrolytes were recently reported (*1*). In acid medium two waves are found, only the second being reversible. The authors have since had occasion to employ high concentrations of sulfuric acid supporting electrolytes for polarographic determinations of selenium in biological samples. In 3*M* sulfuric acid the second selenium wave decreased in height upon standing in the polarographic cell under nitrogen with mercury dropping through the solution; the wave eventually disappeared completely. The wave also shifted to slightly more negative potentials as it decreased in height. Sometimes a milky precipitate occurred with these changes but this was not always the case.

This behavior has been investigated further and the observed changes have been shown to be due to reaction of free mercury ions with intermediate reduction products of the selenium; the free mercury ions are formed from acid dissolution of the mercury electrode.

EXPERIMENTAL

Reagent grade chemicals were used throughout. Stock selenium(IV) solutions were prepared by dissolving spectrograde black selenium powder in a small amount of nitric acid and diluting to volume with water.

All polarographic measurements were made with a Sargent Model XV polarograph. The polarographic cell was equipped with a mercury pool anode unless otherwise stated. Solutions were deoxygenated with Seaford nitrogen (Southern Oxygen Co.) for 10 minutes prior to the running of the polarogram. During the course of the polarogram a nitrogen atmosphere was maintained above the sample solution. All polarograms were obtained on a sample thermostated at 23° ± 0.2° C.

RESULTS

A polarogram was obtained on a solution of 10 μg. of selenium(IV) per ml. in 3*M* sulfuric acid. The original height of the second wave (after 10 minutes in the cell) was 0.90 μa. The wave almost completely disappeared upon standing for 1 hour under nitrogen in the cell [in contact with the mercury pool anode and the dropping mercury electrode (DME)]. This decrease in the second wave height was accompanied by a change in the first wave from a fairly smooth wave to one with several maxima and minima. On further standing (after wave 2 disappeared) wave 1 became even more distorted. The maxima and minima could be eliminated by the addition of gelatin.

The effects of nitrogen and mercury were studied by transferring aliquots of the same solution (10 μg. Se/ml. in 3*M* H_2SO_4) to two flasks, one containing a pool of mercury. Each solution was bubbled for 8 hours with nitrogen. A polarogram was then obtained immediately after adding each of the solutions to the polarographic cell. The solution which contained no mercury yielded a height of 0.98 μa. for wave 2 and wave 1 was not distorted—i.e., no change. After 1 hour in the cell, the height of wave 2 in this solution decreased to 0.85 μa. accompanied by a slight distortion of wave 1. The second solution, which had been over mercury, gave a height of 0.78 μa. for wave 2 and wave 1 was slightly distorted.

Solutions of selenium(IV) in 3*M* sulfuric acid in the presence of air and the absence of mercury showed no change on standing, even after several weeks.

To test whether the observed phenomena were associated with the sulfate species or with the high acidity of the medium, the same studies were made in 4*M* perchloric acid. Essentially the same results were found. The original polarogram, after deoxygenating for 10 minutes, showed wave 1 to be more drawn out in this medium (almost straight). After 3 hours in the cell,

wave 2 disappeared and wave 1 became badly distorted.

The rate of decrease of the wave height was more rapid when the solutions were in the polarographic cell than when in the flask containing a pool of mercury. This was probably because mercury was dropping through the solution from the DME while standing. A larger and continually fresh surface area of mercury was presented to the solution. Supporting this is the fact that when a precipitate occurred, it appeared to be forming around the mercury drops as they fell through the solution (associated with mercury dissolution).

A similar precipitate has been observed to form in a supporting electrolyte of $3M$ sulfuric acid, causing erratic behavior of the residual current. This precipitate was analyzed and found to contain mercury. Therefore, mercury apparently dissolves from the electrode. The precipitate formed around the DME in the presence of selenium(IV) above was difficult to collect without contamination with elemental mercury.

Since it was apparent that free mercury ions were being formed, an experiment was run to show that acid dissolution of mercury occurs at room temperature. Three flasks were prepared, each containing a pool of mercury. In one was placed $3M$ sulfuric acid. In the second was placed $3M$ sulfuric acid containing $10^{-3}M$ selenium(IV), and in the third was placed $10^{-3}M$ selenium(IV) in water. The flasks were allowed to stand for one day. A white precipitate occurred in the second flask and this precipitate was found to contain mercury and selenium. This was apparently the same precipitate as formed around the DME above. A polarogram was run on the solution in flask 3 after acidifying. The normal selenium waves were found. A polarogram on the solution in flask 1 was very ragged and appeared to give an immediate cathodic current (reduction of free mercury ions). Further tests proved the existence of free mercury ions in this solution. After adjusting the pH to ca. 2, the solution was extracted with dithizone in chloroform. An orange color developed in the chloroform layer which was eliminated by back extraction into $6M$ hydrochloric acid. This indicates the presence of mercury ions (*4*). The dithizone extract was also analyzed by atomic absorption spectrometry and the results showed the presence of mercury.

Thus, observed changes of selenium(IV) waves are apparently caused by acid dissolution of the mercury electrode with the formation of free mercury ions. The free mercury ions can then interact with intermediate selenium reduction products in the diffusion layer. This was substantiated by obtaining a polarogram of 1 μg. of selenium per ml. ($1.26 \times 10^{-5}M$) in $3M$ sulfuric acid in a Lingane H-cell equipped with a saturated calomel reference electrode (SCE). The normal waves were recorded. The solution was then made ca. $10^{-5}M$ in mercuric sulfate and the polarogram was immediately rerun. The second selenium wave was nearly eliminated. Doubling the concentration of mercuric sulfate completely eliminated the wave. The first wave was not distorted and remained approximately constant in height.

Quantitative wave height measurements of wave 1 when wave 2 decreased with time were difficult because of the high distortion of this wave which usually occurred. When the wave became distorted, it was usually broken into three steps. It appeared generally that the first two steps remained constant in height while the last step decreased slightly with increasing distortion of wave 2. If the wave was not appreciably distorted, the overall height appeared to remain constant.

DISCUSSION

It is not surprising that elemental mercury can be slowly attacked by $3M$ sulfuric acid (or perchloric acid). It is known that mercury is converted to mercurous or mercuric sulfate when heated with concentrated sulfuric acid (*5*); the product depends on the ratio of mercury to acid and on the time of heating.

The disappearance of wave 2 upon addition of free mercury ions, either externally or from slow acid dissolution of the electrode, can be easily explained. The primary electrode reaction for the first wave is a six-electron reduction (*1*).

$$H_2SeO_3 + 6H^+ + 6e^- = H_2Se + 3H_2O \quad (1)$$

However, at potentials corresponding to the first wave, the DME is depolarized by the hydrogen selenide formed at the electrode surface.

$$Hg + H_2Se = HgSe + 2H^+ + 2e^- \quad (2)$$

Therefore, the first wave is an overall four-electron process.

$$H_2SeO_3 + Hg + 4H^+ + 4e^- = HgSe + 3H_2O \quad (3)$$

At potentials more negative than the second selenium wave, reaction 2 does not occur and the overall process is reaction 1. Thus, wave 2 corresponds to a two-electron process because of depolarization of DME by hydrogen selenide at potentials more positive than this wave. When free mercury ions are present at the electrode surface as the hydrogen selenide is formed, these ions will react with the hydrogen selenide and precipitate mercuric (or mercurous) selenide.

$$H_2Se + Hg^{+2} = HgSe + 2H^+ \quad (4)$$

Reaction 2 is therefore decreased or eliminated which effectively decreases or eliminates wave 2. One would expect, however, that wave 1 would increase to a six-electron wave as wave 2 disappeared. This is not the case; wave 1 appears to remain constant at a net four-electron process. This again can be explained. Free mercury ions are reduced at potentials more positive than the first selenium wave. However, when the potential resides on the plateau of the selenium wave, part or all of the mercury ions in the diffusion layer (equal to the amount of reaction 2 which is eliminated) are precipitated and removed from the solution as the selenide. Therefore, the mercury ions no longer contribute to the diffusion current at these potentials and the selenium wave appears to remain approximately constant in height. That is, for every faraday of current increase in wave 1 due to the elimination of reaction 2, there is 1 faraday of current decrease due to precipitation of mercury ions. Lingane and Niedrach (*3*) have observed a similar phenomenon with ammoniacal solutions of selenium (IV) containing copper(II).

Further evidence that the elimination of wave 2 is due to precipitation of the hydrogen selenide was obtained by adding either copper(II) or zinc ions to the solution. Copper(II), which precipitates sulfide in acid medium, eliminated the wave. Zinc ions, which do not precipitate with sulfide in acid medium, did not affect the wave.

Wave 1 remains nearly constant in height upon the external addition of mercuric ions and wave 1 is not distorted as wave 2 decreases, indicating that there is very little difference between the diffusion coefficients of the mercury ions and H_2SeO_3 in this medium; also, the mercuric selenide precipitate does not distort the wave. The fact that the last step of the distorted selenium wave decreases slightly could be due to adsorption of insoluble mercury species at the electrode surface. Probably the precipitate formed, which has nothing to do with the electrode processes, is an insoluble mercurous salt which may be adsorbed, resulting in distortion of the wave. This is supported by the fact that the distortion is partially eliminated by the addition of gelatin. Christian and Purdy (*2*) have shown that insoluble mercurous phosphates are adsorbed at the DME.

The mercury-ion concentration in the bulk of the solution when the second selenium wave has disappeared is probably close to that of the selenium

(IV). This would not have to be the case since we are dealing with processes in the diffusion layer at the electrode surface and sufficient (trace) amounts of mercury might dissolve at the electrode surface to react with the hydrogen selenide formed. However, the fact that wave 2 remains eliminated when running a fresh polarogram after the solution has been removed from the cell for several days indicates that there are sufficient mercury ions in the bulk of the solution to diffuse to the electrode surface along with the selenium(IV).

This problem should be considered whenever working with highly acid electrolytes. Residual currents often become ragged and inconsistent results are obtained with samples. The authors have found that difficulties are eliminated if contact with mercury is avoided while the solution is deoxygenated with nitrogen. With an H-cell fitted with an SCE, this problem is eliminated by lowering the mercury reservoir for the DME during deoxygenation. The polarogram is obtained immediately upon raising the mercury reservoir.

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Modification of Ferrous Ion Reduction Method for Nitroglycerin

SIR: Nitroglycerin (NG) is determined in this laboratory by the familiar method of Becker and Shaefer (*1*). This procedure involves the reduction of the nitrate groups with a large excess of iron(II) in glacial acetic acid. The iron (III) formed is then measured directly by titration with titanium(III) chloride using an internal indicator.

Titanium(III) chloride, though a powerful reductant, is not an entirely suitable titrant. The instability of the titrant is such that precision and accuracy of the titration is not always acceptable. The titanium(III) titrant solution is very sensitive to air oxidation and has to be stored under an inert atmosphere. Solutions need daily restandardization. When this titrant is stored in an automatic buret for any length of time, it is necessary to flush a large volume through the system prior to titration. If this is not done, unacceptable precision results.

The disodium salt of (ethylenedinitrilo)tetraacetic acid (EDTA) is a more suitable titrant for iron(III) in the presence of large amounts of iron(II). The satisfactory titration of iron(III) with EDTA has been reported by several workers (*2*, *3*). Solutions of properly stored EDTA are very stable and require only infrequent standardization. When EDTA is used for the determination of iron(III) formed in the NG reduction, much better precision and accuracy result.

This method is applicable to the determination of NG in the absence of any materials capable of reacting with NG, iron(II), iron(III), or the EDTA used as titrant. For samples received by this laboratory, it was necessary to correct only for 2-nitrodiphenylamine (2-NDPA). Other materials present did not interfere or were quantitatively removed during the extraction step.

Table I. Determination of NG by EDTA Method

NG taken, mg.	NG found, mg.[a]
110.0	110.0
125.0	125.1
135.0	135.3
145.0	145.1

[a] Each result is the average of six determinations.

EXPERIMENTAL

Reagents. A 0.20*M* EDTA solution was prepared by dissolving 148.8 grams of disodium (ethylenedinitrilo)-tetraacetate in 1 liter of warm distilled water, cooling to room temperature, and diluting to 2 liters with distilled water. This solution was standardized against calcium after Welcher (*3*). A 0.70*N* iron(II) solution was prepared by dissolving 137.3 grams of ferrous ammonium sulfate in a solution of 35 ml. of concentrated sulfuric acid and 350 ml. of distilled water, and diluting to 500 ml. with distilled water.

Apparatus. An NG reduction flask, 500 ml., with a gas inlet and a standard taper 29/42 ground glass neck fitted with a water-cooled reflux condenser with a ground glass joint, was used for refluxing. A beaker head was prepared by drilling five holes into a number 12 rubber stopper. This "head" simultaneously held a platinum electrode, calomel electrode, glass electrode, buret, and nitrogen bubbler.

Procedure. Place an accurately weighed amount of the NG sample containing 0.10 to 0.15 gram of NG into a 500-ml. reduction flask. Add 25 ml. of glacial acetic acid and 25 ml. of a 1:1 hydrochloric acid solution. Purge with nitrogen to remove air and add 25 ml. of the ferrous ammonium sulfate solution. Reflux until the sample changes in color from yellow-orange to reddish brown and back to a yellow-orange. (This should require 5 to 10 minutes.) After refluxing, cool the flask and disconnect from the condenser. Transfer the solution to a 250-ml. tall form beaker. Place the prepared rubber stopper with the platinum-calomel indicating electrodes, glass pH electrode, buret, and nitrogen bubbler tube into the beaker. Adjust the pH to 2.5 with 30% sodium hydroxide. The glass and calomel electrodes are used in combination to measure pH. Titrate the iron(III) formed in the NG reduction potentiometrically with 0.20*M* EDTA. The platinum and calomel electrodes are used in combination to follow the potentiometric titration. A Beckman Zeromatic pH meter or equivalent potential recording device is suitable. Run a blank in the same manner, with the exception that no sample is added.

RESULTS AND DISCUSSION

End Point Detection. Welcher (*3*) recommended several internal indicators for the iron(III)–EDTA titration. A number of these indicators proved unsatisfactory under the conditions of the NG determination. These included salicylic acid, Pyrocatechol Violet, Eriochrome Black T, Variamine Blue B, Xylenol Orange, and copper-PAN 1-(2-pyridylazo)-2-naphthol. Poor end points resulted for any of a combination of reasons—e.g., iron (II) interference, high iron(III) concentration, and high solution ionic strength.

A potentiometric procedure employing a platinum-calomel indicating couple gave a suitable end point. The slope and magnitude of the end point "break" was pH dependent. A pH of 2.5 gave the best end point.

Interferences. Materials frequently present with NG included varying amounts of triacetin and

about 1% 2-NDPA. Introducing varying amounts of triacetin caused no interference in the NG determination. A nonstoichiometric positive error was caused by 2-NDPA. This error, however, was small but constant and was corrected for in the titration. One milligram of 2-NDPA required the equivalent of 0.0034 meq. of EDTA in the titration.

Precision and Accuracy. To determine the accuracy and precision of the NG determination using EDTA to titrate the iron(III), four standard samples were prepared. Six determinations were made on each sample using the EDTA titration. (The results are shown in Table I.) The method showed a positive bias of 0.09%. The 95% confidence limit for a single NG determination using EDTA was ±0.24% at the 70 to 90% level. Becker and Shaefer reported a 95% confidence limit of ±0.69% at the 100% level for the titanium(III) method using a potentiometric end point.

For further comparison of the methods, this laboratory has also obtained data for the titanium(III) titration with a potentiometric end point. A 95% confidence limit of ±0.33% at the 100% level was established. Previous work here has shown the potentiometric end point gave better precision and accuracy than the visual end point methods, so no precision data was obtained using the visual end point.

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Fluorescence of the Aluminum–[1-(2-Pyridylazo)-2-Naphthol] Complex

SIR: A recent development in our laboratory has been a fluorescent indicator for the qualitative determination of the aluminum ion (*3*). An aqueous fluorometric determination of aluminum using Pontachrome Blue Black R has been reported by Weissler and White (*6*). The present paper reports the use of PAN for the determination of aluminum in ethanol–water solutions. The method consists in preparing an aluminum–PAN complex in 95% ethanol and measuring the aluminum content fluorometrically.

PAN [1-(2-pyridylazo)-2-naphthol], was first reported by Liu (*5*) to form complexes with the heavy metals. Cheng and Bray (*1*) have also noted further properties of PAN; and Flaschka (*2*) has investigated the use of PAN as an indicator in conjunction with EDTA. It has been noted that a number of aromatic fluorescent complexes of aluminum all possess a phenolic hydroxyl group either ortho or para to the complexing site (*4*); PAN belongs in this category since it has its phenolic hydroxyl group ortho to an azo group.

The aluminum–PAN mixture exhibits several properties not shared by other metallo-PAN chelates. No reaction is detectable between the aluminum ion and PAN in aqueous solution; however, an orange or yellow solution results when the two substances are mixed in variety of organic solvents. The fluorescence color of the complex as well as the color of other transition metal complexes is given in Table I. The other property which was observed for the Al–PAN complex is that it fluoresces with an orange-yellow color in alcohol and acetone.

A typical calibration curve can be plotted from the fluorescence observed in a 95% ethanol media. The aluminum–PAN ratio need not be constant since only the complex fluoresces and not the excess PAN. A linear plot was obtained over the range of 4 to 12 × 10^{-2} mg. of Al^{+3} per 50 ml. of 95% ethanol–water solution using 2.5 × 10^{-5} gram per ml. of PAN. These alcoholic solutions were prepared by volumetrically diluting 1 ml. of 5 × $10^{-3}M$ PAN and an appropriate volume of $10^{-3}M$ Al^{+3} ion from $Al(NO_3)_3 \cdot 9H_2O$ to 50 ml. with 95% ethanol. The solutions used to obtain a calibration curve are given in Table II.

The fluorescence was measured with a Coleman Photo-fluorometer (Model 12-B) using the primary filter No. 12-222 (B-2) which passes the 436 mμ line and the secondary filter No. 14-212 (PC-2) which stops light below 530 mμ. Two excitation maxima, 350 mμ and 545 mμ, permit the use of primary filters 320 to 345 mμ or 500 to 550 mμ,

Table I. Fluorescence Color

PAN complex	Solvent				
	EtOH[a]	Et_2O	C_6H_6	CCl_4	$CHCl_3$
Cr	B	Br	Y	Y	Y
Fe	Br	Br	Y	Y	Y
Mn	P	P	Y	Y	Y
Ni	R	Pu	P	R	Y
Zn	R	R	R	R	R
Co	L	L	Y	G	G
Al	O	Y	Y	Y	Y

B-blue, Br-brown, G-green, L-lavender, O-orange, P-pink, Pu-purple, R-red, Y-yellow.

[a] Identical colors were also obtained in MeOH, PrOH, BuOH, AmOH, HexOH and acetone.

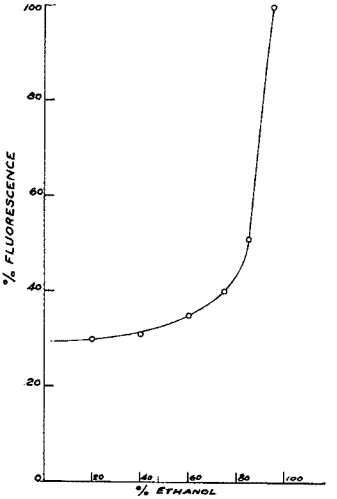

Figure 1. Variation of fluorescence with per cent ethanol

Table II. Aluminum–PAN Solutions

Ml. of $10^{-3}M$ Al^{+3}	Mg. of Al^{+3} per 50 ml.	Al:PAN ratio
1.33	0.036	0.029
2.00	0.054	0.043
2.67	0.072	0.058
3.33	0.090	0.072
4.00	0.108	0.082

respectively. The emission maxima is 590 mμ. The secondary filter should transmit from 560 to 600 mμ. Excellent results were obtained in the detection of 10^{-6} gram of Al^{+3} per ml. and acceptable results with 27×10^{-9} gram of Al^{+3} per ml.

It was also noted that fluorescence decreases as the amount of ethanol decreases. This decrease as shown in Figure 1 was obtained from solutions, each of which contained 2.5×10^{-6} gram of Al^{+3} ion per ml. and 7.5×10^{-6} gram of PAN per ml. of solution. Other working curves using a different per cent by volume of ethanol can also be obtained; however, a 70 to 95% ethanol solution gave satisfactory results.

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Switching Circuitry for Fast Chronopotentiometry

SIR: Recent work involving short-time chronopotentiometry has indicated hazards in switching circuitry which applies the current to the cell (*1*, *2*, *6*). In addition, it is of some interest to carry out chronopotentiometry from an initially biased electrode rather than from the equilibrium potential as is normally done (*3*, *5*). The present correspondence is concerned with a relatively simple switching circuit which may be successfully applied to both problems.

It is advantageous to utilize make-before-break high-pressure mercury relays in chronopotentiometric switching. While having the disadvantage of momentarily shorting the indicator and counter electrodes together, this shorting does prevent fluctuation in the constant current source, regardless of type. However, the shorting may result in a large indicator electrode polarization for the approximately 0.5 msec. involved.

A fourth electrode against which the counter electrode may be prebiased represents a solution to this problem (*1*), as does the use of break-before-make relays which, however, may cause current source fluctuation (*2*). If it is desired to prebias the indicator electrode, the bias must be removed just prior to application of the constant current, or else a parallel path for current flow may be present.

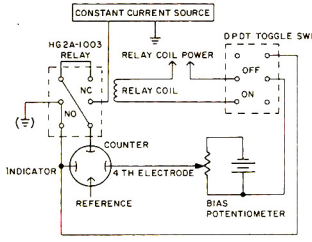

Figure 1. Switching circuitry

The circuit in Figure 1 indicates one solution to the problem. Relay 1 is a Clare HG2A1003 make-before-break high-pressure mercury relay. SW1 is a double pole, double throw toggle switch. The potentiometer serves to bias the indicator and counter electrodes, which are shorted together when SW1 is in the off position. When SW1 is thrown on, the bias potentiometer is first removed, then the relay coil energized. When Relay 1 is energized, it momentarily shorts all the contacts together, prior to breaking from the "Normally Closed" position. However, because the indicator and counter electrodes have been biased as a shorted pair, no significant polarization takes place; further, because the current source is shorted, no current flows through the cell until the contacts break.

Figure 2*a* shows a potential-time trace using a make-before-break relay but without the use of the fourth electrode and related switching circuitry. The initial equilibrium potential of about −0.4 volt corresponds to a thallium amalgam. The potential excursion observed when the relay was shorted polarized the electrode to mercury dissolution, as the platinum counter electrode had been strongly anodic prior to the chronopotentiogram shown. When the relay breaks, applying the constant current to the cell, mercuric reduction is noted, followed by a rise to thallous reduction.

Figure 2*b* shows the start of two chronopotentiograms with the switching circuitry of Figure 1. The lower curve is biased at 0 volt, the upper at −0.3 volt *vs.* the SCE. There is no potential excursion, and the rise to the start of the thallous reduction corresponds to double layer charging.

The constant current source employed was a portion of an operational amplifier set-up, similar to that previously described (*4*). However, any constant current source may be used with this switching circuitry.

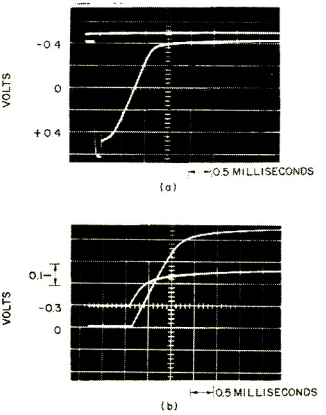

Figure 2. Hanging drop mercury electrode

5mM Tl(I) in 1M $HClO_4$; horizontal axis, 0.5 msec. per div.

(a) Make-before-break relay, Tl(Hg) hanging drop formed from a prior chronopotentiogram. Vertical axis, 0.2 volt per division

(b) With switching circuitry of Figure 1; lower curve prebiased at 0 volt; upper curve prebiased at −0.3 volt; vertical axis, 0.1 volt per division

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An Improved Method for Determination of Selenium in Biological Material

SIR: In the past several years many excellent methods have been published for determining the concentration of selenium in biological material. But even with these improved methods many analytical problems remained unsolved. For example, all of the practical methods were very time consuming, requiring from 8 hours in some cases to as long as 48 hours in others. Many of these methods required expensive instruments not found in many analytical laboratories. Therefore, realizing the great demand for a rapid and accurate quantitative method of analysis which could detect microquantities of organic-bound selenium, we developed and published a method which appeared to solve all of these problems (*2*). However, after this method was published, an improved method was devised which allows one to analyze a single sample in less than an hour or 15 samples in about 2 hours, and the results appear to be better than those obtained with our previous method. The only other practical methods that can compare with this method on a time basis and still retain their sensitivity are neutron activation analysis and atomic absorption spectrophotometry. The cost of the equipment alone makes these methods prohibitive in many laboratories. Also, neutron activation analysis becomes impractical if one wishes to analyze a large number of samples.

