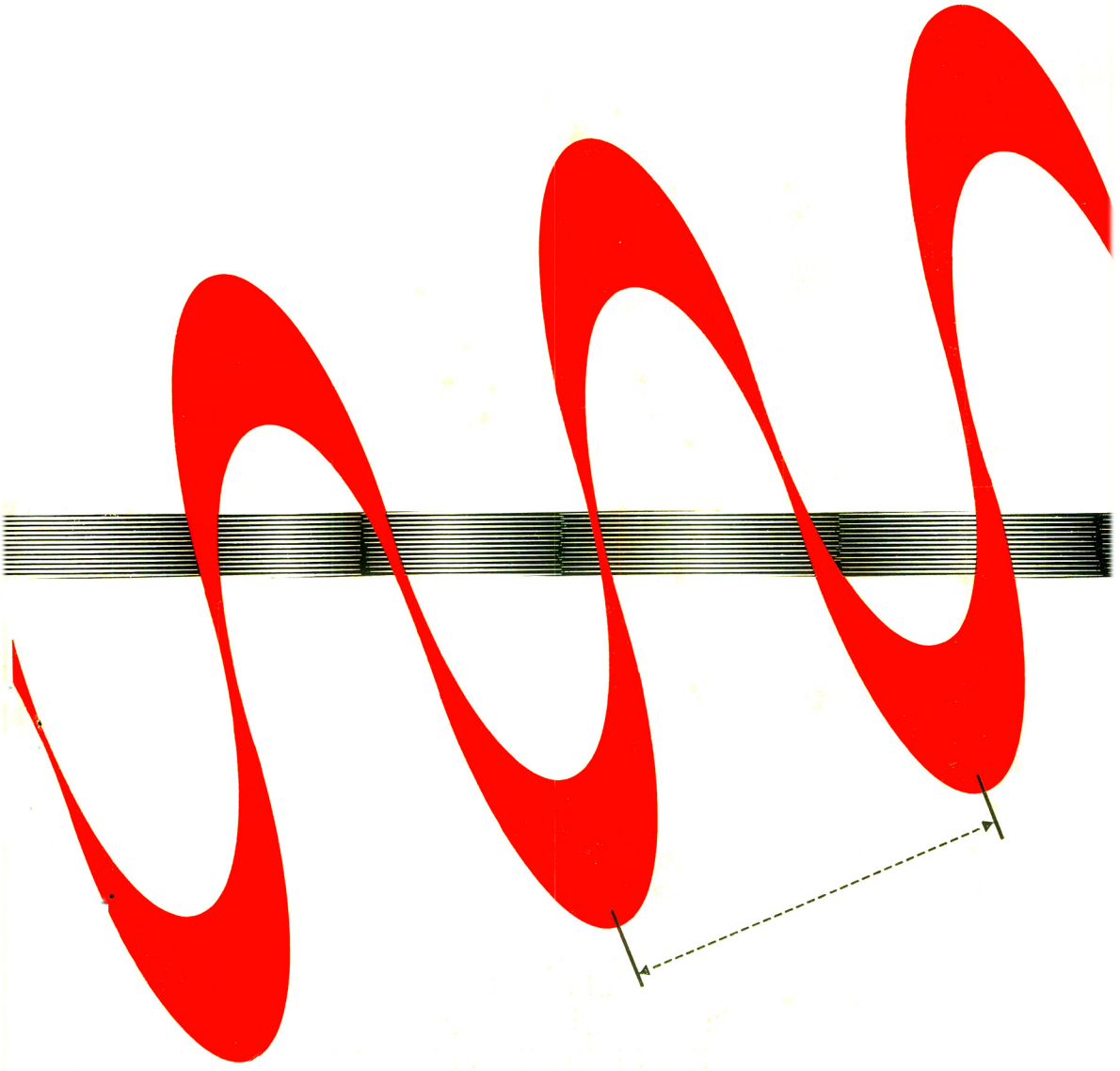
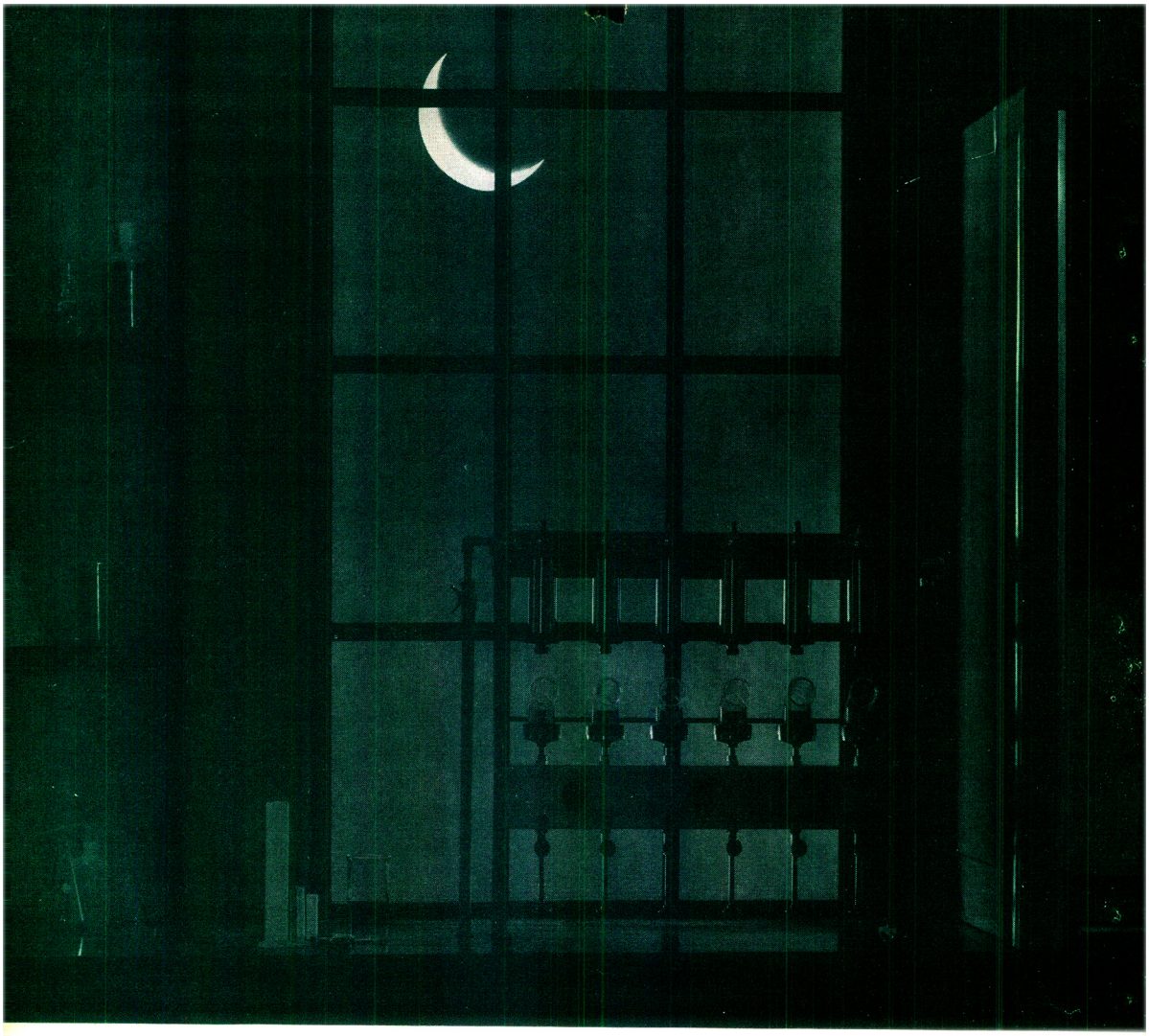
NOVEMBER 1964

ANALYTICAL CHEMISTRY



AVAILABILITY OF STANDARD REFERENCE MATERIALS 23A



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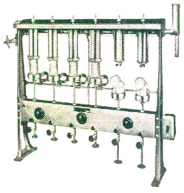

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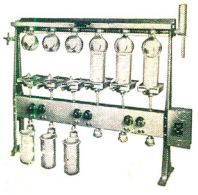

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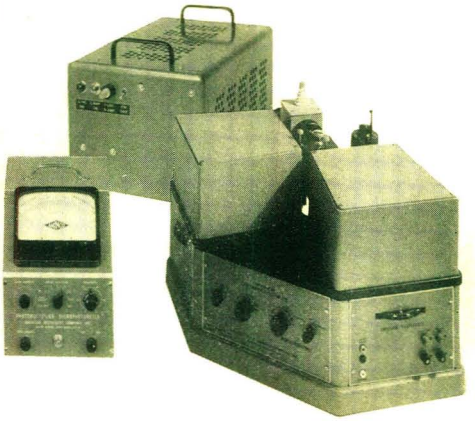

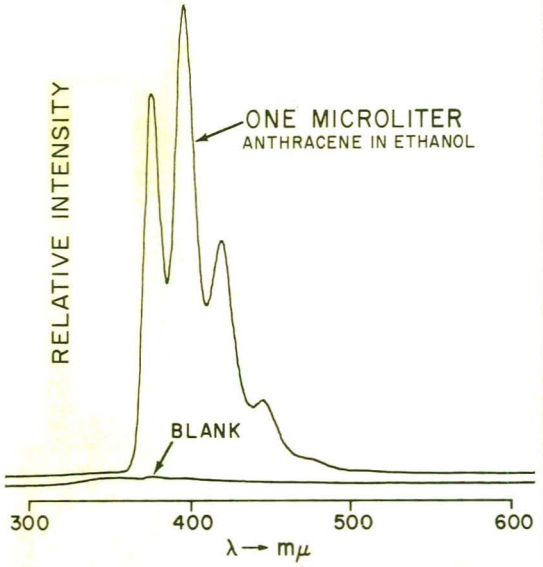

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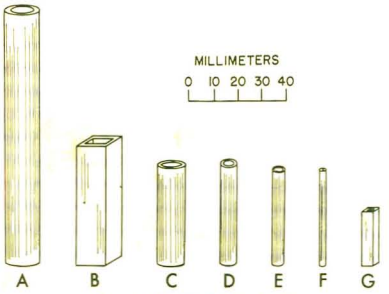

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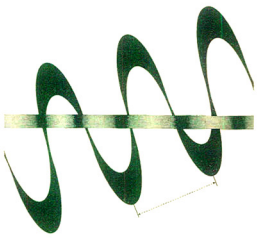

AVAILABILITY OF STANDARD REFERENCE MATERIALS 23A

This month's cover illustrates the international standard of length, the wavelength of the orange-red light emitted by excited atoms of the krypton isotope 86. The November Report for Analytical Chemists, "The Availability of Standard Reference Materials," begins on page 23 A.

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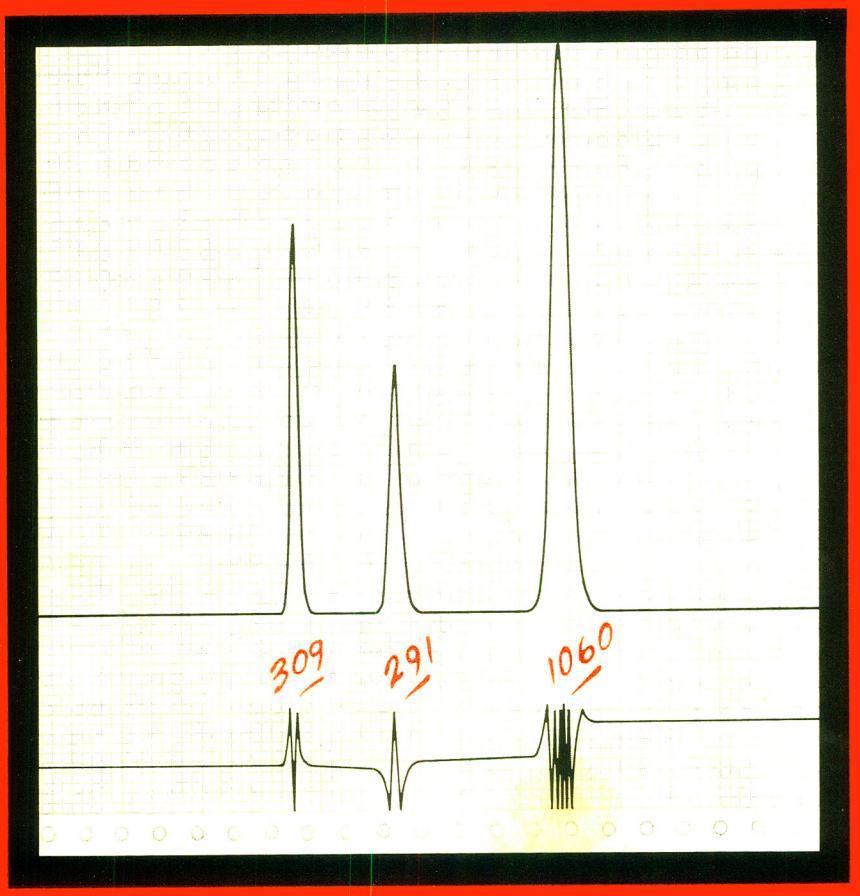

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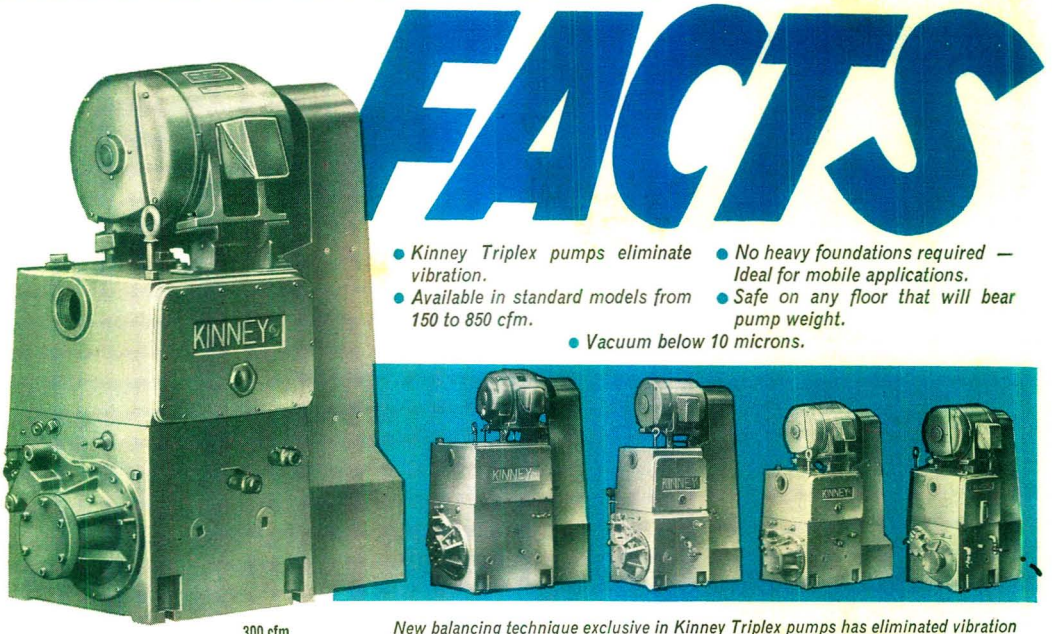

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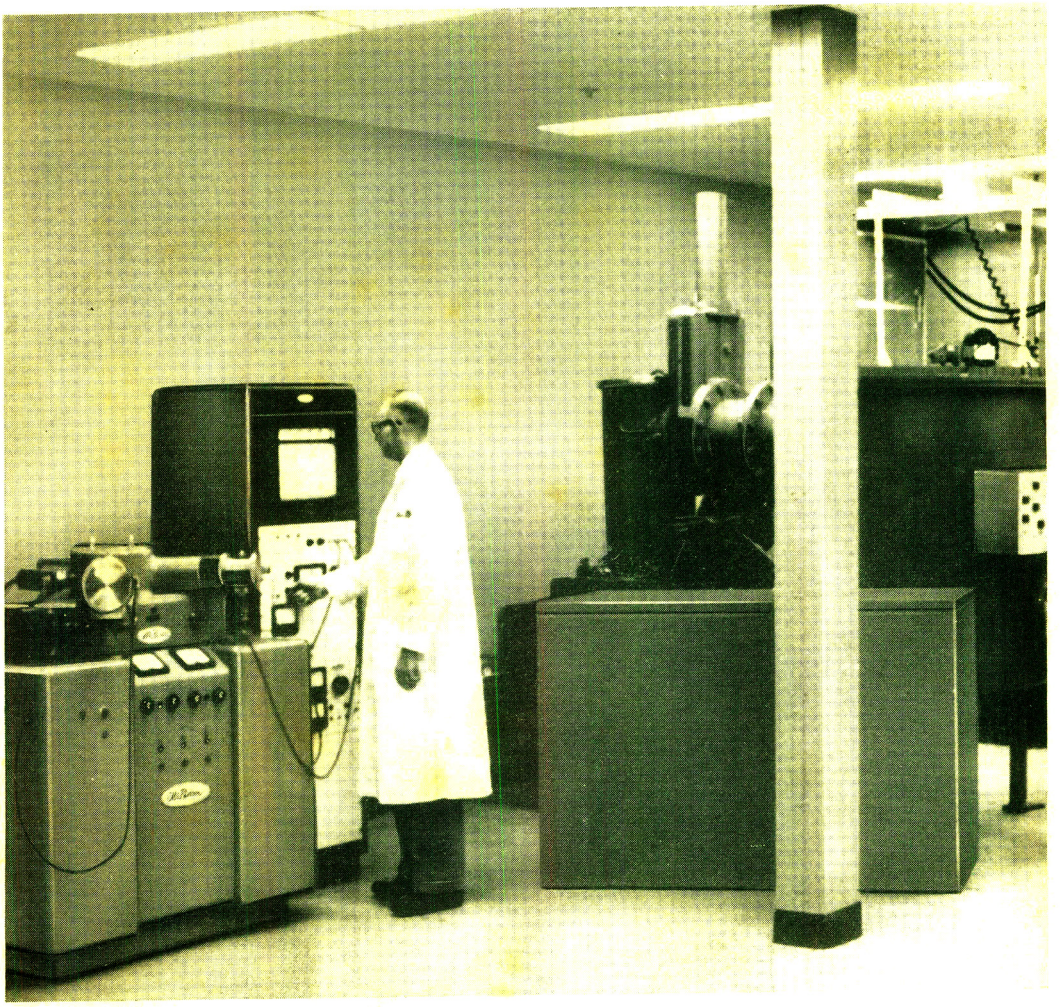

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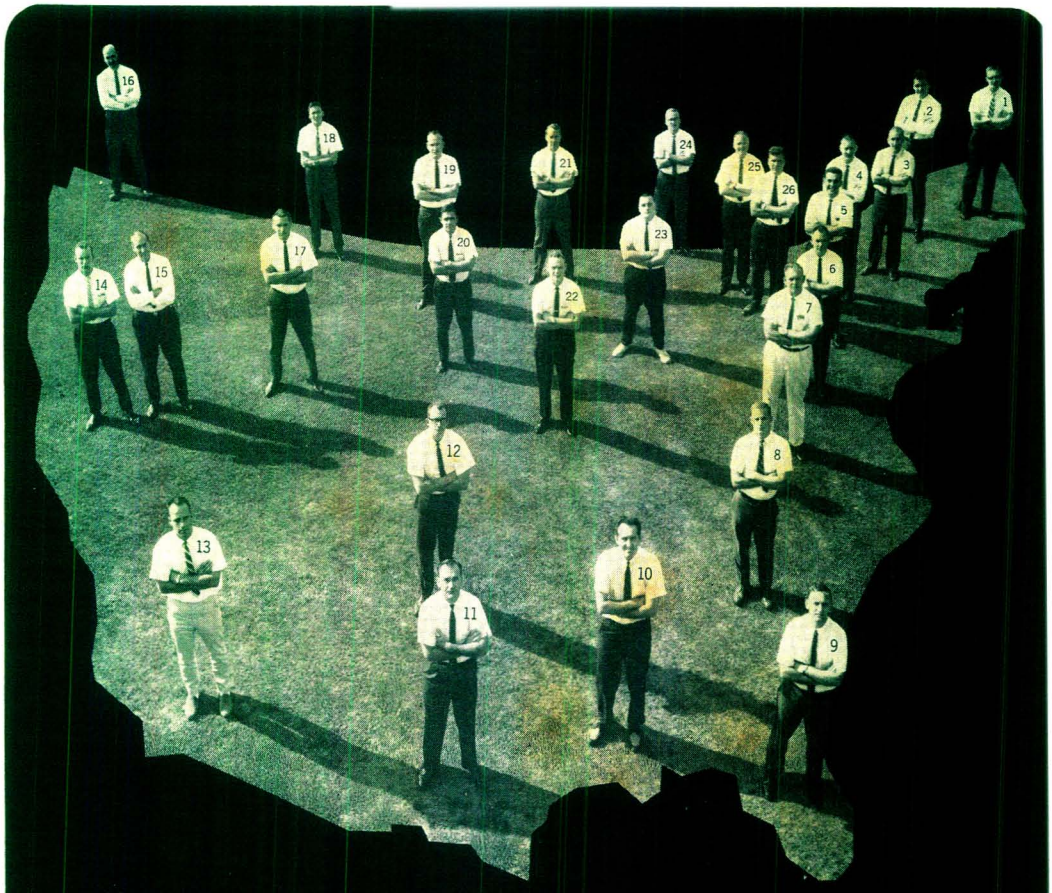

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AC BRIEFS

Highlights for the scientific and technical articles in this issue

Porous Layer Glass Bead Column Packing in Gas Adsorption Layer Chromatography

Porous layer glass beads coated with highly dispersed ferric oxide or zirconium oxide and impregnated with triethylene glycol are used to separate aliphatic and aromatic hydrocarbons and to separate aliphatic compounds containing oxygen or halogens.

ISTVÁN HALÁSZ and CSABA HORVÁTH, Institut für physikalische Chemie der Universitat, Frankfurt am Main, Germany.

Anal. Chem. 36, 2226 (1964)

Vapor Pressure of Stationary Phases over Gas Chromatographic Supports

Studies by various methods of the vapor pressure of stationary phases over gas chromatographic supports show that this value approaches the bulk form, with attendant bulk properties, at most practical loadings.

STEPHEN J. HAWKES and J. CALVIN GIDDINGS, Department of Chemistry, University of Utah, Salt Lake City, Utah

Anal. Chem. 36, 2229 (1964)

Zone Melting Considered as a Chromatographic Separation Technique

Elementary theory for ZC (zone chromatography) is compared with the theory for gas liquid chromatography. Requirements of the apparatus and variants of the basic technique are discussed.

W. G. PFANN, Bell Telephone Laboratories, Inc., Murray Hill, N. J.

Anal. Chem. 36, 2231 (1964)

Gradient Loaded Columns in Gas Chromatography

The case of a continuous linear decrease in k (partition ratio) down the column is considered theoretically and experimentally. Theoretical predictions and experimental results agree well on a 16-stage step-wise approximation to a continuous linear gradient column.

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

Anal. Chem. 36, 2234 (1964)

Gas Chromatography of Free Fatty Acids

Free fatty acid homologs and isomers from C_2 through C_5 can be separated on columns made with a polar liquid phase and an acidic additive coated on acid-washed glass microbeads.

J. G. NIKELLY, Department of Chemistry, Philadelphia College of Pharmacy and Science, Philadelphia, Pa. 19104

Anal. Chem. 36, 2244 (1964)

Gas Chromatographic Determination of Acetylsalicylic Acid

Quantitative separation is achieved on a 1- to 2-meter column of 0.25% Carbowax 20M and 0.4% isophthalic acid coated on acid-washed glass microbeads. Precision is 1% or better and the limit of detection is about 50 p.p.m. or 10^{-11} gram.

J. G. NIKELLY, Department of Chemistry, Philadelphia College of Pharmacy and Science, Philadelphia, Pa. 19104

Anal. Chem. 36, 2248 (1964)

Sulfonation and Dehydrogenation as an Aid to Gas Chromatography in Evaluating 90° to 150° C. Petroleum Fractions

Procedures are given to determine most of the individual components through *n*-heptane, individual aromatics through C_8 compounds, ethylcyclohexane and the four isomers of dimethycyclohexane (*cis* and *trans* structure combined), combined total of C_9 and C_{10} aromatics, and an approximate carbon number distribution of paraffins and naphthenes above C_7 compounds.

W. J. HINES and D. E. SMITH, Phillips Petroleum Co., Bartlesville, Okla.

Anal. Chem. 36, 2250 (1964)

Gas Chromatographic Separation of 2,4-Dinitrophenylhydrazone Derivatives of Carbonyl Compounds

Separation is accomplished using SF-96 (100) silicone oil as a liquid phase at temperatures from 200° to 250° C. The reagent does not interfere and recrystallization of the derivatives is not necessary.

R. J. SOUKUP, R. J. SCARPELLINO, and ELLEN DANIELCZIK, Jell-O Research Laboratories, General Foods Corp., White Plains, N. Y.

Anal. Chem. 36, 2255 (1964)

Quantitative Determination of Parts-per-Million Quantities of Nitrogen Dioxide in Nitrogen and Oxygen by Electron-Capture Detection in Gas Chromatography

The advantages of this method include that of short time (5 minutes *vs.* 3–4 days with the ASTM method) and small sample size (0.5 cc. *vs.* about 1 liter).

M. E. MORRISON, R. G. RINKER, and W. H. CORCORAN, Chemical Engineering Laboratory, California Institute of Technology, Pasadena, Calif.

Anal. Chem. 36, 2256 (1964)

Investigation of Trace Impurities in Solids by Electron Paramagnetic Resonance. Distribution of Manganese in Calcium Carbonate

The study shows that trace impurities are not distributed on the basis of homogeneous probability when mutual interaction among atoms of the impurity occurs.

SHIZUO FUJIWARA, Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo, Japan

Anal. Chem. 36, 2259 (1964)

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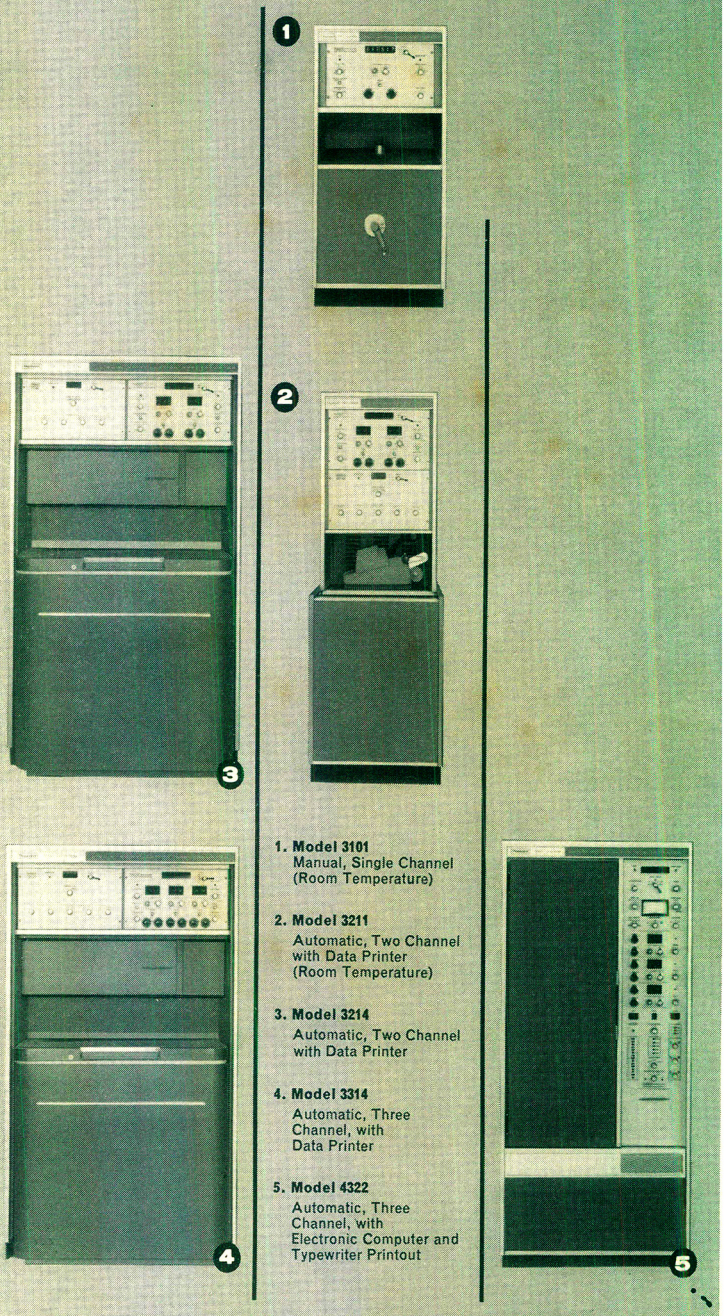

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Kinetics and Mechanism of Extraction of Zinc, Nickel, Cobalt, and Cadmium with Diphenylthiocarbazone, Di-o-Tolylthiocarbazone, and Di-α-Naphthylthiocarbazone

Each of the reactions studied was first order in metal ion and, with one exception, first order in reagent anion. The reaction of zinc with di-α-naphthylthiocarbazone was second order in reagent anion. Values of the distribution coefficients, $K_{D,r}$, between $CHCl_3$ and water are reported.

B. E. McCLELLAN and HENRY FREISER, Department of Chemistry, The University of Arizona, Tucson, Ariz.

Anal. Chem. 36, 2262 (1964)

Study of Kinetics of Iridium(III)–Chlorate Reaction by Steady-State Controlled-Potential Coulometry

Steady-state controlled-potential electrolysis in the investigation of kinetics of redox reactions has been examined with regard to types of systems amenable to study.

G. A. RECHNITZ and J. E. McCLURE, Department of Chemistry, University of Pennsylvania, Philadelphia, Pa. 19104.

Anal. Chem. 36, 2265 (1964)

Analysis of Mixtures of Hydroxyl Compounds Using Differential Reaction Rates

The hydroxyl group of binary and ternary mixtures of alcohols is reacted with phenyl isocyanate. The reaction is followed by the disappearance of the NCO band at 4.42 microns in the infrared spectrum.

FRISO WILLEBOORSE and F. E. CRITCHFIELD, Union Carbide Corp., Chemicals Division, Technical Center, South Charleston, W. Va.

Anal. Chem. 36, 2270 (1964)

Identification of 2-Quinolones in a California Crude Oil

Infrared spectra of heavy gas oils vacuum distilled from a few crude oils sampled from wells in the Ventura Basin, Calif., showed a unique absorption band at 6.07 microns which by chemical and chromatographic methods proved to be caused by the amide carbonyl group of 2-quinolones.

EDWARD C. COPELIN, Union Oil Co. of California, Union Research Center, P. O. Box 76, Brea, Calif.

Anal. Chem. 36, 2274 (1964)

Thickness Measurement of Polymer Films for Infrared Spectrometry by Beta-Ray Absorption. Analysis of Ethene–Propene Copolymers

The relative error in the determination does not exceed 1%. The method which is applicable to rubber and to films with rough surfaces is used for illustrative purposes for the determination of the propene content of ethene–propene copolymers.

Th. A. VEERKAMP, R. J. De KOCK, A. VEERMANS, and M. H. LARDINOYE, Central Laboratory, Staatsmijnen in Limburg, The Netherlands

Anal. Chem. 36, 2277 (1964)

Diffusion Method for the Determination of Silicon in Inorganic Materials

The procedure eliminates most interfering cations and anions and is rapid and accurate. The concentration range studied in this investigation was between 0.003 and 2.7%.

ROBERT HOUSEHOLDER and R. G. RUSSELL, Olin Mathieson Chemical Corp., New Haven, Conn.

Anal. Chem. 36, 2279 (1964)

Determination of Residual Monomers and Other Volatile Components in Styrene Based Polymers by Gas Chromatography

The method is based on the direct injection of solutions or dispersions of polymers in *N,N'*-dimethylformamide using toluene as an internal standard. Additives, pigments, and stabilizers do not interfere in the determination.

PETER SHAPRAS and GEORGE C. CLAVER, Monsanto Chemical Co., Plastics Division, Research Department, Springfield, Mass.

Anal. Chem. 36, 2282 (1964)

Determination of Polyphenyls in Working Environments of Organic Reactors by Spectrophotometric Methods

Two analytical procedures were devised for the determination of polyphenyls: a colorimetric method and an ultraviolet method. Three types of air sampling procedures were also developed.

CORRADO TESTA and GIUSEPPINA MASI, Medical Service, Casaccia Nuclear Center, C.N.E.N.-Rome, Italy

Anal. Chem. 36, 2284 (1964)

Polarographic Determination of Submicrogram Quantities of Molybdenum

The method has a sensitivity of 0.005 μg. of molybdenum per ml. of solution and has been used for the determination of this metal in a number of pure materials.

AURORA T. VIOLANDA and W. D. COOKE, Department of Chemistry, Cornell Univeristy, Ithaca, N. Y.

Anal. Chem. 36, 2287 (1964)

Use of Self-Sealing Elastomer Septums for Quantitative Operations with Volatile Solvents

Sorption, permeation, diffusion, and resealing ability of a representative group of elastomers and volatile solvents have been studied. Merits and limitations of the septums and techniques for decreasing sorption–permeation losses are given.

NORMAN ADLER, Chemical Division, Merck & Co., Inc., Rahway, N. J.

Anal. Chem. 36, 2291 (1964)

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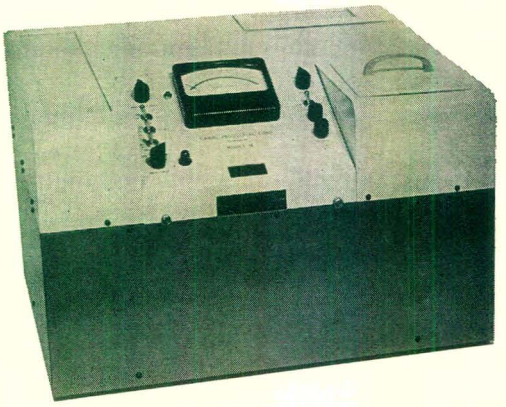

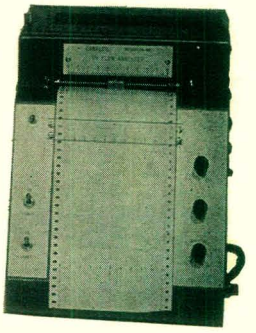

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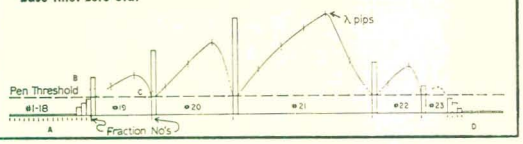

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Time Constant of a Thomas Autometer and Significance of Indicated Response

A time constant theory based on a first order response of the sensor, as developed for thermometers and other meteorological instruments, has been applied to the continuous measurement of air pollutants.

H. P. SANDERSON, P. E. PENNER and MORRIS KATZ, Occupational Health Division, Dept. of National Health and Welfare, Ottawa, Canada.

Anal. Chem. 36, 2296 (1964)

Analysis of Pentaerythritol Tetranitrate and Its Hydrolysis Products by Thin Layer Chromatography and Radio Scanning

The hydrolysis of C^{14}-tagged pentaerythritol tetranitrate by 1*N* HCl in 75% aqueous dioxane was studied. Thin layer chromatography was used to resolve the mixtures and radio scanning was used to locate the compounds.

FREDERICK J. DiCARLO, JAMES M. HARTIGAN, Jr., and GEORGE E. PHILLIPS, Biochemistry Department, Warner-Lambert Research Institute, Morris Plains, N. J.

Anal. Chem. 36, 2301 (1964)

Separation of Scandium from Yttrium, Rare Earths, Thorium, Zirconium, Uranium, and Other Elements by Anion Exchange Chromatography in Ammonium Sulfate Media

The described procedure can also be used for separating five metals—rare earths(III), Sc(III), Zr(IV), Th(IV), U(VI), consecutively using $(NH_4)_2SO_4$ and very common mineral acids.

HIROSHI HAMAGUCHI, ATSUHIRO OHUCHI, TSUNEO SHIMIZU, NAOKI ONUMA, and ROKURO KURODA, Department of Chemistry, Tokyo Kyoiku University, Koishikawa, Tokyo

Anal. Chem. 36, 2304 (1964)

Cation Exchange Separation of Titanium and Zirconium Using Perchloric Acid. Application to the Analysis of PZT Ceramics

The separation procedure uses $HClO_4$–NH_4F mixtures and $HClO_4$ as eluents. Solutions containing titanium and zirconium in amounts between 10 to 100 mg. of each element were separated from each other.

R. G. DOSCH and F. J. CONRAD, Organization 1122, Sandia Laboratory, Albuquerque, N. M.

Anal. Chem. 36, 2306 (1964)

Anion Exchange Separation of Gallium, Indium, and Aluminum

Two methods are described for the quantitative separation of milligram quantities of gallium and indium even when aluminum is present in great excess. The methods can be applied to the analysis of aluminum for gallium and indium.

JOHANN KORKISCH and ISIDOR HAZAN, Analytical Institute, University of Vienna, IX., Währingerstrasse 38, Austria

Anal. Chem. 36, 2308 (1964)

Anion Exchange Behavior of Alkali and Alkaline Earth Elements in Dioxane–Mineral Acid Media

A separation of Group I from Group II elements using dioxane–HCl–H_2O as eluent was demonstrated. Effects of dioxane content, acid concentration, and loading are discussed. Analytical applications are considered.

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

Anal. Chem. 36, 2311 (1964)

Thermal Expansion Apparatus for Use with Differential Thermal Analysis Equipment

The apparatus described used with DTA can determine coefficients of thermal expansion of solid samples over a wide temperature range. Sample expansion is mechanically and electrically amplified and recorded automatically and accurately.

EDWARD M. BARRALL II, ROGER S. PORTER, and JULIAN F. JOHNSON, California Research Corp., Richmond, Calif.

Anal. Chem. 36, 2316 (1964)

Automatic Data Processing, Interpreting, and Reporting of Results of Emission Spectrographic Analyses

A generalized Fortran computer program is given which calculates and reports the results for the common-matrix method of emission spectrographic analysis. Elements determined, lines used, and element used for internal standard are left to the option of the user.

D. D. TUNNICLIFF and J. R. WEAVER, Shell Development Co., Emeryville, Calif.

Anal. Chem. 36, 2318 (1964)

Spectrophotometric Determination of Tin(IV) by Extraction of Stannic Iodide into Ethyl Iodide

The Sn concentration can be determined within 1% of the total Sn present. The method was applied to the determination of Sn in alloys whose other principal constituents were Cu, Pb, Zn, and Sb. Interference studies are reported.

ARMINE D. PAUL and JOHN A. GIBSON, Jr., Department of Chemistry, West Virginia University, Morgantown, W. Va.

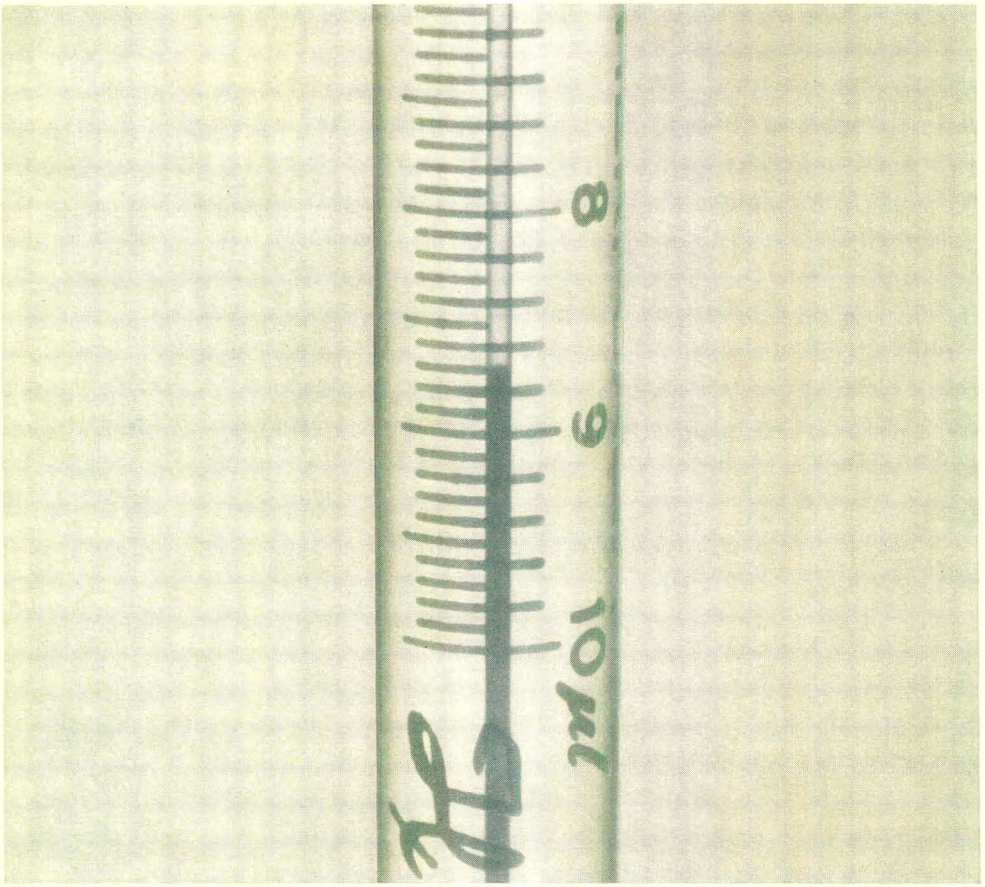
Anal. Chem. 36, 2321 (1964)

Optimum Conditions for Chemical Analysis by X-Ray Absorption-Edge Spectrometry

The related problems of optimizing sample path length (absorber thickness) and x-ray detector timing periods for chemical analysis by absorption-edge spectrometry are considered. Numerical solutions of the derived equations are given.

CHARLES G. DODD, Owens-Illinois Glass Co., Toledo, Ohio 43601, and DAVID J. KAUP, University of Oklahoma, Norman, Okla.

Anal. Chem. 36, 2325 (1964)



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Separation of Americium from Curium with Calcium Fluoride

Americium(VI) is soluble in fluoride solutions and passes through a column of calcium fluoride. Curium(III) and other trivalent actinides and lanthanides are not soluble and are retained. This method offers a 50-fold greater separation of americium from curium than is obtained by the precipitation technique.

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

Anal. Chem. 36, 2329 (1964)

Infrared Spectra of Transition Metal Alkoxides

The infrared spectra of a number of transition metal isopropoxides and tetra-*tert*-butoxides have been obtained from 5000 to 285 $cm.^{-1}$ Results show that the region from 715 to 285 $cm.^{-1}$ would be satisfactory for characterizing *tert*-butyl compounds.

C. T. LYNCH, K. S. MAZDIYASNI, J. S. SMITH, and W. J. CRAWFORD, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio

Anal. Chem. 36, 2332 (1964)

Thermoanalysis of Some Inorganic Fluorides and Silicofluorides

Experiments were performed at one atmosphere pressure over a temperature range 25° to 800° C. with the following compounds: potassium fluoride dihydrate, calcium fluoride, lead fluoride, ammonium silicofluoride, sodium silicofluoride, magnesium silicofluoride hexahydrate, calcium silicofluoride dihydrate, and zinc silicofluoride hexahydrate.

ELI S. FREEMAN and VIRGINIA D. HOGAN, Pyrotechnics Laboratory, Picatinny Arsenal, Dover, N. J.

Anal. Chem. 36, 2337 (1964)

Infrared Analysis of Suspended Particulates with Millipore Filters and Attenuated Total Reflection

The described technique is particularly effective for separating particulate material from fluid media and also presents a nearly ideal type of sample to the attenuated total reflectance crystal. Several examples of the usefulness of this method are given.

ROBERT W. HANNAH, The Perkin-Elmer Corp., Norwalk, Conn., JAMES L. DWYER, Millipore Filter Corp., Bedford, Mass.

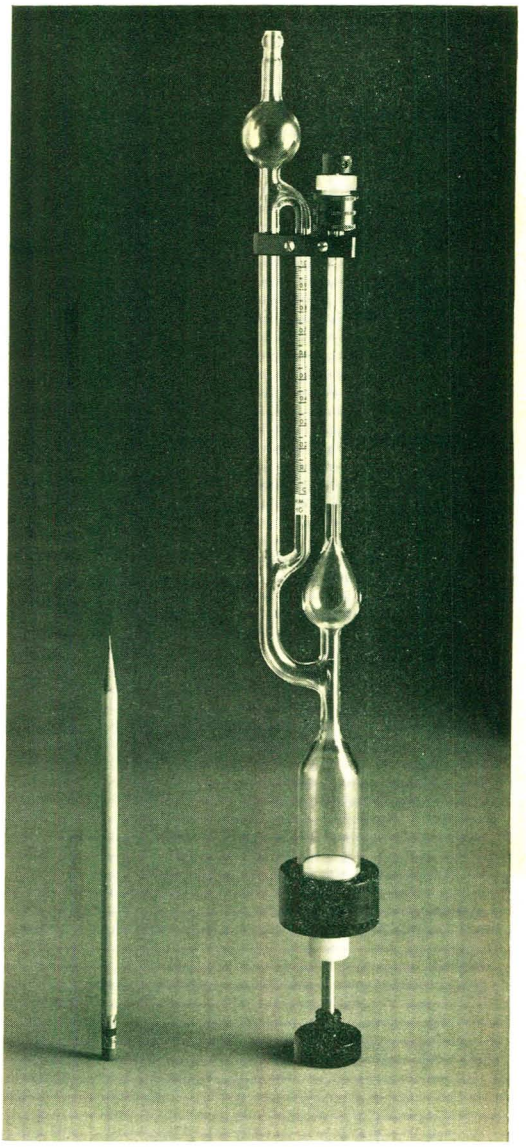
Anal. Chem. 36, 2341 (1964)

Estimation of a Few Nanograms of Fluoride in Presence of Phosphate by Use of Liver Esterase

Optimum conditions are given for the inhibition of liver esterase by fluoride and the attendant modification of the method of Linde. Enzyme activity was measured by titration of the butyric acid formed from ethyl butyrate with NaOH.

CHARLES McGAUGHEY and ELLERY C. STOWELL, Dental Research Laboratory, Medical Research Programs, Veterans Administration Hospital, Long Beach, Calif.

Anal. Chem. 36, 2344 (1964)



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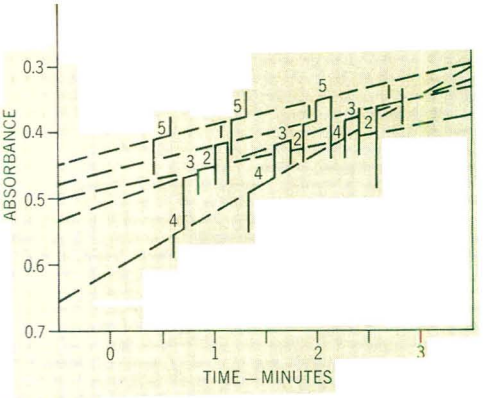

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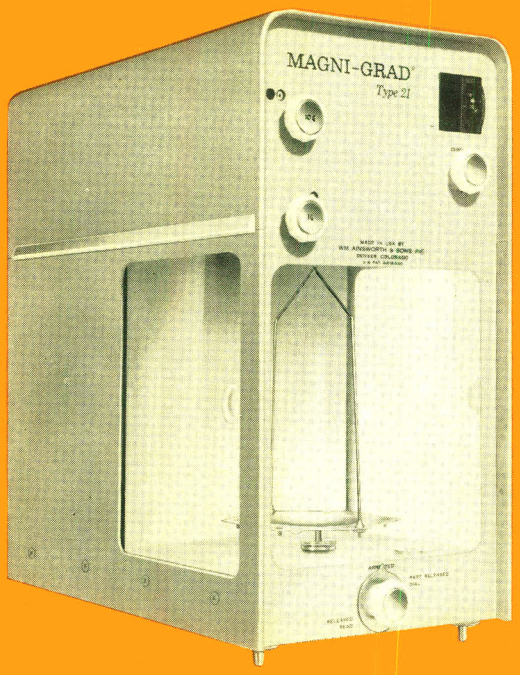

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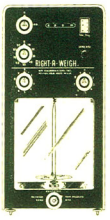

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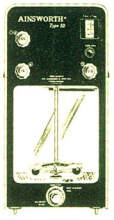

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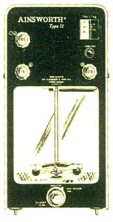

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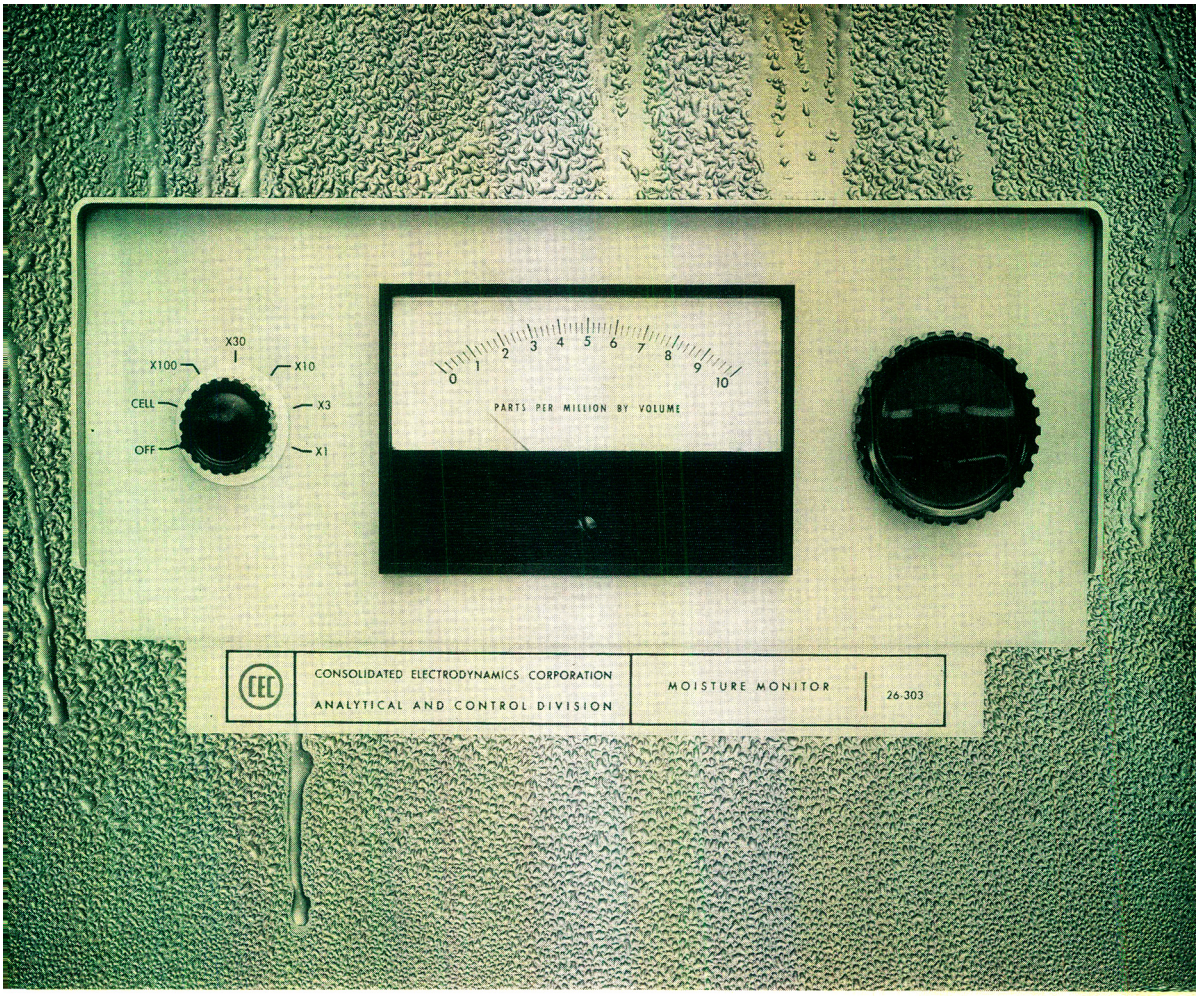