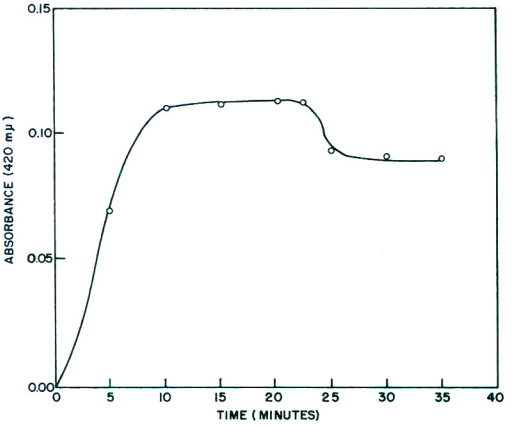

Figure 1. Time required for maximum color development of the Se-DAB complex at 60° C.

4 μg. Se per 4.0 ml.

EXPERIMENTAL

Apparatus and Reagents. STANDARD SELENIUM SOLUTION. Prepare a stock solution containing 1 mg. of selenium per ml. by dissolving 2.190 grams of carefully dried sodium selenite in distilled water to which approximately 80 ml. of 48% hydrobromic acid has been added. Dilute this solution to 1 liter. Standardize this solution gravimetrically. Prepare a solution containing 1 p.p.m. by diluting the stock solution.

DIGESTION MIXTURE. Dissolve 10 grams of sodium molybdate in 150 ml. of distilled water. Slowly add 150 ml. of concentrated sulfuric acid to the molybdate solution. After cooling, add 200 ml. of 70–72% perchloric acid.

Saturated NaOH, 90% formic acid, 40% hydroxylamine hydrochloride, 0.2*M* EDTA (disodium salt), 3,3′-diaminobenzidine (DAB), (0.5% aqueous solution freshly prepared from the tetrachloride), metacresol purple, (0.1% in 0.0026*N* NaOH).

Constant temperature bath, pH meter, and a Spectronic-20.

Procedure. Digest 0.1 to 0.2 gram of dried material or 0.5 to 1.0 gram of wet material in 5 ml. of the digestion mixture. Digest in either a 50-ml. digestion tube or in a micro-Kjeldahl flask. Add 5 to 6 boiling stones to prevent bumping. (The boiling stones should be boiled for several minutes in the digestion mixture and thoroughly washed with distilled water prior to use. This removes trace amounts of selenium which we have found in some boiling stones obtained commercially.) Heat the tube or flask over a low flame with continuous swirling. In about 5 to 10 minutes the solution begins to boil, and vigorous oxidation takes place soon thereafter. Most samples, such as skeletal tissues, hair, blood, and plant material are completely digested in about 15 to 20 minutes, and the solution becomes clear at that time. Upon digesting bone tissue, however, a white insoluble precipitate appears at the completion of the digestion, and it should be removed before continuing the analysis by means of a fine-porosity fritted glass filter.

After digestion, allow the tube to cool and then wash its contents plus the boiling chips into a 250- ml. beaker with about 20 ml. of distilled water. Bring the pH up to about 7 with saturated NaOH using metacresol purple as an indicator. At this pH the indicator changes to a purple color. The pH is then lowered to between 2 and 3 by adding 2 ml. of 90% formic acid. Add 4 ml. of 40% hydroxylamine to reduce any excess oxidative reagent.

Table I. Selenium Content in Dried Tissue

	Described method		Neutron activation analysis
	μg. Se recovd. from 0.10 g.	μg. Se recovd. from 0.15 g.	p.p.m. Se recovd. from 0.36 g.
	3.90	5.95	37.0 ± 0.9[a]
	4.00	5.70	35.4 ± 0.9
	4.00	6.10	39.6 ± 0.9
	4.25	5.95	
	4.20	6.18	
	3.90	6.25	
	4.00	5.95	
	4.07	6.37	
	4.20	6.37	
	3.90	6.25	
Av. μg.	4.04	6.11	
Std. dev. μg.	±0.13	±0.23	
Av. p.p.m.	40.4	40.7	37.3

[a] Plus or minus values given are standard deviations estimated from counting statistics only.

The solution now starts to change to a greenish color. Add 4 ml. of 0.2*M* EDTA to mask the interfering ions. It is now advisable to check the pH to see that it is still between 2 and 3. If not, either add concentrated NH_4OH or 90% formic acid for the adjustment. Add 2 ml. of 0.5% 3,3'-diaminobenzidine, and complex in a constant temperature bath at 60° C. in subdued light for only 20 minutes. After removal from the bath, adjust the pH to between 7.0 and 7.5 with concentrated NH_4OH. Since the solution at this point is quite colored, the indicator change is not distinct and a pH meter must be used. Rinse the solution into a 125-ml. separatory funnel with a few milliliters of distilled water, and extract with exactly 4 ml. of toluene by shaking the mixture vigorously for 1 minute. Allow 3 to 4 minutes for complete layer separation and discard the aqueous layer. Transfer the toluene extract to a centrifuge tube and centrifuge for a few minutes. Determine the absorbance of the extract at 420 mμ with a Spectronic-20 using a toluene blank.

Prepare a standard curve by adding 2, 4, 6, 8, and 10 ml. of the 1 p.p.m. standard solution to 5 ml. of the digestion mixture and heat to boiling for about 5 minutes, then carry out the remainder of the procedure.

RESULTS AND DISCUSSION

The advantage of this method over our previously published method (*2*) is in the elimination of the ascorbic acid reduction step which was necessary to isolate the selenium from interfering ions. Gutenmann and Lisk (*3*) reported that the selenium–DAB complexing reaction can be carried out in the presence of EDTA. EDTA masks ions such as Fe(III), Cu(II), and V(III) which have likewise been shown to complex with DAB (*1*). The elimination of the ascorbic acid reduction step reduces the analysis time by at least 1 hour. In addition, another 40 minutes can be saved by hastening the rate of the complexing reaction. We found that at 60° C. maximum complexing occurs in 20 minutes (Figure 1). After about 23 minutes it appears that decomposition of the selenium–DAB complex starts to occur.

To determine the efficiency of this method 20 analyses were carried out on samples of acetone-dried liver obtained from sheep whose diets were supplemented with subtoxic levels of sodium selenate. [The preparation of this dried tissue is described in (*2*).] Some of the same dried tissue sample was sent to General Atomics (General Dynamics/General Atomic Division, Activation Analysis Service, San Diego, Calif.,) for neutron activation analysis. After comparing the results obtained from the neutron activation analysis with those obtained by this method, it must be concluded that this method is capable of recovering virtually all of the organic-bound selenium. These data are summarized in Table I.

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Use of In Situ Reactions for Characterization of Alcohols and Glycols by Nuclear Magnetic Resonance

SIR: Esterification of hydroxy compounds produces downfield shifts of nuclear magnetic resonance peaks which are caused by hydrogens alpha to hydroxy groups (*2*). The magnitude of the shift, the multiplicity of the shifted peaks, and the relative areas of the shifted peaks are valuable aids in determining structures. Such shifts often separate peaks which are overlapped in the spectrum of the hydroxy compound so that multiplet patterns can be determined and their areas measured.

The addition of a reactive isocyanate or ketene to an alcohol or glycol in the NMR sample tube is a simple and rapid means for effecting the desired changes in the NMR spectra. These reagents produce no by-products and the urethanes and esters which are produced do not need purification.

EXPERIMENTAL

The proton magnetic resonance spectra were recorded using a Varian A-60 NMR spectrometer equipped with a V-6031 variable temperature probe. Peak positions are given in parts per million, relative to tetramethylsilane as an internal standard. Diphenylketene was prepared by the procedure of Staudinger (*4*). Trichloroacetyl isocyanate was prepared by the method described by Speziale and Smith (*5*). The sample of 2,2-dimethyl-5-phenyl-1,3-pentanediol was synthesized in this laboratory by a method similar to that described in the literature (*1*). All other materials used were commercially available, reagent grade compounds and were used without further purification.

RESULTS AND DISCUSSION

Reagents which were used in this work are diphenylketene, phenyl isocyanate, and trichloroacetyl isocyanate. Diphenylketene is the least desirable of the three reagents because it is not readily available, because it does not have a long shelf life, and because its reactivity toward hindered hydroxy groups is limited. Phenyl isocyanate is a satisfactory reagent but it is also slow to react with hindered hydroxy groups. The reactivity can be increased by using catalysts and elevated temperatures. Complete reaction is not always necessary since the alpha hydrogen peaks in the spectrum of the derivative can often be seen if the isocyanate is 50% reacted.

Trichloroacetyl isocyanate is the most effective of the three reagents. It reacts almost instantaneously with primary or secondary hydroxy groups and requires only 2 or 3 minutes to react with tertiary hydroxy compounds and phenols. This reagent produces no NMR peaks of its own and it has a good shelf life. Its derivatives are fairly soluble. Concentrations of about 10% in common solvents are attainable at elevated temperatures. The main disadvantage of trichloroacetyl isocyanate is that it is not readily available; however, it can be prepared without great difficulty.

The most obvious method of determining whether a hydroxy group is primary or secondary is to measure the area of the peaks which shift and thereby determine the number of hydrogens alpha to the hydroxy group. If this is impossible because of overlapping of peaks, the magnitude of the shift will furnish the answer. Shifts of about

0.5 to 0.9 p.p.m. occur for hydrogens alpha to primary hydroxy groups compared with shifts of about 1.0 to 1.5 p.p.m. for hydrogens alpha to secondary hydroxy groups, as shown in Table I.

Because tertiary hydroxy compounds have no alpha hydrogens, the only major changes in their spectra upon reacting with isocyanates will be the disappearance of the hydroxy peaks and the appearance of NH peaks.

NH peaks from the derivatives of trichloroacetyl isocyanate are fairly sharp and usually are found near 10 p.p.m., as shown in Table I. The NH peak areas can be measured with fair accuracy and can be used to determine the total number of hydroxy groups per molecule regardless of the types of hydroxy groups present. Water does not interfere with this analysis because the products of the reaction between trichloroacetyl isocyanate and water are carbon dioxide and trichloroacetamide. The NH_2 peak of the amide occurs near 7.8 p.p.m.

Figure 1 shows a portion of the NMR spectrum of 2,2-dimethyl-5-phenyl-1,3-pentanediol at a concentration of about 10% in 1, 1, 2, 2-tetrachloroethane at 100° C. before and after reaction with trichloroacetyl isocyanate. The resonance peaks caused by the hydrogens on the first and third carbon atoms are near 3.45 p.p.m. and are overlapped so that the multiplet patterns cannot be determined. The spectrum of the derivative was recorded a few minutes after addition of an excess of trichloroacetyl isocyanate to the glycol solution and shows clearly the peaks of interest.

The peak at 4.16 p.p.m. has an area equivalent to two hydrogens per molecule and shows that the glycol had one primary hydroxy group. The observed shift of 0.71 p.p.m. confirms that the hydrogens are alpha to a primary hydroxy group. The fact that a single peak is observed shows that the second carbon atom is fully substituted. The triplet at 5.07 p.p.m. has an area equivalent to one proton per molecule and confirms the presence of one secondary hydroxy group in the glycol. The observed shift of 1.62 p.p.m. agrees with this assignment. The triplet shows the presence of two hydrogens on carbon atoms beta to the secondary hydroxy group.

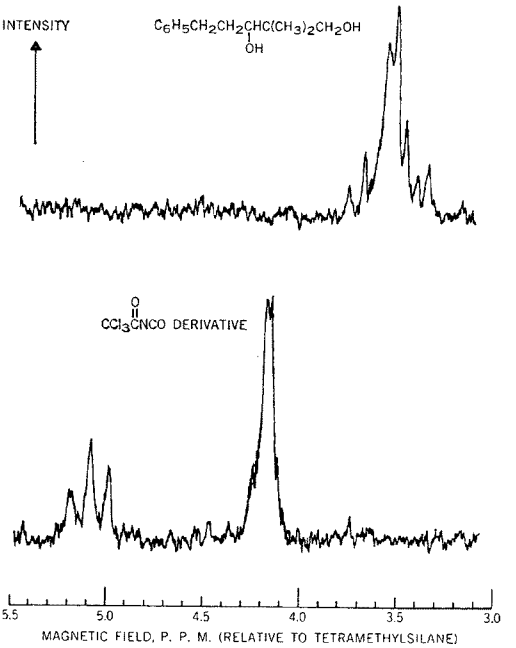

Figure 1. NMR spectra of 2,2-dimethyl-5-phenyl-1,3-pentanediol and its trichloroacetyl isocyanate derivative

In addition to the large shifts described above, it is sometimes found that reacting an alcohol or glycol with trichloroacetyl isocyanate produces small shifts of peaks other than those caused by hydrogens alpha to hydroxy groups; then the spectrum of the derivative is helpful in determining structural features other than those of the hydroxy portion of the molecule.

By choosing a reagent of the proper reactivity, and adjusting concentrations and temperature, one can produce reactions which proceed at measurable rates. This is a simple and rapid method for determining the relative reactivities of different types of hydroxy groups in the same molecule or in a mixture of alcohols. Careful work will give data suitable for determining reaction kinetics. A detailed kinetic study is presently underway.

Table I. NH Peak Positions and α-Hydrogen Shifts for Trichloroacetyl Isocyanate Derivatives[a]

Compound	α-Hydrogen shift, p.p.m. Primary hydroxy	α-Hydrogen shift, p.p.m. Secondary hydroxy	NH peak position, p.p.m.
Butyl alcohol	0.72		10.1
sec-Butyl alcohol		1.24	10.1
Isobutyl alcohol	0.70		10.2
1,3-Butanediol	0.60	1.08	10.2, 10.3
2,2,4-Trimethyl-1,3-pentanediol	0.67	1.07	10.3, 10.4
tert-Butyl alcohol			9.8
p-Cresol			10.6

[a] Recorded as 10% solutions in acetone.

ACKNOWLEDGMENT

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Mass Spectrometric Differential Thermal Analysis

SIR: In the previous article dealing with mass spectrometric thermal analysis (MTA) and differential thermal analysis (DTA) (*2*), it was mentioned that progress was being made toward the incorporation of MTA and DTA into a single instrumental method. The purpose of this communication is to describe one of the possible methods, the basic mechanical and physical aspects of the system, and some of the preliminary data which are compared to those previously obtained by MTA experiments.

The basis of the system is the remote cell adapter that can be purchased as an accessory to the Du Pont Differential Thermal Analyzer (*1*). The bell jar, base plate, and furnace assembly can be readily transferred between the main instrument and the remote cell adapter. A gasket supplied by the manufacturer separates the base plate–bell jar–furnace assembly from the base plate of the adapter assembly and allows either vacuum or high pressure modes of operation.

Mechanical connections are made to the base plate of the adapter (Figure 1) in the following manner: Opening 1 is fitted with $^1/_4$-inch o.d. copper tubing which is connected to a two-way valve opening to the atmosphere and is the purge gas exit. Opening 2 is plugged. Opening 3 is fitted with $^1/_4$-inch o.d. copper tubing which is connected to a vacuum pump through a valve. Opening 4 is fitted with $^1/_{16}$-inch o.d. stainless steel tubing connected to a three-way valve (*3*), which connects to a vacuum pump on the second arm and opens to the mass spectrometer on the third arm. Opening 5 is fitted with $^1/_4$-inch o.d. copper tubing connected to a two-way valve and is used to conduct a purge gas into the system as desired. The system is thus equipped to provide a sample to the mass spectrometer from any pressure between roughly 10^{-3} torr to 2 atmospheres with any desired purging gas.

Openings 1, 3, and 5 open through the gasket directly into the bell-jar and furnace assembly. Opening 4 is connected to the furnace by $^1/_8$-inch o.d. tubing as described in Figure 2. This permits direct sampling of any gas evolved from the sample during the heating process into the mass spectrometer. The heater block was drilled as shown to accommodate the tubing.

The vacuum pump is connected by one line directly at the valve controlling gas flow to the mass spectrometer in an effort to provide as good a control over the gas flow into the mass spectrometer and as small a "dead volume" as was possible. The latter consideration is perhaps the most important if the changes occurring in the vapors evolved from the sample are to be studied with any degree of fidelity.

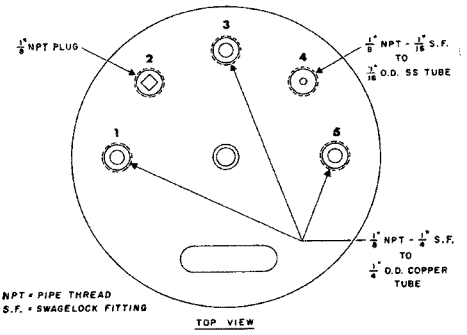

Figure 1. Base plate adapter

The first compound studied utilizing this system was triphenyltin hydroxide. An MTA scan of this compound (*4*) at a mass spectrometer (and hence sample) pressure of $<10^{-6}$ torr indicates that water is released in a diffusion controlled process over a wide temperature range. Maximum water release is noted at 65° C. When the system described above is used, at a pressure of 10^{-3} torr, two endotherms are noted on the DTA trace, one occurring at 100° C., and another occurring at 124° C. The second of these is the characteristic melting point of bis(triphenyltin)oxide as previously established by DTA at atmospheric pressure (*4*). A comparison with the trace from the scanner on the mass spectrometer monitoring water at *m/e* 18 shows a maximum occurring at about 103° C., indicating that the first endotherm is due to water release from the sample. The slight temperature difference (actually a time lag) is due to the time necessary for the gas to flow from the sample in the DTA well to the ionizing region, a distance of about 70 cm. This time lag, usually of the order of 30 sec., is caused by an excessive gas volume on the high pressure side of the valve. Changes are contemplated to

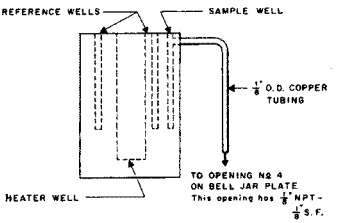

Figure 2. Furnace assembly

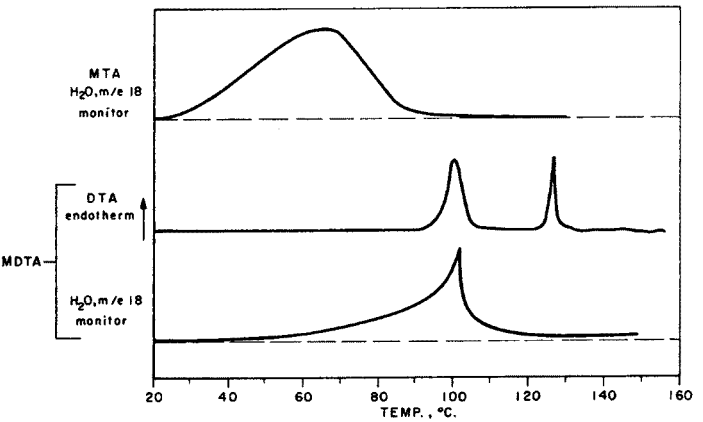

Figure 3. Ph_3SnOH

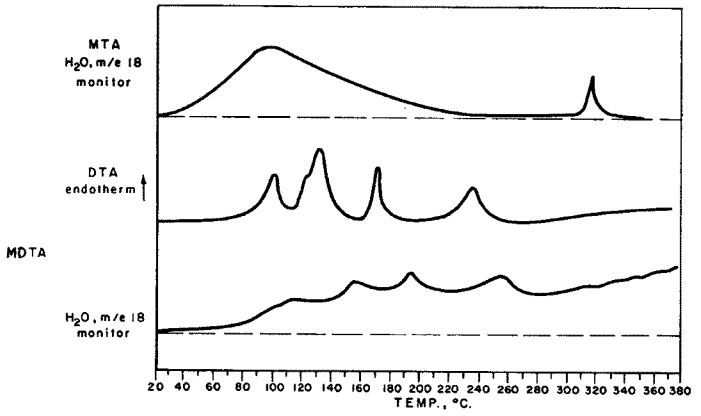

Figure 4. $MgCl_2 \cdot 6\ H_2O$

reduce this volume and with this the time lag. Figure 3 compares the various runs.

As a second example, $MgCl_2 \cdot 6H_2O$ was studied, also at a pressure of 10^{-3} torr. Again, H_2O at m/e 18 was monitored. A comparison of the data from the MTA scan monitoring water and from the combined instrumentation can be made by examining Figure 4. The apparatus functions quite well and will prove to be very useful in monitoring thermal decomposition products and phase changes in one operation. Discrepancies initially noted between the MTA and DTA scans in this work are probably caused by the pressure difference between the two operations; MTA work being done at a factor of 10^3 to 10^4 lower pressure. This is particularly evident for a fast release of water at about 310° C. and 10^{-7} torr (sharp peak in the MTA scan in Figure 4) as compared with a slow diffusion process at 10^{-3} torr [gradual increase in base line for both MDTA (mass spectrometric differential thermal analysis) scans].

The technique of MDTA will, then, be particularly useful in the study of pressure dependent thermal reactions.

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Determination of Americium-243 by Separation and Counting of Neptunium-239 Daughter

SIR: A rapid, precise method was developed for determining low concentrations of Am^{243} in actinide-fission product mixtures. The determination is based on the separation and counting of 56-hour Np^{239}, the decay daughter of Am^{243}.

Although Am^{243} is an active α and γ emitter, it is frequently encountered in systems in which its contribution to the total activity is so low as to make direct measurement by α or γ spectrometry impossible. Methods involving the separation of Am from Cm and fission products are time consuming and require an exacting technique. The mass spectrometric isotope dilution method reported previously by Banick, Carothers, and Donaldson (*1*) is the most precise of those that have been used in this work. However, the method not only requires the use of an expensive mass spectrometer, but requires chemical purification to obtain a sample that is very low in solids and β-γ radioactivity.

A convenient method for determining the concentration of Am^{243} consists of separating and counting Np^{239}, the product of the Am^{243} α decay. The Np count at secular equilibrium (Np eq.) is compared with that of samples of known Am^{243} concentration.

EXPERIMENTAL

The ratio Np eq./Am^{243} was established by analyses of eight samples standardized by the mass spectrometric method referred to above. Samples were undisturbed for at least twenty days to allow the Am^{243}–Np^{239} system to reach equilibrium. Aliquots of the samples containing between 0.1 and 5.0 μg of Am^{243} were taken, and Np^{239} was then extracted into 2-thenoyltrifluoroacetone (TTA) by the method of Murray (*2*). Of the gamma emitters present (Zr^{95}–Nb^{95}, Ce^{144}–Pr^{144}, $Cs^{134,137}$, $Ru^{103,106}$), only Zr^{95}–Nb^{95} was extracted with the Np^{239}. The extract was

Table I. Ratio of Np^{239} Activity to Weight of Am^{243} in Solutions of Irradiated Pu^{239}

Am^{243} (mg./ml.)	Np^{239} eq. (c./s./ml.)	Np^{239} eq. (c./s./mg.) Am^{243}	Apparent[a] counting efficiency, %
0.0173	2.01×10^4	1.16×10^6	16.23
0.0173	1.98	1.14	15.94
0.0173	1.93	1.12	15.60
0.0173	1.98	1.12	15.66
0.0173	1.96	1.13	15.80
0.1555	17.0	1.09	15.24
0.1555	16.8	1.08	15.10
0.1555	16.8	1.08	15.10

Average = 15.59 ± 0.39

[a] Apparent counting efficiency = $\frac{Np^{239}\ c./s./mg.\ Am^{243}}{7.15 \times 10^8\ d./s./mg.}$ with $T_{1/2}$ Am^{243} = 7950 years.

counted in a 5- × 5-inch NaI (Tl) well crystal connected to a 256-channel pulse height analyzer. The portion of the γ spectrum between 0.20 and 0.50 m.e.v., which included the 0.22 and 0.28 photopeaks, was used to calculate the Np^{239} count rate. This count rate was corrected for the contribution made by the Zr^{95}–Nb^{95}.

DISCUSSION

Table I is a summary of the eight determinations that were made to establish the relationship between Np^{239} counts and Am^{243} concentrations at equilibrium (Np eq./Am). The figure in column 4 is referred to as an "apparent counting efficiency," since it also includes the errors involved in separating the Np.

The results of Table I were then applied to the analyses of sixteen samples from laboratory scale studies of proposed processes for actinide-lanthanide separation and americium-curium separation. Where the age or history of the sample was uncertain, two extractions were necessary. The first Np extract was discarded and new Np was allowed to "grow in" for a specified time, usually about twenty-four hours. The "in-grown" Np was then extracted, counted, and corrected to equilibrium. The amount of Am^{243} in the samples was also determined by the mass spectrometric method. The average recovery of Am^{243}, when analyzed by separating and measuring its Np^{239} daughter activity, was 99.5% of the value obtained by the mass spectrometric method. The relative standard deviation of an individual determination was ±3.3%.

ACKNOWLEDGMENT

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Mass Spectrometer Used as Detector and Analyzer for Effluent Emerging from Capillary Gas Liquid Chromatography Column

Sir: One of us (*5*) recently described a combination mass spectrometer–gas chromatograph which employed two molecular separators coupled in series between the column and the inlet line of the mass spectrometer. With this technique, the sample-to-helium ratio is increased at least 100 times, and good spectra were obtained from less than 1 μg. of material. This communication describes the extension of this combination instrument to capillary gas liquid chromatography columns. The increase in resolution normally obtained with capillary columns is extremely useful in analyzing mixtures of compounds having similar properties—i.e., the fatty acid esters, C_{18}, $C_{18:1}$, $C_{18:2}$, and $C_{18:3}$. With this combination instrument, capillary or packed columns can be used without modification of the inlet system of the mass spectrometer. The time required to change from a packed column to a capillary column is less than $^1/_2$ hour.

Other differently designed combination instruments using capillary columns have been described (*1*, *3*, *4*, *6*), but attention has been directed chiefly to the analysis of compounds with low molecular weight.

EXPERIMENTAL

Apparatus. The arrangement used for connecting the capillary column to the mass spectrometer varies from that previously reported (*5*) in that only one molecular separator is used and that a part of the total ion current is collected on a plate in the analyzer tube rather than in the source. Continuous registration of the total ion current serves as the gas chromatographic record. The helium pressure at the sample inlet side was in most cases 1.0 kg. per sq. cm., giving a flow rate of about 0.5 ml. of He per minute. The operating temperatures were: ion source, 250° C.; injection port, 285° C. The column was run either isothermally or programmed linearly. The temperature programmer was the same as that used earlier (*5*).

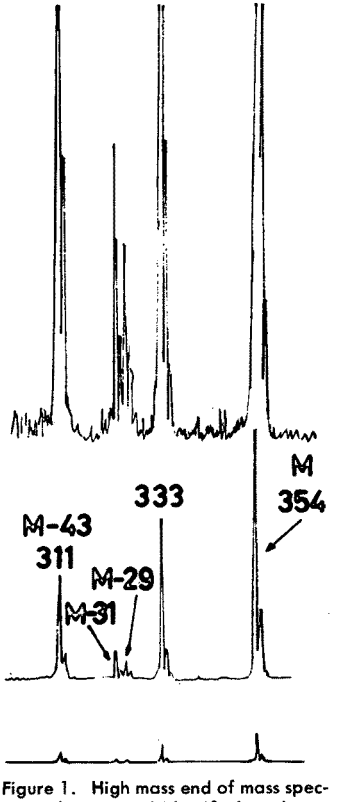

Figure 1. High mass end of mass spectrum of compound identified as docosonoate

Galvanometers sensitivity ratios, 1:10:100

GLC Column. A 90-foot stainless steel capillary column, 0.01-inch i.d., 20% diethyleneglycolsuccinate (DEGS) (Applied Science Laboratories, State College, Pa.) supplied by M. E. Mason, Oklahoma State University, was used. Methyl undecanoate was obtained from Applied Science Laboratories. It was equipped with a 7:1 precolumn split device. Methyl esters were prepared from peanut oil by the method of Mason, Eager, and Waller (*2*). The samples were injected onto the GC column in 0.1 to 0.5 μl. of redistilled acetone. Temperatures above 170° C. were avoided because of excessive bleeding.

RESULTS AND DISCUSSION

Figure 1 shows the high mass end of the mass spectrum of docosanoate from the injection of 10 μg. of peanut oil methyl esters. The peaks in the *m/e* 333 region are caused by column bleeding. This spectrum was recorded when the concentration was less than 0.2 μg. [calculation based on the average content of docosanoate in peanut oil (*2*)], the retention time was 46 minutes, and the GC peak height was 32 mm. The most sensitive galvanometer deflection was 470 mm., which indicated that the molecular ion of a mass spectrum taken

at a concentration of 2 nanograms (about 6 μμmoles) would be visible (about 5 mm. high on the most sensitive galvanometer). A GC peak height of 1 mm. would correspond to approximately 0.6 nanogram. A GC peak of 56 mm. was obtained from 28 nanograms of standard methyl undecanoate (retention time, 14.5 minutes). Because a 1-mm. peak is visible, it follows that 0.5 nanogram or 2.5 μμmoles can be detected. It is possible to make the total ion current detecting unit at least 10 times more sensitive, but routine operation of the combination instrument at this setting was unsatisfactory.

This combination mass spectrometer–gas chromatograph can detect as little as 0.5 nanogram of a substance, provide a molecular ion peak at a concentration of 2 nanograms, and provide an interpretable mass spectrum from 20 nanograms. These values are typical for methyl esters of fatty acids such as methyl undecanoate or methyl docosanoate.

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Molybdenum(V)—Thiocyanate Complex Extracted into Chloroform

SIR: The reduction of acidic solutions of molybdate by stannous chloride in the presence of thiocyanate has been used as the basis for the spectrophotometric determination of molybdenum. Because this reaction is kinetically and mechanistically complex, careful regulation of the many variables in the system is required to achieve analytical reproducibility. One representative procedure is that of Crouthamel and Johnson (*3*) involving an aqueous-acetone solution for the reduction medium. Another approach was used by Wilson and McFarland (*12*) in which the thiocyanate complex of the reduced molybdenum is extracted into chloroform in the presence of a quaternary ammonium thiocyanate. Although the thiocyanate complex measured in these procedures contains molybdenum in the +5 oxidation state, the exact identity of the colored species is uncertain. Perrin (*9*) concluded that uncharged $MoO(SCN)_3$ is formed in aqueous-acetone. It is the purpose of this communication to report the isolation of oxypentathiocyanatomolybdate (V) ion from a chloroform extract.

Solid molybdenum(V) chloride is dimeric with an octahedral arrangement of the chlorine atoms about the molybdenum, and a similar structure has been assigned by Mitchell and Williams (*8*) to pyridinium salts of $[MoO_2(SCN)_3]^{-2}$ from an analysis of infrared spectra. Recently, Allen *et al.* (*1*) examined several salts containing the oxyhalide ions, $[MoOX_4]^-$ and $[MoOX_5]^{-2}$, and deduced that the latter is an octahedral monomer.

Aryl "onium" ions, including tetraphenylarsonium, tetraphenylphosphonium, and quaternary ammonium ions, have been useful both in the extraction of inorganic anions into water immiscible polar solvents (*4*) and in the precipitation of anionic coordination complexes (*13*). In these applications the union between the complex ion and the "onium" cation is an associated ion pair in the nonaqueous solvent and an ionic bond in the solid (*11*, *13*). For the present study, triphenylsulfonium bromide was used to extract and precipitate oxypentathiocyanatomolybdate(V) ion from acidic media, as shown by the net reaction in Equation 1.

$$[MoOCl_5]^{-2} + 5\,SCN^- + 2\,(C_6H_5)_3S^+ \rightarrow [(C_6H_5)_3S]_2[MoO(SCN)_5] + 5\,Cl^- \quad (1)$$

The solution of oxypentachloromolybdate(V) ion was obtained by dissolving molybdenum(V) chloride in dilute hydrochloric acid.

EXPERIMENTAL

The absorption spectrum of the thiocyanate complex of molybdenum(V) was determined with a Beckman Model DU spectrophotometer.

Reagents and Solutions. Triphenylsulfonium bromide was prepared by the Grignard reaction reported by Potratz and Rosen (*10*). The melting point of the product was 285–6° C., after recrystallization from acetone. A 0.01*M* solution was made in water.

Molybdenum pentachloride was synthesized by the direct union reaction analogous to that for tungsten(IV) chloride (*7*). Manipulations of this compound were made in a dry nitrogen atmosphere. A 0.05*M* stock solution of molybdenum(V) was made by dissolving $MoCl_5$ in 3*M* HCl.

Preparation of Bis(triphenylsulfonium)Oxypentathiocyanatomolybdate (V). An aqueous solution containing 0.24 mmole of the stock molybdenum(V) and 8 mmole of ammonium thiocyanate in a final volume of 80 to 100 ml. was allowed to stand in a separatory funnel for 30 minutes. A 0.24 mmole portion of the triphenylsulfonium bromide solution was added, and the mixture was immediately extracted with successive 50-ml. volumes of reagent grade chloroform until no red color appeared in the chloroform phase. The combined extracts were dried over calcium sulfate, and this solution was slowly concentrated at room temperature in a vacuum desiccator with gentle suction from a water aspirator. When crystals began to form, the chloroform solution was cooled in an ice bath and the solid was filtered with suction.

The crude product was recrystallized from chloroform to give a final yield of 9.3%. The dark red solid had a melting range of 161–2° C. and an absorption band at 466–7 mμ in chloroform. Results from elemental analysis by micro methods are summarized in Table I.

Table I. Elemental Analysis

Element	Exptl. %	Calcd. % $[(C_6H_5)_3S]_2[MoO(SCN)_5]$	Calcd. % $(C_6H_5)_3S[MoO(SCN)_4]$
C	52.0	52.9	35.6
H	3.20	3.26	2.49
Mo	11.15	10.35	15.8

RESULTS AND DISCUSSION

The addition of triphenylsulfonium ion to the acidic reaction mixture containing Mo(V) and thiocyanate yields a deep red amorphous precipitate in the absence of chloroform. Since the identity of the chloroform-soluble species was the principal concern in this work, isolation of the water-insoluble product was not attempted. When the chloro-complex of Mo(V) in 3*M* hydrochloric acid was treated directly with the triphenylsulfonium bromide, no precipitation occurred.

A trial preparation of tris(tetraphenylarsonium) hexathiocyanatoferrate (III) was undertaken as a model for synthesis of the corresponding Mo(V) compound. Finely divided crystals were obtained from a water solution of the reactants; however, analyses for C, H, As, and Fe differed by more than 5% from the theoretical values. The visible and near ultraviolet spectrum for chloroform extracts of the reaction mixture contained a sharp absorption peak at 315 mμ, indicating tetraphenylarsonium thiocyanate was present. The same band was found in the chloroform extract of the aqueous mixture of Mo(V), SCN^-, and tetraphenylarsonium ion (*6*). It was concluded that tetraphenylarsonium ion is not suitable for the precipitation of anionic thiocyanate complexes without coprecipitation.

The results in Table I indicate that $[MoO(SCN)_5]^{-2}$ is extracted into chloroform when a large organic cation is present. In the earlier application of the method of continuous variations to the molybdenum–thiocyanate system the measurement of the maximum absorbance in the chloroform phase corresponding to a given ratio in the aqueous phase (*6*) does not necessarily give a correct value for the Mo:SCN ratio in the extract. Although the distribution ratio for the complex was not determined, it is likely that the 1:6 ratio for Mo:SCN obtained earlier reflects a displacement of the maximum in the continuous variations plot toward a higher ratio because of incomplete extraction of the complex. Babko (*2*) found evidence for a Mo:SCN ratio of 1:5 in solutions of reduced molybdate containing high concentrations of thiocyanate, but he assumed this represented an uncharged species.

It is clear that one of the pentavalent molybdenum thiocyanate complexes is anionic. Haight (*5*) assigned a dimeric structure in Equation 2 for the Mo(V) species formed by the Sn(II) reduction of molybdate in 3*M* hydrochloric acid.

$$Mo(IV) + Mo(VI) \rightarrow [Mo(V)]_2 \quad (2)$$

The 2:1 stoichiometry of the onium ion–molybdenum complex above does not distinguish between a monomeric or dimeric structure for the oxypentathiocyanatomolybdate(V); however, Wilson and McFarland (*12*) obtained a distribution ratio in chloroform indicating a 1:1 association of a quaternary ammonium ion with Mo(V) at very low concentrations of the complex.

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Spectrophotometric Determination of Calcium in Uranium Using Glyoxal Bis-(2-Hydroxyanil)

SIR: Glyoxal bis-(2-hydroxyanil) (hereafter glyoxal) is a specific reagent for spot test detection of calcium (*1*). The spectrophotometric determination of calcium using this reagent was applied by Williams and Wilson (*3*) for solutions of calcium in the presence of common cations including magnesium, strontium, and iron.

Nuclear pure ammonium diuranate and uranium oxides (UO_3, UO_2, and U_3O_8) have been analysed in our laboratory for their calcium content with this reagent, after the separation of the uranium with hydrogen peroxide precipitation (*2*), tributyl phosphate (TBP) extraction in nitric acid, or retention of the uranyl sulfate complex on an anionic ion exchange resin(sulfate form).

EXPERIMENTAL

Apparatus. Measurements were made with a Hilger spectrophotometer (Hilger & Watts, Ltd., London), using 1-cm. matched, square cells. Conical glass centrifuge tubes (12 cm. of height and 12-ml. capacity, with glass stopper) were used for the color extraction.

Reagents. Glyoxal (E. Merck Ag. Darmstadt). Make a 0.4% w./v. solution of glyoxal in ethyl alcohol. Prepare this solution fresh daily.

Prepare a color developing solution by dissolving 10.0 grams of sodium hydroxide and 0.5 gram of sodium carbonate in 100 ml. of water.

Ion exchange column. Transfer 5 ml. of Nalcite SAR (30–50 mesh) anionic ion exchange resin to a glass tube (8-mm. i. d.) column and condition the resin by passing 25 ml. of 1*M* H_2SO_4 and wash with 50 ml. of water.

Procedure. SEPARATION OF URANIUM.

Precipitation of Uranium by Hydrogen Peroxide.

Use uranyl nitrate solution prepared by dissolving the samples (U_3O_8, UO_2, UO_3, or ammonium diuranate calcinated to U_3O_8) with minimum amount of 6*M* HNO_3 and dilute to desired volume with water. The optimum pH of the final solution is 1–3.

Pipet 2 to 10 ml. of uranyl nitrate containing 100 to 500 mg. of U_3O_8 (2 to 14 μg. of calcium) into a centrifuge tube, add 1 ml. of 30% hydrogen peroxide, mix thoroughly with a glass rod and keep in the refrigerator for 20 minutes. Centrifuge and pour the supernatant through a Whatman 41 filter (previously washed with water), recovering the filtrate directly into a platinum crucible (to avoid calcium from glass). Add 2–3 drops of 30% hydrogen peroxide to the centrifuge tube and make the volume 5–7 ml. with demineralized water, mix the precipitate thoroughly with a glass rod and centrifuge again. Collect the second supernate using the same filter. Evaporate the filtrate to 3–5 ml. on a hot plate, transfer to a 25-ml. volumetric flask and make up to the mark with water. Use aliquots of this solution for the determination of calcium.

Extraction of Uranium with Tributyl Phosphate.

To 2 ml. of uranyl nitrate solution (100 mg. of U_3O_8), add 5 ml. of 6*M* HNO_3 and extract 5 times with 1 ml. of 20% TBP in CCl_4, and finally wash the aqueous phase twice with 2 ml. of

pure CCl_4. Filter the aqueous phase through a Whatman filter paper previously washed with water. Evaporate the aqueous phase to dryness using a platinum crucible, after adding one drop of $HClO_4$. Wash the crucible using 2 ml. of water containing one drop of $2M$ HCl and transfer the solution into a 10-ml. volumetric flask. Take an aliquot for the determination of calcium.

Ion-exchange Separation.

Use uranyl sulfate solution prepared by fuming uranyl nitrate solution with minimum amount of sulfuric acid for complete elimination of nitric acid and finally dilute with water to a desired volume. In the case of ammonium diuranate, dissolve 5.0 grams of ammonium diuranate of nuclear purity on a hot plate with $1M$ H_2SO_4 adding the last amounts of the acid drop by drop; transfer the solution to a 100-ml. volumetric flask and dilute to the mark with water. The pH of this solution should be 1–2.

Dilute an aliquot of the uranyl sulfate solution containing 100 mg. of U_3O_8 to 10–12 ml. with water and percolate through the anionic exchanger column with a flow rate of 5–8 drops per minute. Wash the column with 10 ml. of water. Collect the effluent and wash into a platinum crucible and evaporate to dryness. Add 1 drop of $1M$ H_2SO_4 to the platinum crucible and transfer the content to a centrifuge tube using 2 ml. of water dropwise.

To prepare the column for the next experiment elute the resin with 25 ml. of $1M$ HNO_3 and wash with 25 ml. of water, 25 ml. of $1M$ H_2SO_4, and 50 ml. of water, successively.

Extraction and Estimation of Calcium. For the color development and extraction of calcium, pipet 2 ml. of solutions obtained in any of the above steps, into the centrifuge tube, add 2 drops of 10% hydroxylamine hydrochloride, stopper, and mix thoroughly. Add 2 ml. of glyoxal solution, mix well, and add 0.5 ml. of color-developing solution. Finally, add 4 ml. of chloroform, stopper, and extract the calcium–glyoxal complex inverting the tube about 20 times. (It is essential to do the extraction like this since violent mixing results in a decrease in the absorbance, thereby giving lower values for calcium. A similar behavior has been observed also when the organic phase is filtered. The reasons for both have not been investigated.) Centrifuge for one minute (2400 r.p.m.) and remove the supernate using a pipet. Transfer the organic phase into the spectrophotometer cell and measure the absorbance at 535 mμ using chloroform in the other cell.

For the determination and standard curve, develop the color and extract the glyoxal–calcium complex of two centrifuge tubes one at a time and make the measurements immediately.

Reagent Blank. Prepare a reagent blank using the same amounts of reagents. Develop the color and measure the absorbance exactly as for the calibration curve. Subtract this value from the determination for the exact correction.

Calibration Curve. Prepare a standard curve using 2-ml. aliquots of the solutions containing 1, 2, 3, 4, 5, 6 and 7 μg. of calcium per ml., and follow the procedure given for the extraction of calcium for the determination of the absorbance of the calcium complex. Plot calcium in micrograms against absorbance.

RESULTS AND OBSERVATIONS

Table I shows typical results of the determination of calcium in one batch of nuclear grade uranium. The results are in good agreement for the three different methods used for the separation of uranium. However, the hydrogen peroxide method is preferred to the other two because it is more simple, less time consuming, and the blank corrections are small.

For the TBP extraction a relatively large amount of HNO_3 is used and because even C.P. nitric acid contains considerable amounts of calcium, the reagent blank correction is higher than in the hydrogen peroxide or ion exchange separation procedures. With TBP extraction the last traces of TBP have to be washed carefully with CCl_4; otherwise the phosphate ions produced by the decomposition of TBP lower the calcium values.

In the anion exchange resin separation, the flow rate for the small column used has to be controlled and the acidity of the sulfate solution is critical, the optimum pH being 1–2. Finally, there is a relatively large volume of solution to be evaporated.

Table II contains the results of the determination of calcium in the same batch of uranium analyzed by this procedure after the separation of uranium by precipitation with hydrogen peroxide. In these analyses the recovery of calcium is controlled by adding a spike of calcium.

Table III shows the results of calcium determination performed using uranyl nitrate solution with negligible content of calcium. This solution is prepared by dissolving the uranium oxide which was obtained from nuclear grade uranium by hydrogen peroxide

Table I. Calcium in Uranyl Nitrate Solution (H_2O_2 and TBP Procedures) and Uranyl Sulfate Solution (Ion Exchange Procedure)

Procedure	No. of determinations	Ca/U_3O_8 Av., p.p.m.	Ca/U_3O_8 Std. dev.
H_2O_2	5	46.0	1.6
	3	44.0	1.7
	4	46.8	1.9
	5	46.4	2.1
	5	42.4	2.1
	6	47.6	4.1
Ion-exchange	6	46.8	1.9
	5	48.0	1.8
TBP	4	46.5	3.7
	4	44.8	1.0

Table II. Calcium in Uranyl Nitrate Solution (H_2O_2 Procedure)

Calcium, μg. Total	Added	Found	Ca/U_3O_8 P.p.m.	Average	Std. dev.
9.4	5.0	4.4	44		
9.7	5.0	4.7	47		
4.6	...	4.6	46		
4.8	...	4.8	48	46.8	1.9
4.9	...	4.9	49		
4.8	...	4.8	48		
9.4	5.0	4.4	44		
9.6	5.0	4.6	46		
9.5	5.0	4.5	45	46.4	2.1
4.8	...	4.8	48		
5.3	...	5.3	53		
4.6	...	4.6	46		
5.2	...	5.2	52		
7.6	3.0	4.6	46		
9.2	5.0	4.2	42	47.6	4.1
4.3	...	4.3	43		
4.5	...	4.5	45		
8.0	4.0	4.0	40		
9.1	5.0	4.1	41		
9.3	5.0	4.3	43	42.4	2.1

Table III. Calcium in Uranyl Nitrate Solution (H_2O_2 Procedure), Previously Purified by H_2O_2 Precipitation

Group	Calcium μg. Total	Added	Found	Ca/U_3O_8 p.p.m.
A	0.1	...	0.1	1
	0.2	...	0.2	2
	0.2	...	0.2	2
	0.1	...	0.1	1
B	4.8	5.0	...	...
	5.2	5.0	0.2	2
	4.9	5.0	...	...
	5.0	5.0	...	...
	5.1	5.0	0.1	1

precipitation, and subsequent calcination.

In the three separation techniques there always remain traces of uranium that interfere by imparting a violet color to the chloroform glyoxal extract. Color development experiments were made which showed that when 100 to 500 mg. of uranium were used, 0.2 to 5.0 mg. remained after separation by the three methods suggested. When hydroxylamine was added, the same experiments showed no interference. The experiments were made with or without calcium present and uranium was detected in the organic phase, chloroform, after evaporation and destruction of organic matter with HNO_3–HCl and evaporation to dryness, addition of 3–4 drops of acetic acid and 2 drops of 3% potassium ferrocyanide solution. In those experiments in which hydroxylamine was present no uranium was detected.

It has been observed that the chloroform extract of calcium–glyoxal complex starts fading after 5–10 minutes and for a series of determinations the last readings give systematically lower results. To avoid this, the color development and extraction are carried out only on two samples at a time.

Calcium is usually and routinely determined by flame photometry, which is a relatively insensitive method compared with the spectrophotometric one. Beer's law is obeyed from 0 to 18 μg. of calcium.

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Rapid Gas Chromatographic Analysis of Fractional Microgram Concentrations of Lebaycid

SIR: In the past year, Hirano and Tamura (*4*) published a spectrophotometric method for the determination of Lebaycid {*O*-dimethyl-*O*-[4-(methylthio) - *m* - tolyl]phosphorothioate}; the reported method obeying Beer's law at concentration levels ranging from 10 to 100 μg. In their procedure, the phosphorothioate compound is hydrolyzed with an alcoholic sodium hydroxide solution and the 4-methylthio-*m*-cresol obtained is condensed with 4-aminoantipyrine by the modified method of Emerson (*2*) in an alkaline sodium carbonate buffered medium in the presence of sodium periodate. The orange-colored condensation product is extracted with chloroform and determined spectrophotometrically at 458 mμ with a relative error of 3% in the 10- to 100-μg. range. The authors substituted sodium periodate for potassium ferricyanide in order to obtain lower blanks.

To circumvent the time-consuming hydrolysis by refluxing, buffering with CO_2 gas and sodium carbonate, coupling or condensation reaction and chloroform extraction steps specified in this colorimetric procedure, this communication presents a direct, rapid gas chromatographic method for the determination of fractional microgram concentrations of Lebaycid.

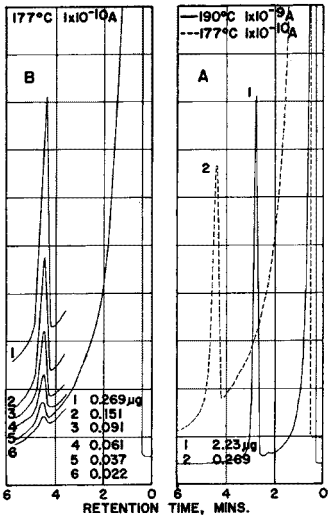

Figure 1. Gas chromatograms of Lebaycid at column temperatures of 177° and 190° C. and sensitivity settings of 1×10^{-9} and 1×10^{-10} amperes (flame ionization detector)

EXPERIMENTAL

The Jarrell-Ash Model 28-710 equipped with electron affinity and flame ionization detectors and the Bristol Dynamaster Model 1P12H560, 11-inch strip-chart recorder, 0- to 10-mv., was used for this study.