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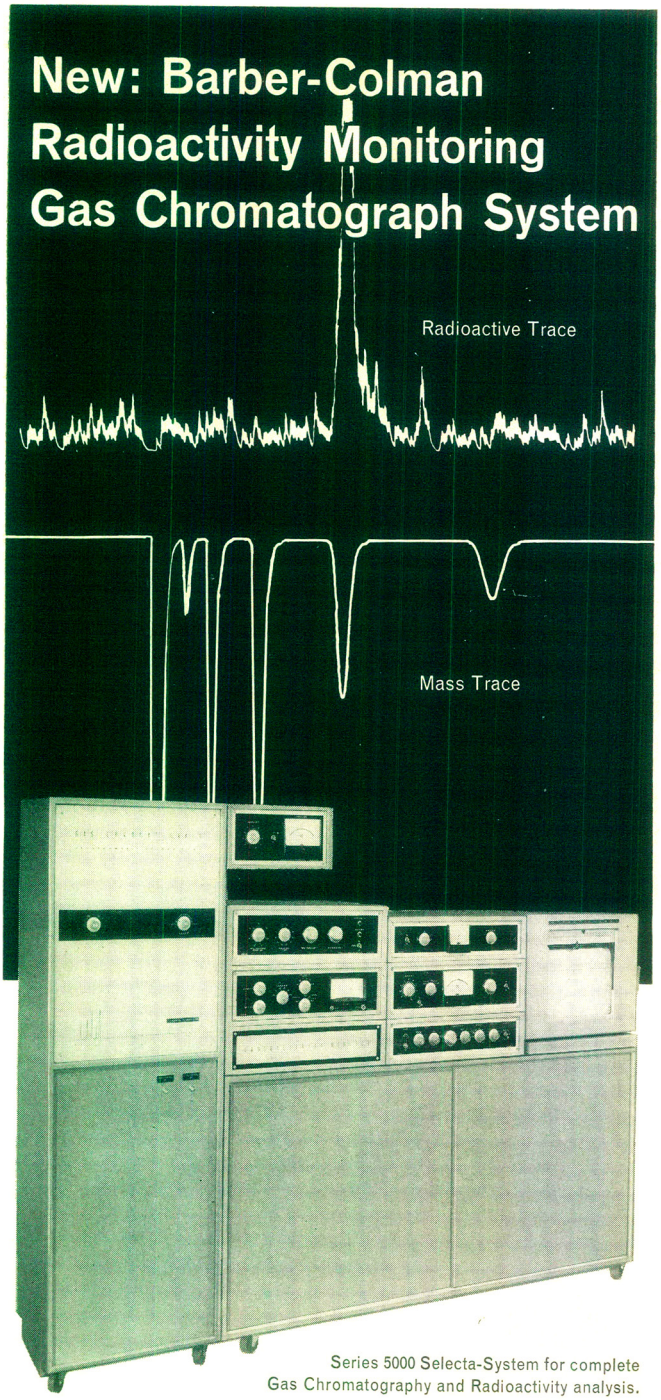

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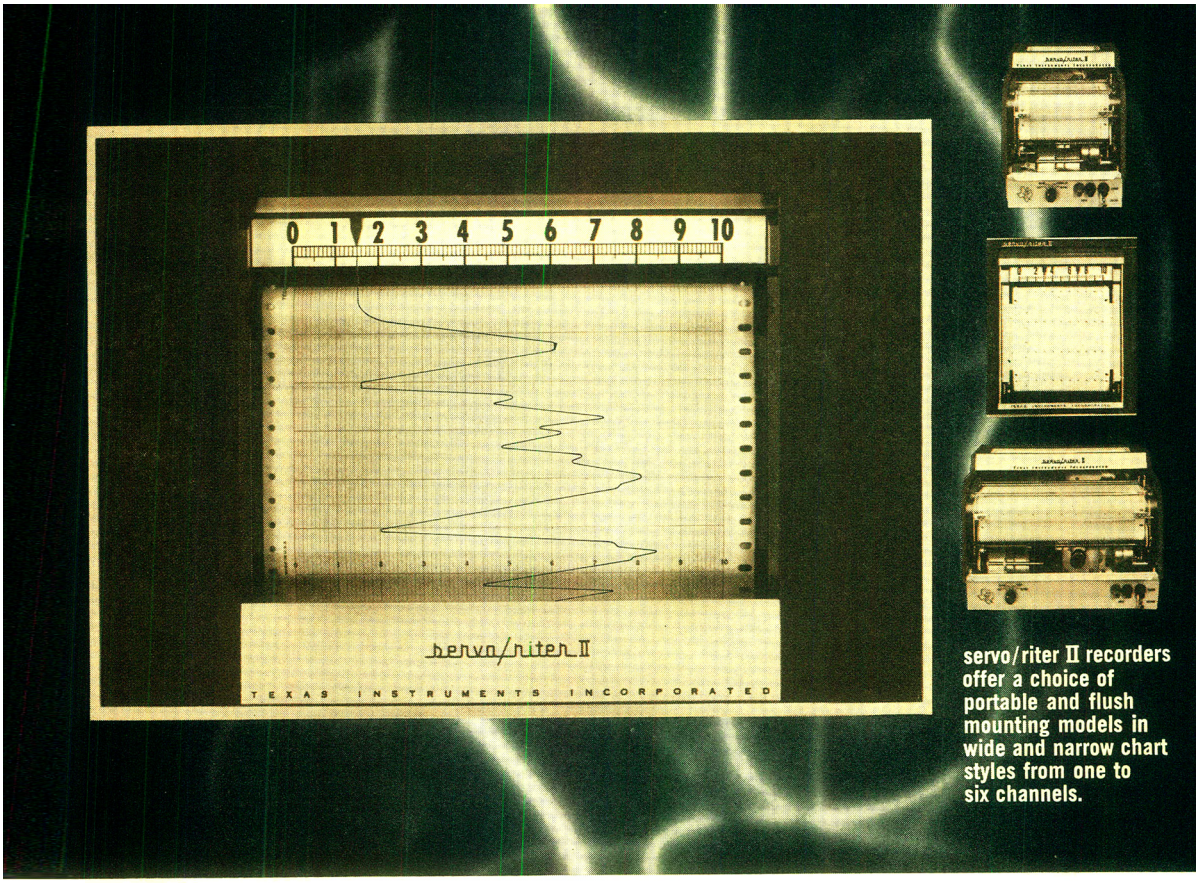

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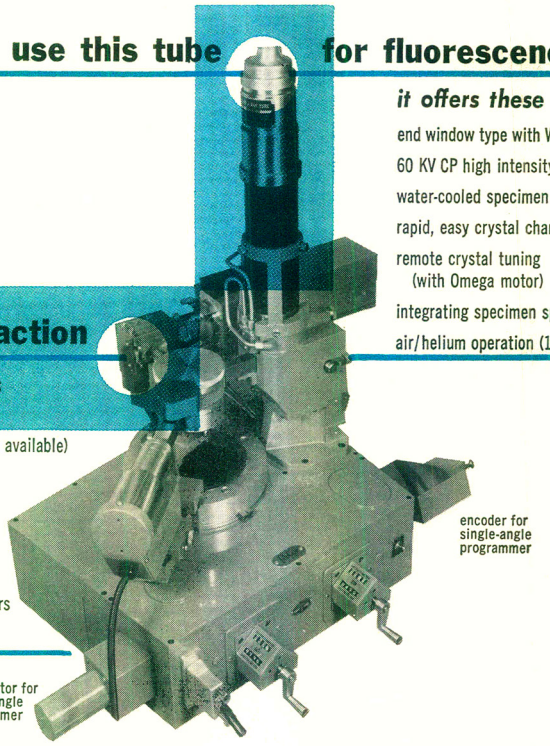

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The Availability of Standard Reference Materials

WITH THE RAPID GROWTH of new instrumental analytical techniques in the last two decades, the need has arisen for a wider variety of reliable standard reference materials. There is a lack of samples of certified high purity. Along with the shortage of certified samples is the need for accurate data on pure compounds including physicochemical properties. These problems were among those discussed at the Symposium on Standard Reference Materials and the Symposium on National and International Standards held by the ACS Divisions of Analytical Chemistry, Chemical Marketing and Economics, and Industrial and Engineering Chemistry in cooperation with the ACS Committee on Standardization Relations at the 148th National ACS Meeting in Chicago on September 3. Twenty-five scientists representing industry, government agencies, academic institutions, and scientific associations took part in the symposia.

Dr. F. D. Rossini of Notre Dame University reported to the Symposium on Standard Reference Materials on the two-day National Academy of Sciences–National Research Council on Reference Standards held June 22 and 23, 1959. Although this conference was held over five years ago, its conclusions and recommendations are equally valid today. Among the conclusions reached at this conference, Dr. Rossini noted, was that there is a lack of samples of certified high purity. Accurate data on basic compounds are needed, including physiochemical properties. Research investigations are hampered by lack of thermal, spectral, and physical data. Systematic study on pure compounds is needed with rapid publication of results. The biggest need may be a method for coordination of scientific efforts in establishing specifications for reference materials, the Conference participants felt.

It was concluded at the Conference that a strong scientific program with great depth be established in the field of reference standards. Government, industry, and university scientists must all take part in order to make the program successful. It was recommended that some existing organization should establish a permanent information center for compounds of certified purity. The establishment of a permanent central technical organization for the preparation, analysis, and certification of purity and to provide for compound distribution was recommended. It was further recommended that the program on reference standards cover a broad spectrum of compounds, take cognizance of foreign countries, implement communication and exchange of ideas, and encourage research on the preparation and analytical examination of pure compounds. The proceedings of this conference are being reprinted and will be available from the Office of Technical Services.

Dr. W. W. Meinke of the National Bureau of Standards and Chief of the Bureau's new Office of Standard Reference Materials discussed the standard reference materials program at NBS. The Bureau presently has available more than 600 standard reference materials as summarized in NBS Miscellaneous Publication 241 available from the Office of Technical Services. It is also working on the development of about 50 new ones and has on hand requests for the preparation of many others. The requests have always far exceeded the Bureau's capacity to produce and certify these materials.

One of the main functions of the NBS Institute for Materials Research is to develop, produce, and distribute standard reference materials which provide a basis for comparison of measurements on materials and aid in the control of production processes in industry. To help carry out this function the Office of Standard Reference Materials evaluates the requirements of science and industry for carefully characterized reference materials, and directs their production and distribution. Emphasis is given to providing NBS Standard Reference Materials (a) where attainment of needed accuracy of analysis or accuracy of measurement of characteristics is not economically or technically feasible elsewhere, and where such accuracy is generally important to users, (b) where industry-wide standards for commerce are needed from a neutral supplier who is not otherwise available, and (c) where continuing availability of highly characterized material from a common source is important to science or industry.

NBS recognizes the need for broadening the present program on reference materials to include all types of well-characterized materials than can be used to calibrate a measurement system or to produce scientific data that can be readily referred to a common base. With this broadening, however, it still remains apparent that the demand for new standard reference materials will continue to far exceed the Bureau's capacity for development. Therefore, requests for new standard reference materials which will have limited use and for which the need is not very great will have to be passed by in favor of requests clearly showing a critical need. For determining which requests are to receive top priority, the Bureau will need the information supplied by industry, either through its own representatives or through interested

committees, such as those of the American Society for Testing and Materials, the American Standards Association, and the International Organization for Standardization.

While the Bureau welcomes all requests for the development of new standard reference materials, it will help both the Bureau, and industry as well, if requests are accompanied by such information as will permit an assessment of the urgency and importance of proposed new reference materials, Dr. Meinke pointed out.

In discussing future plans for the NBS Standard Reference Materials Program, Dr. Meinke said that the NBS is actively working on standards for Mössbauer spectrometry. This technique, he pointed out, gives information on binding of atoms in molecules. The Bureau is calibrating a number of crystals of sodium nitroprusside. This work will hasten routine application of the Mössbauer Effect in analysis, Dr. Meinke believes.

AMERICAN PETROLEUM INSTITUTE STANDARD SAMPLES

Manufacture of petroleum products and petrochemicals such as aviation gasoline and monomers for synthetic rubber requires careful analysis in research, A. J. Streiff of Carnegie Institute of Technology told the Symposium on Standard Reference Materials. Spectral measurements by infrared, ultraviolet, mass, Raman, and nuclear magnetic resonance, together with gas chromatography, have become valuable tools for fast and precise analyses. The instruments developed for these purposes need to be calibrated, and calibration is dependent on the purity of standards from which it is determined.

During World War II, the American Petroleum Institute Research Project 6 on the composition of petroleum began to purify standard samples of hydrocarbons and to certify their purities in a joint effort with NBS. Since 1950 this activity has been a cooperative effort of the American Petroleum Institute (API) and the Carnegie Institute of Technology. All of this work has been consolidated into a single project designated API Research Project 58 on the Synthesis and Purification of Standard Hydrocarbons. The part of the Project concerned with synthesis, directed by E. J. Eisenbraun, is located at Oklahoma State University; purification and certification of purity is directed by Mr. Streiff at Carnegie Institute of Technology.

Standard samples of organic sulfur compounds and organic nitrogen compounds have been produced by API Projects 48 and 52, respectively, located at the laboratories of the U. S. Bureau of Mines in Laramie, Wyoming, and Bartlesville, Oklahoma.

API standard samples of 310 hydrocarbons, 38 organic sulfur compounds, and 9 organic nitrogen compounds may be purchased from the API Samples Office at Carnegie Institute of Technology. These standards have certified purities. (The target is a purity of 99.9%.) They are made available in units of 5 ml., completely degassed and sealed under their own vapor pressure in glass ampoules. Carbon number range of the hydrocarbons is C_4 to C_{19}. Present emphasis is being placed on synthesizing and purifying new standard hydrocarbons in the C_{12} to C_{18} range. Some standard hydrocarbons used for checking instruments and techniques have recommended values of refractive index and density supplied with the samples.

When a hydrocarbon is purified, several hundred milliliters of material of the very highest purity which can be produced is reserved for research measurements of needed physical, thermodynamic, and spectral data. These API research hydrocarbons are loaned to qualified investigators for a wide variety of measurements. The data which are obtained on API research hydrocarbons can be found in the Tables of Selected Values of Properties of Hydrocarbons and Catalogs of Spectral Data of the API Research Project 44 which is located at Texas A&M University.

Purification of API standard and research hydrocarbons is accomplished by the use of the following fractionating processes: high efficiency distillation, both regular and azeotropic, liquid-solid chromatography, crystallization or zone refining, and formation of solid molecular compounds. Distillation is used most often, and a completely equipped laboratory for distillation containing 14 columns, each 20 feet in height, is part of the facilities at Carnegie Tech.

Careful purification of hydrocarbons must be followed by equally careful determination of purity. Methods are used which measure quantitatively very small amounts of impurity. The purity of hydrocarbons which can be crystallized is determined by calorimetric cryoscopic measurements. For compounds which do not crystallize, the purity is evaluated from careful gas-liquid chromatographic measurement using capillary columns 20 to 600 feet in length with hydrogen flame detection.

Continuing efforts to improve methods of purification and determination of purity ensure that American Petroleum Institute standard and research hydrocarbons continue to be major chemical guidelines for research, development, and control.

THE OAK RIDGE RESEARCH MATERIALS INFORMATION CENTER

One of the continuing needs in materials research is information on the availability of high quality research specimens whose purity or composition is precisely known, T. F. Connolly of Oak Ridge National Laboratory told the Symposium on Standard Reference Materials. Although a large number of interesting materials are produced by commercial, government, and university laboratories, open literature publications or sales catalogs seldom indicate the source and purity of starting materials, methods of further purification, crystal growth, and assay of the end product, Mr. Connolly pointed out.

The Research Materials Information Center was established as a part of the Pure Materials Program of the Solid State Division of the Oak Ridge National Laboratory to collect and provide this information to both producers and users. The primary emphasis is on high

purity inorganic research materials (usually single crystals) such as metals, alloys, semiconductors, refractory or insulating compounds, laser and optical materials, and magnetic materials. Structural materials, devices, and radioisotopes are not included, since these are covered by the Defense Metals Information Center at Battelle Memorial Institute and the Isotopes Information Center at Oak Ridge National Laboratory.

An aperiodic bulletin, newsletters containing selected articles on materials preparation and evaluation, and lists of available and desired materials are published and distributed to all participants in the program. No purchases, loans, or exchanges are handled directly. However, recipients of information are asked to notify the Center of results on any specific material in order that its records can be adjusted accordingly.

General searches of the entire collection for the purpose of reviews are made on occasion, and the collection and searching mechanism is available for use by visitors to the laboratory. Where the searches turn out to be extensive and there is a possibility of their being of general interest, a record is kept of the references sent out. The lists are filmed and are then available as the core of future searches. Lists of references on ferroelectric materials (inorganic single crystals), iron crystals and films, and refractory metals and compounds have been compiled.

Equipment has been installed that will conduct an automatic search for coded entries that have been placed on film (including more than 1500 data sheets). Requested material for which no information is available is also listed, and the requester notified if such material becomes available.

Background information on materials is also collected and encoded. A list of more than 300 coding terms has been established under such general categories as Type and Form of Material, Crystal Structure, Electrical Properties, Growth Techniques, etc. Each category is further divided into additional coding terms. Open literature publications, company reports, abstracts, and preprints have been collected and coded; and the collection contains about 9,000 documents on about 30 reels (100 ft. each) of 16-mm. film. Each reel can be searched for set of coding terms in about 15 seconds.

Mr. Connolly emphasized that close cooperation is required between the Center and those who analyze, grow, and characterize research quality materials. The most immediate and continuing need of the Center is for completed data sheets from all producers of such materials, and for a rapid notification of any significant new result or development via internal reports, preprints, or personal communication.

THE INTERNAL COMPANY STANDARD

In discussing the internal company standard, M. D. Cooper of General Motors Research Laboratories pointed out that it has been the practice of some companies to make their company standards available outside of their own organizations. However, these are *company* standards not *primary* standards, Mr. Cooper emphasized. By definition, primary standards must be certified by a recognized standardizing agency, generally as the averaged result of the work of two or more laboratories performing entirely independently. Although the values assigned to company standards may reflect the work of two or more laboratories, absolute assurance that they perform independently is lacking. Therefore company standards can rate no higher than *secondary* standards and, as such, their use should be limited to internal control analyses. In the case of disagreement between producer and consumer with regard to the composition of commercial items, primary standards may be used with much greater confidence; and the use of company standards in these instances should be only an interim arrangement while awaiting the availability of primary standards.

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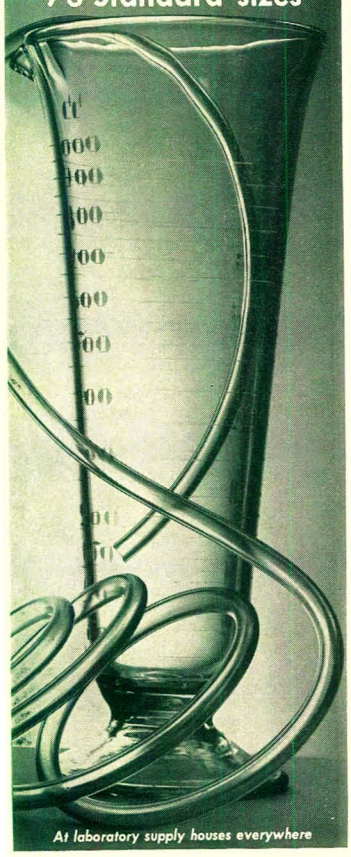

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given time with regard to types, concentration ranges, and amounts required, suggest that a lag between the development of a need and its fulfillment is inevitable, Mr. Cooper pointed out. For example, x-ray fluorescence methods that became practical about ten years ago imposed special demands with regard to dimensions of standard specimens; and vacuum optical emission instruments introduced four years ago permitted for the first time the determination of certain light elements which now must be provided in spectro-chemical standards.

Although the internal company standard should and does have an important place in our laboratories, primary standards evolving from the seasoned judgment and objectivity of the NBS are considered indispensable, Mr. Cooper concluded.

COMMITTEES OF IUPAC, NAS–NRC, AND MCA

The needs for standard substances are not peculiar to the United States, but are international in character, Dr. Daniel R. Stull of the Dow Chemical Company pointed out. One of the international scientific bodies recognizing the need for standard substances is the International Union of Pure and Applied Chemistry (IUPAC), which has a Commission on Physico-chemical Standards and Data. The members of an IUPAC commission represent their country in the affairs of the commission. It is usual practice in the U. S. to have a domestic committee whose function parallels that of the IUPAC commission. Thus, the Committee on Physical Chemistry of the National Academy of Sciences–National Research Council (NAS–NRC) has established a Subcommittee on Physico-chemical Standards.

The Subcommittee on Physico-chemical Standards has been active at various times in the past, and is again becoming active because of the growing need in this area. Efforts are being made to consolidate the national needs for physico-chemical standards, and since international trade requires it, to mesh these national needs with similar international needs. The cooperation of academic, industrial, and governmental scientists will ensure the formulation of a sound program to meet the needs for standard substances, Dr. Stull concluded.

Dr. Stull pointed out the need of the chemical industry for a fund of physical properties on the chemicals of importance. In 1955 the Manufacturing Chemists' Association (MCA) funded a Physical Properties Research Project whose goal was the preparation of reliable numerical data on chemical materials of importance. This project has recently been made a part of the National Standard Reference Data Program, and experimental measurement of physical properties of chemical materials has begun.

For these measurements, materials of superior purity are needed, and the MCA Physical Properties Project Advisory Subcommittee visualizes the need for the establishment of a bank of materials of superior purity. This MCA Subcommittee recently prepared a list of about 100 organic compounds of primary importance. This MCA Priority List of Organic Compounds defines the areas where experimental measurements will first be made, and also the specific compounds requiring a sample of superior purity. Although the details remain to be worked out, the establishment of a sample bank of priority compounds is an important objective of the MCA program.

ROLE OF ASTM

In a paper presented to the Symposium on National and International Standards, J. W. Caum of the American Society for Testing and Materials (ASTM) and Harold M. Smith of the U. S. Bureau of Mines discussed the organization and functions of ASTM. The purpose of ASTM is "the promotion of knowledge of the materials of engineering and the standardization of specifications and the methods of testing."

That part of ASTM work which has to do with "the promotion of knowledge of the materials of en-

gineering" is effected through investigations and researches by committees and individual members of the Society and by joint efforts with other groups. The results of these investigations and researches are presented as papers, reports, and discussions at Society and committee meetings. Most of them are subsequently published to add to the store of knowledge about the materials of engineering—properties, performance under varying or stated conditions, and other information to advance our technology. This is the knowledge on which sound standardization of both specifications and methods of testing is based.

The "standardization of specifications and methods of testing" is carried out chiefly by the technical committees of the Society. Each of these committees has under its jurisdiction engineering materials in a definitely prescribed field or some specific phase of testing. Each is a vital and inherent part of the Society.

THE INTERNATIONAL STANDARDS ORGANIZATION

The work of the International Standards Organization (ISO) is neither known nor understood by a majority of the people of United States industry who really stand to profit most by its efforts. This is the belief of A. C. Webber of E. I. du Pont de Nemours & Co. and F. C. Frost of the American Standards Association (ASA), expressed in a paper on ISO and ASA given before the Symposium on National and International Standards.

The object of ISO is to "promote the development of standardization in the world with a view to facilitating international scientific, technological, and economic activity." In effect, this scope permits the consideration of any matters of standardization excepting those concerned with electrical and electronic standards which have been the responsibility of the International Electrotechnical Commission since 1904. The standards bodies of 50 countries are now members of ISO, each participating in those technical committees of interest or economic importance to it.

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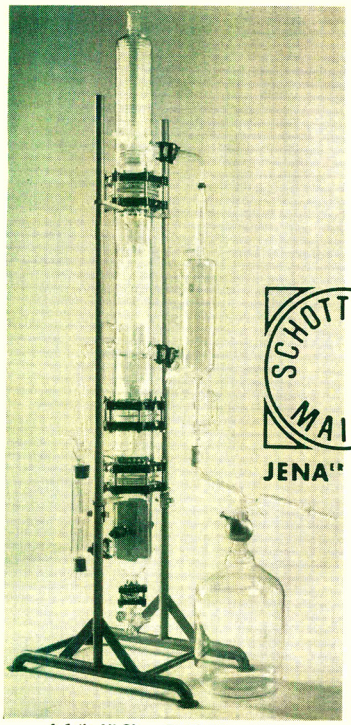

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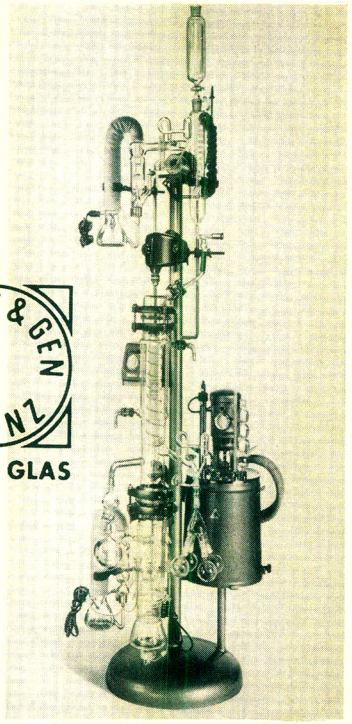

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REPORT

The technical work of ISO is carried out in technical committees. Each technical committee is made up of representatives of those member countries which wish to participate in its work. There are now 107 technical committees covering a very wide range of subjects. Each technical committee has a secretariat, which is responsible for the conduct of the work of the committee and for reporting annually to the Council on the results of the year. The secretariats are usually accepted on the basis of a major interest of the member body and ability to pay the costs of the operation. The United Kingdom holds 25 secretariats. The United States holds only 10 secretariats and is obviously not carrying a share commensurate with its world trade.

All technical committees have plenary sessions, some annually and others only when the secretariat feels such a meeting is needed. Many of the technical committees have divided the work into specific categories, assigning these to subcommittees or working groups under the leadership and responsibility of a separate secretariat. In any case, much of the work must be carried out by correspondence and by small meetings of interested technical personnel.

When a working group of a technical committee has completed a draft of nomenclature, method of test, or specifications, it is submitted to the member bodies of the technical committee as a Draft Proposal. When the ballot of these members shows acceptance by the majority, the draft, revised if necessary, is submitted to the general secretariat and through it to all 50 member bodies of ISO as a Draft ISO Recommendation. Agreement by these members and approval by the Council is then followed by publication of the matter as an ISO Recommendation.

It must be emphasized that these documents are not international standards binding upon the member bodies. They are recommendations which are intended to provide a guide to each member body for the preparation of its national standards.

The member body in ISO for the United States is the American

Standards Association (ASA). ASA was established to coordinate the standardization efforts of the major standards-writing bodies in the United States. Its present membership consists of about 140 technical societies and trade associations and 2200 companies.

When the question of American participation in an ISO technical committee arises, all interested industries and organizations are informed and consulted by ASA. If sufficient interest exists, the United States indicates that it wishes to participate either actively (P membership) or as an observer (O membership) in the proposed technical committee. A committee is then organized to represent the United States in the work of the technical committee. This committee is assigned the full responsibility for the technical work, for the establishment of the American position on each item under consideration, and for the provision of delegates to meetings. The dues to ISO are paid by ASA from its budget, and staff services are provided for the necessary documentation and correspondence. In this manner the United States now participates in 66 of the 107 technical committees, holding observer status in the remaining 41 committees.

To those who are familiar with the work of ISO and who recognize its importance, it is clear that the United States participation on the whole is not adequate. While this general low level of participation is traceable principally to lack of economic pressures, there is not a sufficient understanding of the nature of these international recommendations and their potential importance to the economic welfare of the United States.

In the plastics field, the interrelationship among the American Chemical Society, ASTM, ASA, and ISO has been effective and productive, C. Howard Adams of Monsanto Chemical Company told the Symposium on National and International Standards. One reason for this may be that in many cases one individual wears the necessary number of hats to cover the various societies and organizations concerned with getting the standards job done.