The chromatographic column was made of borosilicate glass (6-foot by $^3/_{16}$-inch o.d.) packed with 5% by weight Dow-Corning QF-1 (trifluoro propyl methyl silicone polymer) on 80/90 mesh Anakrom AS (Analabs, Inc., Hamden, Conn.). Prior to use, the column was conditioned at 250° C. for 48 hours to minimize column bleed.

Flame ionization detector sensitivity settings of 1×10^{-9} and 1×10^{-10} amperes were used for this study in addition to the following chromatographic operating conditions: hydrogen gas pressure, 7.0 psi.; air flowrate, 1.25

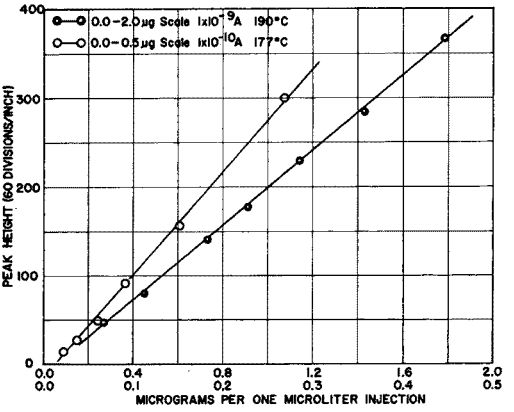

Figure 2. Plot of peak height *vs.* micrograms of Lebaycid per one microliter injection (flame ionization detector)

c.f.h.; column temperature, 177° and 190° C.; detector temperature, 250° C.; injector temperature, 280° C.; nitrogen carrier gas flowrate, 71.5 cc./minute.

To compare the area response per microgram of Lebaycid with both the electron affinity and flame ionization detectors, the electron affinity detector's senistivity was optimum when operated at 12 volts at a 1×10^{-9} ampere gain setting. With this detector, the 6-foot column was packed with 5% SE-30 (General Electric's methyl silicone gum rubber) on 80/90 mesh Anakrom AS. This liquid phase was used in view of the high background and noise level resulting from the QF-1 phase. At a column temperature of 177° C., the nitrogen carrier gas flowrate was increased to 150 cc./minute in order to obtain equivalent retention times with both liquid stationary phases. All other operating parameters were maintained similar to those noted above for the flame detector with the exception of the detector temperature which was held at 210° C.; this was limited by the detector's tritium source.

One-microliter Hamilton microsyringe injections of varying Lebaycid concentrations dissolved in benzene as solvent were made directly onto the coated column solid support; thereby eliminating the possibility of catalytic degradation at metallic surfaces.

DISCUSSION OF RESULTS

Using the conditions cited in the experimental section for the flame detector, typical chromatograms obtained for Lebaycid at 177° and 190° C. are shown in Figure 1. Chromatogram A compares the peaks obtained at two different sensitivity and column temperature settings for known amounts of the phosphorothioate compound injected, whereas Chromatogram B shows superimposed gas chromatographic peaks resulting from different concentrations of Lebaycid at 177° C. and 1×10^{-10} ampere.

By plotting peak-heights *vs.* concentration of Lebaycid at gain settings of 1×10^{-9} and 1×10^{-10} ampere, nearly linear relationships are obtained as shown in Figure 2. At 1×10^{-10} ampere and a column temperature of 177° C., as little as 22 nanograms of this compound is easily detected; thus showing the gas chromatographic procedure to be about 500 times more sensitive than the spectrophotometric analysis.

This study has also shown that the area response in square millimeters per microgram of compound at 1×10^{-9} ampere with the flame detector (1517 mm^2) is approximately 1.53 times greater than that obtained with the electron affinity detector (995 $mm.^2$). This indicates that the  grouping in Lebaycid has a poor affinity for electrons and confirms and is consistent with the findings of Cook *et al.* (*1*) and Gudzinowicz *et al.* (*3*).

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AIDS FOR THE ANALYTICAL CHEMIST

Quartz Window Cuvette Prepared by Sealing Quartz to Borosilicate Glass

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WITH THE ADVENT of commercially available automated liquid flow analytical systems, many laborious and time-consuming analyses can now be run at the rate of 60 per hour. The modular approach, extensively used for these analyses, also allows the operator to incorporate a wide variety of other laboratory instruments into an analytical scheme.

The relatively low liquid flow rate of such systems coupled with the fact that air bubbles often find their way into optical systems, either by accident or intentionally, places severe limitations on existing small volume flow cuvettes. A variety of commercial flow cuvettes designated as microcuvettes were tried as cells for a commercial spectrophotometer. These cells ranged from rectangular quartz cells and small diameter cylindrically shaped cells to the recently available microaperture flow cell. At low flow rates (several milliliters per hour), bubbles either lodged within the optical path of the cell or peak distortion was observed. At higher flow rates (several milliliters per minute), channeling was a problem in cells with large cross sectional area.

This paper describes in detail the fabrication of a streamlined, liquid flow, small volume, deep path, UV transmitting cuvette for the Beckman DB or similar spectrophotometer. Air bubbles do not lodge within the cell and peak distortion is no problem at low or high flow rates.

PROCEDURE

Prepare a heat resistant form, the dimensions of which correspond to the desired internal width and depth of the cell, from Morganite (Morganite, Inc., Canoga Park, Calif.). A form with dimensions of $^5/_{64}$ inch $\times$ $^1/_4$ inch $\times$ $1^1/_4$ inch gives a finished cell with an active volume of about 0.3 ml.

Push the form into the middle of a 12- to 14-inch length of borosilicate glass

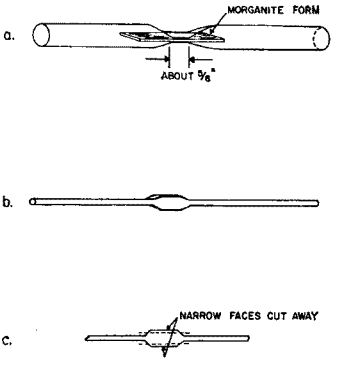

Figure 1. Steps in the fabrication of a quartz window flow cell

(a) Cell body molded over Morganite form (b) Shoulders drawn down to form inlet and exit tubes.
(c) Quartz windows are sealed onto narrow faces after borosilicate glass portion has been cut away

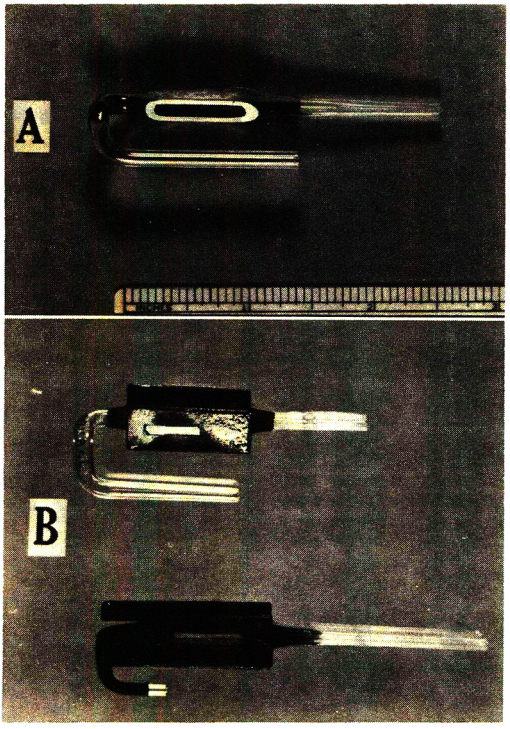

Figure 2. View of flow cells in various stages of completion

(A) Platinized borosilicate glass body ready for bonding to quartz. (B) Shorter cell, complete with exception of spacers; completed assembly, longer cell

tubing of such internal diameter that there is little clearance between the walls of the tube and the corners of the forming piece. Heat the assembly to about 200° to 300° C. while flushing the tube with nitrogen or other inert, nonpoisonous gas to drive out most of the entrapped air. At once cork one end of the tube with a solid cork and place a one-hole cork in the other end. Heat the central portion of the tube with rotation until the glass softens and begins to collapse onto the form. Continue the heating until the glass becomes quite fluid and then quickly remove the assembly from the flame and suck strongly on the end containing the one-hole stopper. At this point the assembly should appear as shown in Figure 1*a*.

After the assembly is cool, remove the form by pushing it out with a small-diameter metal rod. Gentle tapping with a mallet may be required.

The glass is then thickened near each shoulder and drawn out into heavy wall, small-bore inlet and outlet tubes as shown in Figure 1*b*. The glass forming the walls of the narrow portion of the borosilicate glass piece are removed by holding the cell against a rotating carbide-composition, wet cut-off wheel (Figure 1*c*). Use care to keep the faces parallel. Finish by grinding on a glass plate with a slurry of 300- to 400-mesh carborundum powder in water followed with 600-mesh powder and finally jewelers' rouge. Figure 2*A* shows the cell at this point. This particular cell has been platinized prior to receiving quartz windows by the second sealing method described below. Windows are salvaged from broken rectangular quartz cuvettes and are cut to shape with the wet cut-off wheel. The inlet tube has been bent so that the assembly will fit into the 1-cm. wide cell compartment of the DB.

Windows can be mounted onto the borosilicate glass body by one of two methods. The first method, which is the easiest, uses Helix R-363 epoxy resin (Carl H. Biggs Co., Inc., Santa Monica, Calif.) as the bonding agent. The ground surfaces of the borosilicate glass body are given a thin coating of the prepared resin and the windows are carefully put in place. When the resin has cured, a fillet of Helix R-318 is flowed in around the outside of the cell where the quartz meets borosilicate glass. Both R-363 and R-318 show excellent resistance to aqueous salt solutions, acids, and bases of moderate strength and a wide variety of organic solvents.

Helix-363, unlike many epoxy resins shows a slight amount of elasticity in the cured state, hence the glue line does not fail when glasses of differing coefficients of expansion are sealed to-

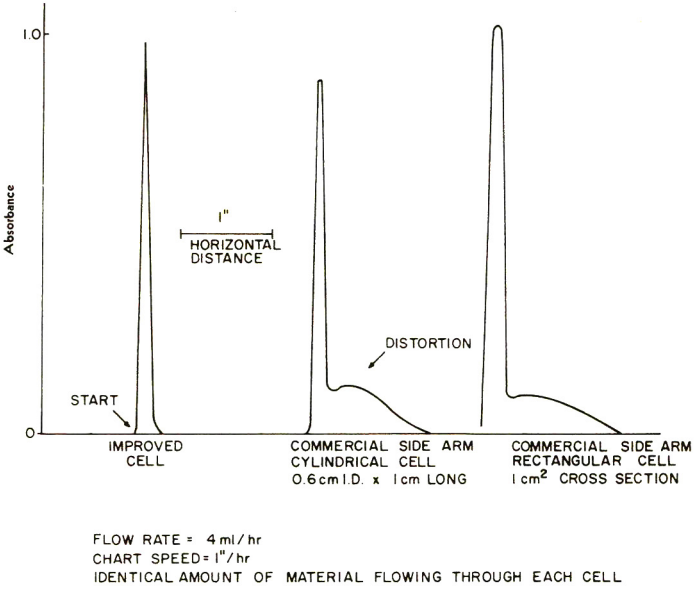

Figure 3. Flow characteristics for cells of the type described in this paper are compared with those of two commercial cells at a low flow rate

gether as in this example. Finally, the window areas are masked with narrow strips of Scotch tape, the lower inlet tube is plugged and the assembly is dipped repeatedly into a thin acetone slurry of Eccobond 51 black epoxy resin (Emerson and Cuming, Inc., Canton, Mass.) until a black deposit has been built up. After cure, the masks are removed and small rectangular Plexiglas spacers are sealed onto the broad borosilicate glass faces of the cell to make the finished cell wide enough to fit correctly into the spectrophotometer cell compartment.

If solutions of thiosulfate, cyanide, and ammonium hydroxide, which attack silver salts, are not to be encountered, the quartz windows can be sealed to the borosilicate glass in a more elegant fashion. First, the ground surfaces of the borosilicate glass body are coated with Liquid Bright Platinum No. 05 (Hanovia Liquid Gold Division, Engelhard Industries, Inc., East Newark, N. J.) and fired at 1025° F. in a furnace or lehr. The quartz windows are masked with tape and coated on the masked side with the platinizing solution.

After the coat has dried, the masks are carefully removed and the windows are fired at 1200° F. A thin layer of a thick slurry of silver chloride in glycerine–water (50/50) is applied to the platinized borosilicate glass body. The windows, platinized side toward the borosilicate glass body, are then carefully put in place. In place of the silver chloride slurry, a "gasket" of silver chloride can be cut from sheet silver chloride (A. D. Mackay, Inc., New York 38, N. Y.).

The assembly is then heated in the oven at 840° F. for 10 minutes and the cell is then allowed to cool slowly to room temperature. Masking of the outer surface of the windows and blackening of the cell is conducted as in the first method.

The cell with the longer (straight) exit tube shown in Figure 2*B* is a finished assembly; windows have been epoxy bonded. The shorter cell, assembled by the silver chloride technique, is complete with the exception of plastic spacers. Flow characteristics for two commercial cells are compared in Figure 3 with that obtained for cells described in this paper.

The silver chloride–platinized glass technique finds general use for sealing together glasses with the same or differing coefficients of expansion (*1*); seals are vacuumtight (1×10^{-10} Torr). Nickel, nichrome, copper, alumel, and tungsten wires can be sealed directly into holes drilled in glass with silver chloride as sealant (*2*).

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Trade names referred to in this paper do not imply endorsement of commercial products.

A Scanning Potentiostat

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THE PRESENT apparatus was designed to provide controlled electrical conditions for studying the electrolytic reduction of groups such as disulfides in peptides and proteins (*2*). Reduction could be effected either directly at the mercury cathode surface or indirectly in the presence of a trace amount of carrier—e.g., thiol—which is continuously regenerated to the fully reduced state by electrolysis.

The apparatus has a scanning feature for automatically producing a current-voltage curve. This enables progress of preparative reduction to be quickly checked by pushing a button, rather than by taking an aliquot from the potentiostat cell and using a separate polarograph for estimations.

The cell used, Figure 1, was similar to that of Meites (*3*) having a conical 500-ml. cathode compartment containing mercury of about 40 sq. cm. surface area. A glass stirring propeller is used to agitate the mercury cathode surface as vigorously as possible without causing detached droplets to be formed. This rapid and efficient stirring keeps the thickness of the diffusion layer to a minimum, permitting increased currents to flow, which expedites the electrolytic process. As a result of this stirring, the internal resistance of the cell is not steady and its value fluctuates in phase with the stirring motion.

Potentiostats described in the literature have the disadvantage of being slow in response where a reversible motor has been used to control the power output from a rheostat or Variac, or inefficient in supplying large currents if entirely electron tube operated. Those where the output is controlled by power transistors (*1, 4, 5*) appear to offer the best solution to the requirements of high current handling capacity and an adequately rapid rate of correction.

The present potentiostat is entirely line operated and transistorized through-

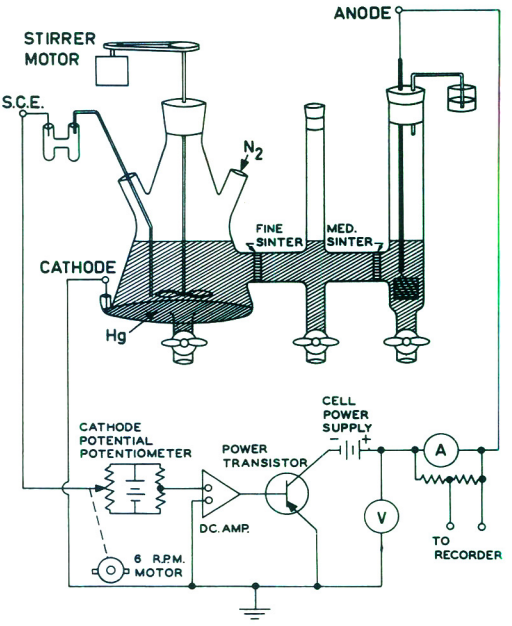

Figure 1. Cell and basic circuit

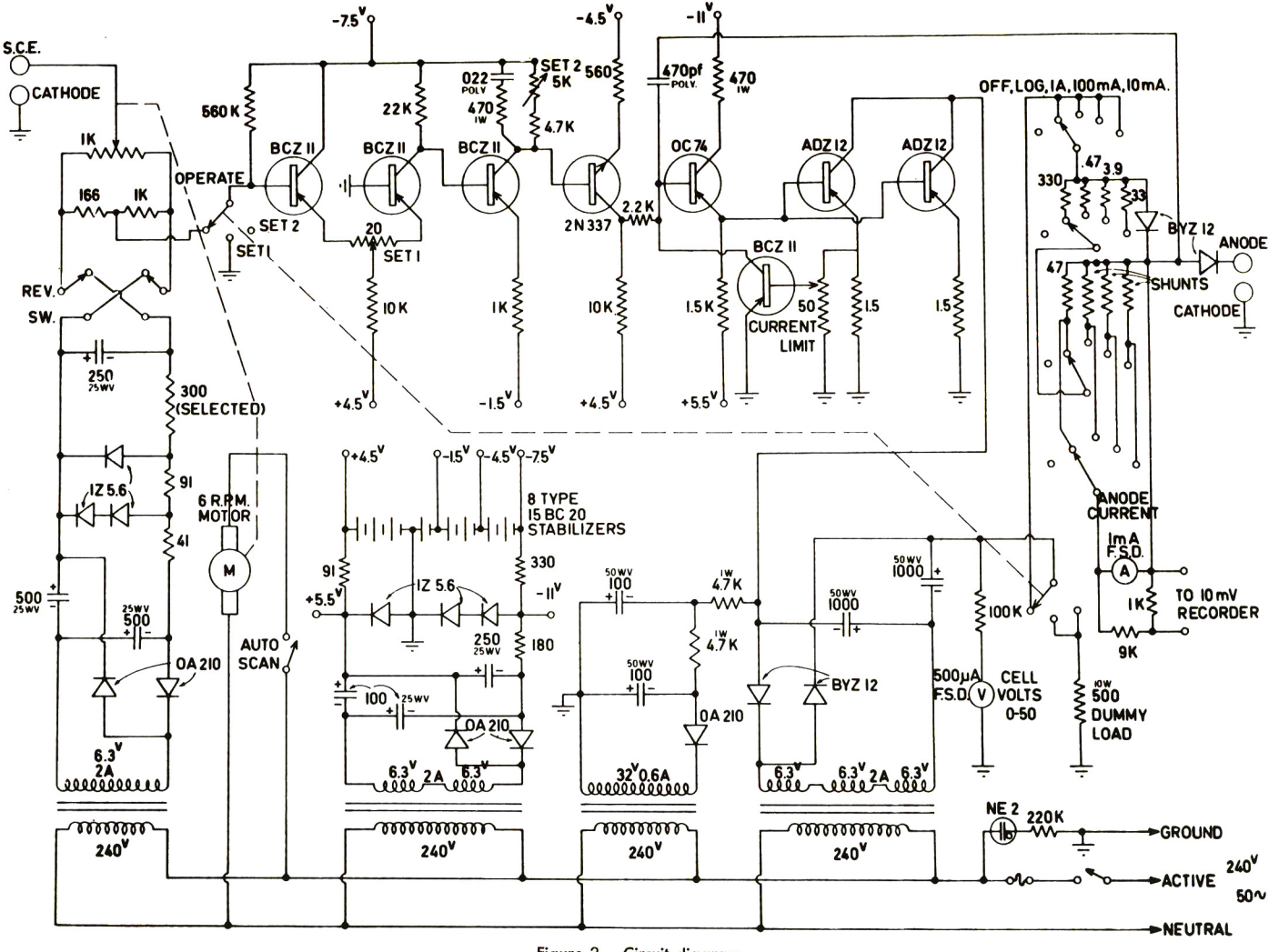

Figure 2. Circuit diagram

out, capable of supplying currents up to 1 ampere, and a maximum of 50 volts is available when cell current is small.

Figure 1 represents the basic setup. The current flowing from anode to cathode through the cell is controlled to maintain a constant preset value of potential between the mercury cathode and a standard calomel electrode (S.C.E.) immersed in the solution. This cell is used both analytically and preparatively. For the examination of a sample, a 6-r.p.m. synchronous motor coupled by a cork friction clutch, rotates the cathode potential potentiometer. The range covered by this potentiometer for the present work was chosen to be +0.5 to −3.0 volts but a reversing switch was included to extend the positive range should the need arise.

The cathode potential is scanned and the applied current, which is controlled by the potentiostat, is simultaneously plotted with a 10-mv. strip chart recorder having a chart speed of 12 inches per minute. The resulting current-voltage curve may be examined for plateau indicating reducible sites.

For preparative electrolytic reduction, the cathode potential corresponding to each plateau may be read from the curve, enabling the apparatus to be set to electrolyze at a desired cathode potential. This allows selective reduction to be carried out, as only those sites where the half-wave potential is exceeded will be reduced.

ELECTRONICS

The current applied to the cell from the voltage doubler power supply is controlled by two parallel-connected germanium power transistors type ADZ12, mounted on air convection cooled heat sinks of 80 square inch surface area each. Housing of the electronic gear in two separate units and grouping the power supply components and these heat sinks together, allowed the controls and input amplifying stages to be operated remotely from undesirable heating effects and hum pickup.

The power transistors are driven by the output from a high gain d.c. amplifier comprised of 5 transistors. The two input transistors type BCZ11 connected as a "long-tailed pair," were closely mounted in tight fitting, silicone smeared holes in a brass block to minimize the temperature difference between them. The BCZ11 fed from this input pair was also mounted in this brass block to increase its thermal inertia.

The operating conditions of the d.c. amplifier input were chosen to give good voltage sensitivity while drawing least current from the standard calomel electrode.

This was achieved by an initial setting up procedure which ensured that the point where zero input current flowed was about in the middle of the controlled cell voltage range. As shown in the circuit diagram Figure 2, a switch labelled Operate, Set 1, Set 2, and two potentiometers are provided for this purpose. These are located at the rear of the control unit and by successive adjustment of potentiometers Set 1 and Set 2, the cell voltage reading is brought to 25 volts on dummy load with the switch in each Set position.

A measured input current required to turn the cell voltage from midscale down to zero and up to the maximum of 50 volts on dummy load was less than 10^{-8} ampere of appropriate polarity. The overall gain of the system was such that a change from plus to minus 300 μv. was sufficient to change the cell voltage from zero to 50 volts under these conditions.

To achieve stable, oscillation-free operation, the two phase-correcting networks and amplifier gain were adjusted for optimum on the completed setup. This was necessary as the cell forms part of the feedback loop and extremes of experimental conditions within the cell were explored for possible instability with a high gain, broadband oscilloscope. The circuit values were chosen for maximum safe gain for the cell used and no untoward tendency to instability has been shown over a $2^1/_2$ year period. If a reduction of gain is necessary for some other experimental conditions not yet encountered, a series resistance can be added externally to the S.C.E. input lead.

The power supplied to the cathode potential potentiometer is regulated by 2 stages of Zener diodes operated under conditions to give low temperature coefficient. Some care in transformer placement and shielding of components was necessary here to prevent hum being injected into the input from this floating supply. This was achieved satisfactorily provided the active and neutral line leads were not reversed. A neon indicator was included which glows to indicate the correct connection.

Total ripple voltage from all sources between S.C.E. terminal and cathode under typical experimental conditions was less than 100 μv. peak to peak.

The power supplied to the transistor amplifying stages is also regulated by Zener diodes and use is made of 1.5-volt cadmium–nickel electrolytic stabilizers to provide convenient low impedance voltage tappings.

For reasons of economy, PNP germanium rather than silicon power transistors were used for the output stage and an additional small power supply was included to cancel their leakage current. By this means the cell current may be reduced to zero, but to prevent any reverse current being applied to the cell during part of the Auto. Scan cycle, a series power diode is included in the anode current lead.

To protect the power transistors in the event of an overload, a limiting circuit is employed which prevents a current greater than the maximum permissible from being exceeded. The current limit potentiometer is set so 1-ampere cell current causes about 600 mv. to be fed to a silicon transistor which then conducts and prevents any further significant increase in current through the power transistors.

Cell current is measured on a multirange meter protected against overload by a power diode, which includes a Log position (*1*) to enable a small residual end current to be detected after a large initial current without recourse to range changing. The output to operate a 10-mv. recorder is taken from a voltage divider across this meter.

STABILITY

The electrical zero drift of the potentiostat system was assessed in the following way.

The cathode potential potentiometer was set at 1.2 volts and an accurately measured input voltage from an adjustable source of 1.2 volts nominal, with an internal resistance of 2 kohms, was connected between the S.C.E. and cathode terminals. This input voltage was adjusted for a reading of 25 volts on the cell volts meter with a 500-ohm dummy load connected between anode and cathode terminals. Variation with time from this set reading of 25 volts was corrected by re-adjustment of the applied input voltage.

Once the apparatus had come to temperature equilibrium within an air-conditioned laboratory, the maximum equivalent input drift variation was less than ±1 mv. for periods of several hours.

COMPONENT PARTS

This apparatus was constructed with components readily available in Australia.

Operation from a 117-volt, 60-cycle line however, could be achieved by choosing the 6-r.p.m. motor and transformer primaries to suit this line instead of 240-volt, 50-cycle as shown.

Wire wound resistors and potentiometers were used in most instances for stability reasons rather than their 3-watt rating. Where carbon resistors have been used they are of 1-watt rating and are labelled 1*W* on the circuit diagram. Standard filament-type transformers were used for the power supplies.

Some suggested American-type re-

placements for the Philips semiconductors used are as follows—change ADZ12 to Motorola 2N174A, BCZ11 to Amperex 2N2617, OC74 to Motorola 2N1496, 0A210 to RCA 1N3193, and BYZ12 to RCA 1N1614. Type 2N337 was manufactured by Texas Instruments Inc. and type 1Z5.6 by International Rectifier Corp.

Cadmium-nickel stabilizers type 15BC20 made by L'Accumulateur Etanche, Belgium, would be available from Gould National Batteries Inc., St. Paul, Minn.

ACKNOWLEDGMENT

The author thanks P. J. Beck for his assistance in the construction of the apparatus.

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Powdered Sugar Adsorbent for Detection of Chlorophyll Components in Thin Layer Chromatography

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IN THE COURSE of an investigation of chlorophyll pigments in green vegetables (*8*) a simple microtechnique was needed for detection, identification, and proof of the purity of various chlorophyll components in amounts of 5×10^{-3} microgram. Spectrophotometric determinations were satisfactorily made on 5 μg. per ml. However, an amount of contaminant too small to cause a change in the shape of the visible range absorption spectrum might go undetected if masked by a component of greater concentration. Mangold (*5*) in 1961 suggested that "all adsorbent materials used in chromatography may also be applied in TLC." Since sugar columns had been successful for the separation of pigments in large amounts for many years and the available methods of glass strip (*1, 3, 4, 7*) and glass plate (*2, 6*) TLC showed promise, various trial runs were made to determine a usable procedure.

A mixture of confectioners powdered sugar containing 3% starch could be mixed with isopropanol 4:3 w./w. and after standing tightly covered overnight formed a smooth paste. This paste was applied to glass plates 20 × 20 cm. with any of several commercial spreaders or a simple aerosol sprayer to give a satisfactory thin layer 0.25 to 0.35 mm. thick. After application of the adsorbent, the plates were dried at 40° C. for one hour which produced a stable film that did not flake off appreciably on handling. The adsorbent was then scribed into 10 to 14 strips 1 to 2 cm. wide which produced strips similar to the ridged plates of Gamp *et al* (*2*). A tongue depressor whittled to a blunt end 2 mm. wide was used as a scraper by guiding along a straight-edge laid across a 2- × 2-inch block on either side of the plate to completely and cleanly remove the adsorbent without scratching the glass.

Each strip was spotted 2.5 cm. from the bottom of the plate with 2 to 10 μl. of 100% acetone or ether solution containing a concentration of 5 to 15 × 10^{-3} μg. (Solutions must be anhydrous when spotted on the sugar plates.) The solvent is allowed to evaporate from the spots for 15 minutes and the spots are developed in a closed tank with a solvent consisting of 5% acetone in Skellysolve B, v./v. for 3½ hours.

Figure 1 shows a plate which had been spotted with known solutions of pheophytin *a* and pheophytin *b*, developed in upward direction and subsequently photographed under ultraviolet light.

The advantages of this method are its simplicity of preparation and the use of a readily available, inexpensive adsorbent which allows detection of very small amounts of pigment material. An amount of contaminant which failed to change the shape of the visible range absorption spectrum of the classical curve was discernible as a separate spot on a sugar plate when viewed under ultraviolet light.

Strips 6 and 11 on Figure 1 were spotted with 1.0×10^{-3} μg. of purified pheophytin *a* and showed one pink fluorescent band which had traveled with the blue solvent front but was not distinguishable on a black and white print. Strips 1 and 13 contained no pigment material and were blue on the solvent front under ultraviolet. Strips 4 and 8 were spotted with 2×10^{-3} μg. of pheophytin *b* which contained a trace of pheophytin *a*. Strips 3, 7, 9, and 10 illustrate various stages of purification of crude material repre-

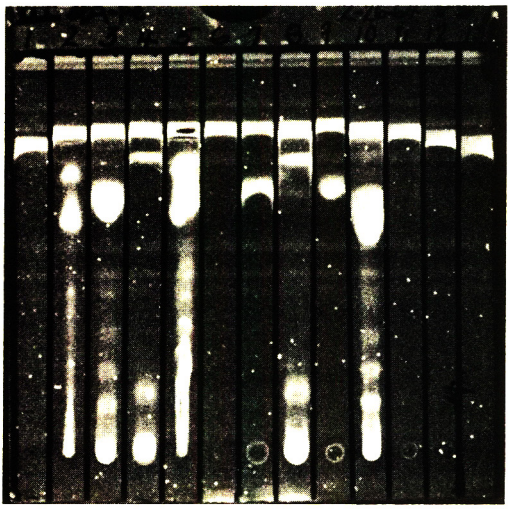

Figure 1. Thin layer powdered sugar plate of known and unknown components

Spotted, dried, and developed with ascending 5% acetone in Skelly solve B, v./v. for 3½ hours. Photograph taken under ultraviolet light, 80-second exposure

sented on strips 2 and 5. Strip 12 shows a purified sample of pheophytin *b*. (The small white specks visible in the black and white photograph are due to imperfectionsi n the layer of sugar.)

The fluorescent areas clearly visible under ultraviolet can be marked, scraped from the plate, and eluted from the sugar to recover the desired material for further identification.

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Variable-Speed, Motorized Buret for Rapid, Semiautomatic Neutralization of Small Volumes

Lorne F. Ebell, Department of Forestry of Canada, Victoria, British Columbia[1]

IN THIS laboratory large numbers of soxhlet residues of woody tissues are ground in 15-ml., tapered, glass tissue grinders with 6 ml. of 1*N* HCl. After hydrolysis, the ground material requires precise neutralization prior to enzymatic determination of starch as glucose. The standard electromagnetic, pinch-cock-type, titrimeter valve proved unsatisfactory for the purpose. This valve provided extremely slow delivery of titrant during the initial phases of neutralization, when set finely enough for a good end point, required excessively large volumes of relatively weak titrant, and constant attention to avoid disastrous overshoot. Commercially available, motor-driven burets were too limited in speed flexibility for the logarithmically decreasing titrant volumes required for a fast approach to neutrality. The inexpensive, motor-driven buret described in this note has permitted use of concentrated sodium hydroxide for neutralization of hydrolyzates, with a time requirement of approximately 1 minute per sample under good mixing conditions.

Table I. Output Shaft Speed and Titrant Delivery Characteristics with 2-ml. Micrometer Buret Delivering 0.1 ml. per Revolution

Motor	Output shaft r.p.m. over operational voltage: 30 volts	3 volts	Range of speed reduction	Range of titrant delivery rate μl. per minute
Fast motor	4	0.1	40:1	400 to 10
Slow motor	0.1	.005	20:1	10 to 0.5

GENERAL DESCRIPTION

A stepless, buret drive-speed control of 800:1 was obtained by varying the voltage to two 30-volt d.c. motors driving a common output shaft through a differential gear system (Cramer type 800 d.c. motors on type 152 dual motor gearing system, Cramer Division, Gianinni Controls Corp., Centerbrook, Conn.). A 2-ml. capacity, micrometer syringe was mounted to the motor gear housing and connected to the dual-motor, output shaft with a slotted drive system, as illustrated in Figure 1. The output shaft speed and titrant delivery rate ranges obtainable over the operational voltage range of the motors are given in Table I. Motor speeds are linearly proportional to applied voltage.

Further reduction in the rate of titrant delivery, providing a smooth, automatically controlled approach to the end point, was obtained by intermittent operation of the slow-speed motor through a relay compatible with the valve circuit output of an automatic titrimeter. Under intermittent operation delivery rate is governed by motor voltage setting, titrimeter proportional band setting, and proximity to the end point.

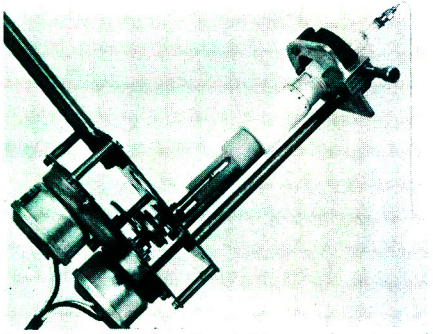

Figure 1. Mounting of variable-speed, motorized buret

Buret is aligned and held to the dual motor gear housing by two rods and a finger-tight screw clamp. A machined nylon, slotted drive extension, press-fitted to the micrometer barrel, permits advancement of the micrometer as it is turned by the output shaft of the motors

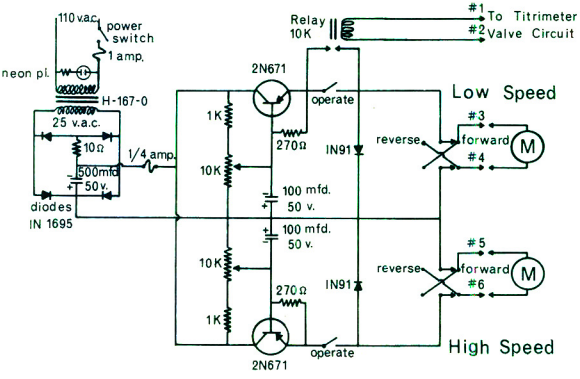

Figure 2. Circuit diagram of power supply

POWER SUPPLY DESIGN

The circuit diagram for the power supply, which provides a continuously variable range of 0 to 32 volts d.c. to the motors, is given in Figure 2. Power from the 110-volt a.c. line is applied to a step-down transformer to provide 25 volts a.c. to a bridge rectifier consisting of four IN1695 diodes, and partially filtered by a 500-mfd. condenser. A 10-ohm series resistor limits the initial surge current when power is first applied so that the diode ratings are not exceeded.

Two identical regulators are employed for the high- and the low-speed motors. By employing transistors as filter elements the need for large bulky chokes is eliminated. The voltage at the emitter of each transistor is set by the 10-K potentiometer in its base circuit, the emitter voltage being nearly equal to the base voltage. The effective filtering action of the 100-mfd. condensers is magnified by the current gain of the transistors and appears much larger than its actual value. When the operate button is pushed, voltage is applied to the motor through the forward-reverse switch. This switch reverses the polarity of the voltage applied to the motor and permits operation in either direction. The two motors and the relay coil are connected to the power supply through a six-pin, Jones connector. When the relay coil is energized by the titrimeter valve circuit, the relay contacts close, activating the slow-speed motors. The motor remains operational, or is operated intermittently, for the length of time the relay coil is energized. The IN91 diodes are transient suppressors, used to eliminate the large inductive voltages appearing across the motors when switched on or off. If the power supply is used for other applications, current drain should be limited to a maximum of 100 ma.

OPERATION OF BURET

The slow motor is automatically started by the titrate control of the titrimeter. The fast motor is simultaneously operated manually as required to move the meter off the extreme ends of the pH scale, and neutralization is completed with the slow motor. Motor voltage controls are set according to the desired rate of titrant delivery. The buret may be refilled simply by running the fast motor in reverse at an appropriate speed. For somewhat more convenient titrimetry with this motor system, a digital readout buret with manual re-set could be substituted for the buret in present use. Since the power supply is independently line-operated, provision was made for bypassing the slow motor relay to permit use of the system for manually controlled titrimetry with a standard pH meter or for use of the motors for other than buret drive applications.

ACKNOWLEDGMENT

Appreciation is expressed to Anthony Moilliet, R. W. Chappell, and J. W. Parker of the Pacific Naval Laboratory, Esquimalt, B. C., for assistance in development of this apparatus.

[1] Department of Forestry, Canada, Forest Research Branch Contribution No. 658.

Simultaneous Dual Column Gas Chromatographic Modification

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THE APPLICATION of multi-column gas chromatography has become increasingly popular. Most of the commercial gas chromatographs being manufactured today are dual column instruments. A multi-column gas chromatograph has been described recently which uses a single detector and recorder (*4*). The advent of dual column chromatography was prompted by the desire to maintain a straight base line when temperature programming. Many workers, however, have utilized the dual column chromatograph containing columns with different liquid phases (polar and nonpolar) to have them conveniently available for certain applications without having to bother to change columns.

Meritt (*3*) has described a dual column instrument containing two independent detectors and recorders. This instrument enables the operator to make a single injection and obtain simultaneously gas chromatographs on two different columns. Such a system is very advantageous insofar as saving time is concerned when one wishes to employ the retention volume constant system described by Meritt (*2*) or the well known Kovats retention index system (*1*, *5*). By the same token, if one wishes to determine the purity of a sample (in many cases a gas chromatographic trapping), one can make a single injection and then observe the separations obtained on the two columns simultaneously.

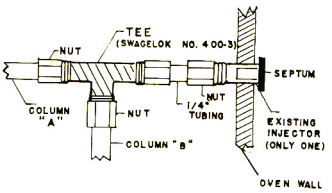

Figure 1. Construction of tee and its attachment to columns and injector

Unfortunately, the gas chromatograph described by Meritt (*3*) is not available commercially and if it were it would be too expensive for general use, thus prohibiting its widespread application.

In our laboratory, we have modified a commercially available dual column instrument in such a manner that a sample is injected into one of the existing injectors, it is then divided by means of a tee (in the oven) so as to go to the two different columns. The tee is shown on Figure 1. The existing single detector is used without any modifications and the recorder supplied with the unit is also used without change. The pen of the recorder is adjusted so as to ride at mid scale prior to injecting the sample. A simple schematic is shown in Figure 2.

We have found that such a system serves admirably for cataloging materials, according to the Kovats retention index system mentioned previously. It is also ideal for testing the purity of trapped materials as well as others.

The outstanding advantage of the device described in this paper is the saving of 50% in the time required for the applications described previously.

EXPERIMENTAL

An F and M Model 810 was modified by placing a tee (shown in Figure 1) after the injector, *A*. An 8-foot, $^1/_4$-inch o.d. by $^3/_{16}$-inch i.d. copper column filled with 20% Carbowax 20M on 60–80 mesh Chromosorb P, was attached to one arm of the tee and the other end of the column was attached to the *A* portion of the detector. An 8-foot, $^1/_4$-inch o.d. by $^3/_{16}$-inch i.d. copper column filled with 20% SE-35 on 60–80 mesh celite was attached to the other part of the tee and the other end of the column was attached to the *B* portion of the detector. Column *A* (Carbowax) had a flow rate of 100 ml. per minute at an inlet pressure of 35

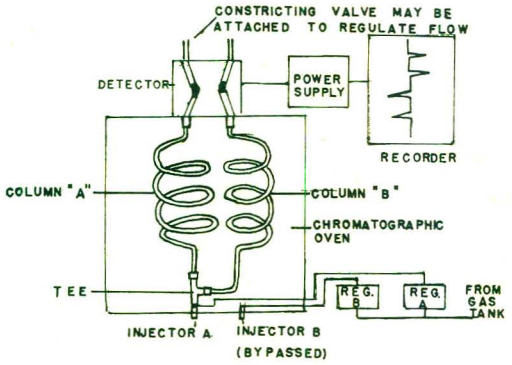

Figure 2. Schematic diagram of modified instrument

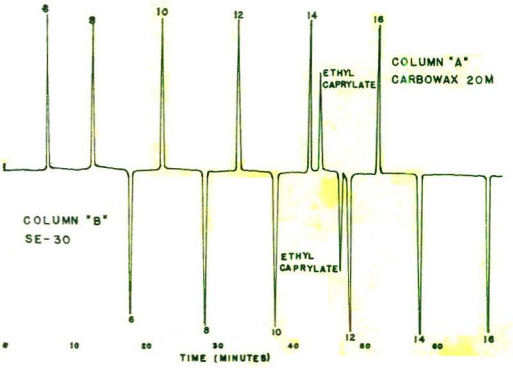

Figure 3. Programmed gas chromatogram of hydrocarbons plus ethyl caprylate

p.s.i. helium (75° C.). Column *B* (SE-30) had a flow rate of 70 ml. per minute and an inlet pressure of 35 p.s.i. of helium. (Columns *A* and *B* will always have the same inlet pressure because they are attached to a common tee.) The oven was programmed from 70° C. to 220° C. at a rate of 2 degrees per minute. The injector was at 250° C. and the detector was at 300° C.

RESULTS

Figure 3 represents an injection of $2^1/_2$ μl. of a mixture of C_6, C_8, C_{10}, C_{14}, C_{16}, normal hydrocarbons to which a single material, ethyl caprylate, has been added to show the applicability of this system for cataloging data via the Kovats retention index system.

Figure 4 represents an equal mixture of hexyl butyrate and terpinenol-4. (These materials occur in natural Lavender and could represent a trapping obtained on a nonpolar column.) As can be readily observed, the carbowax column clearly separates the mixture into its components while the SE-30 column shows only a single peak. ($2^1/_2$-μl. injection).

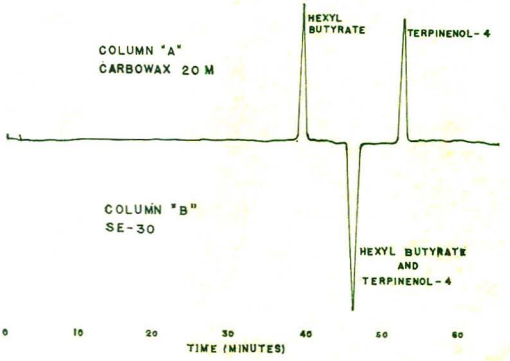

Figure 4. Programmed gas chromatogram of mixture of hexyl butyrate and terpinenol-4

DISCUSSION

We feel that the system described above will be invaluable where equipment is at a premium and advantage can be taken of the savings of time (especially when cataloging materials for a system such as the Kovats retention index system). One must bear in mind that no permanent change is made to the dual column gas chromatograph since only an inexpensive tee is added, which can be removed in seconds, leaving the instrument in its original state.

It is obvious this system has only one serious drawback—i.e., if a peak elutes simultaneously on both columns. However, experience has shown that such an occurrence is easily recognizable by a skewed and distorted peak. This effect can be remedied by changing the flow rate of one of the columns. The flow rates of the two columns can be changed, if desired, by placing a restricting valve at the exit of the detector to which one of the columns is attached. Also, experience will enable the operator to choose just the correct amount of sample to prevent the recording from going off the chart.

The modification described in the paper is intended primarily for instruments equipped with thermal conductivity detectors. However, it is apparent that older instruments designed with only one column can be easily modified using the method described herein. To accomplish this, one has to connect a second column between one leg of the tee and the reference side of the detector. In many instruments, the reference side of the detector is merely a helium bleed to the atmosphere and is ideally suited for the attachment of the second column. This is actually what is done in dual column instruments equipped with thermal conductivity detectors.

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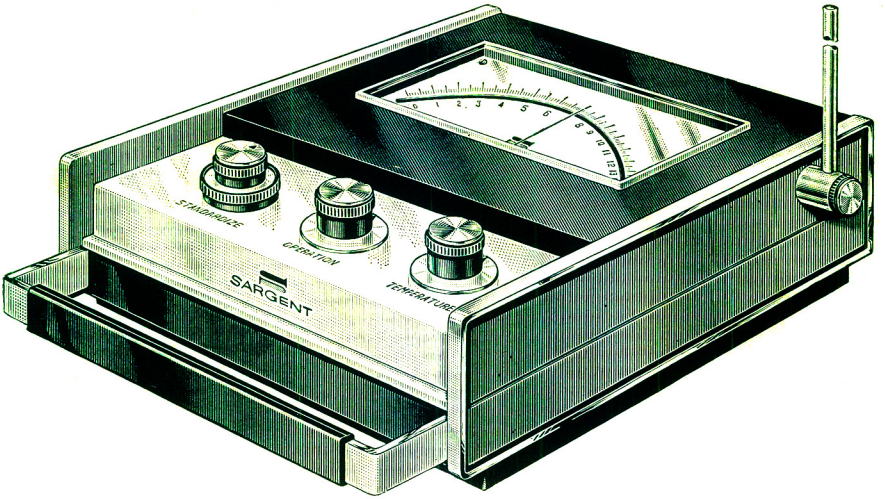

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■ **Rugged Construction** ■ for use in any locale, any climate; moisture-proofed, transistorized circuitry, shock-proof case.

MODEL PB Cat. No. S-30007 with batteries, buffers and electrodes . . . $255.00
Cat. No. S-30007-10 with batteries only, for use with any electrodes . . . $215.00
MODEL PL Cat. No. S-30008 with line power source, buffers and electrodes . . . $295.00
Cat. No. S-30008-10 with line power source only, for use with any electrodes . . . $255.00
Power Supplies Cat. No. S-30007-15 Zener Line Source for substitution in Model PB meters . . . $60.00
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For complete information write for bulletin pHP.

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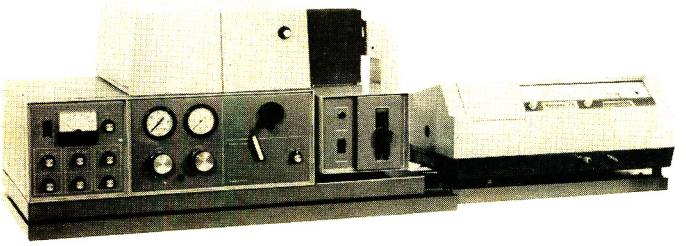
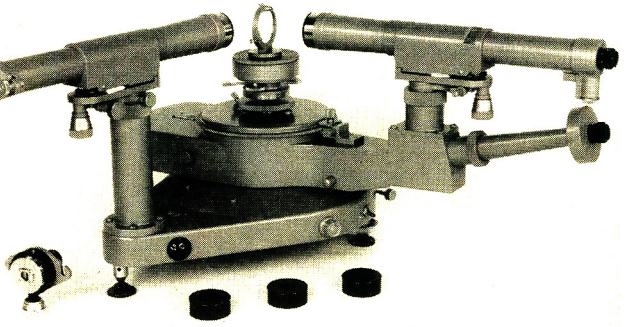
NEW PRODUCTS

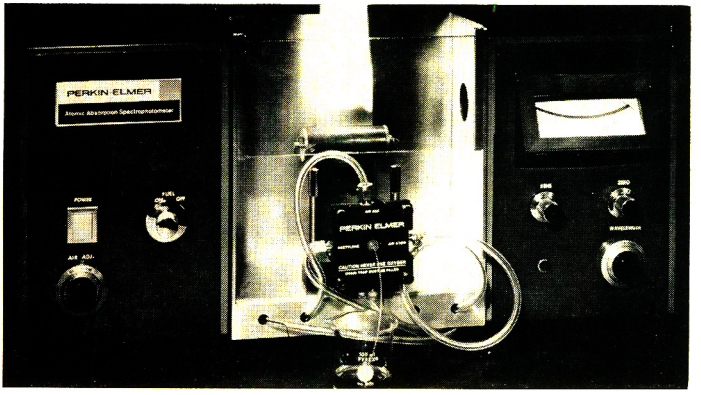
EQUIPMENT APPARATUS INSTRUMENTS



Atomic absorption accessory is shown with the DB ultraviolet spectrophotometer. The DU, DU-2, or DB spectrophotometers equipped with the accessory provide three methods of measurement: atomic absorption, flame photometry, and standard UV spectrophotometric absorption analysis. Located within the main accessory housing are the source lamp power supply, up to five source lamps, and all pressure and feed controls for the burner fuel and air supply. A special optical system allows the beam from the source to be passed through the flame (two types of burners are available) up to three times before it is reflected into the spectrophotometer where it falls on the photodetector. The signal is amplified and readout is provided by the instrument or an auxiliary recorder. Beckman Scientific and Process Instruments Division, 2500 Harbor Blvd., Fullerton, Calif. 92634. **401**

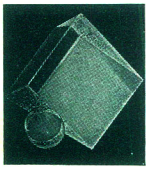
Goniometer/spectrometer is the first instrument of its kind which allows simultaneous observation of two circle positions. The optical system can be used with white or nonchromatic light and consists of a telescope with objective and eyepiece, collimator, scale observation microscope, and graduated circle. The principal uses as a goniometer are the measuring of angles on prisms and wedges by direct or differential methods, the testing of glass surfaces for parallelism by autocollimation, the determination of the focal length of optical systems, etc. The graduated circle has a 150-mm. diameter; the smallest division is $1/6°$. Brinkmann Instruments, Inc., Cantiague Rd., Westbury, N. Y. 11590. **402**





Model 290 atomic absorption spectrophotometer can analyze a large number of samples for one or two elements; successive determinations of the same element, Ca, Mg, Zn, or any of 30 other metals, can be made at the rate of four per minute. Readout of the instrument is directly in concentration. The instrument is supplied with a book of analytical methods. Perkin-Elmer Corp., Main Ave., Norwalk, Conn. **403**

HARSHAW
POLISHED OPTICS



Materials available include lithium fluoride, calcium fluoride, barium fluoride, sodium fluoride, sodium chloride, potassium chloride, potassium bromide, silver chloride, KRS-5, KRS-6, thallous chloride, thallous bromide, cesium bromide and cesium iodide. Special crystals can be custom grown to customer specifications. Other products include specially oriented crystals, attenuated total reflection components, and X-ray monochrometer plates. For additional information write to the Crystal-Solid State Division, The Harshaw Chemical Company, 1945 East 97th Street, Cleveland, Ohio 44106, phone area code 216, 721-8300.