In Mr. Adams' opinion, if there is to be healthy international trade, it must operate within the frame of international test methods and international specifications. As more and more items move freely in international trade, the use of ISO test methods and specifications will be an automatic development. A further thought is that the agressive development and promotion of ISO test methods and specifications can do much to stimulate international trade.

Many factors will affect future exports from the United States, some of which may be far more important than whether or not international standards are widely used, Mr. Adams believes. ISO methods and specifications will most certainly be highly effective catalytic agents. Standards and specifications internationally agreed upon are perhaps the most effective aids to overcoming language barriers. Where international standards and specifications exist, the U. S. commercial position should be the healthiest since materials and products of submarginal quality cannot compete with U. S. quality products. The U. S. strength in the standards arena stems almost completely from an industry recognition of the standardization need and vigorous industry support of the standards program, Mr. Adams pointed out.

It seems that one of the basic questions is how far this whole standards thing should go, Mr. Adams remarked. Certainly if one has a proprietary product—i.e., is the sole supplier of that product or material (except in those areas where its use may have a bearing on the public safety and welfare)—then the standardization matter is primarily one of quality control by the company offering the product. However, it is a commercial fact of life that there are fewer and fewer proprietary products that are completely controlled by a single enterprise. It is Mr. Adams' opinion that supplier and consumer will operate in a much healthier commercial climate if standards defining product type and quality are more broadly available, not only domestically, but worldwide.

■ END

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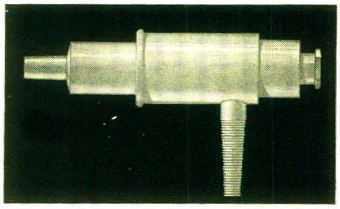

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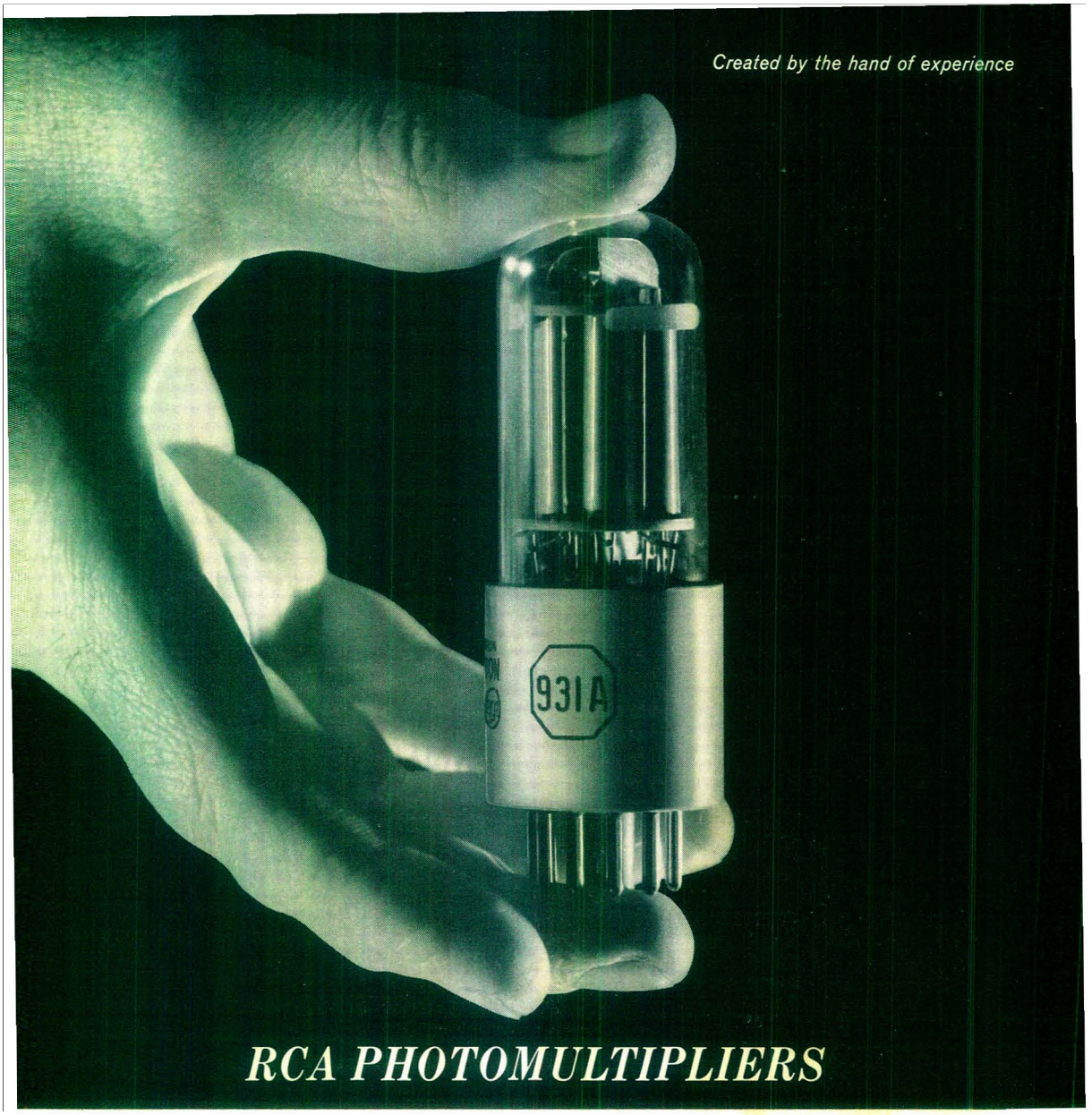

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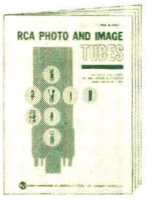

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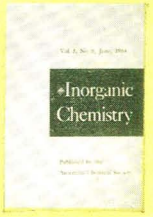

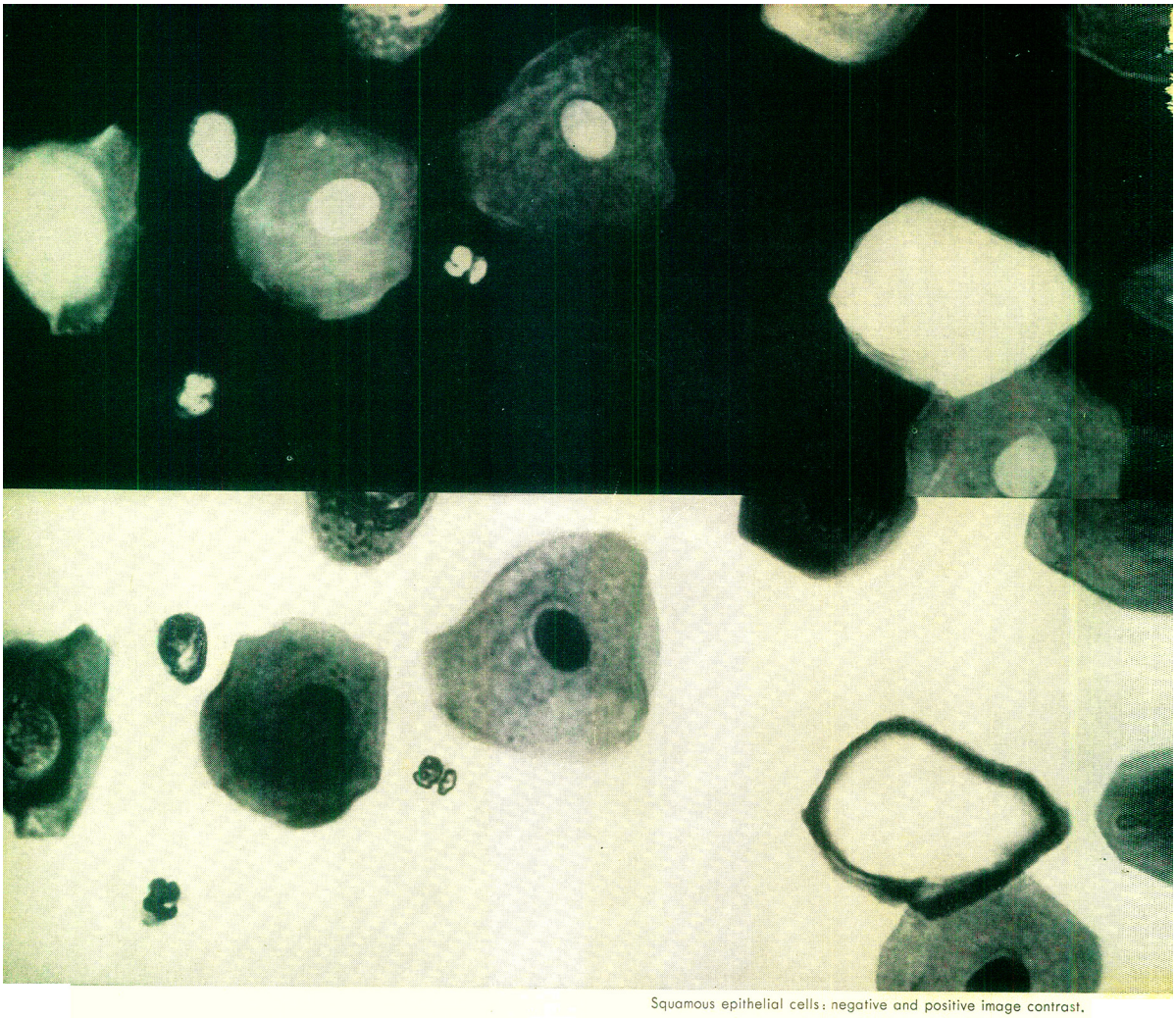

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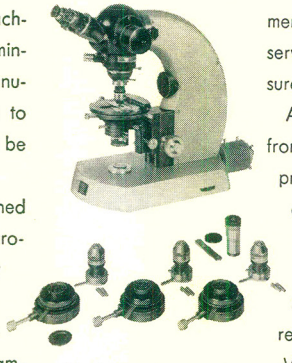

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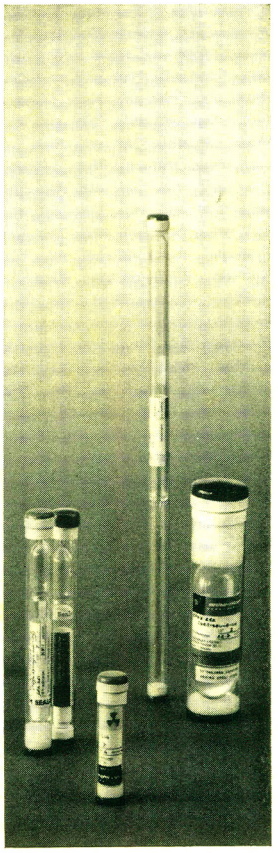

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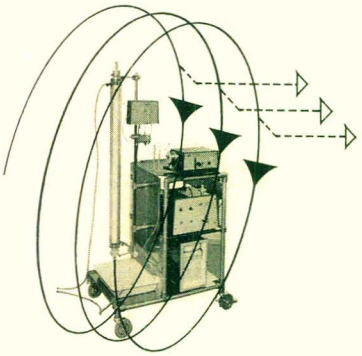

The ReCyChrom is equally applicable for preparative and analytical separation of mixtures of large-sized or of small-sized molecules. These molecules do not have to be electrolytes and restrictions on the type of buffer used are less than with other types of chromatography. Components within a narrow range of molecular sizes, usually not resolved on simple gel filtration columns, are separated in the ReCyChrom by allowing the sample to pass repeatedly through the bed, thereby multiplying its effective height many times. Separated fractions and uninteresting or disturbing parts of the effluent may be bled out of the stream after any cycle without interrupting the separation of the remaining components.

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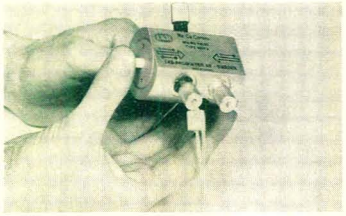
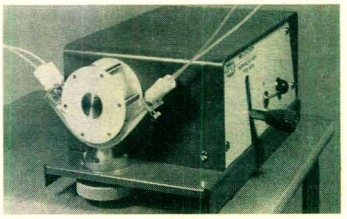
*According to J. Porath and H. Bennich

Request literature file 4900A11 for details.



The simple push of a button on the Selector Valve alters the flow circuit from injection or bleeding to recycling.



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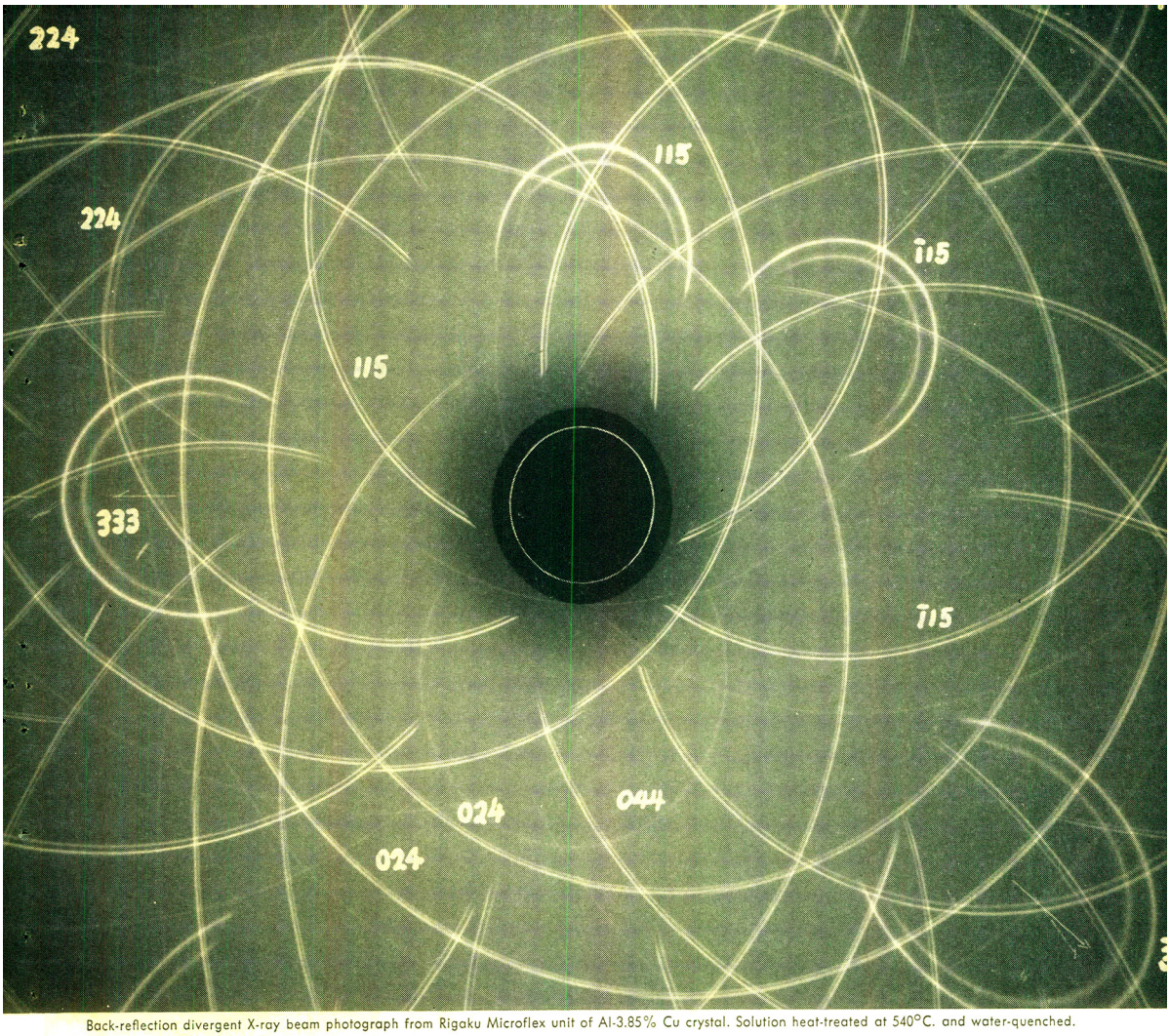

Back-reflection divergent X-ray beam photograph from Rigaku Microflex unit of Al-3.85% Cu crystal. Solution heat-treated at 540°C. and water-quenched.

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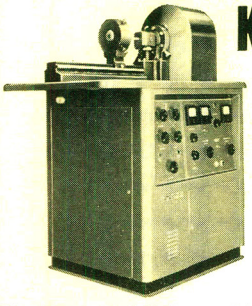

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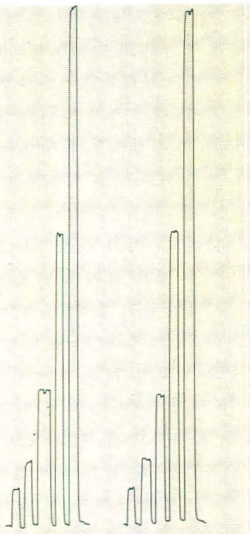

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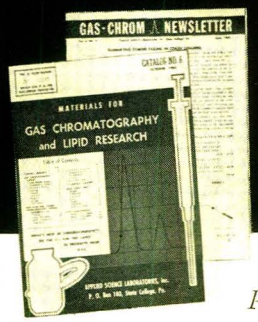

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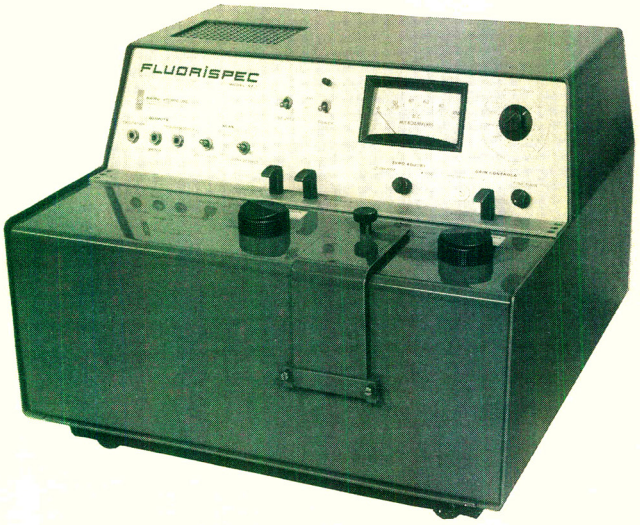

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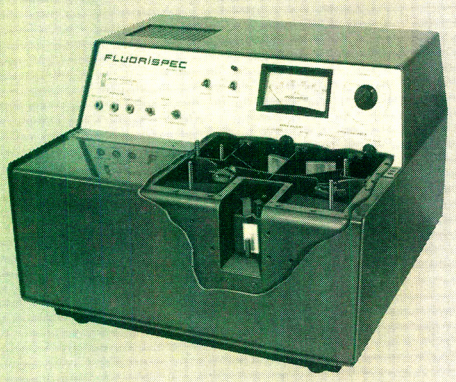

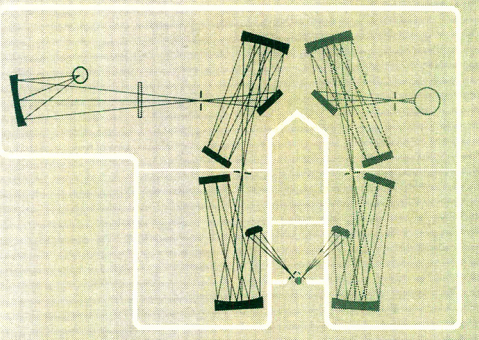

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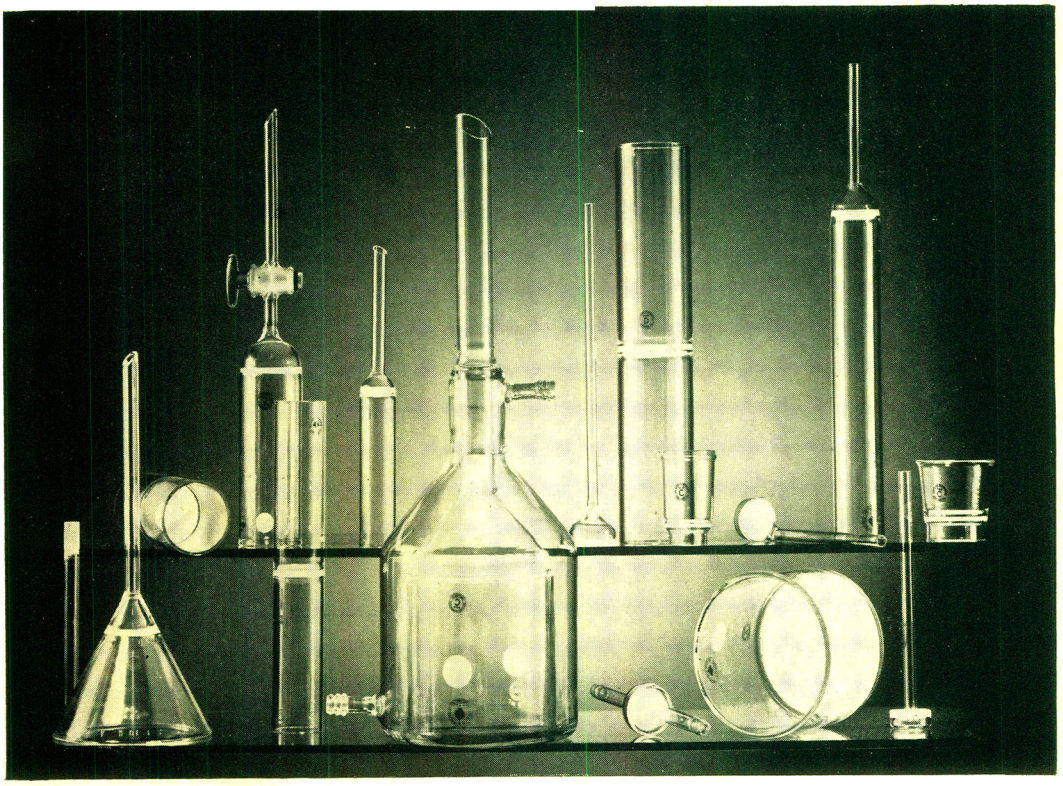

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Quality and Greater Abrasion Resistance. Ace filters, the first American made sintered glass filters, feature a glass fiber structure, more abrasion resistant because it is fused together on a larger area. Particles do not detach from the filter body as easily as spherical granules. The shock and chemical attack resistance of glass is unimpaired as the Ace fiber glass sintered filter is made entirely of glass. You are assured of Ace Glass quality: each filter plate is individually tested for porosity and hardness.

Selection and Economy. Ace fiber glass sintered filters have been incorporated into a wide variety of Ace glassware, with new items being made available. The Dannley Pressure Filter Funnel shown at right is a good example. Ace fiber glass sintered filters are economically priced. For instance, the filter funnel (Cat. No. 7186 in the 20 ml. cap. with 20 mm. disc) shown in photograph above, is listed at $3.95. The wide selection of Ace fritted ware is incorporated in the Ace Catalog 64. See your copy or send for new Ace Fritted Ware Brochure.

ACE GLASS INCORPORATED

Vineland, New Jersey

LOUISVILLE, Ky. BOX 996 SPRINGFIELD, MASS. BOX 1688

Circle No. 116 on Readers' Service Card

Dannley Pressure Filter Funnel

makes pressure filtration practical for the first time for small scale use.

7188

For details, send for NEW Ace Fritted Ware Brochure!

the question is . . . WHO EVER HEARD OF A

Hoke needle valves have been a stable laboratory commodity for almost as long as the Bunsen burner. And in more recent years, the habit has spread to instrument engineers, gas analysts, pilot plant engineers — even aerospace scientists.

Among such distinguished people, we've worried a little about the looks of our favorite product . . . gas chromatographs, mass spectrometers and autoclaves are sophisticated company for a plain jane.

The 1965, super-duper Hoke Needle Valve is new from top to bottom. Let's take it apart in that order so you can judge for yourself.

This little screw is a necessary evil. Removable handles must be restrained somehow.

This is, of course, the removable handle. It looks so neat and simple that you wouldn't believe how long we worked to get it that way. Molded nylon makes it strong and the ridges make it easy to grip. We even make color discs to insert in that top recess for fluid identification.

This is our whiz-bang packing nut combination. On the left is the garden variety, standard nut. On the right is the interchangeable panel mounting adapter. Result: You can stock standard valves (at lower cost) and convert them for panel mounting as needed.

And what goes under the packing nut? You have a choice yet. An O-ring for temperatures under 200°F. and non-corrosive service. For tougher duty, Hoke's new Dyna-Pak consisting of alternate thin layers of Teflon and Stainless is the answer. The Teflon lips seal tight under pressure (the higher the better) with negligible wear (no adjustments!) and easy turning even at 5000 psi.

HOKE

SOPHISTICATED NEEDLE VALVE?

So we took the plunge and redesigned our pride and joy. We haven't discarded any of those features painfully acquired during the last 50 years but we re-styled the body and made a new handle to dress up your new instruments and panel boards. We added interchangeable and replaceable parts to make your storekeeper's life easier.

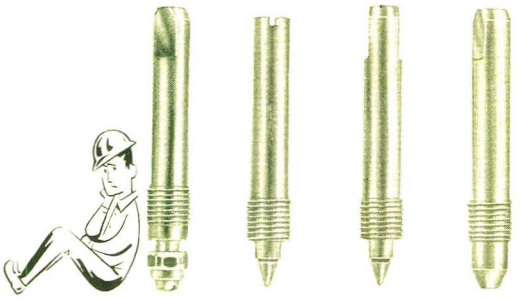
See for yourself . . . here's the whole story, part-by-part.

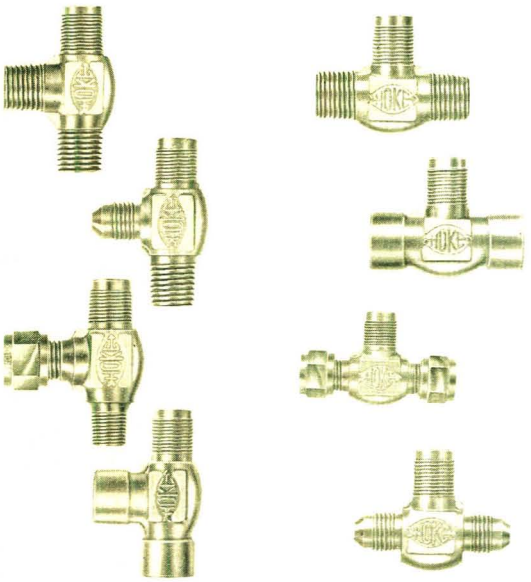
The stem is the business end of any valve so we gave it our most careful attention. We came up with three different stem tips to choose from, depending on your mood (and need).

For shut-off service and high flow capacity we offer a blunt stem point with two orifice sizes: .170″ or .219″.

And, in case you worry about minute seat leakage or corrosive fluids, the blunt stem is available with a Kel-F tip. Abuse it all you want — the tip is easily and inexpensively replaced.

For those of you who need an honest-to-goodness needle valve, the V-point stem tip with a .059″ orifice is a real squeezer.