Write for our booklet "Harshaw Polished Optics".

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CRYSTAL-SOLID STATE DIVISION
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Taylor's new Catalog has twelve pages filled with all the information you need for specifying liquid-in-glass thermometers. It lists all the data on the complete line of Precision quality, Laboratory quality and Standard quality thermometers and accessories. It also explains the many advantages of Taylor's new SURFAMARK* method of marking. Send for your free copy of **Bulletin 98280-B** today. Taylor Instrument Companies, Asheville, North Carolina.

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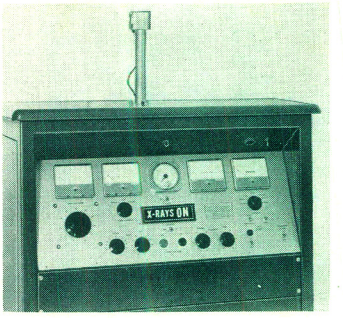
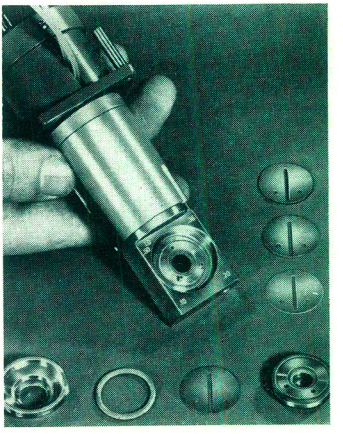
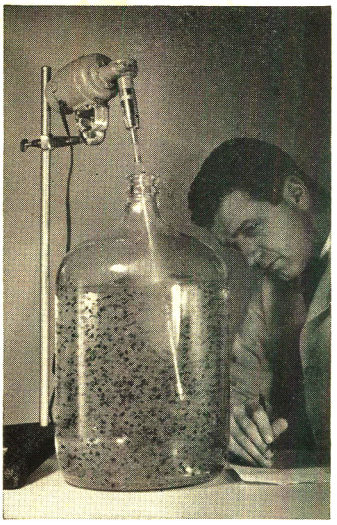
NEW PRODUCTS



Y-33B microfocus x-ray generator provides the highest power level available; with tube loading of 50 kv. at 10 ma. Demountable tubes give the minimum focus area for greatest energy density. The 40-micron diameter spot focus gun may be interchanged with others to provide 100 micron 600 micron line focus. Horizontal and verticle tube housing, guns, targets, filters and cathode are completely interchangeable with the demountable tubes. The rigid one-piece aluminum top serves for a full complement of cameras and diffractometers. This instrument is manufactured under a Hilger & Watts license. Engis Equipment Co., Morton Grove, Ill. **404**



Components of short path flow-through cuvette are shown with a complete set of shims. Numbers on cuvette let the operator know which shim is in use. This cuvette is used with the Spectronic 20 colorimeter in the company's data acquisition system. It provides a path length capability between 0.1 mm. and 1.0 mm., and is interchangeable with the standard flow-through cuvette. Bausch & Lomb, Inc., Rochester, N.Y. 14602. **405**



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If you had to standardize on just one kind of mixer in your laboratory, this gear drive unit would be a good choice.

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And you can purchase it in a gear ratio that matches the kinds of mixing you do most; 1800 rpm for general service, 1000 or 600 rpm for viscous fluids.

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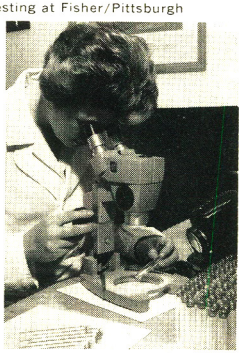
J-401

Electrode production and testing at Fisher/Pittsburgh





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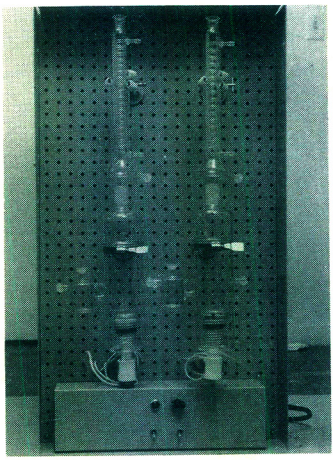
NEW PRODUCTS



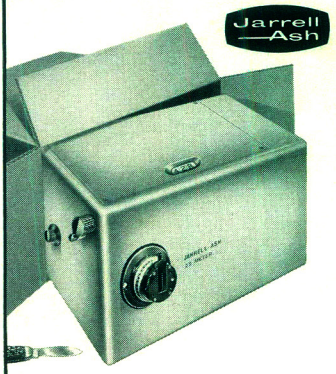
Model 2642 Sartorius analytical balance permits fast pre-weighing. Weight additions can be made when the knives are not sitting on the bearings, thus protecting the knives and saving time. Optical range is 100 grams for coarse beam and 1000 mg. for fine beam, total maximum capacity is 220 grams, sensitivity is 0.1 mg., and direct digital reading is to 1.0 gram with torsion spring, and 0.1 mg. with fine beam. Brinkmann Instruments, Inc., Cantiague Rd., Westbury, N. Y. 11590. **406**



Panel-mounted, all-glass water distillation apparatus features two distillation stages of 600 watts each, thermostatic cut-off, and an outlet for single-stage use. The Model 64-1 will provide one half liter per hour continuously. Lab-Items Assoc., P. O. Box 321, San Francisco, Calif. 94101. **407**

A first-class Monochromator for under $900.00

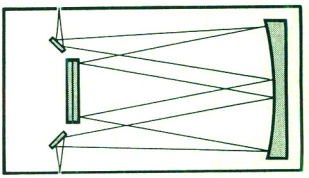
Jarrell—Ash



Here is more monochromator than ever before available at twice the price. Advanced Jarrell-Ash optics is one reason. Another is exceptional versatility. Features like two gratings in place which may be interchanged simply by turning an external knob make this new instrument the standard monochromator for general use in every physics, chemistry and biology laboratory. Wide wavelength range from ultraviolet to infrared. Write for complete specifications.

MODEL 400 JARRELL-ASH
0.25 METER EBERT MONOCHROMATOR

OPTICAL LAYOUT



APERTURE RATIO f/4.3
RESOLUTION . . As good as 1A with 10 micron slits
SLITS . . . . . Focusable for optimum resolution
READOUT . . . Digital counter
WEIGHT . . . . . Approx. 12 pounds

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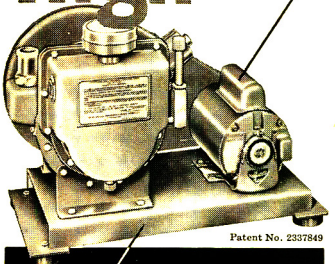
High CAPACITY VACUUM



Patent No. 2337849

WELCH DUO-SEAL VACUUM PUMP WITH VENTED EXHAUST

Welch "Duo-Seal" No. 1397 is a two-stage, oil sealed, rotary vacuum pump with a free air capacity of 425 liters per minute and a guaranteed vacuum performance of 0.1 micron or better with the vented exhaust closed . . . 1.0 micron with vent open. The performance is uniformly high over a range to 1 x 10-4 mm Hg (Torr). It is especially suited for application to large systems involving substantial vapor removal.

The 1397 s are equipped with vented exhausts to eliminate condensation of vapors which raise the vapor pressure of the sealing oil, contaminate and break down the oil, and corrode the metal parts.

IMPORTANT FEATURES:

- High pumping speed— 425 liters per minute
- Low ultimate pressure— 1 x 10-4 mm Hg (Torr)
- Quiet, vibration-free operation
- Compact, rugged design
- Air-cooled
- Vented Exhaust— eliminates condensed vapors, oil filters and separators
- Belt guard
- Trouble-free, low maintenance

Over the years, Welch "Duo-Seal" Vacuum Pumps have gained a world-wide reputation for best performance, greatest reliability and quietest operation. They are available in a wide selection of capacities and ultimate vacuum characteristics, ranging in capacities from 21 to 1400 liters/ minute and ultimates from 2 x 10-2 mm Hg (Torr) down to 1 x 10-4 mm Hg (Torr).

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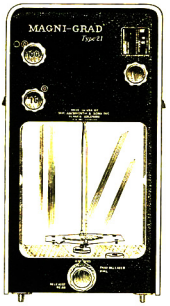

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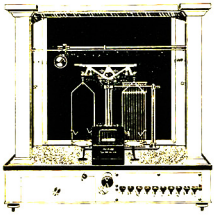
Capacity	160 gr.	160 gr.	200 gr.	80 gr.
Total load	—	220 gr.	—	120 gr.
Sensitivity	0.1 mg.	0.1 mg.	0.1 mg.	0.01 mg.
Readability by estimation	0.05 mg.	0.05 mg.	0.05 mg.	0.005 mg.
Reproducibility	±0.05 mg.	±0.03 mg.	±0.03 mg.	±0.01 mg.



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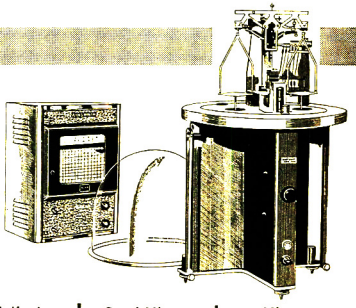
VERSATILE • ECONOMICAL

. . . wide range of capacities and sensitivities

	Model LCB Analytical	Model TCY Analytical	Model FHM Micro
Capacity	200 gr.	100 gr.	20 gr.
Sensitivity	0.1 mg.	0.01 mg.	0.001 mg.



FULL LINE of recording vacuum-pressure balances

For accurately recording weight, or other variables, vs. time in a controlled vacuum, pressure, temperature or gaseous environment.

	Analytical	Semi-Micro	Micro
Capacity	200 gr.	100 gr.	10 gr.
Sensitivity	1 mg/div.	0.1 mg/div.	0.01 mg/div.
Readability by estimation	0.1 mg.	0.01 mg.	0.001 mg
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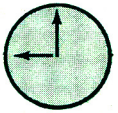
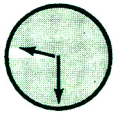
TIMES ARE CHANGING

. . . in AMINO ACID ANALYSIS



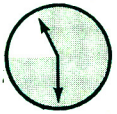
9:00 A.M.

INTRODUCE SAMPLE INTO NEW PHOENIX SPHERIX® RESIN COLUMNS



9:30 A.M.

ANALYSIS OF BASIC AMINO ACIDS COMPLETED



11:30 A.M.

ANALYSIS OF ACIDIC AND NEUTRAL AMINO ACIDS COMPLETED AND START OF AUTOMATIC REGENERATION

Yes, times really are changing when you progress from a complete analysis in 22 hours to a complete analysis in just under 2½ hrs.

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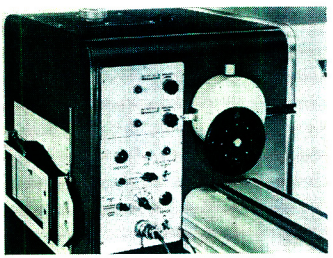
NEW PRODUCTS

Spectrum Accumulator

The JNM-RA-1 spectrum accumulator is designed for enhancement of detectable sensitivity for ESR, broad line NMR, and high resolution NMR. Applications include spectrum analysis, integral and differential calculus of spectrum, cancelling background signal, and calculation of second order moment. The system consists of an operation unit, a computation control unit, a memory drive unit, a magnetic drum, an AD-DA converter, and an input and output circuit, all housed in a single console. Detection sensitivity is increased 10 times or more when this instrument is used. Japan Electron Optics Laboratory Co., Ltd., 461 Riverside Ave., Medford 55, Mass. **408**

Residual Gas Analyzer

The new Ultek/EAI residual gas analyzer claims to have order-of-magnitude improvement in performance over conventional mass spectrometers because it was designed with the aid of an analog computer. The instrument operates in the range from 10^{-4} torr to extreme high vacuum; it is capable of scanning an entire mass range in 10 milliseconds. Scan rate is continuously variable from 500 μseconds to 6 minutes per a.m.u. Sensitivity is 10^{-15} torr (for nitrogen), resolution is better than 100 at mass 100. The complete instrument consists of a small, light-weight tube, bakeable to 400° C. and no magnets, and an electronics console. Ultek Corp., Box 10920, Palo Alto, Calif. **409**



Two 4″ × 5″ gratings are mounted back-to-back in a rotatable turret in this new research spectrograph. The instrument has a numerical aperture of f/15.5 when the paired gratings are used. For work requiring higher speeds, up to f/12.1, a single grating can be specified. For high resolution studies using a 300 groove/mm. echelle grating at an incidence angle of 65°, photographs up to the 28th order can be taken. The spectrograph can be used for isotope and laser work. Bausch & Lomb, Inc., Rochester 2, N. Y. **410**

what you should know about VYCOR® BRAND

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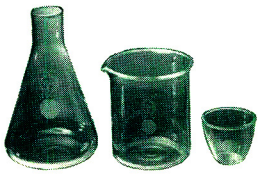

Our octagon design trademark means it is VYCOR brand ware. Nearly pure silica, it is capable of continuous service at 900°C. It can be quenched safely and repeatedly in ice water from that temperature. It may be safely used in place of fused silica or quartz.

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Laboratory Glassware Dept., Corning Glass Works, 3903 Crystal St., Corning, N. Y.

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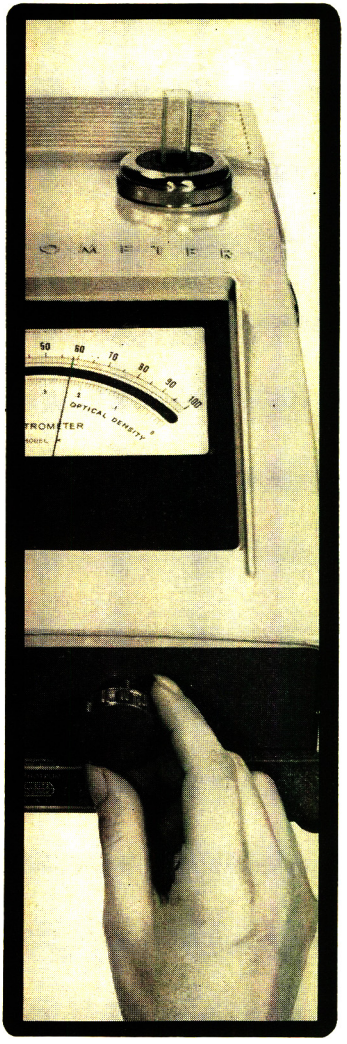

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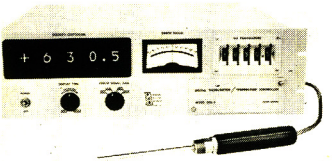
NEW PRODUCTS



Model DTS-1 is a resistance type digital thermometer which acts simultaneously as a thermometer and a temperature controller. Temperature readings are presented on a numeric display consisting of 4 decimal digits and a plus or minus sign. Measured temperature information is available in binary coded, 10-line decimal, or pulse code modulated form. Temperature range of instrument is −192.0° C. to +999.9° C. Princeton Applied Research Corp., Box 565, Princeton, N. J. **411**

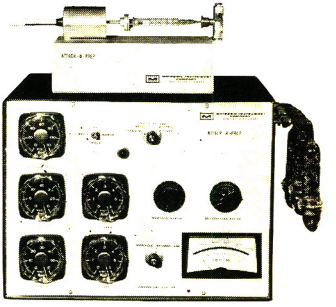
Metal Membrane Filter

The Flotronics filter—a very thin membrane of pure silver—is said to be the first metal membrane filter ever developed for microfiltration and microanalysis. The filter is available in six distinct grades with maximum pore diameters ranging from 5 microns down to 0.2 micron. Filter disks are supplied in diameters ranging from 13 mm. to 293 mm. Standard membrane thickness is 2 mils. The filters have a large percentage of open area and are stable in any atmosphere at temperatures ranging from −200° F. to +700° F. Because of high compressive strength, the metal membranes may be used in almost any type of fluid system at a pressure differential of 15,000 p.s.i. without distorting the porosity structures. Selas Flotronics, Spring House, Pa. **412**

Mössbauer Spectrometer

The electromechanical-drive Model AM-1 Mössbauer spectrometer operates with constant acceleration over the complete velocity range from 0 to 60 cm. per sec. Equipped with cryogenic accessories, the spectrometer permits studies of the Mössbauer effect in iron, tin, tellurium, europium, iodine, and other elements. System linearity is better than 1% over 95% of the half-period of the velocity wave form. Velocity calibration is ±1%, reproducible to ±0.5%. Various operating modes permit the instrument to be used with source and absorber cooled; absorber cooled; source cooled; or room temperature. Nuclear Science & Engineering Corp., P. O. Box 10901, Pittsburgh, Pa. 15236. **413**

Use Your Existing Gas Chromatograph



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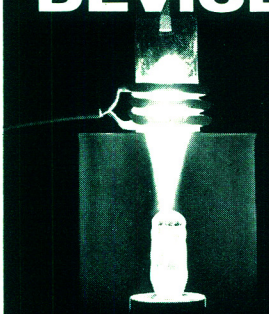

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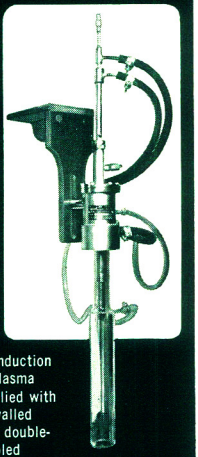
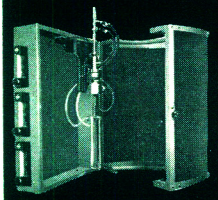


The new Lepel inductively coupled plasma device is a low cost unit designed to permit laboratories and research departments to conduct experimental work within a modest budget. It can readily be mounted on existing laboratory fixtures or directly on the induction generator. The plasma unit can be supplied with either a single-walled quartz tube or a double-walled water cooled quartz tube. The adjustable water cooled feeder tube provides for passage of solid particles through the plasma.



Enclosure for plasma device includes hinged protective shield of tinted plexiglas and flow meters.

Lepel HIGH FREQUENCY LABORATORIES, INC.

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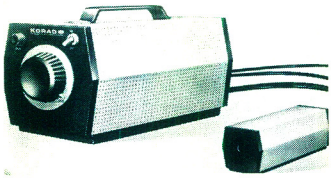
NEW PRODUCTS

Spectroradiometer

A new spectroradiometer uses a rotating integrating sphere which alternately compares radiation from the standard lamp and unknown source. The undispersed radiation from the sphere is directed to a monochromator. After being dispersed by the monochromator, the radiation is received by a single photo tube or PbS detector as alternate pulses of standard and unknown energy. The instrument records directly and linearly in microwatts per square millimeter per nanometer at a wavelength range of 2500–25,000 A. The photometric system is a modified version of the system used in the Model 14 spectrophotometer. Internal controls permit adjustments of 63 points within the wavelength range for a working reference lamp. The reference lamp is a 1000-watt tungsten quartz iodine lamp. Applied Physics Corp., 2724 South Peck Rd., Monrovia, Calif. **414**

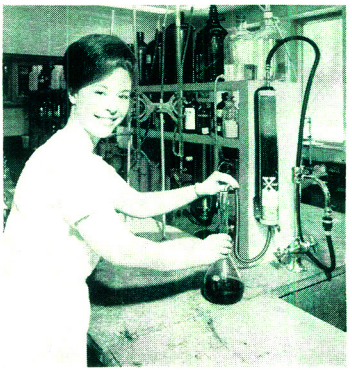


A portable yttrium aluminum garnet laser, 20 pounds, is excited by long-life tungsten lamps to produce a continuous output of ½ watt at a wavelength of 1.06 microns. Power output may be varied continuously. The laser is ideal for ranging experiments when mounted on a telescope, for calibration of spectral data with an interferometer, and for general laboratory use on optical benches. A 110-volt outlet will operate the laser. Korad Corp., 2520 Colorado Ave., Santa Monica, Calif. 90406. **415**

Thermometer Adapter

The A92 recording adapter can be used with any potentiometric recorder to expand the temperature scale of the Atkins thermometer used. The nominal 0 to 60 mv. output of the indicator is used with a 10 mv. or even 1 mv. recorder setting to achieve scale expansion of 5 times, 20 times, etc. Temperature sensitivity of 0.01° C. is possible. The scale expansion and range selection is completely adjustable. The adapter is mercury battery powered and connects to any company thermometer at the standard recorder output. This is one item of a large line of electronic temperature measuring, controlling, alarm, and recording equipment de-

WATER



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And how pure is that? Well, how does less than ½ part per million total dissolved solids sound to you? This our Research Model CARTRIDGE DE-IONIZER can deliver — and right out of your own faucet, as the young lady is demonstrating in the picture above. We have two versions of this handy, reliable, versatile Cartridge. ■ Our ILLCO-WAY UNIVERSAL Model removes all ionizable solids except silica and CO_2, is suitable for general pure water needs, has a rated capacity of 1000 grains as $CaCO_3$, has a flow rate of 5 gph maximum, and is priced at $9.75. ■ Our ILLCO-WAY RESEARCH Model removes all ionizable solids, including silica and CO_2, reduces total solids to less than 0.5 ppm, has a capacity of 500 grains as $CaCO_3$, a flow rate of 5 gph maximum, and is priced at $12.50. ■ We have two types of holders: a Wall Bracket for push-on tap attachment at $7.50, and a Mounting Fixture for permanent in-line installation at $12.00. ■ The capacities shown above are reliable and conservative, as demonstrated by careful comparative tests at an independent laboratory. ■ A color indicator shows when the resin in the Cartridge is nearing exhaustion, at which time you simply discard the Cartridge and replace it with a fresh one. ■ If you are curious to learn more about this handy-dandy, do-it-yourself type of instant-pure-water supply, ask the man from your lab supply house, or address your questions to Mr. A.W. Michalson, Illinois Water Treatment Company, 840 Cedar St., Rockford, Illinois 61101.