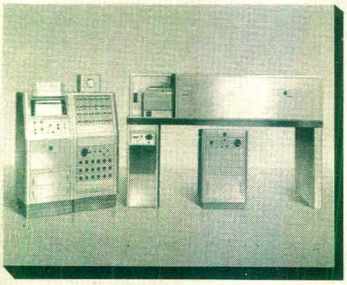
Last, but far from least, consider our new valve body (or bodies we should say — there's quite a variety). We start with a bigger, huskier forging — take a look at the size of the wrench pads. This forging is made in three sizes to cover the range from ⅛″ to ⅜″ pipe or tube. Materials are brass, stainless and aluminum. We make angle and globe pattern, pipe and tube ends . . . and combinations thereof. The variety of patterns, materials and sizes has our production control man muttering to himself — but you now have the greatest choice of Hoke needle valves in our long and checkered history.

If you'd like to see a sample of our latest offspring, write to the proud parents on your company letterhead . . .

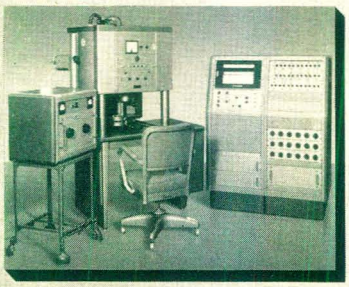
HOKE INCORPORATED 1 Tenakill Park, Cresskill, N.J.

Circle No. 20 on Readers' Service Card

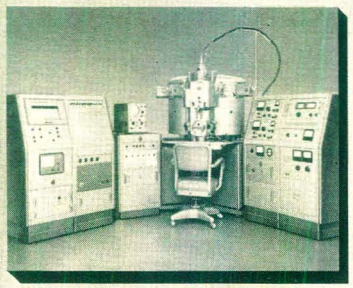
FIRST IN SPECTROCHEMICAL INSTRUMENTATION



FIRST with *vacuum* optical emission spectrometer. Nearly 200 Quantovac installations world-wide, provide precise, quantitative analysis in less than 2 minutes of as many as 23 elements, including C, P, & S.



FIRST with *simultaneous* multi-element analysis using x-ray fluorescence. Rapid, precise, push button analysis of elements above atomic number 11, to meet the increasingly complex requirements of industry.



FIRST in *number* of microprobe installations. The EMX and EMX Mark II, today's ultimate analytical research tools, have made ARL the acknowledged leader in the field of electron probe microanalysis.

To remain FIRST, ARL has established the Hasler Research Center for research and development.

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Circle No. 3 on Readers' Service Card

HONEYWELL

INSTRUMENTATION NEWS

LABORATORY EDITION

Number 2-AC

ElectroniK 19 Has Range For Research, Test Applications

PHILADELPHIA — The range of Honeywell's new *ElectroniK 19* portable lab recorder has aroused wide interest among prospective users. The new instrument is the first of its type to measure voltages ranging from 100 microvolts to 100 volts.

The following features of the recorder are especially attractive:

Small size: 8¾ x 8¾ x 11 inches.

Two recorders can be placed side by side in a standard 19-inch relay rack.

Light weight: Less than 20 pounds.

Low power requirement: 30 watts.

Span flexibility: 100 μv. to 100 v., in 19 manually selectable calibrated ranges.

Zero flexibility: Calibrated and continuously adjustable to ±100% of span.

Fast response: Less than 0.5 second full scale with frequency response of 5 cycles at 10% peak to peak.

Calibrated accuracy: ±¼ of 1% of span or 1 microvolt, whichever is greater.

Chart drive will either re-roll paper on takeup reel or feed it out across lab bench or table.

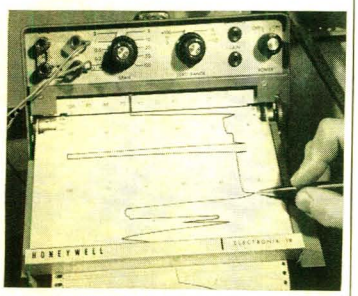
Chart speed flexibility: 10 manually selectable speeds from 10 min/in to 1 sec/in.

High stray rejection: Transverse, 55db; longitudinal, 170 db.

To order: Specify Model 19 Portable Lab Recorder.

Price: $1,100 net f.o.b. U. S. factory.

CIRCLE 1 ON READER SERVICE CARD



ELECTRONIK 19 **PORTABLE recorder is shown recording spectral power density phenomena in the far infrared region.**

ElectroniK 16 Line Satisfies Wide-Chart Recorder Needs

PHILADELPHIA—"Our new *ElectroniK 16* recorder has been designed to satisfy your wide chart recorder requirements," says C. W. Wilkins, Honeywell's laboratory equipment market manager.

"It uses solid-state circuitry for the utmost in reliability and is modernly packaged for bench, rack, or apparatus cabinetry mounting."

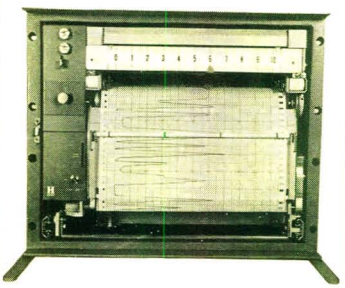
Wilkins pointed out that the new recorder has been built with future needs in mind, too. "Most of the options and accessories have their own unique locations on the chassis. If you want to add something later, you can do it yourself; it won't require sending the instrument back to the factory.

"This built-in flexibility is only one of the reasons we feel you'll find the *ElectroniK 16* recorder easy to install, use, maintain and work with."

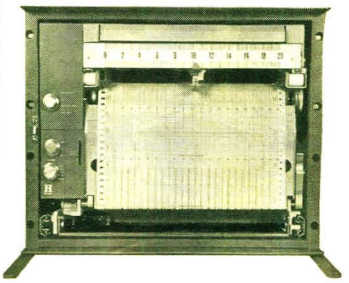
The new instrument is available in one- and two-pen or multipoint versions.

Wilkins noted that while a number of customer "most-wanted" features are standard in the *ElectroniK 16* line, many of the options may prove attractive to laboratory users.

"I'm thinking particularly of our optional pre-loaded chart transport that permits charts to be changed in approximately 10 seconds. This is particularly useful where you're using a fast chart speed and you don't want to waste time."



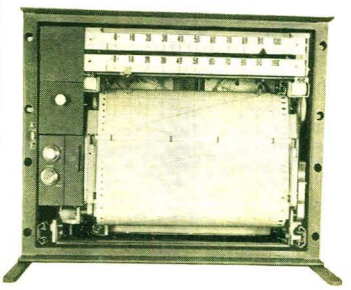
THE ***ELECTRONIK 16*** **SINGLE-PEN Recorder is available with left or right zero on the chart, integrator readout, operation pens, and many other options to meet specific requirements.**



ELECTRONIK 16 **MULTIPOINT Recorder is shown printing 24 points (bottom portion of chart); selected points, using *Select-O-Print* option (center portion of chart), and producing a graphic record with optional recording pen (top portion of chart).**

Complete specifications and other descriptive material can be obtained from your local Honeywell salesman or by writing Philadelphia headquarters.

CIRCLE 2 ON READER SERVICE CARD



IN THE TWO-PEN ***ELECTRONIK 16*** **Recorder there are two independent servos, each available with options to satisfy your many needs. Pens cross with displacement of ⅛-inch or less or can operate over ½-scale width on the same time line.**

Honeywell

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PHILADELPHIA, PA. 19144

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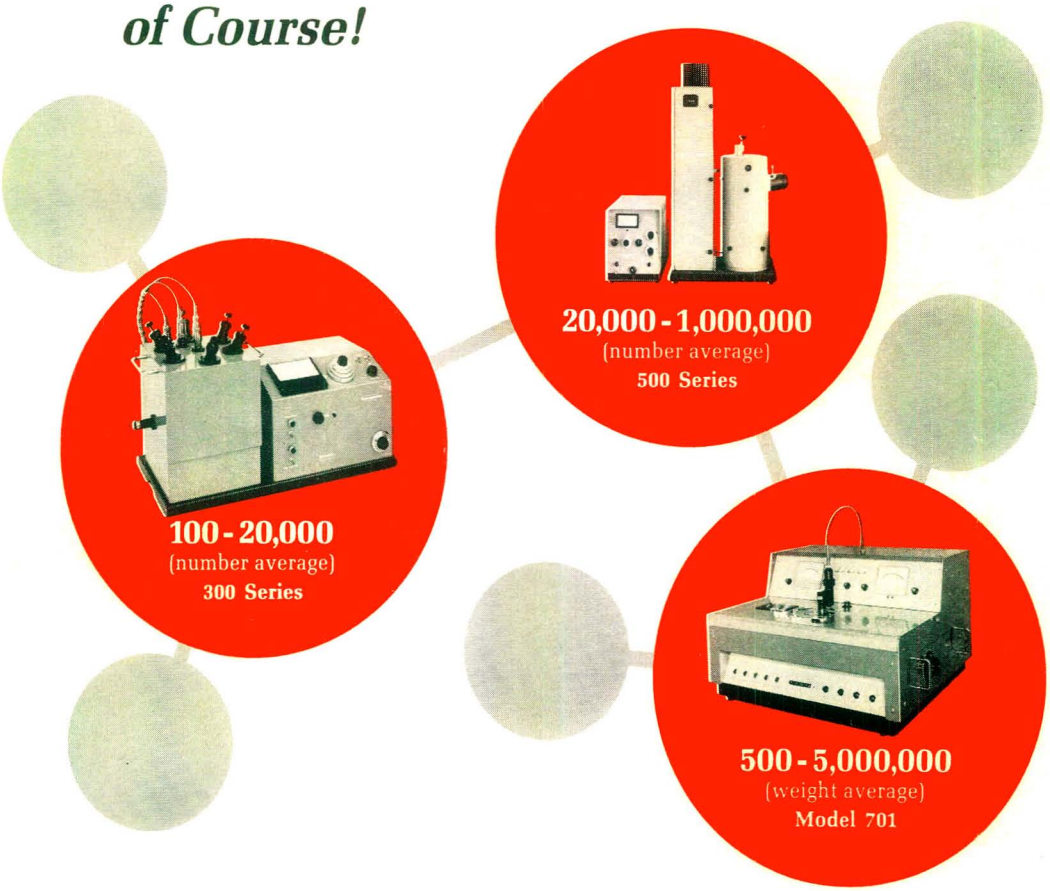
Sales and service offices in principal cities of the world. Manufacturing in United States, United Kingdom, Canada, Netherlands, Germany, France, Japan.

Measure Molecular Weight in 30 Minutes??

of Course!



Any one of the Mechrolab instruments you see here will give you a complete determination of molecular weight within 30 minutes. There is no faster, no more efficient, no simpler and no more dependable means of measuring molecular weights.

Hundreds of these instruments are now used routinely in chemical and biomedical laboratories and universities for polymer research and many other studies.

We'll be happy to send complete details and/or arrange a demonstration at your convenience. Write to us at 1062 Linda Vista, Mountain View, 25, California.

For the Range of 100-20,000 (number average)
300 Series Vapor Pressure Osmometer

Molecular weights are determined by thermoelectrically measuring temperature differences caused by vapor pressure lowering of solvent by solute. A series of standard two minute readings at progressive concentrations enables molecular weights to be determined in twenty minutes or less with an accuracy of 1% up to 5,000.
Price: Model 301A $2,390

For the Range of 20,000-1,000,000 (number average)
500 Series High-Speed Membrane Servo-Osmometer

Determines molecular weights by measuring osmotic pressures to ±.01 cm. of solvent. An optical detector and a servo-operated pressure system automatically establish osmotic equilibrium. This instrument is capable of measuring up to four concentrations in less than one hour. Output is provided for continuous strip chart readout.
Price: Model 501 $3,850

For the Range of 500-5,000,000 (weight average)
Model 701 Light Scattering Photometer*

*Manufactured by S.O.F.I.C.A.; sold and serviced exclusively in the U.S.A. by Mechrolab.

The new improved Model 701-42,000 Light Scattering Photometer measures size, shape, mass, and solvent-solute interaction of macro-molecules. A goniometer unit, carrying the scattered light beam and photo-multiplier tube, can be rotated electrically between 0° to 180°. Fine sensitivity, wide temperature range, and broad molecular weight range combine to make this a productive and versatile laboratory instrument. Price: $9,525

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Southwest Regional Meeting

The 20th Southwest Regional Meeting of the ACS will be held in Shreveport, Louisiana, December 3 to 5 at the Captain Shreve, Washington-Youree, and Downtowner Hotels. Seventeen papers will be presented at the analytical chemistry sessions.

The scientific program for analytical chemistry is given below. Further information is available from Dr. Edward C. Greco, United Gas Corp., P. O. Box 1407, Shreveport, Louisiana 71102.

PROGRAM

Kinetic Study of the Precipitation of Copper-8-Quinolate from Acetone-Water Mixed Solvents. Lester C. Howick and Tony Rihs, Department of Chemistry, University of Arkansas, Fayetteville, Ark. 72701.

The Aluminum Salt of 8-Hydroxyquinaldine. Hans A. Suter, 1002 Chamberlain, Corpus Christi, Tex.

Chemical Microscopy of the Platinum Metals: Reactions with 1,5-Naphthyridine. Harold F. Schaeffer, Department of Chemistry, Westminster College, Fulton, Mo.

The Validity of the Cobaltinitrite Test for Potassium Ion and the "Confirmatory Flame Test." Robert E. McCoy, Francis T. Nicholls, State College, Thibodaux, La.

Spectrophotometric Study of 2-Mercaptoacetanilide Carbamate as a Colorimetric Reagent for Rhodium(III) and Palladium(II). Suresh Srivastava and Mary L. Good, Chemistry Department, LSUNO, Lake Front, New Orleans, La. 70112.

1-Nitroso - 2 - Naphthol - 3,6 - Disulfonic Acid (Disodium Salt) as a New Reagent for the Spectrophotometric Determination of Ruthenium(III). David Miller, Suresh Srivastava, and Mary L. Good, Chemistry Department, LSUNO, Lake Front, New Orleans, La. 70122.

Procedures for the Identification of Small Quantities of Carbonyl Compounds by Way of Their 2,4-Dinitrophenylhydrazones. Michael E. Mason and Bobby Johnson, Oklahoma State University, Stillwater, Okla., and Mynard Hamming, Continental Oil Co., Ponca City, Okla.

Copper-Copper Oxide Flame Reactions of Selected Organohalogens in the Presence of Methane and Air. E. A. Eads and Paul Lynas, Department of Chemistry, Lamar State College of Technology, Beaumont, Tex., and D. A. Payne, Jr., Department of Chemistry, Tulane University, New Orleans, La.

Organic Nitrogen by Sealed Tube Kjeldahl. William S. Ferguson, Marathon Oil Co., P. O. Box 269, Littleton, Colo.

Reduction of Alkyl Disulfides with Triphenylphosphine. Ray E. Humphrey, Department of Chemistry, Sam Houston State College, Huntsville, Tex., and Lloyd M. McCrary and Rodney C. Webb, Dow Chemical Co., Freeport, Tex.

Voltammetry of Iodide, Iodine, and Iodate with the Pyrolytic Graphic Indicating Electrode. F. J. Miller and H. E. Zittel, Analytical Chemistry Division, Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tenn. 37831.

Simple Room Temperature Gas Chromatography. K. V. Wise and T. J. Lemoine, Monsanto Co., Texas City, Tex., and L. H. Holves, Jr., Southeastern Louisiana College, Hammond, La.

Special Techniques of Trace Analysis by Gas Chromatography. John Q. Walker, Wilkens Instrument & Research, Inc., 2510 Broad St., Houston, Tex.

A Statistical Evaluation of Some Important Parameters in the Preparation of Gas Chromatographic Packings. Edgar D. Smith, University of Arkansas, Graduate Institute of Technology, P. O. Box 3017, Little Rock, Ark. 72203, and J. M. Oathout, Hendrix College, Conway, Ark.

A Method for Activation Analysis of Ruthenium in Sea Water. B. W. Dixon, J. F. Slowey, and D. W. Hood, Department of Oceanography & Meteorology, Texas A & M University, College Station, Tex.

Mass Spectrometric Ionization Sensitivity for Positive and Negative Halogen Ions. H. M. Klein and A. Max Bryant, Central Research Laboratories, Texas Instruments Inc., P. O. Box 5474, Dallas, Tex. 75222.

Emission Spectrometric Determination of Barium, Strontium, Boron, Manganese, and Iron in Oilfield Waters Using Plasma Arc. A. Gene Collins, Bartlesville Petroleum Research Center, U. S. Department of the Interior, Bureau of Mines, Bartlesville, Okla.

Congress on Molecular Spectroscopy

The Eighth European Congress on Molecular Spectroscopy will be held August 14 to 20, 1965, in Copenhagen, Denmark. The Congress is sponsored by the International Union of Pure and Applied Chemistry and by the Royal Danish Academy of Sciences. Papers are invited on the following topics: Raman and infrared spectra, ultraviolet spectra, microwave spectra, nuclear magnetic resonance spectra, electron spin resonance spectra, spectral theory, and novel analytical applications. Participants wishing to present a paper should return the provisional registration form, to be received in Copenhagen not later than December 15, 1964. For registration forms and additional information write: Eighth European Congress on Molecular Spectroscopy, Universitetsparken 5, Kobenhavn, Denmark.

Industry Items

Bell & Howell Co., Chicago, Ill., has formed a new subsidiary, Bell & Howell Instrument Co., which will manufacture, in Puerto Rico, precision components used in scientific and recording equipment produced by Bell & Howell's Electronic Instrumentation Group.

Itek Corporation, Lexington, Mass., has reorganized its Research Division to reflect an increased emphasis on basic and applied science. The new structure focuses on the three fundamental disciplines of chemistry, physics, and applied mathematics. The Research Division will continue to support all operating divisions in both a problem-solving and long-range research capacity.

Leeds & Northrup Co., Philadelphia, manufacturers of electronic instruments and automatic controls has formed a Mexican subsidiary, Leeds & Northrup Mexicana S. A., to manufacture and sell Leeds & Northrup products in Mexico.

E. H. Sargent & Co. has purchased The Laboratory Supply Division of Mine & Smelter Supply Co., Denver, Colo. Acquisition of the Laboratory Supply Division will provide Sargent with broader distribution for its products in the Rocky Mountain area.

Technical Measurement Corp., North Haven, Conn., manufacturers of digital computers and instrumentation systems, has acquired **Vanguard Instruments Corp.**, La Grange, Ill. Vanguard produces chemical analytical equipment using radiochemical and ultraviolet absorption techniques.

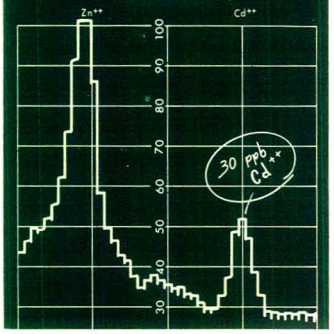
Warner-Chilcott Laboratories, a division of Warner-Lambert Pharmaceutical Co., Morris Plains, N. J., has established an Instruments Division. The nucleus of the new division is the former Research Specialties Co. of Richmond, Calif., recently purchased by Warner-Lambert. The new division will be responsible for the development and manufacture of automated equipment for use in medical and industrial laboratory procedures.

Melabs ANNOUNCES

TRACE METAL ANALYSIS TO

PARTS PER BILLION

WITH MELABS' NEW PULSE POLAROGRAPHIC ANALYZER



Test trace showing 30 parts per billion of cadmium in .01M sodium sulfate solution. The zinc is an impurity in the distilled water.

See it at the EASTERN ANALYTICAL SYMPOSIUM Booth 41A

Model CPA-3

Three-electrode, controlled potential circuitry for use with high resistance solutions.

Pulse measurements for high sensitivity.

Single sweep mode for rapid analysis.

Drop-rate control and temperature control incorporated in companion electrode stand, Model CDM-1.

Sensitivity demonstrated above obtained with differential pulse method. Similar results obtained with most metals normally analyzed by polarography.

Other instruments in our line, designed especially for the analytical chemist, include:

- CCM-1 Conductivity Meter
- CTC-1 Temperature Controller
- CTB-1 Temperature Bridge
- CDM-1 Electrode Stand

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CALENDAR OF EVENTS

Nov. 4 to 6	**Pittsburgh Diffraction Conference.** Mellon Institute, Pittsburgh, Pa. *Contact:* Dr. W. M. Biagas, Crucible Steel Co., P. O. Box 7257, Pittsburgh, Pa. 15213. Page 76 A, Sept.
Nov. 5 to 6	**Eighth Annual Fall Conference of the Chemical Division of the American Society for Quality Control.** Mountain View Hotel, Gatlinburg, Tenn. *Contact:* Hubert M. Hill, Tennessee Eastman Co., Kingsport, Tenn.
Nov. 11 to 13	**Sixth Eastern Analytical Symposium.** Statler-Hilton Hotel, New York City. *Contact:* Leo Safranski, E. I. du Pont de Nemours & Co., Plastics Department, Experimental Station, Wilmington 98, Del. Page 45 A, Oct.
Nov. 13 to 14	**26th Meeting of the Association of Clinical Scientists.** Washington Hospital Center, 110 Irving St., N. W., Washington, D. C. *Contact:* Dr. F. W. Sunderman, 1933 Delancey Place, Philadelphia, Pa. 19103.
Nov. 26 to Dec. 4	**Fourth Exhibition of Chemical Equipment.** Palazzo dell'Arte by the Park, Milan, Italy. Sponsor: Italian Chemists National Association. *Contact:* Italian Chemist National Association, 29 via Marianna Dionigi, Rome, Italy.
Nov. 30 to Dec. 3	**American Nuclear Society Winter Meeting in conjunction with the 12th Hot Laboratory and Equipment Conference and the Atomic Industrial Forum Meeting.** San Francisco, Calif. *Contact:* W. H. Nutting, Pacific Gas & Electric Co., 245 Market St., San Francisco, Calif.

Coming Events

Dec. 3 to 5—**Twentieth Annual Southwest Regional Meeting of the American Chemical Society.** Captain Shreve Hotel, Shreveport, La. *Contact:* Edward C. Creco, United Gas Corp., P. O. Box 1407, Shreveport, La. 71102. Page 45 A, Nov.

1965 Meetings

Jan. 22 to 23—**Symposium on Hydrocarbon Analysis—Future Requirements and Applications.** Sheraton-Lincoln Hotel, Houston, Tex. Sponsor. ASTM. *Contact:* R. R. Wright, American Society for Testing and Materials, 1916 Race St., Philadelphia 3, Pa.

Jan. 27 to 30—**Fifth Seminar on Electrochemistry.** Central Electrochemical Research Institute, Karaikudi-3, South India. *Contact:* Dr. M. A. V. Devanathan, Central Electrochemical Research Institute, Karaikudu-3, South India.

Feb. 1—**Metropolitan Regional Meeting, ACS.** Stevens Institute of Technology, Hoboken, N. J. *Contact:* Dr. Arthur Kemper, Manhattan College, Dept. of Chemistry, New York, N.Y. 10471. Page 76 A, Sept.

Feb. 4 to 5—**12th Annual Conference of the Western Spectroscopy Association.** Asilomar, Calif. *Contact:* Dr. M. W. Windsor, TRW Space Technology Laboratories, One Space Park, Redondo Beach, Calif.

Feb. 8—**Toronto Symposium on Thermal Analysis.** Seaway Towers Hotel, Toronto, Ontario, Canada. Sponsor: Chemical Institute of Canada. *Contact:* H. G. McAide, Ontario Research Foundation, 43 Queen's Park Crescent East, Toronto, 5, Canada.

Feb. 8 to 12—**ASTM Committee Week.** Statler-Hilton Hotel, Cleveland, Ohio. *Contact:* American Society for Testing and Materials, 1916 Race St., Philadelphia 3, Pa.

Mar. 1 to 5—**Sixteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.** Penn-Sheraton Hotel, Pittsburgh, Pa. 15213. Page 75 A, Sept.

Mar 17—**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. 29 to Apr. 2—**LABEX 1965—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.

Apr. 4 to 9—**149th ACS National Meeting.** Detroit, Mich.

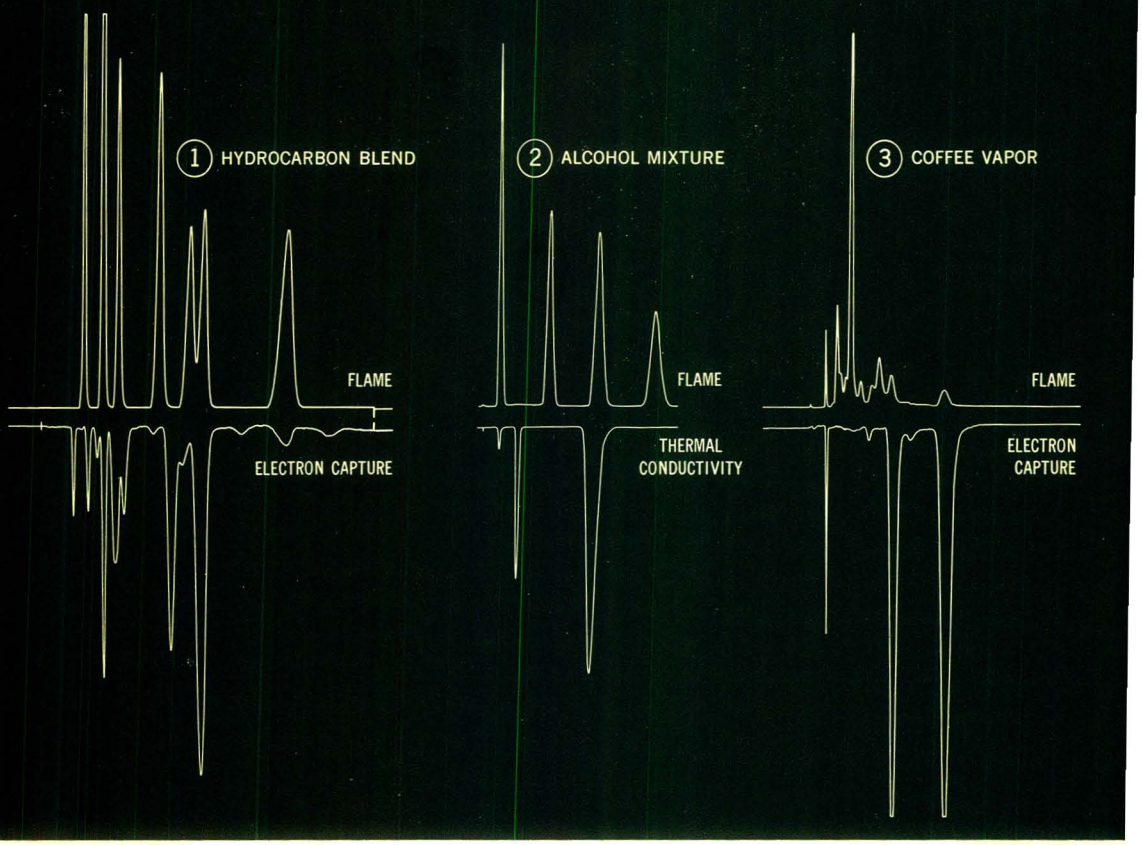
Apr. 7 to 9—**Anniversary Meeting of the Chemical Society.** Glasgow, Scotland. Symposia on Physical Methods of Structure Determination and Non-Aqueous Solvents and Melts will be included. *Contact:* General Secretary, The Chemical Society, Burlington House, London, W1, England.