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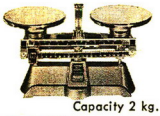

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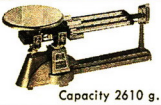
HARVARD TRIP BALANCES
from $21.50
0.1 g. Sensitivity



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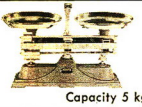
1 g. Sensitivity



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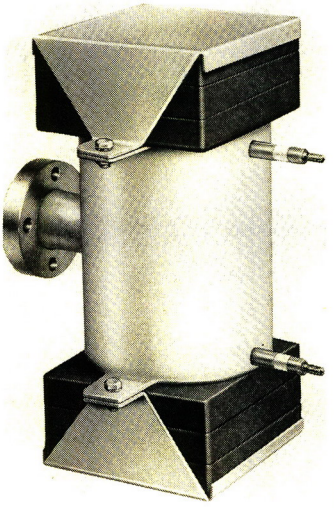
scribed in a 24-page catalog available from the company. Atkins Technical, Inc., P. O. Box 14405, University Station, Gainesville, Fla. 32603. **416**



Ion Pump Model HV-015, a 15-liter-per-second pump, is especially well suited for vacuum tube processing, mass spectrometer evacuation, and general research applications. This pump's special design results in improved gas-handling capability. Titanium cathodes provide well over 40,000 hours life at 10^{-6} torr. The complete ion pump and magnets may be operated at temperatures up to 300° C.; with magnets removed, the pump may be baked to 550° C. Andar Corp., 185 East Evelyn Ave., Mountain View, Calif. 94041. **417**

X-Ray Diffraction Attachment

An x-ray diffraction attachment allows researchers to study the characteristics of materials at pressures up to 1,500,000 p.s.i. The XKB-100 camera can be used with any standard x-ray diffractometer to study phase equilibria and structural change as a function of pressure. A pair of optically flat, especially oriented diamond crystals—piston and anvil—is used to mount the powder specimen. The piston diamond is attached to a gas-pressurized piston, which provides a mechanical advantage of about 2500 times the applied gas pressure. The exact area constant for the piston diamond is given so that pressure is readily calculated by reading the gas pressure (dry nitrogen from a standard gas cylinder). Materials Research Corp., Orangeburg, N.Y. 10962. **418**

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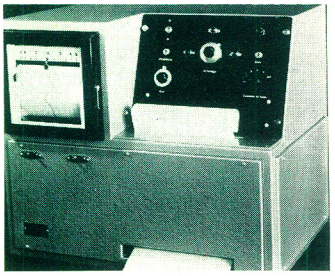


Surface profile of materials in sheet form, such as paper or plastics, weighing between 0.003 and 6 ounces per square foot, is measured with the alpha-beta radiation profile recorder shown. The instrument is made by Caratom Corp., Paris, France. A selection of five sample feed speeds and recorder speeds and either an alpha or beta source, depending on the thickness of the sample, are available. Variations in superficial weight around an indicated nominal value are presented graphically. Precision of measurement is better than ±1%. Numec Instrument and Controls Corp., Apollo, Pa. 15613. **419**

Scanning Photometer

An automatic scanning, high resolution, low angle light scattering photometer allows light scattering techniques to be applied to larger particle sizes and high molecular weights. The instrument has high angular resolution of 0.02° with a minimum detection angle of 0.05° from the incident beam, an automatic scanning capability with five push-button selectable speeds from 0.1 to 20 degrees per minute, over an angular range of 0° to 140°. Direct recorder plots of all functions which include intensity of scattering, speed of scanning, and angular position of photodetector marked in 0.1° increments are provided. Cenco Instruments, Corp., 1700 W. Irving Park, Chicago, Ill. 60613. **420**

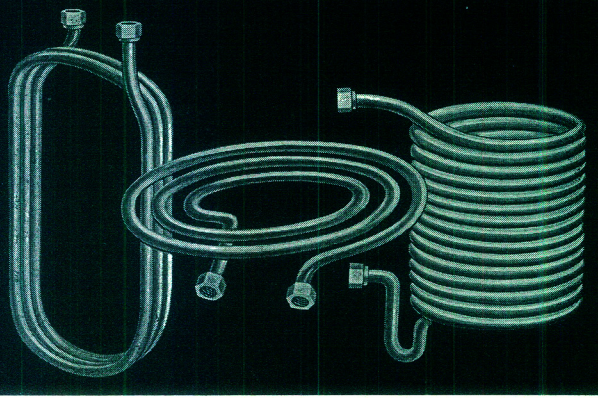
Leak Detector

A new mass spectrometer leak detector uses solid state electronics and modular construction. The unit detects leaks as small as 2×10^{-11} cc. per sec. The detector is available in two models: LC-20 with a built-in automatic test station; and LC-10 without a test station. Maximum operating pressure is rated at 0.2 micron at the analyzing tube. Amplifier drift does not exceed 2% of full scale per hour after warm-up. General Electric, Schenectady 5, N. Y. **421**

Gas Chromatograph and Accessories

Process gas chromatographs used for multiple or single stream detection and multicolumn operation are simple low cost instruments designed to provide excellent temperature control, high sensitivity, and fast response. A new peak picker accessory can be installed in the bar graph recorder to send a signal to a memory unit at the peak of any chosen component readout. The peak picker couples to the slidewire motion train and incorporates a retransmitting slidewire to provide to the memory unit a voltage proportional to the peak height. The memory unit normally provides an output signal in millivolts proportional to the voltage stored in its input, but the unit is capable of delivering about 0 to 2 volts at approximately 50 μa. A sup-

Curtin Custom Chromatographic Columns for any standard or special chromatograph



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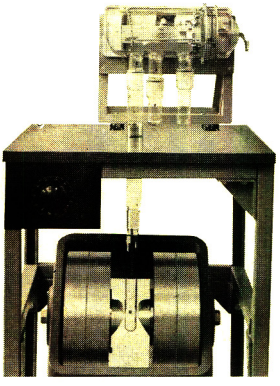

Magnetic susceptibility data are useful in molecular and crystal structure studies, and analytical chemistry, especially in the study of transition elements and coordination compounds. Their utility has been described as being comparable with X-ray and electron diffraction data. Their cost is substantially less.

You can assemble your own magnetic susceptibility system somewhat as you put together a hi-fi system. The first thing you need is a balance. The Faraday method requires one sensitive to 1 microgram or finer, with loads of about 50 mg, including container. The Cahn Electrobalance is ideal for this work. It is sensitive to 0.1 microgram, and has a capacity of over 1 g. It works well in the presence of vibration, temperature changes and gradients, and external magnetic fields which would disable an ordinary microbalance. Budget $1100-$3500, depending on degree of automation and atmosphere control desired.

Then you'll need a magnet and power supply. About 15,000 gauss, with an actual gap of about 2 inches, is the most popular. Homogeneity is no problem. Power supply regulation requirements are happily modest. Figure about $2000-$3000 for this part of the system.

When you're not measuring magnetic susceptibility, you can use the components for adsorption isotherms, TGA, and many other measurements.

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plementary unit can be supplied to boost the output to about 20 to 25 ma. at about 40 volts. The current output is intended to operate a current-to-pressure transducer to provide a control signal directly. Analytic Systems Co., 370 South Fair Oaks Ave., Pasadena, Calif. **422**

Immersion Heaters

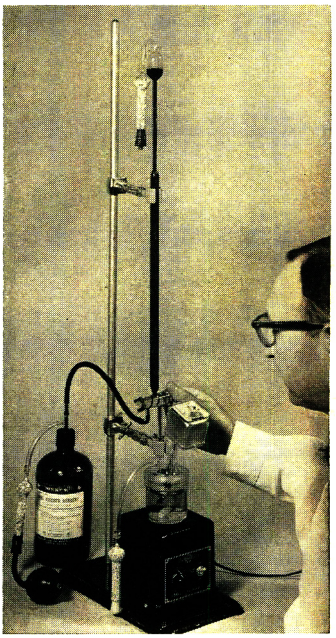
Redesigned immersion heaters with built-in thermostatic controls have optional full length polypropylene tube guards for complete protection. Slimline Thermersion heaters are made of fused quartz tubes and vaporproof epoxy heads and are highly resistant to all acids, except HF. Three sizes are available: 300, 600, and 1000 watts, each requiring only $2^3/_8$ inches of tank space when guard is used; $1^3/_8$ inches for heater alone. Sethco Manufacturing Corp., 1 Bennington Ave., Freeport, N.Y. 11520. **423**

Improved Spectroanalyzer

The Spectroanalyzer previously applicable for the measurement of trace concentrations of nitrogen in argon has extended its capabilities to include the measurement of nitrogen in helium and xenon. For nitrogen in argon the instrument has a maximum sensitivity of 0 to 5 p.p.m. full scale with linear ranges up to 1000 p.p.m. For nitrogen in helium and xenon, maximum sensitivity is 0 to 20 p.p.m. with linear ranges up to 1000 p.p.m. There is no interference from oxygen, hydrogen, or hydrocarbons; or from water vapor in concentrations approaching saturation. Mine Safety Appliances Co., 201 North Braddock Ave., Pittsburgh, Pa. **424**

Gel Permeation Chromatography

A gel permeation chromatography assembly is now available as a complete apparatus including a fraction collector. The system may be used to analyze polymers, and determine molecular weights, both for number average and weight average. Minute samples of the polymer are dissolved in suitable solvents and eluted through 4-foot stainless steel columns packed with a special polystyrene spherical gel material. The effluent of the column can be collected in narrow fractions. The assembly is complete with recorder, temperature control system, and flow control system as well as an integral syphon counter and fraction collector. Waters Associates, Inc., 45 Franklin St., Framingham, Mass. **425**



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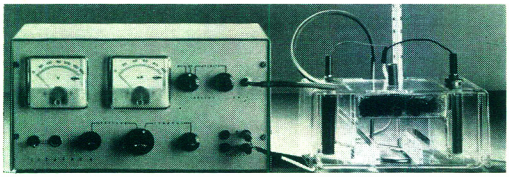

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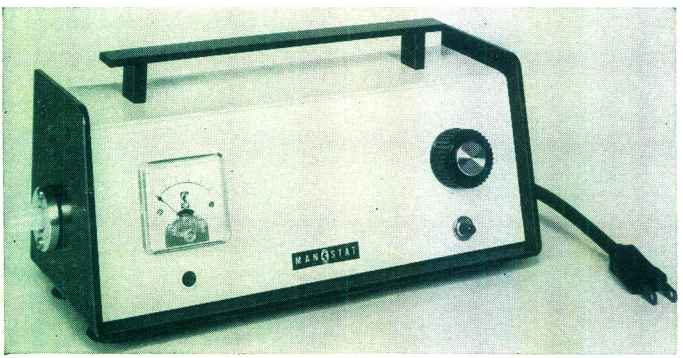

New! Ministaltic Pump delivers drops to 1800 cc per minute, uniform flow, one-knob control of corrosive liquids

Designed for continuous pumping, this sturdy, accurate little workhorse has been tested for over 10,000 continuous hours of operation. No moving parts are exposed — liquids come in contact only with chemically inert polyethylene. A simple knob controls flow rates from a few drops to 1800 cc per minute, indicated on dial type electrical meter. Self-priming operation; compact, handsome all-metal two-tone cabinet.

72-894-21 MINISTALTIC PUMP, 10" long by 4¼" deep by 4" high, operates on 115 volt, 50-60 cycles. each . . . $79.00

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NEW CHEMICALS

Naphthoresorcinol

Naphthoresorcinol is now produced in ampules, packed under nitrogen. The compound is a reagent for the colorimetric determination of glucuronic acid in urine according to Tollens, as described in Kurze's "Handbuch der Kohlenhydrate" (Springer-Verlag). Since this material deteriorates when exposed to air and light, the new product should be of considerable importance. Gallard-Schlesinger Chemical Mfg. Corp., 580 Mineola Ave., Carle Place, L. I., N. Y. 11514. **501**

Custom Tritiation

A custom tritiation service is available. This is accomplished by labeling by the Witzbach method (exposure of the compound to tritium gas in a closed ampule for a period of several weeks) or labeling by catalytic exchange or reduction using tritium gas and noble metal catalysts or tritiated metal hydride reagents. The 8th edition of the catalog lists over 1100 compounds labeled with carbon-14, tritium, deuterium, including deuterated solvents for NMR which are available from the company. Nuclear Research Chemicals, Inc., 100 No. Crystal Lake Dr., P. O. Box 6458, Orlando, Fla. **502**

New Carbon-14 Labeled Compounds

New compounds of particular interest to biochemists, medical researchers, etc., include thymidine, deoxyadenosine, deoxyguanosine, and deoxycytidine uniformly labeled with carbon-14 at specific activities in the range 200 to 350 mc./mM. They have been prepared by the degradation of deoxyribonucleic acid obtained from chlorella grown on CO_2–C^{14} as the sole source of carbon. Purification is by ion exchange and paper chromatography. Materials are better than 97% radiochemically pure. Chemical purities are established by ultraviolet spectra. The materials are dispensed in aqueous solutions, sealed under vacuum, and autoclaved at 15 lb./sq. inch for 30 minutes. Nuclear-Chicago Corp., 359 East Howard Ave., Des Plaines, Ill. 60018. **503**

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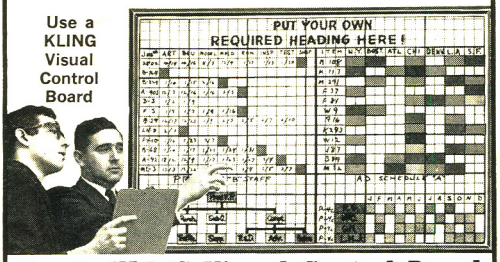

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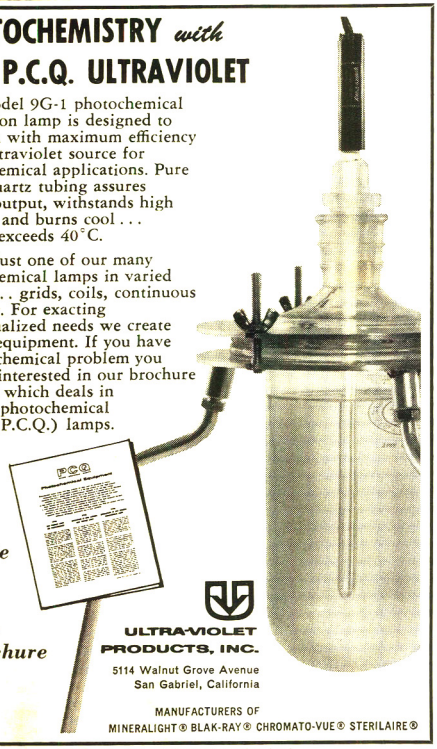

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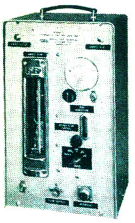

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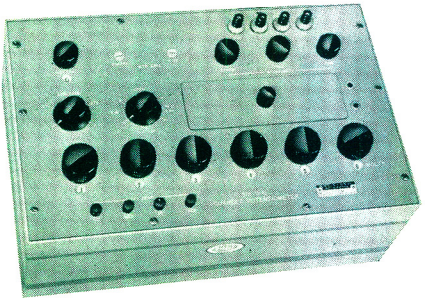

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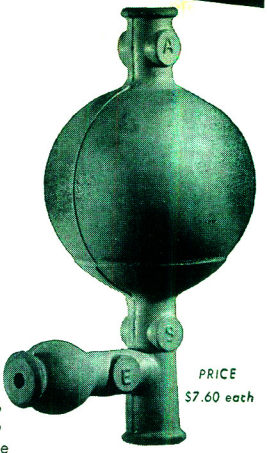

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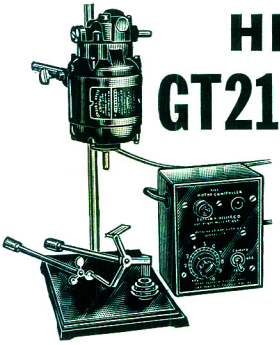

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MANUFACTURERS' LITERATURE

Carbon-14 Labeled Compounds. A new schedule of carbon-14 labeled compounds, 20 pages, contains over 400 items listed alphabetically, each with its specific activity range, useful purity check, and packaging information. Nuclear-Chicago Corp., 359 East Howard Ave., Des Plaines, Ill. 60018. **601**

Residual Gas Analyzer. An 8-page bulletin describes the 21-614 residual gas analyzer. This instrument uses a double focusing cycloidal analyzer and operates over a mass range of 2 to 200 at a unit resolution of 150. Consolidated Electrodynamics Corp., 360 Sierra Madre Villa, Pasadena, Calif. **602**

Moisture in Solids. A 4-page bulletin describes the Model 26-321 solids moisture analyzer. This instrument which operates on the coulometric electrolytic principle has a range fom 0.1 μg. to 100 mg. Consolidated Electrodynamics Corp., 360 Sierra Madre Villa, Pasadena, Calif. **603**

Gas Chromatograph Liquid Sample Valve. A 2-page sheet gives specifications and application suggestions for the Model LSV-220 liquid sample valve. Reproducible volumes of 0.3, 1.0, 3.0, or 10 μl. may be introduced into laboratory or process gas chromatographs with this valve. Loenco, Inc., 2092 North Lincoln Ave., Altadena, Calif. **604**

Raman Spectrometry Bibliography. A 23-page bibliography contains references to articles covering applications and techniques of the Cary Model 81 Raman spectrophotometer. Applied Physics Corp., 2724 South Peck Rd., Monrovia, Calif. **605**

CHN Analyzer. An 8-page bulletin describes the Model 180 carbon, hydrogen, nitrogen analyzer. Included is a discussion of this instrument along with photographs and captions to show the 3-step procedure for a complete analysis in 10 minutes. F & M Scientific Corp., Route 41 and Starr Rd., Avondale, Pa. 19311. **606**

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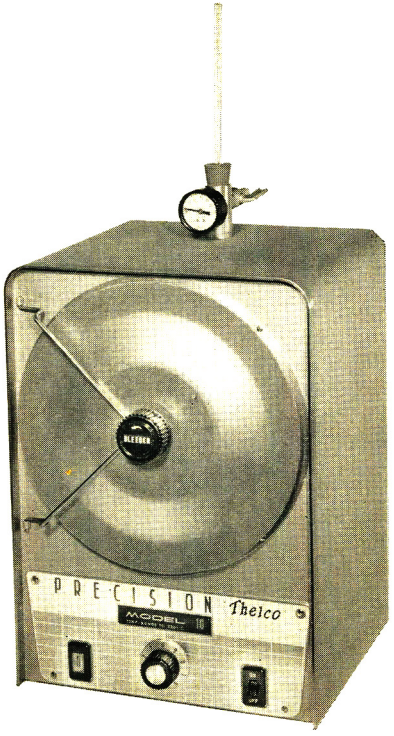

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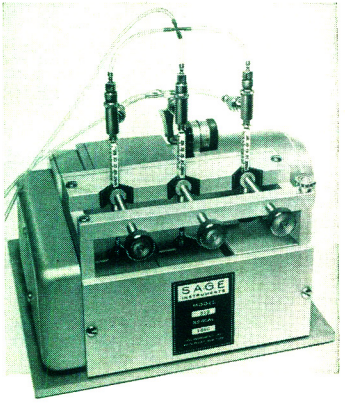

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MANUFACTURERS' LITERATURE

Environmental Equipment. A 6-page folder is a product guide for refrigerated and heated baths; low temperature, and humidity controlled environmental chambers, portable coolers, ovens and sterilizers, incubators, etc. Forma Scientific, Inc., Box 649 Marietta, Ohio 45750. **607**

Laboratory Products. A 32-page catalog lists, pictures, and describes laboratory equipment such as racks, brackets, baskets, trays, frames, electrical and portable equipment. Penn-Chem Corp., 232-238 N. Marshall St., Lancaster, Pa. **608**

Solid State X-Ray System. A 4-page brochure describes a new solid state system which provides stability and accuracy, works with all types of detectors, and is compatible with major x-ray diffraction and fluorescence systems. Hamner Electronics Co., Inc., P. O. Box 531, Princeton, N. J. **609**

Wet Chemical Analyzer. A 4-page bulletin, 4057, describes the Model 100 continuous wet chemical analyzer. This is an instrument for making continuous on-stream analyses of liquid or gaseous streams. Typical analyses are silica, hardness, chloride ions, hydrazine, phosphate, copper, iron, and residual chlorine. Beckman, Scientific & Process Instruments Division, 2500 Harbor Blvd., Fullerton, Calif. 92634. **610**

Metallurgical Microscopy. A 28-page publication, No. E-260, "Applications of Metallurgical Microscopy" by Hendrickson and Iannone, contains photomicrographs supported by a text covering the ground from basic definitions to unconventional applications of the metallograph. Single copies are free, multiple copies are available at $1 each. Bausch & Lomb Inc., Rochester, N. Y. 14602. **611**

Carbonaceous Analyzer. Bulletin 4059, a 6-page folder, describes an instrument that monitors water pollution by determining either total carbon or total organic carbon content of a dilute water sample in two minutes. The instrument is available for use in the laboratory or on-stream. Beckman Scientific and Process Instruments Division, 2500 Harbor Blvd., Fullerton, Calif. 92634. **612**

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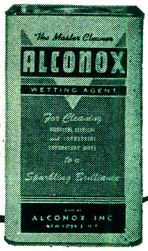

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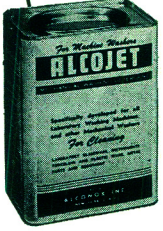

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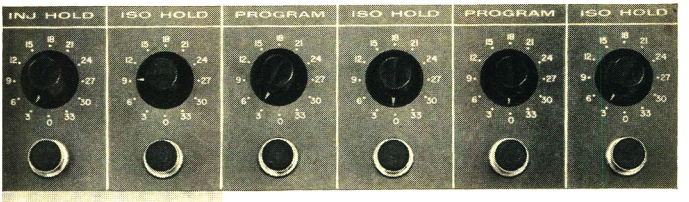

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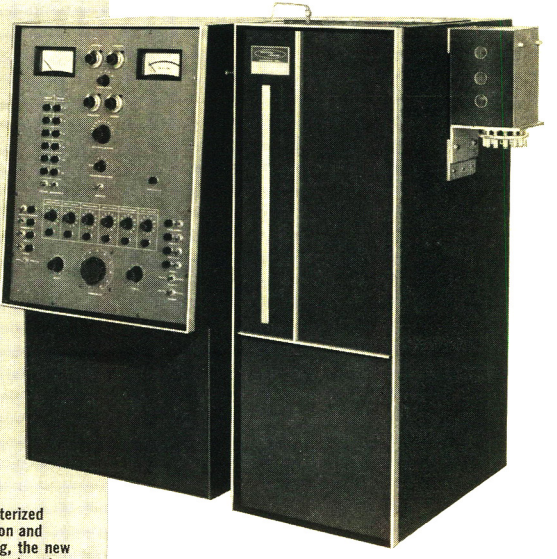

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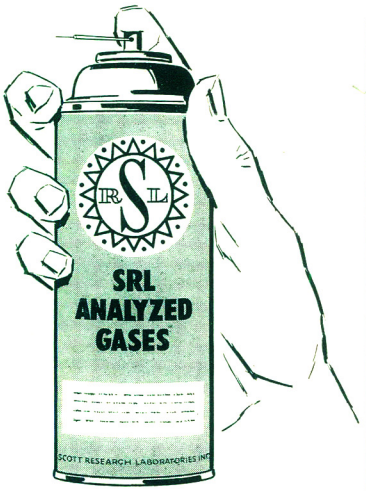

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MANUFACTURERS' LITERATURE

Research Biochemicals. The 1965 Price List and Reference Guide, 84 pages, contains information on some 3500 biochemicals including 170 new products. Mann Research Laboratories, Inc., 136 Liberty St., New York, N. Y. 10006. **613**

Plastic Labware. Catalog 0-165, 36 pages, describes the complete line of Nalgene plastic laboratory ware. Some products are new, some have been redesigned, and some have been reduced in price. The Nalge Co., Inc., 75 Panorama Creek Dr., Rochester, N. Y. 14625. **614**

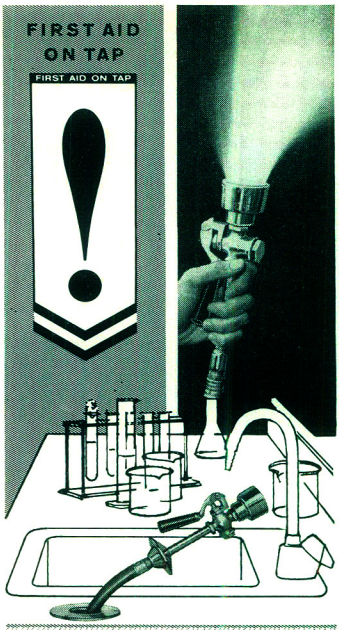
Plastics Labware. The 1965 S/P Catalog of Plastics and Disposables, 32 pages, presents products specifically designed for laboratory use, some with the added convenience of disposability. Scientific Products, 1210 Leon Place, Evanston, Ill. 60201. **615**

Spectrator. A 4-page bulletin describes the Spectrator (spectro-calculator) Type RO-201, a semiautomatic electrical analog computer for use in quantitative emission spectrography. Hollywood Instruments, Inc., P. O. Drawer 1400, Hollywood, Fla. **616**

Conductivity Monitor. Data Sheet B2.2121, 4 pages, describes the method of operation, presents schematic drawings, and gives a full list of specifications for the company's fluid conductivity monitor. Leeds and Northrup Co., 4901 Stenton Ave., Philadelphia, Pa. 19144. **617**

Radiochemical Catalog. A new catalog contains information on more than 900 radioactive chemicals and sources, plus numerous other products and services provided by the company. Purity, shelf life, specific activity, and prices are given. Tracerlab, 1601 Trapelo Rd., Waltham, Mass. 02154. **618**

Radioactivity Counting Systems. Bulletin 7056, 24 pages, describes and illustrates the Lowbeta II and the new Widebeta II planchet counting systems. It also covers the technique of low level counting, comparison of counting systems, and applications of low level counting. Beckman Scientific and Process Instruments Division, 2500 Harbor Blvd., Fullerton, Calif. 92634. **619**



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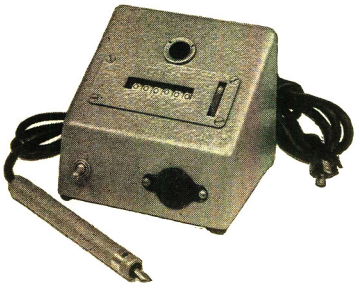

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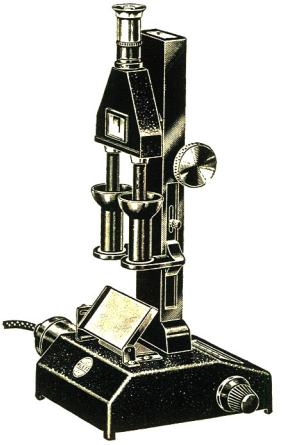

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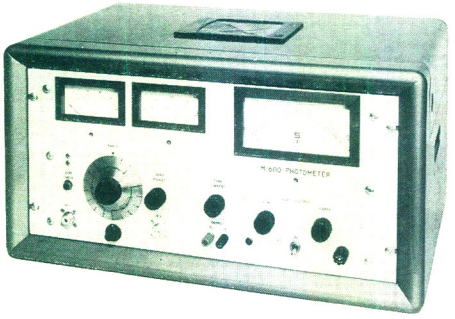

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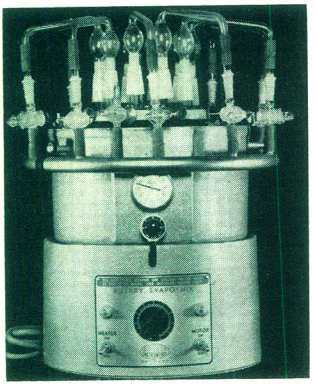

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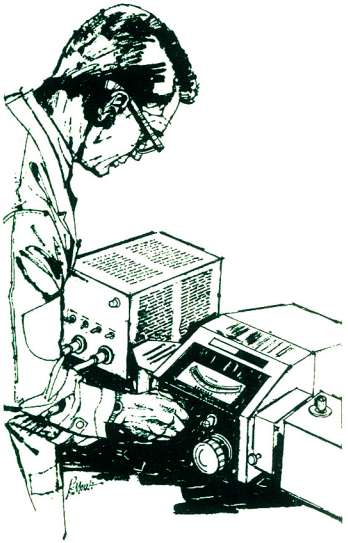

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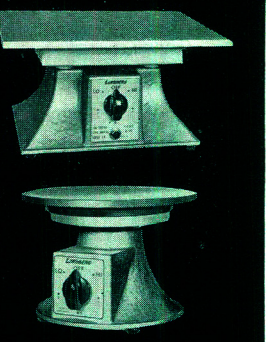

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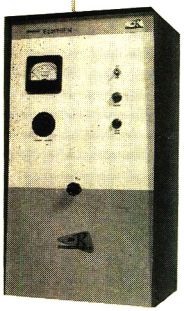

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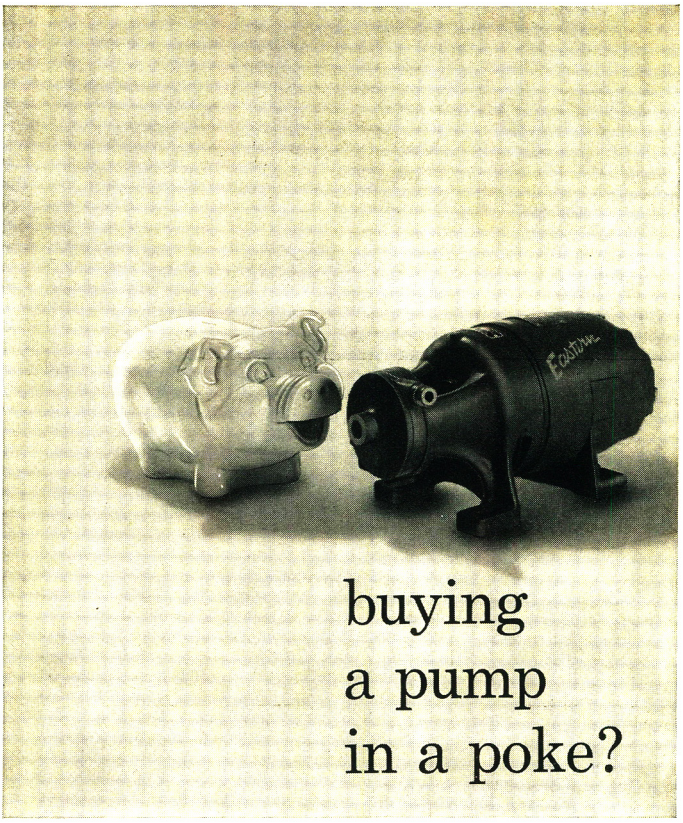

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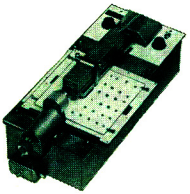

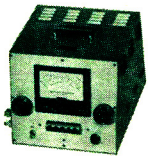

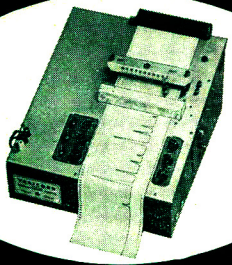

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JEOL News. Vol. 2, No. 4. This 16-page issue contains technical notes and information on new products. Among the new products are a new laser system, a specimen heating attachment for the company's electron microscope, and a standard recording chart system for the 100 Mc. NMR. Japan Electron Optics Laboratory Co., Ltd., 461 Riverside Ave., Medford 55, Mass.

Fritzsche Library Bulletin. Vol. 9, No. 1. This 6-page issue with a new format contains references to current literature covering research on essential oils, aromatic chemicals, perfume and flavor raw materials, and their application in industry. Included are 22 references to analytical methods. Fritzsche Brothers, Inc., 76 Ninth Ave., New York, N. Y. 10011.

Engelhard Industries Technical Bulletin. Vol. V, No. 3. This issue devotes 30 pages to a paper covering advances in the art and science of temperature measurement. This article emphasizes the importance of noble metals in thermometry. Engelhard Industries, Inc., 113 Astor St., Newark, N. J. 07114.

CEC/Recordings. This 24-page special edition contains 4 technical papers. Two of the articles are "Mass Spectrometer Plus Gas Chromatograph—A Powerful Research Tool" and "A Building Block Approach to Industrial Instrumentation Systems." Consolidated Electrodynamics, 360 Sierra Madre Villa, Pasadena, Calif.

Arcs and Sparks. Vol. 9, No. 8. This 16-page issue includes photos and a write-up on the Eastern Analytical Symposium and on the 3rd Pacific Meeting in San Francisco. "Labora-Story of the Month" is the Physical Science Center of the Monsanto Co. in St. Louis, Mo. Ultra Carbon Corp., P. O. Box 747, Bay City, Mich.

Chemist-Analyst. Vol. 54, No. 1. This 32-page issue includes articles on the extraction and photometric determination of vanadium using Kojic acid; reagent purification for photometric determination of iron by use of 1,10-phenanthroline, spot tests for dixanthogen, and for identification of formamide, and other analytical procedures. J. T. Baker Chemical Co., Phillipsburg, N. J.

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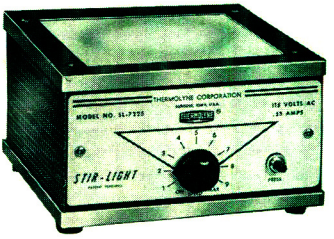

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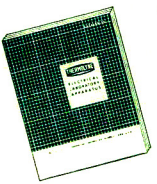

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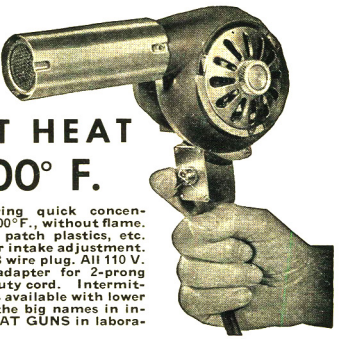

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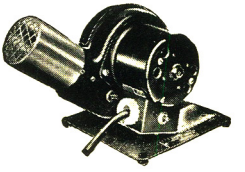

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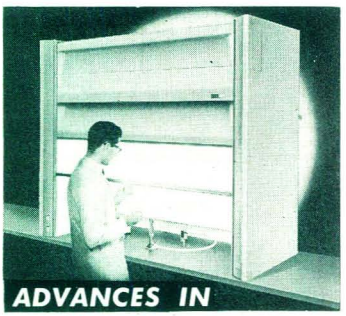

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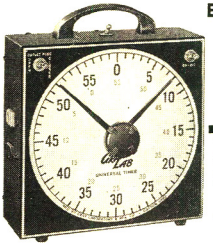

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INDEX TO ADVERTISERS IN THIS ISSUE

Ace Glass, Inc. 18
Heller Creative Advertising

Acton Laboratories, Inc. 91
Engineering Writers

Advanced Instruments, Inc. 138
Tech/Reps

Wm. Ainsworth & Sons, Inc. 131
Walter L. Schump

Alberene Stone, A Div. of the Georgia Marble Co. 77
G. M. Basford Company

Alconox 142
Miller Advertising Agency

Allied Chemical Corp., General Chemical Div., Baker & Adamson Products OBC
Kastor, Hilton, Chesley, Clifford & Atherton, Inc.

Aloe Scientific, Division of Brunswick .. 100
Roman Advertising Co.

American Instrument Co., Inc. 1
G. Bruce West Advertising Agency, Inc.

Analtech, Inc. 88
DeMartin, Marona & Associates, Inc.

Analytical Chemistry Buyers' Guide ... 120

H. Reeve Angel & Co., Inc. 4:106
Eckstein-Stone, Inc.

Applied Physics Corp. 105:122
Charles Bowes Advertising, Inc.

Applied Research Laboratories, Inc. 114
Willard G. Gregory & Company

Applied Science Laboratories, Inc. 104
Barash Advertising

Atomic Accessories, Inc. 45:48
J. B. Rundle, Inc.

J. T. Baker Chemical Co. 21:55
G. M. Basford Company

Barnes Engineering Co. 37
Albert A. Kohler Co., Inc.

Bausch & Lomb, Inc. 53:89:147
Wolff Associates, Inc.

Beckman Instruments, Inc. .....
Scientific Process Div. 73:82:93:113
Spinco Div. 20
Erwin Wasey, Inc.

James G. Biddle, Co. 140
The Michener Company

Bio-Rad Laboratories 139
Cappel, Pera & Reid, Inc.

S. Blickman, Inc. 130
J. M. Kesslinger & Associates

Brinkmann Instruments, Inc. 69–72:108
The Shaller-Rubin Co., Inc.

Briscoe Mfg. Co. 77
Charles Taft Peters, Inc.

Buchler Instruments, Inc. 146
Selvin & Jaffe

Cahn Instrument Co. 137
Haas, DeGrasse, Zimmerman

Canal Industrial Corporation 60
G. Bruce West Advertising Agency, Inc.

Chemical Materials Catalog, Reinhold Publishing Corp. 139
Persons Advertising, Inc.

Coleman Instruments, Inc. .. 38–39:119:124C
Hollander Advertising Agency

Consolidated Electrodynamics Corp. 68
Hixson & Jorgensen, Inc.

Corning Glass Works 123:132
The Rumrill Co., Inc.

Crawford Fitting Co. 33
Falls Advertising Co.

Cryonetics, Inc. 50
S. Gunnar Myrbeck & Co.

W. H. Curtin & Co. 136
Robinson-Gerrard, Inc.

Disc Instruments, Inc. 5
Jay Chiat and Associates

E. I. du Pont de Nemours & Co.. Inc. .. 46:47
The Rumrill Co., Inc.

Eastern Industries, Division of Laboratory for Electronics, Inc. 149
Hepler & Gibney, Inc.

Engelhard Hanovia, Inc., Lamp Div. ... 106
Keyes, Martin & Co.

F & M Scientific Corp. 64
Richardson, Thomas & Bushman, Inc.

Farrand Optical Co., Inc. 91
Snow & Depew Advertising

Fisher Scientific Co. 49:97:129
Fuller & Smith & Ross, Inc.

Forma Scientific, Inc. 44
O-Val Advertising, Inc.

Gilford Instrument Laboratories, Inc. .. 51:86
Evans Type-Art

Greiner Scientific Corp. 138
Fairfax, Inc.

Hamilton Co., Inc. 23
Swain/Mealer, Inc.

W. A. Hammond Drierite Co. 156

The Harshaw Chemical Co. 128

Haws Drinking Faucet, Inc. 144
Pacific Advertising Staff

Heath Co. 65
Advance Advertising Service, Inc.

Gerald K. Heller Co. 140
R & L Advertising Agency, Inc.

Heusser Instrument Company 79

Hewlett-Packard, Mechrolab Division .. 40
Bonfield & Associates, Inc.

Hitachi Ltd. 110
Dentsu Advertising Ltd.

Hoke, Inc. 112
Tek-Mark, Inc.

Honeywell, Inc. 62
The Aitkin-Kynett Co., Inc.

Illinois Water Treatment Co. 134
Cummings, Brand, McPherson Associates, Inc.

Instrumentation Associates, Inc. 140
A. D. Norbeck Co., Inc.

Instrumentation Laboratory, Inc. 107
Pazolt & Co.

Isomet Corporation 124B
Kalmar Advertising

Japan Electron Optics Laboratory Co., Ltd. 66
Fuller & Smith & Ross, Inc.

Jarrell-Ash Co. 34:130
Culver Advertising, Inc.

Kahl Scientific Instrument Corp. 135

Kensington Scientific Corp. 151
Smith-Reynolds

Klett Mfg. Co., Inc. 145

Kontes Glass Co. 74
Garceau, Hargrave & McCullough, Inc.

Laboratory Construction Co. ..... IFC
Valentine-Radford, Inc.

Labindustries 137:155
Bonfield Associates, Inc.

Laboratory Plasticware Fabricators 81
Kalikow Advertising Co.

E. Leitz, Inc. 133
L. W. Frohlich & Co., Inc.

Lepel High Frequency Laboratories, Inc. 134
Apex Graphic Co.

Lindberg/Hevi-Duty Marketing Services 148
Klau-Van Pietersom-Dunlap, Inc.

The London Co. 84
James Lovick & Co., Ltd.

Mfrs. Engineering & Equipment Corp. ... 140
H. Lesseraux Advertising

Master Appliance Corp. 151
Richard-Allen-Winter

The Matheson Co., Inc. 87
Leonard M. Sive & Associates, Inc.

Matheson, Coleman & Bell, Division of the Matheson Co., Inc. 98
Leonard M. Sive & Associates, Inc.

Matronic Instrument Co. 133
Lovekin Advertising

McPherson Instrument Corp. 96
Davis Advertising, Inc.

E. Merck AG 35
Deutsche Anzeigen GMBH

Mettler Instrument Corp. 8:124C
Harold Cressingham

Millipore Filter Corp. 151
Culver Advertising, Inc.

Mixing Equipment Co., Inc. 129
The Rumrill Co., Inc.

Nester & Faust 143
Evans, Dill & Co.

Nikon, Inc. 24
Gilbert and Felix, Inc.

Nuclear-Chicago Corp., Radiation Instrument Development Laboratory, Div. 109
Sidney Clayton & Associates

Nuclear-Chicago Corp., Texas Nuclear Corp., Subsidiary 36:56:57:67:76
Sidney Clayton & Associates

Nuclear Data, Inc. 6
Fulton, Morrissey Co.

Ohaus Scale Corp. 135
Robert M. Baldwin Co.

Pace Engineering Co. 80
Amsterdam Associates

Packard Instrument Co., Inc. 10
Ross Llewellyn, Inc.

Parr Instrument Co. 151
F. Willard Hills

Perkin-Elmer Corp. .....
30:31:58:59:85:95:111:148
Gaynor & Ducas, Inc.

Pfaltz & Bauer, Inc. 81
Givaudan Advertising, Inc.

Pharmacia Fine Chemicals, Inc. 99
Paul Klemtner & Co., Inc.

Philips Electronic Instruments 90
Anders Associates

Phoenix Precision Instrument Co. 132
Product Promotions Agency

Photovolt Corp. 54:150
The M. B. Pearlman Co.

Picker X-Ray Corp. 26
Gotham-Vladimir Advertising, Inc.

Precision Scientific Co. 141
Tri-State Advertising Co., Inc.

Princeton Applied Research Corp. 16
Mort Barish Associates

Professional Tape Co., Inc. 156
Robert Peterson Advertising Agency

Proton Laboratories 32

Radiation Instrument Development Laboratory, A Div. of Nuclear-Chicago Corp. 109
Sidney Clayton & Associates

Radio Corp. of America, Broadcast & Comm. Prod. Division 115
Al Paul Lefton Company, Inc.

INDEX TO ADVERTISERS IN THIS ISSUE

Regal & Wade Mfg., Inc., Kling Systems LBR, Inc. 139

RGI, Inc. 43
Garceau, Hargrave & McCullough, Inc.

Milton Roy Company 149
The Harry P. Bridge Co.

Sadtler Research Laboratories, Inc. 145
The Roland G. E. Ullman Organization, Inc.

Sage Instruments, Inc. 142
Lescarboura Advertising, Inc.

E. H. Sargent & Co. 78:125
Fulton, Morrissey Co.

Carl Schleicher & Schuell Co. 29
Wildrick & Miller, Inc.

Schoeffel Instrument Co. 146
Cristina Advertising Agency

James F. Scanlon Company 44
Associated Business Consultants

Scientific Glass Apparatus Co., Inc. 12

Scientific Industries, Inc. 54
Black & Musen, Inc.

Scott Research Laboratories, Inc. 144
George H. McGlaughlin Advertising

Ivan Sorvall, Inc. 118
Arthur B. W. Toft, William Hill Field Advertising

Standard Scientific Supply Corp. 32
Miller Advertising Agency

Taylor Instrument Companies 128
Batten, Barton, Durstine & Osborn, Inc.

Technical Measurement Corp. 63
Culver Advertising, Inc.

Technicon Controls, Inc. 25
Mediad, Inc.

Textronix, Inc. 83
Hugh Dwight Advertising, Inc.

Texas Instrument, Inc. 61
Robinson-Gerrard-McGary, Inc.

Texas Nuclear Corp., A Subsidiary of Nuclear-Chicago Corp. 36:56:57:67:76
Sidney Clayton & Associates

Thermolyne Corp. 150
E. R. Hollingsworth & Associates

Thermovac Industries Corp. 143
M. B. Brucker Co., Inc.

Arthur H. Thomas Co., Inc. 124:124B

Tracerlab, A Div. of Laboratory for Electronics, Inc. 7
Bonfield Associates, Inc.

Ultra-Violet Products, Inc. 139
Willard G. Gregory & Co.

Unicam 22
Arks Publicity Ltd.

Union Carbide Corp., Carbon Products Division 92
J. M. Mathes, Inc.

U. S. Stoneware Co. 52
Ralph Gross, Inc.

Vanguard Instrument Co. 116
Waldie & Briggs, Inc.

Varian Associates 14
Hoefer, Dieterich & Brown, Inc.

Warner-Lambert Pharmaceutical Co. 19
Lambert & Feasley, Inc.

The Welch Scientific Co. 131
Armstrong Advertising Agency, Inc.

Wilkens-Anderson Co. 103
Mandabach & Simms, Inc.

Wilkens Instrument & Research, Inc. 126
Bob Barriskill Advertising

Carl Zeiss, Inc. IBC:121
G. M. Basford Co.

Laboratory Supply Center 152-153
Burdick & Jackson Laboratories
Chemical Control Systems
Clark Microanalytical Laboratory
Dimco-Gray Co.
Ducommun Co.
Eastern Chemical Corp.
General Atomic
George W. Gates Co.
Gollob Analytical Service, Inc.
Guild Corporation
Hill Engineering & Manufacturing Co.
Hollywood Instruments, Inc.
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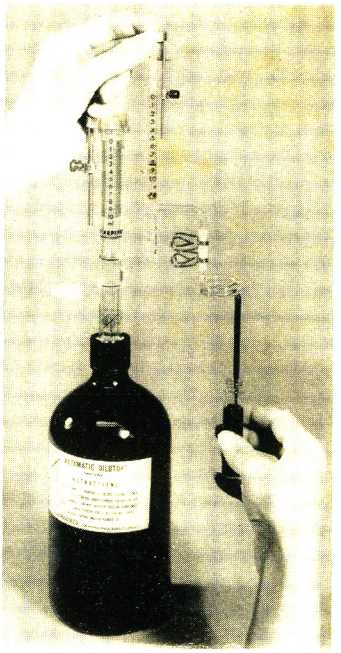

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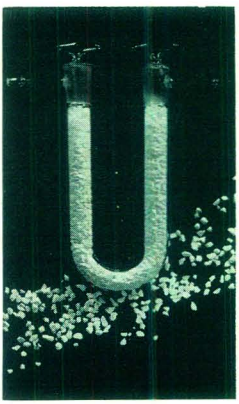

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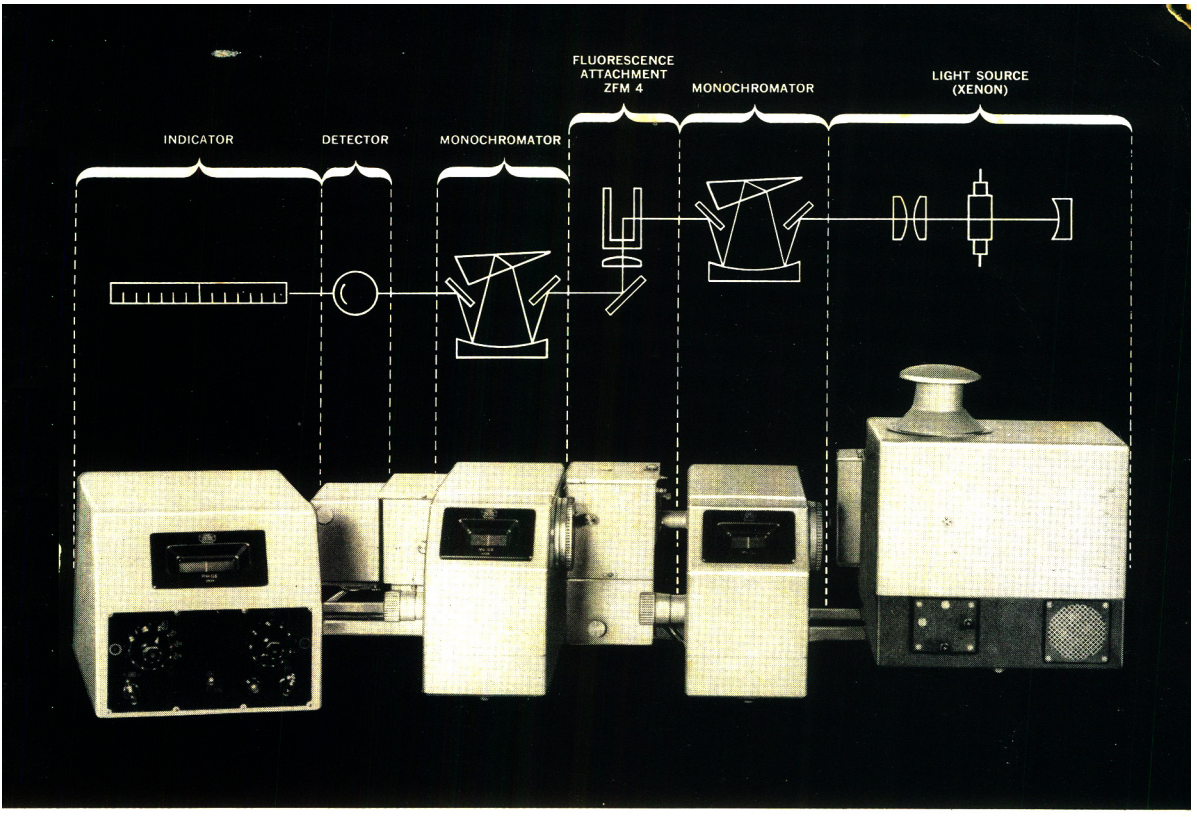

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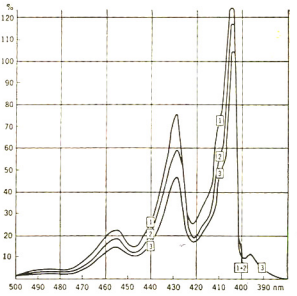

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