Apr. 19 to 22—**1965 International Conference on Modern Trends in Activation Analysis.** Texas A & M University, College Station, Tex. *Contact:* Dr. R. E. Wainerdi, Activation Analysis Research Laboratory, Texas A & M University, College Station, Tex.

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 0 5, Permoserstr. 15, Germany. Page 76 A, Sept.

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.

SIMULTANEOUSLY



The simultaneous detection of a gas chromatograph column effluent by two different types of detection systems places a new degree of utility at the disposal of the analyst. Each of the three simultaneous chromatograms reproduced above, for example, makes possible a more detailed characterization of the sample analyzed than any single-detector run can do.

Chromatogram #1—a simultaneous flame-electron capture analysis of a hydrocarbon blend—not only responds to all the major hydrocarbon constituents in the upper trace but also a surprisingly large number of contaminants in the lower trace.

In chromatogram #2—a simultaneous flame-thermal conductivity analysis of a trace alcohol mixture in aqueous solution—four alcohols are detected by the flame detector operated at high sensitivity while the thermal conductivity detector reveals three inorganic constituents (NH_3, CS_2 and H_2O respectively) that the flame detector does not pick up at all.

Chromatogram #3 is a sampling of the vapor above ground coffee, as detected simultaneously by the flame-electron capture combination.

All three chromatograms were obtained recently in the F & M Applications Laboratory on a Series 810 Gas Chromatograph.

Five important design features make Series 810 Gas Chromatographs particularly well suited to simultaneous detection: (1) the effluent splitter has excellent linearity; (2) any two detectors can be installed and operated simultaneously—the choice is made from dual flame, dual thermal conductivity, electron capture, and micro cross-section detectors; (3) either or both detectors can be changed as frequently as desired; (4) dual column compensation of thermal conductivity or flame ionization detectors is readily accomplished; and (5) collection of samples is possible during most modes of operation.

For more information on this unusually versatile gas chromatograph, write F & M Scientific Corporation, Route 41 and Starr Road, Avondale, Pennsylvania, phone (215) 268-2281. European subsidiary: F & M Scientific Europa N.V., Basisweg, Sloterdijk/Amsterdam, The Netherlands.

F&M

F&M SCIENTIFIC CORPORATION
AVONDALE, PENNSYLVANIA

In the final analysis... it's F&M

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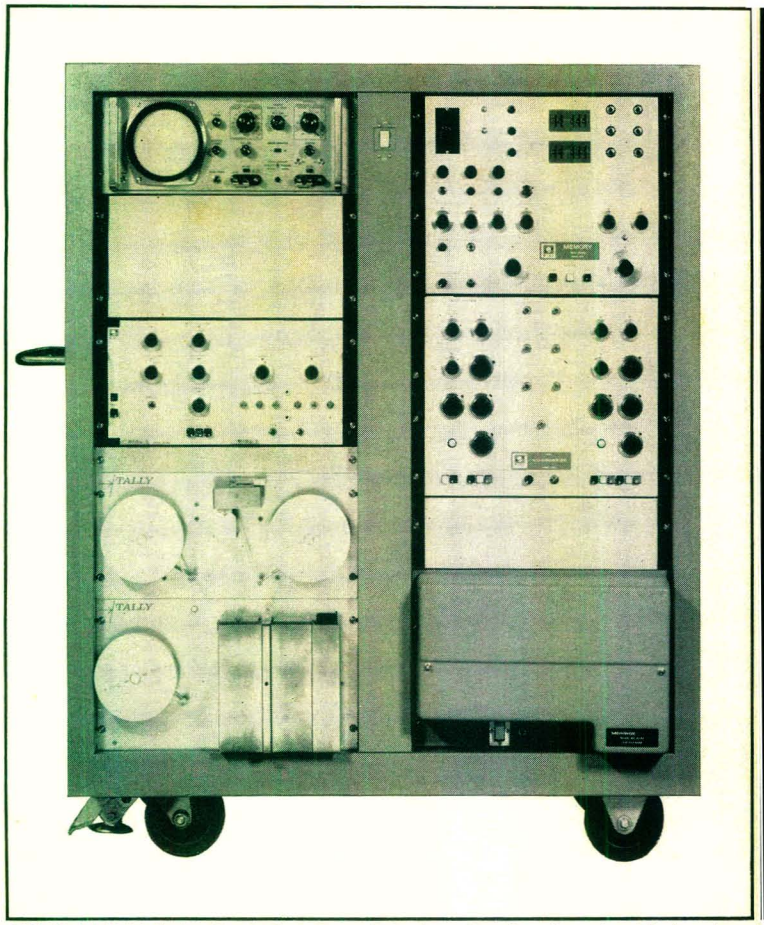
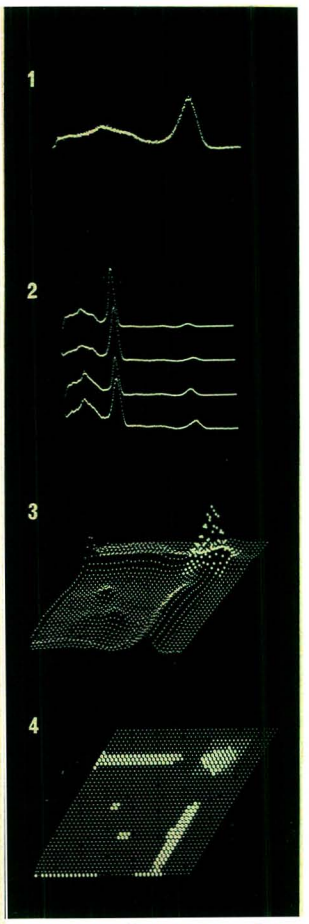


RIDL Model 22-102 Nuclear Counter-Computer consists of 22-01 1600-Word Memory, 22-03 Dual ADC, 29-1B Instrument Case and Power Supply, 52-56 5-in. Display Oscilloscope, 52-52 Data Processor, 52-53 Punch/Type/Read Matrix, 44-15 Tally Punch, 44-23 Tally Reader, 44-25 Monroe Printer, and 29-23 Cart.



*Pictured at right are four of a number of display and operating modes with sodium-22 spectra: **1.** Single-parameter analysis mode provides resolution consistent with most solid-state detectors. **2.** Typical multiple single-parameter application—shown here is 2 x 400 coincidence simultaneously with 2 x 400 anticoincidence. Dual 2 x 800 mode is also available. **3.** Multiparameter 40 x 40 coincidence operation with Region of Interest intensification. Other multiparameter coincidence groups are 16 x 100, 8 x 200, 4 x 400, 2 x 800. System can also be used to monitor data for computer input and analysis. **4.** Unique peak volume integration provided by two-parameter Region of Interest selectors and data level controls which intensify and define area (x and y) in which peak lies and count level above which integration will be performed.*

RIDL 1600-CHANNEL ANALYZER SYSTEMS OFFER VERSATILE READOUT AND DATA HANDLING ABILITY

In addition to the analysis modes portrayed above, versatile RIDL 1600-channel systems provide for multiscaler operation and applications involving time as a "y" parameter. In the latter case, spectra are stored sequentially in time making the system well suited to half-life spectra studies.

Multiple detector operation for up to 16 detector inputs is accommodated by Model 30-27 Mixer-Router. Spectrum analysis/synthesis and peak area integration provisions in the 22-102 system are available as accessories to other systems in the 1600-channel analyzer family.

The dual ADC is available separately and is directly compatible with on-line computers. A computer-compatible magnetic tape system is also offered as an accessory.

Switch-selected wired programming assures simplicity and reliability of operation. The system is operable with the RIDL Digital Stablizer in both the single and multiparameter modes, and the basic system operates with all standard RIDL readout devices including the RIDL Magnetic Tape unit.

Please write for further details and specifications or consult your RIDL sales engineer. NUC:R-4-231

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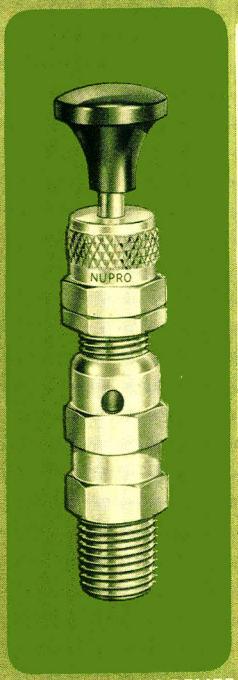

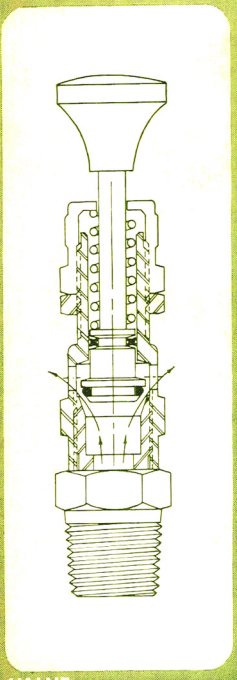

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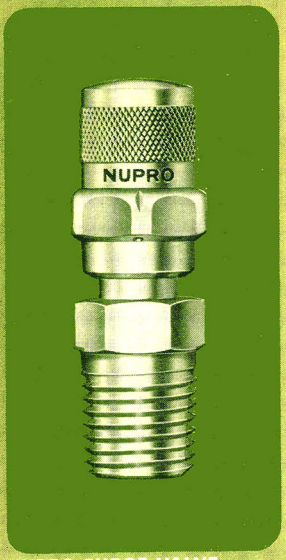

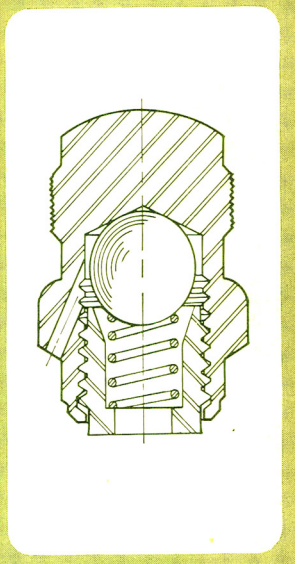

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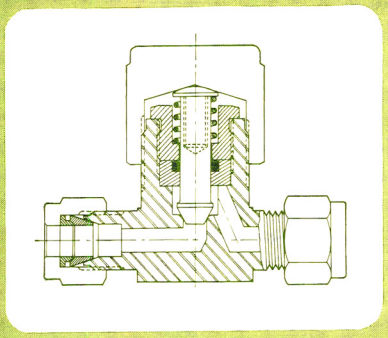

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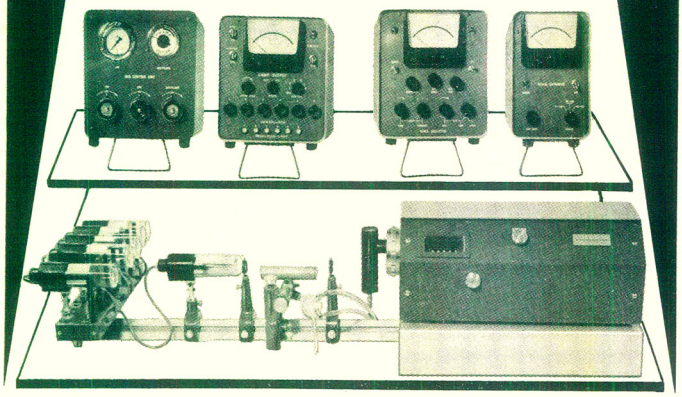
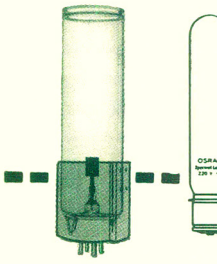


Rapid, highly-accurate metals analysis of many heretofore difficult-to-analyze industrial, agricultural and biological materials is now possible. The atomic absorption technique, with the new Model AA-3, offers many advantages over competitive methods — relative freedom from interelemental matrix interferences, accurate analysis of trace quantities in the presence of large amounts of others, simplicity of operation, and speed in obtaining results are a few such advantages. The AA-3 offers many special features of its own. Among them are a novel "warm-up" bench for up to six source lamps, new slit mechanism for high reproducibility*, designed-in flexibility in the sampling area anticipating future developments, compactness, manual or motor-driven wavelength scan, and the capability to do flame emission analysis. An added bonus is low initial, operating, and maintenance costs!

*Patent applied for



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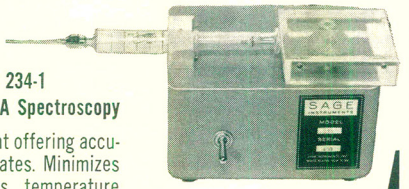

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A simple-to-operate instrument offering accurate control of sample flow rates. Minimizes effect of viscosity variations, temperature changes, and surface tension factors. Flow rates from .341 ml to 16.8 ml per min. possible. Further data on request.

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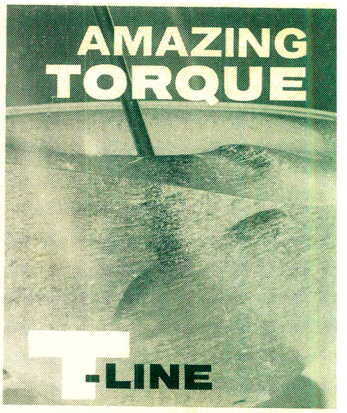

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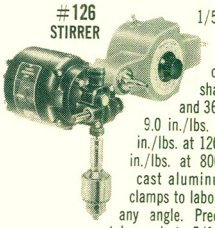
These stirrers are ideal for the most viscous syrups, pastes, paints and petroleum products. Each is a single extremely compact unit—no separate control boxes, rheostats or delicate vacuum tubes. All operate on 115 Volts AC-DC and have three-wire cords and plugs. Finished in pale green epoxy enamel which resists acid and solvents.

#126 STIRRER



1/50 H.P. enclosed motor lessens possibility of damage from corrosive fumes. Three shafts: direct drive, 6:1 and 36:1 reduction. Delivers 9.0 in./lbs. at 20-175 RPM—1.5 in./lbs. at 120-1000 RPM and 0.25 in./lbs. at 800-6000 RPM. Sturdy cast aluminum control housing clamps to laboratory stand—stirs at any angle. Precision Jacobs chuck takes rods to 5/16″. **$165.00**

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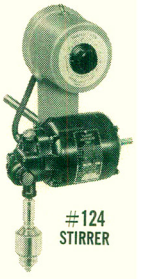

#124 STIRRER

#123 STIRRER

For emulsions, suspensions, etc. requiring high speed and torque. Continuous duty, 1/12 H.P. motor delivers 0.5 in./lbs. at 500-12,000 RPM. Collet type precision chuck* takes 5/16″ rods. **$140.00**

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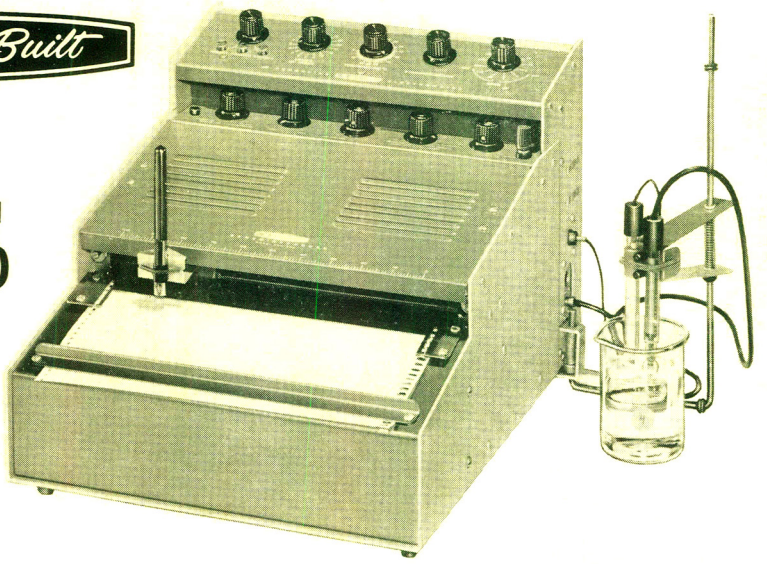

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• **Multi pH Ranges!** Full-scale pH spans of 1, 2, 5, 10 and 14. Any 1 pH unit, 2 pH units (etc.) over entire pH region of interest can be switched for full scale on 10" scale or recorder chart.

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

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Expanded Scales Offer Added Versatility! The expanded scales make it possible to measure the pH very precisely and accurately. Therefore, reliable measurements can be made for the determination of Kw, activity coefficients, formation constants, and function potentials. The unit can be used for Karl Fischer titrations, redox, precipitation and complexation titrations, nonaqueous titrations, the determination of sodium and potassium concentration with the new specific glass electrodes, and all potentiometric measurements. The circuitry is connected for simple modifications by plug-in adapters. One plug-in adapter can convert the pH recording electrometer into a precision recording photometer for use in spectrophotometry, or an ionization detector readout for gas chromatography.

Modular Construction By The Famous Malmstadt-Enke System! The new EUW-301 was designed by Dr. Howard V. Malmstadt, Professor at the University of Illinois. It consists of the Heath EUW-20A Servo-Chart Recorder, coupled with a special pH Module EUA-20-11. It may be purchased as a complete unit, or those who already own an EUW-20A Servo-Chart Recorder may purchase the pH module separately for simple conversion (takes only a few minutes) to a pH Recording Electrometer. A special parts kit, EUA-301-1, is also available for converting the EUW-301 Electrometer to the EUW-20A Servo-Chart Recorder.

A Special Educational Discount Is Available — Write For Details!

EUW-301, pH Recording Electrometer, 26 lbs., (pH electrodes not included) $300.00

EUA-20-11, pH Module Only, 8 lbs. (converts Heath EUW-20A Servo-Recorder to pH Recording Electrometer) $125.00

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NIKON SMZ STEREOSCOPIC ZOOM MICROSCOPE

matched 0.8x to 4x zoom objectives provide wide magnification range with precise parfocality

The Nikon SMZ is equipped with matched 5-to-1 zoom objectives. Used with a pair of 10x oculars it provides a continuously variable range of magnifications from 8x to 40x without any change in focus or working distance. Magnification ranges from 4x to 120x are also obtainable with other eyepieces and by adding supplementary meniscus objective lenses. The following table gives complete details:

OBJECTIVES	SUPPLEMENTARY OBJECTIVE LENSES	EYEPIECES 10X mag.	10X field dia.	15X mag.	15X field dia.	20X mag.	20X field dia.	WORKING DISTANCE
0.8X to 4X zoom	none	8X to 40X	29.7mm to 5.6mm 1.17 in. to .22 in.	12X to 60X	15.3mm to 2.9mm .60 in. to .11 in.	16X to 80X	14.2mm to 2.7mm .56 in. to .11 in.	77.5mm 3.05 in.
	0.5X	4X to 20X	45.5mm to 9.4mm 1.79 in. to .37 in.	6X to 30X	24.8mm to 5.1mm .98 in. to .2 in.	8X to 40X	22.2mm to 4.5mm .87 in. to .18 in.	103mm 4.06 in.
	0.7X	5.6X to 28X	38.0mm to 7.3mm 1.50 in. to .29 in.	8.4X to 42X	19.8mm to 3.9mm .78 in. to .15 in.	11.2X to 56X	18.2mm to 3.5mm .72 in. to .14 in.	95.5mm 3.76 in.
	1.5X	12X to 60X	21.0mm to 4.1mm .83 in. to .16 in.	18X to 90X	11.0mm to 2.1mm .43 in. to .08 in.	24X to 120X	9.0mm to 1.8mm .35 in. to .07 in.	45mm 1.77 in.

One of the advantages of the SMZ is the precise in-focus tracking of the right and left images over the entire zoom range. This is due to meticulously matched optics, and to the fact that the eyepiece tubes are both adjustable for dioptric power. There is a distinct sense of visual ease and comfort even with prolonged use.

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Standard equipment supplied with the Nikon SMZ includes stand, base, reversible white-and-black disc insert and clips, as shown in illustration. Optional equipment includes: substage base for transmitted light observation, illuminators, micrometer stages, reticles, polarizing attachment, half-reflecting mirror attachment for on-axis surface illumination, and a variety of other accessories for numerous applications. Free demonstration provided on request. For detailed catalog, write Dept. AC-11.

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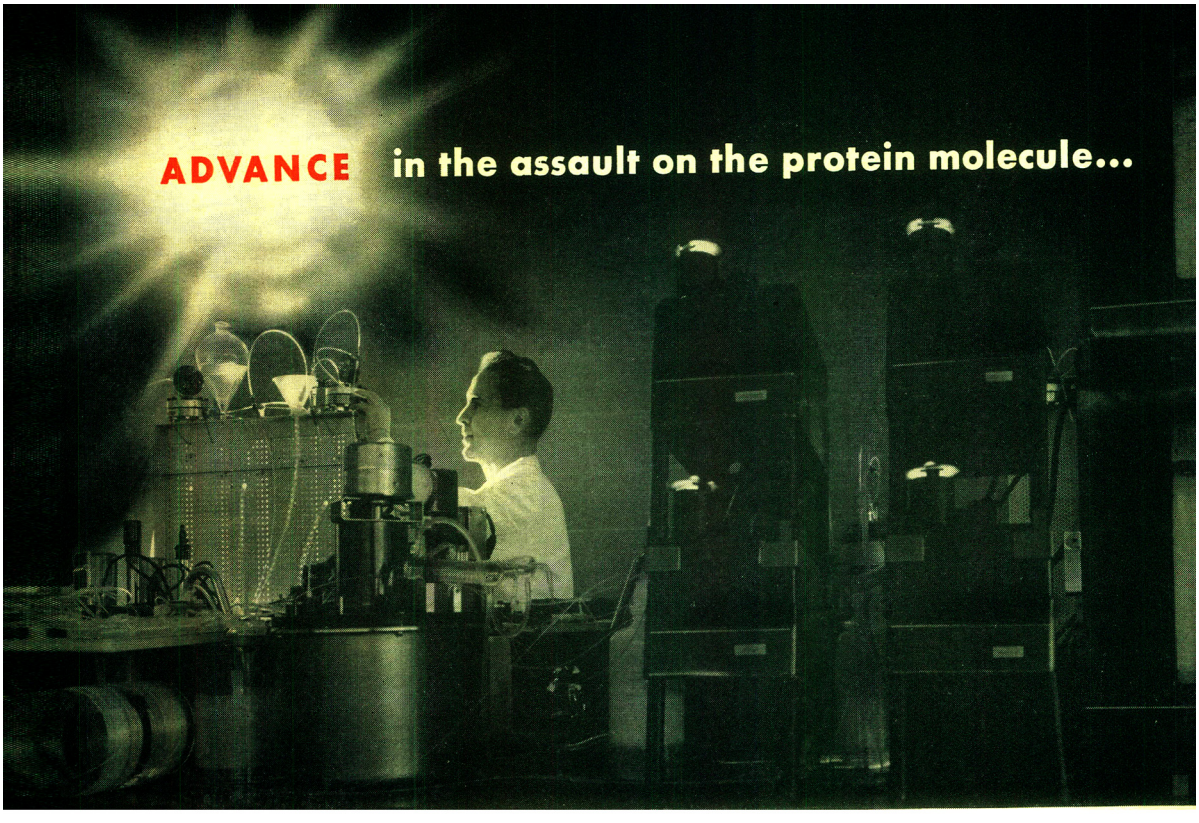

new automated technic provides rapid preparative and quantitative information on peptides ... their size, occurrence and distribution ... and assures detection.

The Technicon AutoAnalyzer system you see above may well make history in protein research. By an ingenious extension of multiple-analysis chromatography, it not only separates peptides for preparative purposes, but at the same time gives quantitative information.

The column effluent is split into many streams. One stream is subjected to a system of continuous hydrolysis. Another stream, unhydrolyzed, is used as control. Both are reacted with Ninhydrin. Comparison of these gives information about the size of the peptide. Other parallel streams can be used simultaneously for specific amino acid reactions. Thus, the basic AutoAnalyzer® train can be augmented and shaped at will to provide more and more analytic information.

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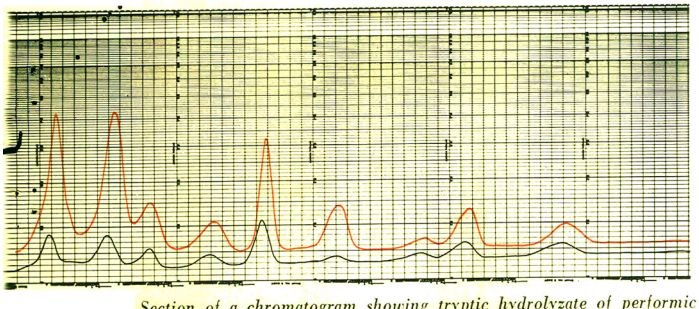
The Technicon® peptide system is automated from beginning to end with thoroughgoing AutoAnalyzer efficiency, rapidity, and reliability. This versatile AutoAnalyzer reduces to *hours* the *days* now conscripted to the tedious task of peptide analysis.



Section of a chromatogram showing tryptic hydrolyzate of performic acid oxidized bovine pancreatic Ribonuclease before and after alkaline hydrolysis.

TECHNICON

CHROMATOGRAPHY COR

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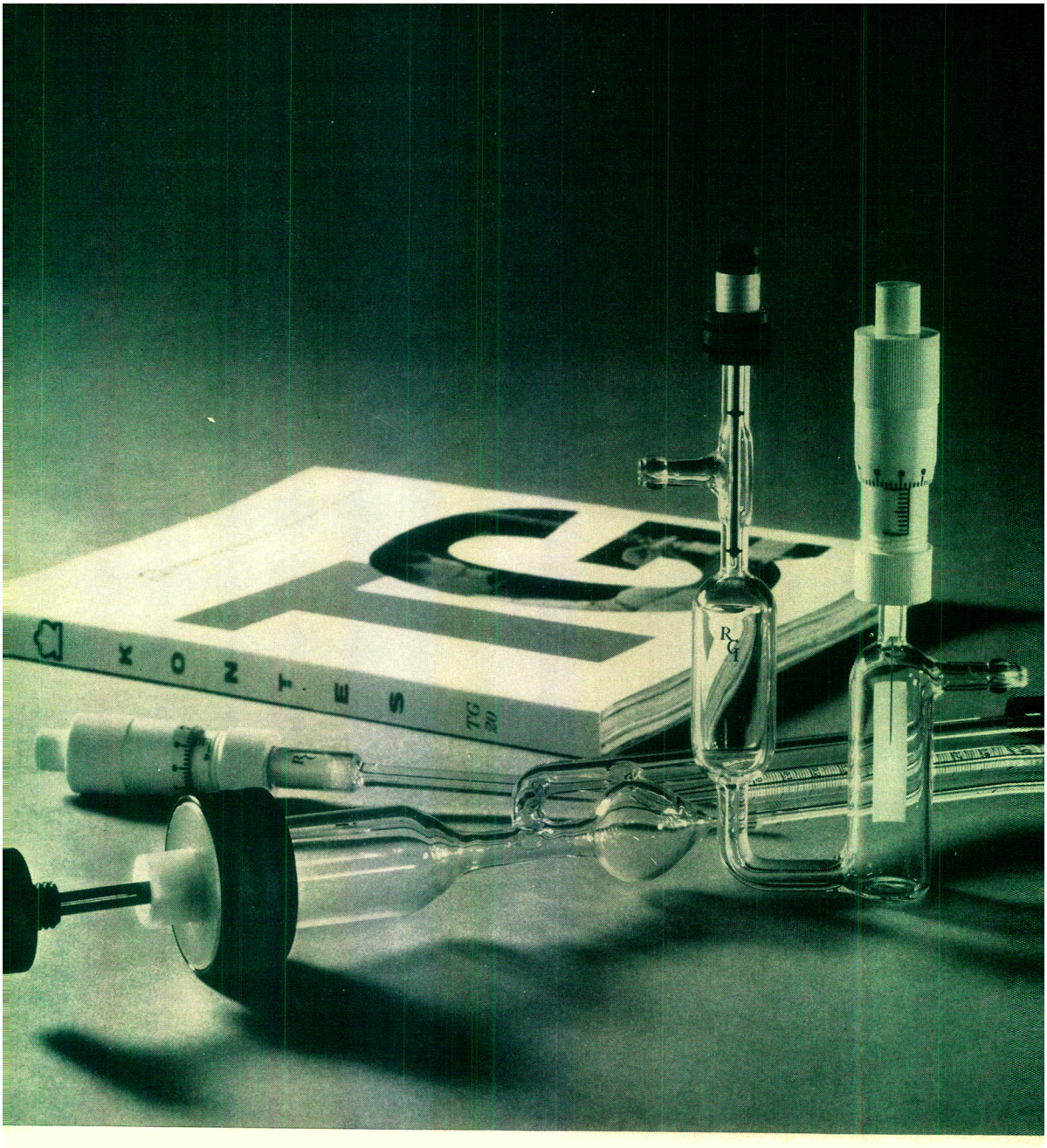

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Analytical Chemistry of Ruthenium. *I. D. Avtokratova. 224 pages. Program for Scientific Translations. 14 Shammai St., Jerusalem, X, Israel. 1964. $11.*

Reviewed by J. C. White, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

This is another volume in the series "Analytical Chemistry of Elements" being published by the Academy of Sciences of the U.S.S.R. In content, scope, and organization the series is quite similar to the treatise being edited by Kolthoff and Elving. There are five chapters; physicochemical and analytical characteristics of ruthenium and its compounds; detection of ruthenium; chemical and physicochemical methods of determination of ruthenium; separation of ruthenium; and determination of ruthenium in natural materials and industrial products. Each chapter is quite complete; the chapter on methods of determination of ruthenium in natural materials includes schemes of analysis in outline form which will be of much use to practicing analysts. The authors have not neglected the radiochemical aspects of ruthenium. This is particularly gratifying because of the importance of the analysis of fission product ruthenium and its complex chemical behavior. Ruthenium can exist in numerous oxidation states and complex ions. Isolation of ruthenium, carrier-free or not, requires knowledge and awareness of these properties.

There is some duplication that inevitably creeps into such an all inclusive volume. For example, there are scattered throughout the text figures of seven apparatuses for the preparation of RuO_4. The separation of RuO_4 by distillation is the most commonly used means of isolating ruthenium, so perhaps there is some justification for including more than one or two distillation set-ups. A bit incongruous is the use of the 1924 figure for the price of ruthenium. Prices of vintage 1924 are but a dream in 1964.

The reader of page 5 will undoubtedly be puzzled by the word "clarke" (ruthenium content in the earth's crust is 5×10^{-6} clarke). A combined search and poll of many colleagues failed to uncover any analytical chemists who claimed either knowledge or prior sight of such a term. With the help of the ORNL library, a glossary was found in a geochemistry text which solved the dilemma. "Clarke" is the unit "average percentage of an element in the earth's crust." This reviewer found the use of the unit more intriguing than exasperating; such may not be the common reaction, however.

It is unfortunate that a book of such excellent editorial content should be published in the style and print that this book has. The paper is too thin to warrant printing on both sides. One becomes irritated and weary attempting to filter the background print from each page. The print is too small for comfortable reading. Bold face type is not used to denote paragraph, section, or chapter headings so that it is difficult to locate specific items on a given page. Most tables are printed in small print. The economic facts of life that publishers face are not completely unknown to scientists. Nevertheless, for the price of $11, one does expect a much higher quality of publishing than this.

Despite these shortcomings, this volume should be in all technical libraries. Many chemists actively engaged in research on ruthenium and the platinum group metals will also want a copy for their personal use.

Paper Chromatography. A Comprehensive Treatise. *I. M. Hais, K. Macek, editors. 955 pages. Academic Press, Inc., 111 Fifth Ave., New York 3, N. Y. 1963. $26.50.*

Reviewed by Erich Heftmann, Division of Biology, California Institute of Technology, Pasadena, Calif.

The third edition of this respected work was written by 22 Czech scholars under the editorship of Hais and Macek, translated into English by Kalina and Němeček with the help of four British editors, and published in America last year. The book is divided into three parts. The general part contains chapters on the history, theory, principles, and techniques of paper chromatography. New material is presented particularly in the chapters on chromatography papers and isotope techniques. Electrochromatography on paper and column chromatography on cellulose powder, which were discussed in earlier editions, had to be omitted to make room for recent advances in paper chromatography.

The special part of the book reviews the applications of paper chromatography to all the inorganic and organic substances from abequose to zymosterol. Biochemical applications have been grouped together in chapters devoted to alkaloids, vitamins, antibiotics, pesticides, etc., while chemical considerations dictated the organization of other chapters, such as organic sulfur compounds and heterocyclic compounds of oxygen or nitrogen. To keep within reasonable limits, some of the obsolete material from earlier editions was eliminated.

The third part of the book contains a particularly valuable collection of practical notes on the preparation of detection reagents, samples, filter papers, and solvent systems for qualitative and quantitative analysis. This is followed by ample author and subject indexes. The text is generously supplemented by illustrations—some of them in color—and tabular material. While the binding is excellent, the paper is apparenty not of the best quality.

Since it is the most recent and comprehensive compilation of information on paper chromatography, no chemistry reference library can afford to be without a copy of this book. On the other hand, at a price of $26.50, very few individual laboratories will be able to afford a copy. Anyhow, progress in chromatography is so rapid that a book such as this, containing practically no references to articles published after 1961, is already to some degree obsolete. For instance, in my own field of interest, the steroids, paper chromatography has for all intents and purposes been superseded by gas and thin layer chromatography. It is particularly unfortunate, therefore, that chromatography on thin layers of cellulose powder, an important modification of paper chromatography, had not progressed sufficiently in 1961, to justify more than a brief mention of this subject.

Progress in the Science and Technology of the Rare Earths. Vol. 1. *LeRoy Eyring, editor. 532 pages. Macmillan Co., 60 Fifth Ave., New York 11, N. Y. 1964. $17.50.*

Reviewed by Donald Cohen, Chemistry Division, Argonne National Laboratory, Argonne, Ill.

Since World War II there has been a tremendous upsurge in the study of the rare earth elements. In addition to several volumes and an annual conference starting in the fall of 1960, it now appears that there will be published an annual survey in this field of rare earth chemistry. The editor, Professor LeRoy Eyring, introduces this volume with the following statement: "This volume presents the first of a series of surveys which will be prepared on an annual basis and to provide a firm foundation for future volumes, the present work covers the years 1955 to 1961."

The book contains sixteen chapters with most of the emphasis upon the science rather than the technology. A novel feature of the volume is that three of the chapters are not in English. "Crystal Chemistry of the Rare Earth Oxides" is in German and "The Analytical Chemistry of the Rare Earths" and "Inorganic and Organic Compounds" are in French. This use of the non-English language will probably cause the average reader to skip these chapters. However, the more frequent use of French and German in reference texts should encourage scientists to practice and improve upon their reading ability in these languages.

In addition to the already named chapters, there are chapters on: geochemistry, mass extraction and separation, ion exchange, solvent extraction, solution chemistry, phase equilibria studies, crystal chemistry, alloys and intermetallic compounds, thermodynamics and magnetic properties of the chalcogenides and uses and applications. Two of the chapters are reviews of Soviet research, one on complexes and the other on analytical chemistry.

The book is well organized and the chapters are in general very well written. The chapters contain a wealth of information with many useful tables and figures. The only serious fault with this book is the time element; a book published in April 1964 should contain work more recent than 1961. Nevertheless this book should be a valuable reference source for anyone interested in this field of rare earth research.

IR—Theory and Practice of Infrared Spectroscopy. *Herman A. Szymanski. xiv + 375 pages. Plenum Press, 227 W. 17th St., New York 11, N. Y. 1964. $15.*

Reviewed by Robert S. Silas, Phillips Petroleum Co., Bartlesville, Okla.

The use of infrared spectroscopy as a tool in research is now common enough that a knowledge of the technique and its applications is becoming an essential part of the education of all chemists. This book is intended for use in an introductory course in infrared for nonspecialists, particularly those who are interested in structure determination and analysis. The major part of the book can be about equally divided into sections of laboratory instrumentation and techniques (three chapters), theory (one chapter), and group frequencies (one chapter). There is, in addition, a brief introductory chapter and a final chapter listing general references, bibliographies, and sources of infrared spectra and information.

The chapter on instrumentation (written by Nelson L. Alpert) is a simple but comprehensive discussion of instrument design and operation, components, and specifications. The discussion is sufficiently general to include the vast majority of instruments now in use, although mention of specific instruments has been avoided. The next chapter mentions virtually

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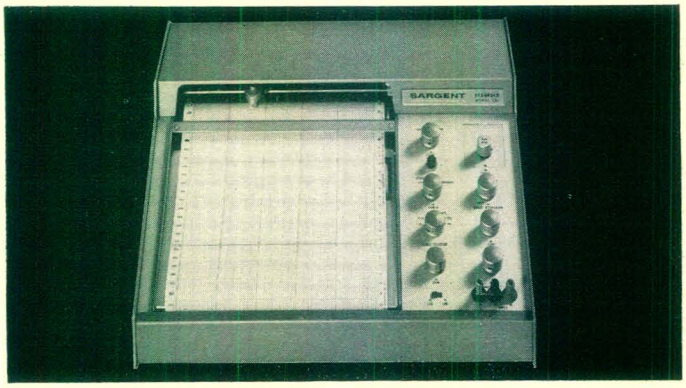

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every sampling technique and sample accessory and discusses the more common ones in some detail. A chapter on quantitative analysis discusses Beer's law, multicomponent and differential analyses, and related topics.

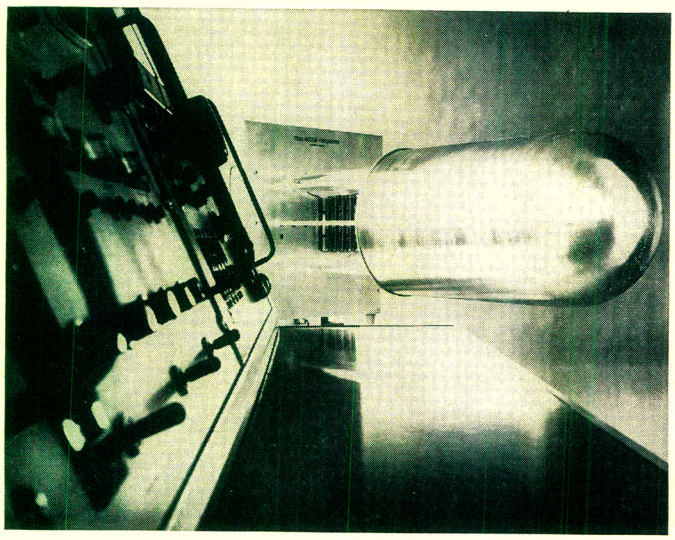
The presentation of infrared theory is principally descriptive, with a minimum of equations. It includes a discussion of point groups (with excellent figures illustrating each), character tables and species of vibrations, calculation of allowed vibrations, and factors affecting band positions and shapes. This is a good presentation of a difficult subject. A number of examples are given, including 17 pages for the reproduction and interpretation of the spectrum of formaldehyde.

The chapter on group frequencies is the longest in the book, but 64 of its 107 pages are given over to figures and tables, including not only graphical summaries of group frequency correlations, but also numerous spectra and tables of experimental frequencies for selected compounds. The presentation is selective; a detailed description and discussion of group frequencies for CH_3 and CH_2 groups, covering more than half of the chapter, is given as an example of the way in which such correlations are developed and used. The rest of the chapter summarizes group frequencies for the most common structural groups.

As can be seen, the range of topics is quite broad. It is at the same time quite selective, some topics being discussed in considerable detail, many others dismissed with a brief mention, if any. This may be unavoidable in a book intended as a textbook rather than a reference, but the choice was not always a happy one, not so much in what was included, but in what was omitted. This is particularly evident in the pages devoted to practical uses of infrared. The author has limited himself to a discussion showing how the methods used with group frequencies are developed. Leaving aside the question whether an extensive listing of group frequencies might be more pertinent to the general user, there are other topics which could be profitably discussed in more detail. Some which come rapidly to mind include band shapes in condensed phases, uses of intensity correlations in conjunction with group frequencies, hydrogen bonding, quantitative functional group analysis, group frequencies in the 15–50 micron region, and the uses of integrated intensities. Their absence is particularly disturbing when one realizes that a considerable part of the discussion of theory is devoted to the description and application of methods of spectral interpretation which the general user will seldom if ever need, limited as they are to a few relatively simple and symmetrical molecules in the vapor phase.

Despite these objections, this book can profitably be utilized by the beginner in infrared, particularly for its survey of basic principles and laboratory technique. The experienced spectroscopists, however will find little here which is not already available to him from standard references and his own experience. The text appears to be relatively error-free. An exception is the consistent misspelling of the name Termatrex.

Treatise on Analytical Chemistry. Part I. Theory and Practice. Volume 4. *Edited by I. M. Kolthoff and P. J. Elving, with the assistance of E. B. Sandell. xxv + 955 pages. Interscience Publishers, Inc., 605 Third Avenue, New York 16, N. Y. $25.00.*



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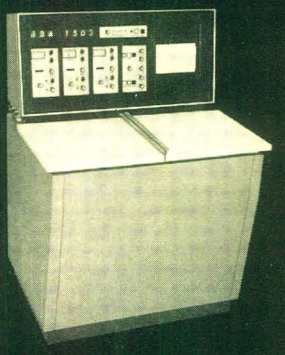

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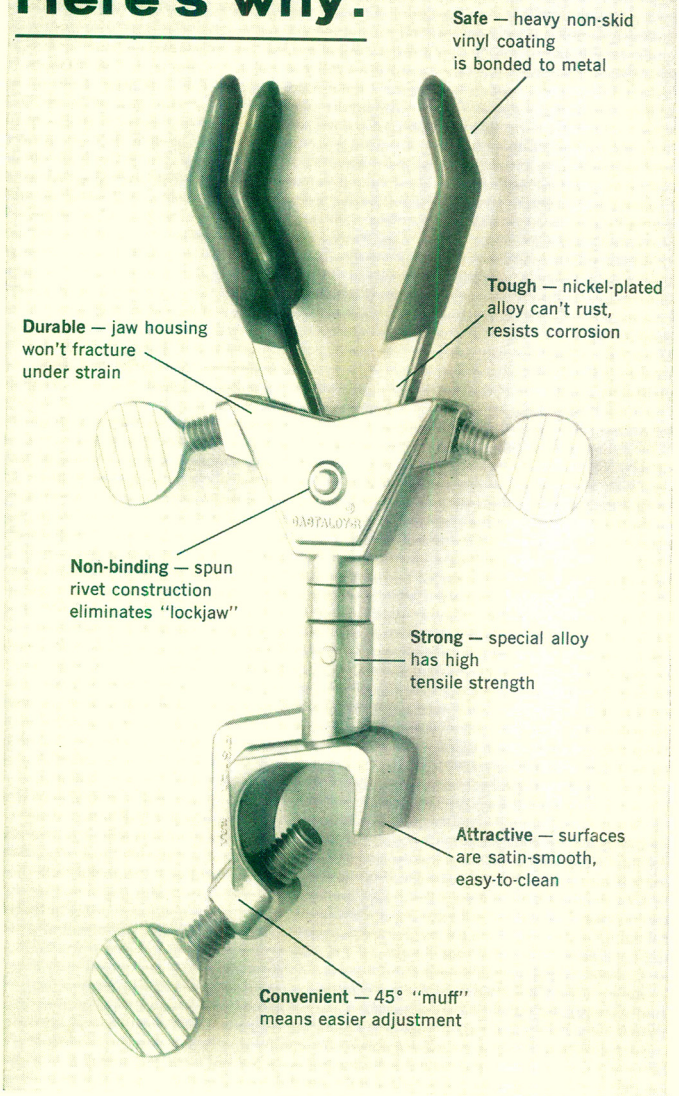

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NEW BOOKS

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

This is the fourth volume to be published of Part I, Theory and Practice, of the extensive treatise on analytical chemistry planned by Professors Kolthoff and Elving. The editors have stated that its purpose is "to present a concise, critical, comprehensive, and systematic, but not exhaustive, treatment of all aspects of classical and modern analytical chemistry." The qualifications of the editors for their stated task are clearly recognized by all chemists. The general plan of the treatise and its organization have been discussed in a previous review of Volume 1, Part I.

Voume 4, Part I, contains a section of Magnetic Field Methods of Analysis and a major section on Electrical Methods of Analysis. This latter section has been prepared with Professor C. N. Reilley serving as a technical adviser, who was assisted by Professor R. W. Murray, both from the University of North Carolina. Their council and advice is clearly evident in this major section of the treatise and has resulted in one of the best discussions of modern electroanalytical chemistry to appear.

This volume contains seventeen chapters by eighteen different authors: 38. Analytical Applications of Magnetic Susceptibility (L. N. Mulay); 39. Nuclear Magnetic Resonance and Electron Paramagnetic Resonance (N. F. Chamberlain); 40. Mass Spectrometry (F. W. Melpolder and R. A. Brown; 41. Ion-Scattering Methods (S. Rubin; 42. Fundamentals of Electrode Processes (C. N. Reilley); 43. Introduction of Electrochemical Techniques (C. N. Reilley and R. W. Murray); 44. Chronoamperometry and Chronopotentiometry (P. Delahay); 45. Potentiometry (N. H. Furman); 46. Voltammetry at the Dropping Mercury Electrode (Polarography) (L. Meites); 47. Voltammetry at Electrodes with Fixed Surfaces (R. N. Adams); 48. Electrodeposition (N. Tanaka); 49. Coulometric Analysis (I. Shain); 51. Conductometry and Oscillometry (J. W. Loveland); 52. Measurement of Capacity: Analytical Uses of the Dielectric Constant (B. W. Thomas and R. Pertel).

This volume again shows the effect of the strong editorial direction of Professors Kolthoff and Elving which has resulted in a well coordinated and readable work. The authors have been carefully selected as well quali-

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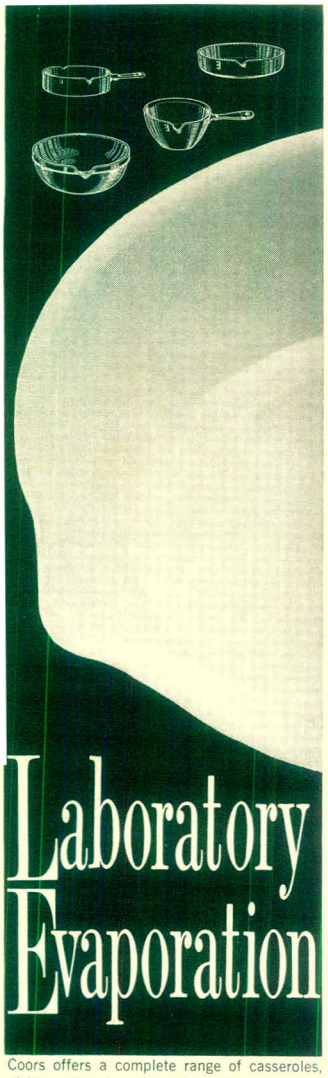

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fied authorities in their particular areas of specialization. Each of the chapters is extensively documented with bibliographies to the current literature and to more intensive and detailed treatments of the subject matter.

The overall quality of this volume is high and maintains the standards set by the previous three volumes. The first section on Magnetic Field Methods of Analysis should prove to be a particularly useful introduction to this increasingly important aspect of analytical chemistry. The chapter on Analytical Applications of Magnetic Susceptibility by Professor Mulay is outstanding and is one of the clearest discussions of the subject that this reviewer has encountered. The other chapters in this section are more introductory, but are a useful starting point for many before going on to the specialized advanced monographs devoted to N.M.R., E.S.R., and mass spectrometry. The final chapter in this section on Ion Scattering is interesting and presents an analytical method that is almost unknown to many analytical chemists.

The major section of Volume 4 is devoted to Electrical Methods of Analysis and it is this section which really makes the volume outstanding. The introductory chapters by Professors Reilley and Murray are extremely lucid and up-to-date. They present the fundamentals of electrochemistry in a clear and concise manner and provide a sound base for the subsequent chapters on specific electroanalytical methods. The chapter on Chronoamperometry and Chronopotentiometry by Professor Delahay also is well done, and should prove useful to many analytical chemists. It is somewhat disappointing that a more extensive discussion is not given of the application of these methods to the study of electrode kinetics and mechanisms. The remaining chapters in this section are all extremely well done and are relatively complete in their coverage. The chapter on Electrodeposition by Professor Tanaka is an especially timely updating of the documentation for this historically important analytical method. Finally, the presentation of chapters on Stripping Analysis and Measurement of Capacity is noteworthy. Neither of these subjects previously has been summarized in a readily available monograph devoted to the interests of analytical chemists. The present discussions should result in an increased interest and utilization of these important techniques.

In summary this is an excellent reference volume and is recommended to all chemists and specifically to analytical chemists.

Comprehensive Analytical Chemistry, Vol. IIA, Electrical Methods. *C. L. Wilson and D. W. Wilson, editors. xvi + 268 pages. American Elsevier Publishing Company, 52 Vanderbilt Ave., New York 17, N. Y. 1964. $11.*

Reviewed by Royce W. Murray, Department of Chemistry, University of North Carolina, Chapel Hill, N. C.

This book, a continuation of the series of publications on analysis by the editors, is the first of two volumes dealing with electrochemical methods. It contains five chapters: Electrochemical Analysis: Introduction, and Electrodeposition, by A. J. Lindsey; Potentiometric Titrations, and Conductometric Titrations, by D. G. Davis, and High Frequency Conductometric Titrations, by T. S. Burkhalter. Each of the four methods chapters presents a description of theory, instrumentation, and methodology, and an extensive discussion of the analytical applications.

The orientation of the chapters is highly practical, in keeping with the editors' philosophy of providing "a working manual offering ... direct and immediate assistance," and deals predominantly with applications in quantitative analysis. Detailed descriptions of many specific analyses are given in the application sections, and literature references are provided to many more. The scope of the types of applications considered is reasonably broad, but cannot be expected to cover every analytical situation. The depth of coverage of the several areas of analysis is somewhat variable; while redox titrations are well represented in the potentiometric chapter, there are no examples given of the many applications of potentiometry in nonaqueous acid-base titrations, only passing mention is made of the existence of pK and pNa glass electrodes, and the novel uses of concentration cells are not considered. There is nevertheless a substantial amount of very useful information contained in the applications sections for the practicing analyst.

The sections on theory and methodology are given with the intention of providing an understanding of the fundamental basis of operation of the techniques. In the last three chapters, this intention is amply fulfilled, and the uninitiated will find them easy to

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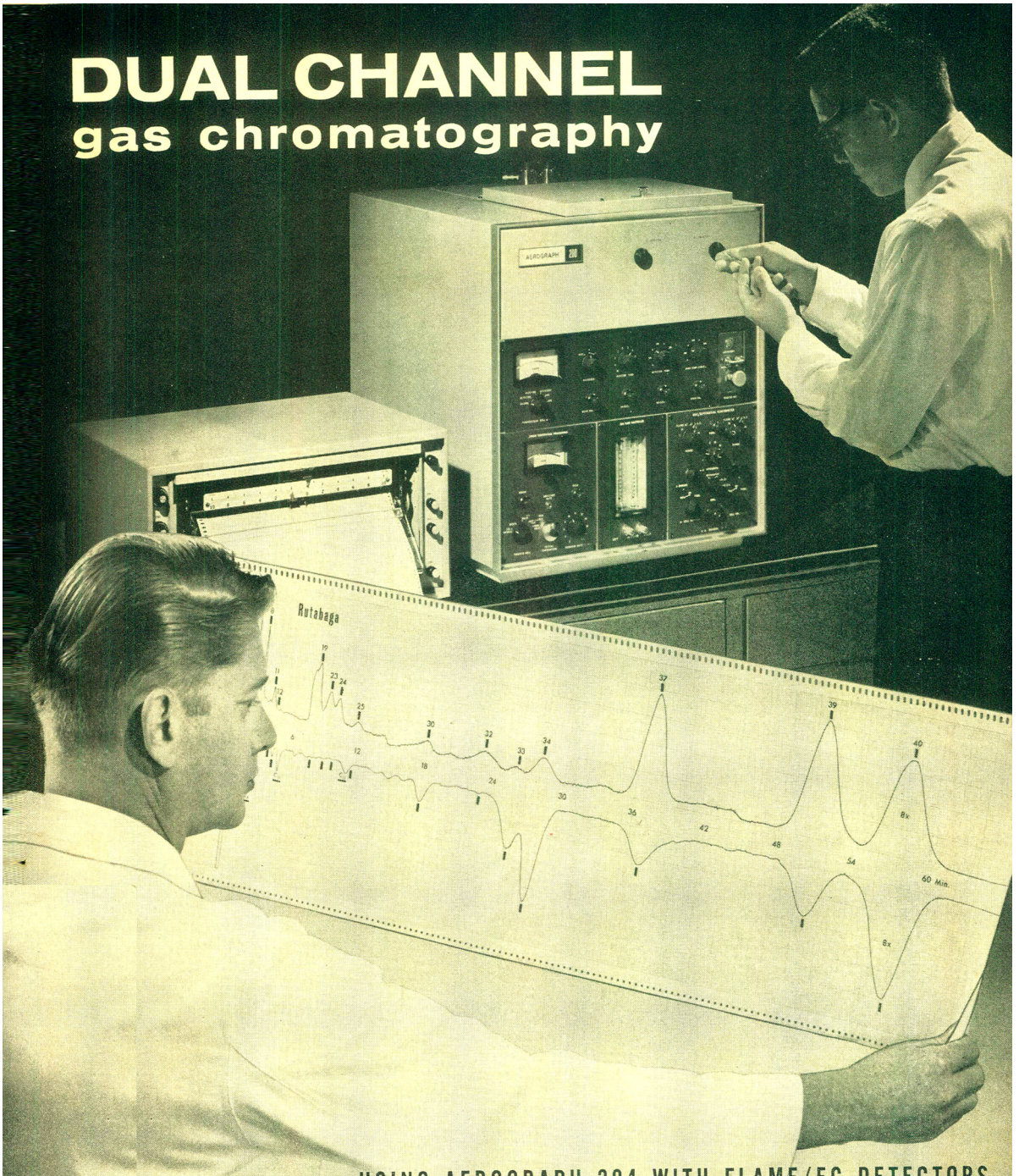

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Analysis of Sulfur Compounds in Garlic, Anal Chem, 36, 1560-1565, July 1964
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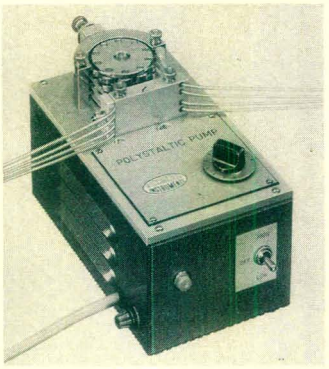

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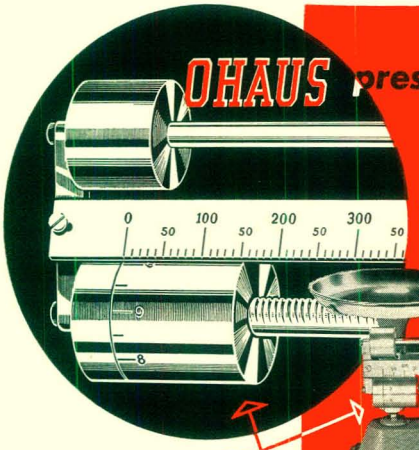

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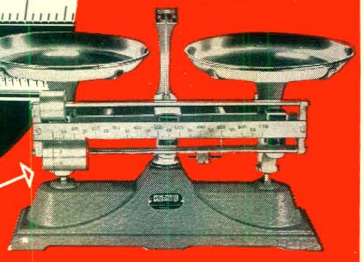

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NEW BOOKS

read and very helpful. Unfortunately, the same does not apply to the theory section of the electrodepositions chapter. This important section is poorly done and would give the novice in this area a distinctly erroneous conception of the important features of an electrodeposition process. For example, much emphasis is placed on the importance of the current-carrying capacity of the electrolyte solution and the aspects of diffusion and convection mass transport and electron transfer rates are not placed in proper perspective.

In spite of this shortcoming, the amount of practical analytical data in this book makes it a worthwhile addition to the library of the analyst.

Bibliography of Vapor Pressure Data for Hydrocarbons. *66 pages. American Petroleum Institute, 1271 Avenue of the Americas, New York, N. Y. 10020. 1964. $1.*

This the second of a series of bibliographies on petroleum data. The bibliography covers the published literature on this subject to Nov. 1, 1963, and is believed to be the most complete list of references available on the vapor pressures of pure hydrocarbons. Included are 28 pages of tables of hydrocarbon vapor pressure data sources, and a related alphabetical listing, by author, of 485 references on the subject.

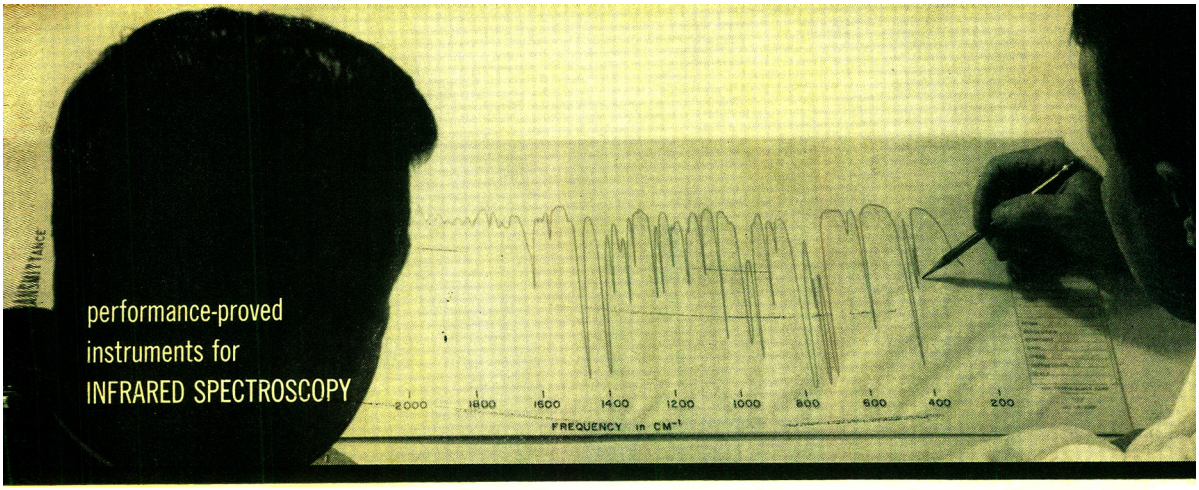
The first bibliography, published in 1963 is titled, "Bibliography of Vapor-Liquid Equilibrium Data for Hydrocarbon Systems." This is also available for $1.

Methods in Enzymology. Vol. VII. *Sidney P. Colowick, Nathan O. Kaplan, editors. ix + 266 pages. Academic Press, Inc., 111 Fifth Ave., New York, N. Y. 10003. 1964. $14.*

This volume is the cumulative subject index for the first six volumes of this series. These books have covered the preparation and assay of enzymes and substrates and special techniques for the enzymologist.

Methods of Biochemical Analysis. Vol. XII. *David Glick, editor. ix + 499 pages. Interscience Publishers, Inc., 605 Third Ave., New York 16, N. Y. 1964. $15.*

This is the 12th in an annual review series designed to meet the needs of biochemical analysis. The following chapters and authors are included in this book: Determination of Elements by X-Ray Emission Spectrometry,



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The Model 521 Interchange is available as a separate unit, and is compatible with Model 221 or 421 Spectrophotometers. For more information, write to Instrument Division, Perkin-Elmer Corporation, 751 Main Avenue, Norwalk, Connecticut.

*U.S. Patent No. 3,144,498.

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"Microcaps" may be used in a number of different ways. The most popular technique is as follows: the pipette is inserted through the rubber cap on the end of the rubber bulb assembly far enough to become visible through the glass tube. A hole in the rubber bulb permits free circulation of air, so that the pipette may be filled by capillary attraction. When filled from end to end, the pipette contains the stated volume. To discharge: hold finger over the hole in the bulb and squeeze. To rinse, repeat the operation with the diluent.

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The bore in the tubing from which "Microcaps" are made is so constant that the volume of a partially filled tube may be determined by simply calculating the volume per linear mm by means of an ordinary metric scale. Example: Suppose a 50 lambda pipette measures 100 mm in length; this means that each mm in length contains 0.5 lambdas. Therefore, should you find that the partial volume measures 46mm in length, you would know that this volume equals 23 lambdas.

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NEW BOOKS

Samuel Natelson, William Whitford; Immunoassay of Plasma Insulin, Rosalyn Yalow, Solomon Berson; Separation and Determination of Bile Acids, Jan Sjövall; Analysis of Natural Radioactive Iodine Compounds by Chromatographic and Electrophoretic Methods, Jean Roche, Raymond Michel, Serge Lissitzky; Chemical and Microbiological Determination of Vitamin B_6, C. A. Storvick, E. M. Benson, M. A. Edwards, M. J. Woodring; Determination of Chloride in Biological Materials, Ernest Cotlove; Thin Layer Chromatography (TLC), H. K. Mangold, H. H. O. Schmid, Egon Stahl.

Nuclear and Radiochemistry. *2nd ed. Gerhart Friedlander, J. W. Kennedy, J. M. Miller. xi + 585 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N. Y. 10016. 1964. $10.75.*

Approximately 50% of the material in the second edition of this text is newly written material. Although appropriate as an undergraduate or graduate textbook, there is much information for research workers. The first four chapters deal with radioactivity, atomic nuclei, equations for radioactive decay and growth, and the interaction of radiation with matter. Thereafter follow chapters on radioactivity measurements and statistics and the use of tracers including their use in analytical chemistry. The remainder of the book deals with various nuclear processes and reactions. Tabular material in the appendixes includes a new table of nuclides with over 1600 entries.

Clinical Chemistry. *Third edition. Joseph S. Annino. xxii + 400 pages. Little, Brown and Co., 34 Beacon St., Boston 6, Mass. 1964. $9.75.*

This is the third edition of a book which is intended to fill the gap between a "cookbook" and a theoretical textbook for practicing laboratory technicians. In addition to general revision and reorganization, methods have been added for oxygen, magnesium, serum glutamic pyruvic transaminase, lactic dehydrogenase, iron-binding capacity, barbiturates, blood alcohol, cerebrospinal fluid gamma globulin, and gastric analysis. New chapters have been added for hormones and lipids.

Part I, 73 pages, deals with basic principles and fundamental information, while Part II deals with specific methods. Although the emphasis is on techniques, the physiological significance of the test results is also discussed.

U. S. Government Publications

The following can be obtained from the Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. 20230.

Automated Analytical Balance. *K-1593. 50 cents.*

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Isotope Abundance in the Elements. *ORNL 3528. $2.*

A tabulation of the isotope content of 55 elements as determined by mass spectrometry.

Mass Spectrometry by Intense Thermal Radiation. *AD 600 159. 50 cents.*

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

Preparation of NBS White Cast Iron Spectrochemical Standards. *R. E. Michaelis, LeRoy L. Wyman. 31 pages. NBS Miscellaneous Publication 260-1. June 1964.*

The method involves casting the molten metal into a grid type of mold on a massive water-cooled copper plate. The method has been applied to the preparation of eight NBS white cast iron spectrochemical standards containing a graded concentration range for some 20 elements, of which the following 10 have been certified: C, Mn, P, S, Si, Cu, Ni, Cr, V, and Mo.

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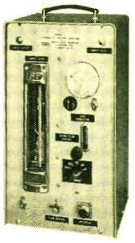

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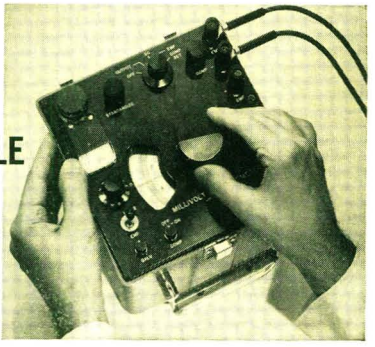

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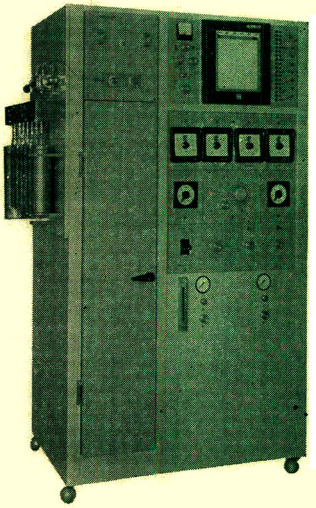

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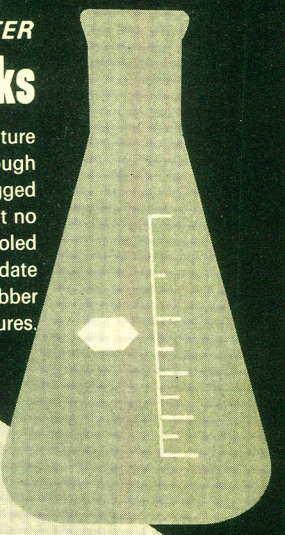

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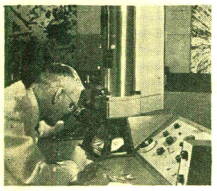

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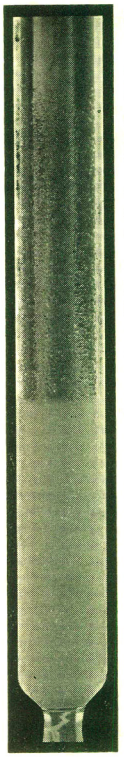

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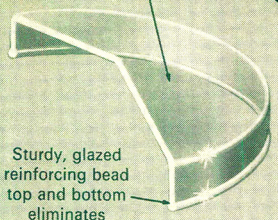

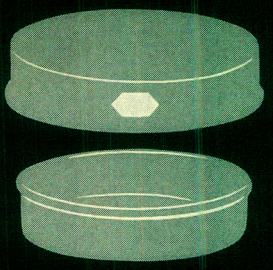

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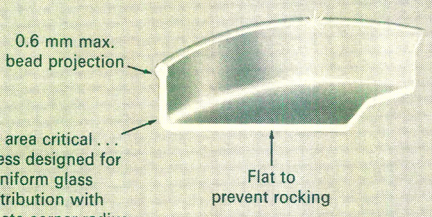

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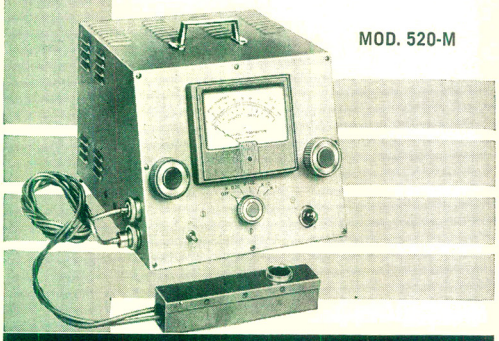

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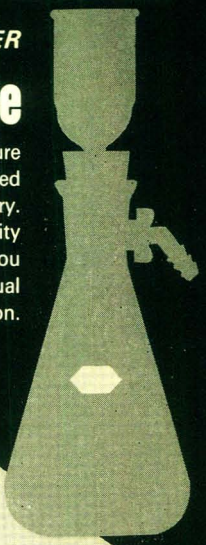

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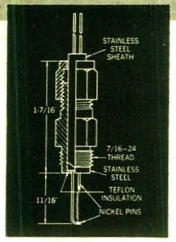

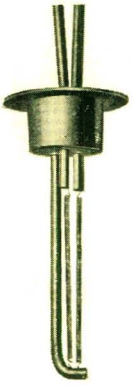

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Camin, D. L., King, R. W. and Shawhan, S. D. Analytical Chem., Vol. 36, No. 7, June 1964

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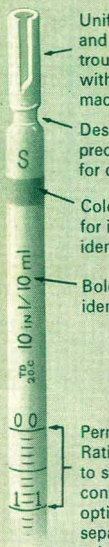

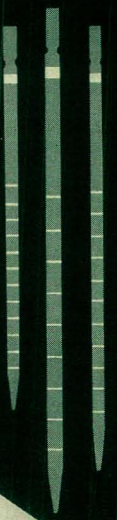

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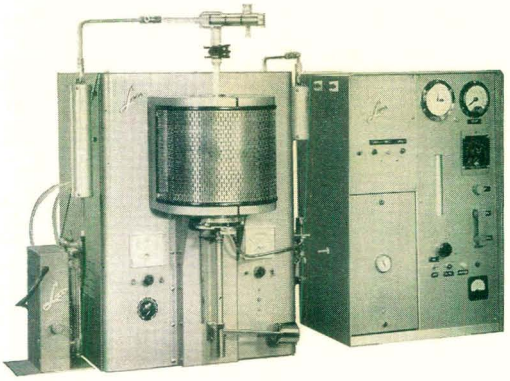

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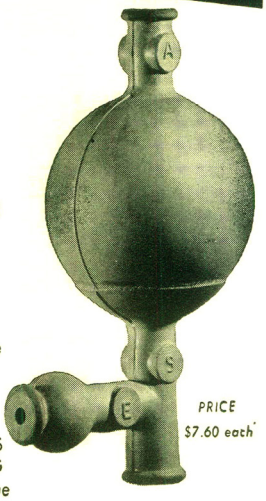

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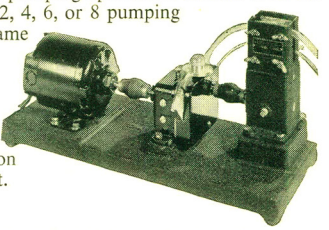

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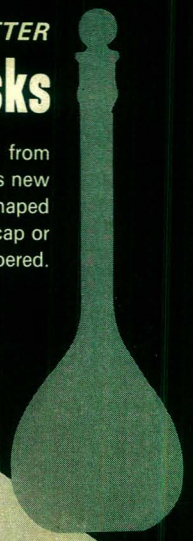

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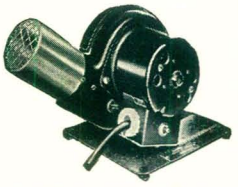

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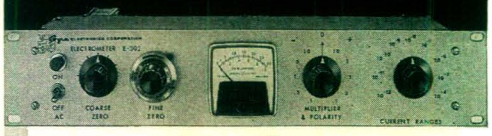

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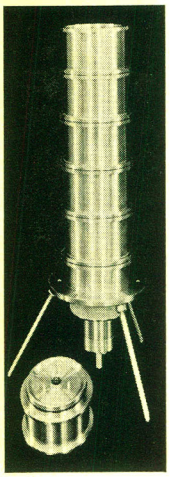

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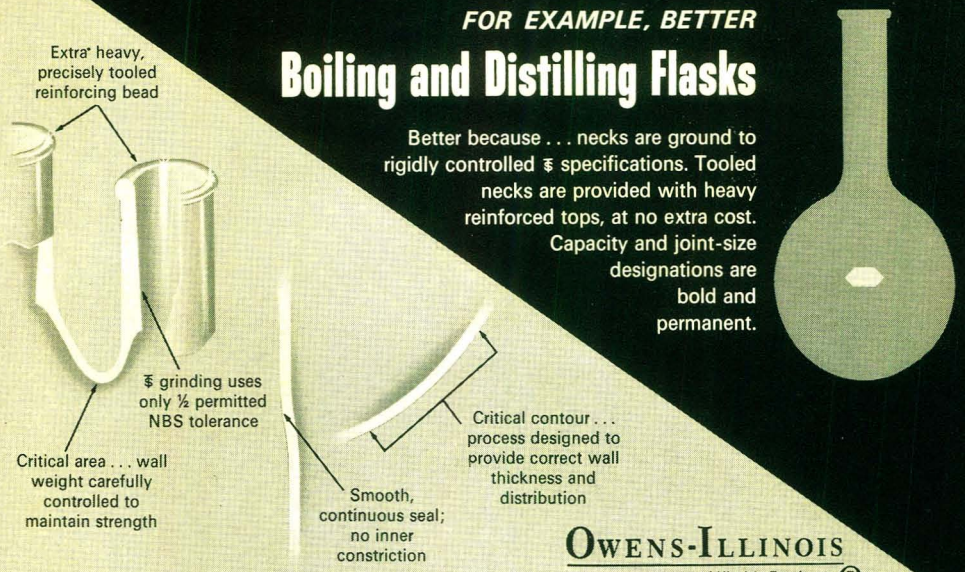

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the EDITOR'S column

L.T. Hallett, Editor

THE THERMODYNAMIC PROPERTIES of solutions of deuterium chloride in heavy water have been determined recently at the National Bureau of Standards Institute for Materials Research ["Thermodynamics of Solutions of Deuterium Chloride in Heavy Water from 5° to 50° C.," Robert Gary, Roger G. Bates, and R. A. Robinson, *J. Phys. Chem.*, **68**, 1186 (1964)]. The study is the first in a series aimed at developing a scale to measure deuterium ion activity in solutions of heavy water.

Increased use of heavy water has renewed interest in the properties of acids and bases in this solvent and has underscored the need for a "pD" scale. In establishing such a scale, precise measurements of the conventional deuterium ion activity, by the electromotive force method, in a variety of useful buffer solutions are necessary. These buffer solutions must cover a wide range of deuterium ion activity. Before the ion activity of buffer solutions can be calculated, however, the standard e.m.f. of the cell, $Pt;D_2(g., 1 atm.)$, DCl in D_2O, AgCl; Ag, designated Cell I, must be accurately measured.

Cell I consists of a solution of deuterium chloride in heavy water, a silver-silver chloride electrode, and a platinum electrode over which deuterium gas is bubbled. The physical configuration of the cell is based on the design of cells used to measure hydrogen ion activity in solutions of hydrogen chloride in ordinary water. However, the present cell is more adaptable for use with different solvents and incorporates a number of new features to increase its accuracy and precision. The e.m.f. of Cell I was compared with that of the "hydrogen" cell in which the deuterium,

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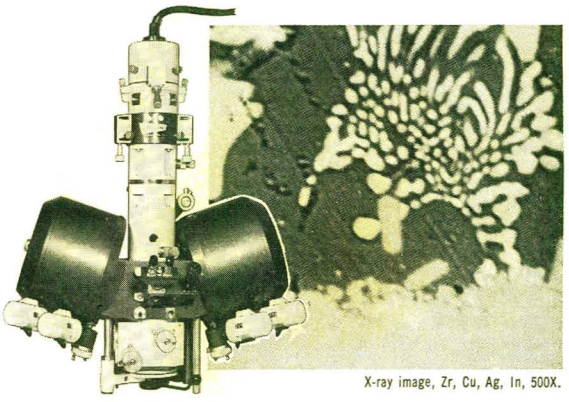

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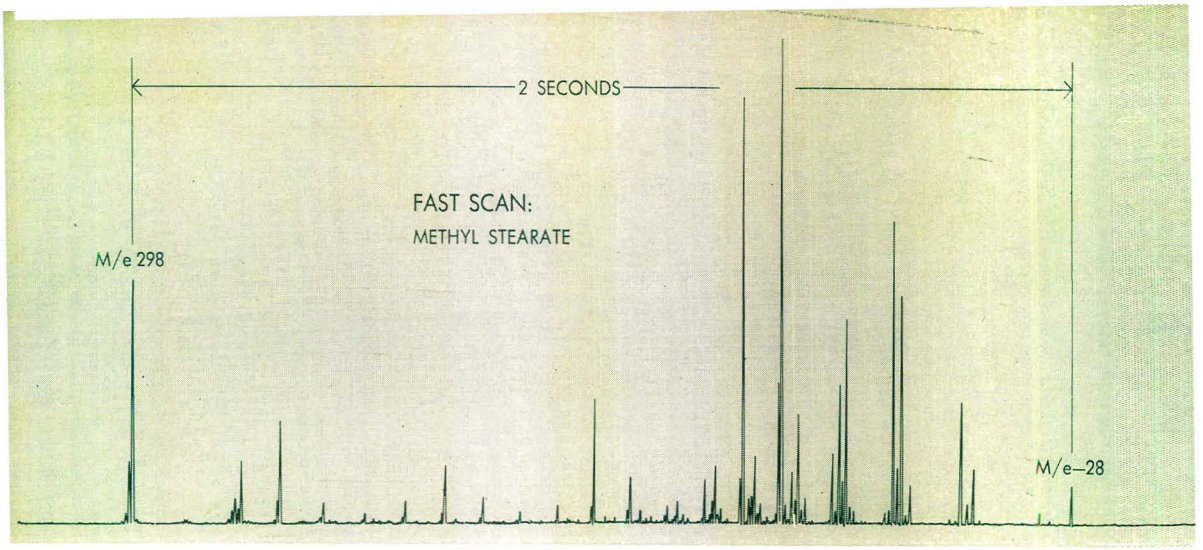

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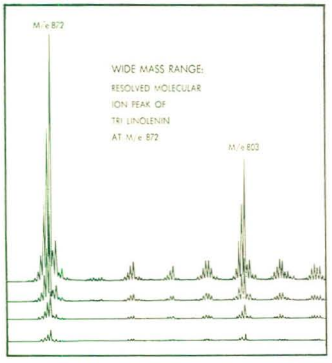

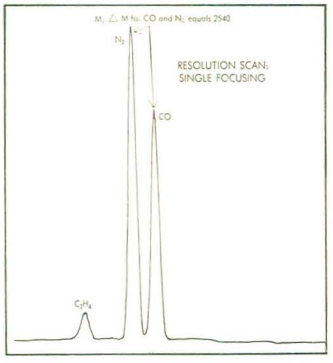

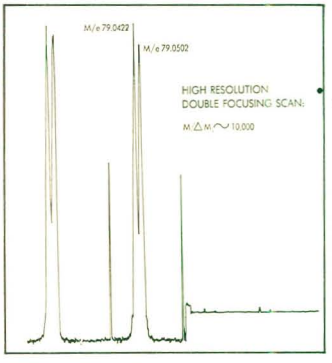

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deuterium chloride, and heavy water are replaced with hydrogen, hydrogen chloride, and ordinary water. The standard electromotive force of Cell I at 298.15° K. was 0.21266 volt on the molality scale. This value is 0.00978 volt lower than that of the corresponding hydrogen cell.

The electromotive force of Cell I was determined for five concentrations (0.01 *M* to 0.05 *M*) of deuterium chloride in heavy water at intervals of 10° from 278.15° to 318.15° K. and at 323.15° K. The findings of this study agree closely with the results of limited work by earlier investigators [C. Noonan and V. K. LaMer, *J. Phys. Chem.*, **43**, 247 (1939)] when all data are converted to the same scale.

Present studies at NBS are directed toward the measurement of the conventional deuterium in activity in buffer solutions which can be used as standards for the pD scale. The pD scale will therefore be fixed by a number of buffer solutions whose e.m.f.'s have been carefully measured. As the standard e.m.f. of Cell I is now known, pD values can be calculated from e.m.f. data on these buffer solutions.

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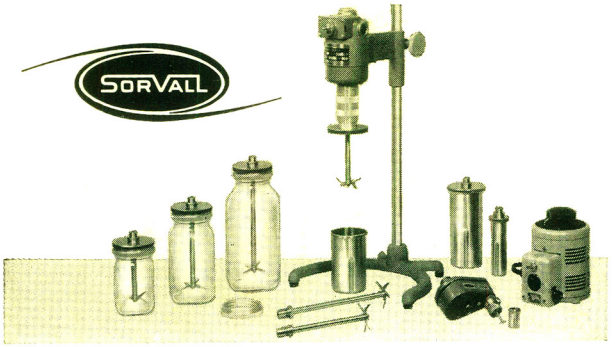
An automated ten-part serum analyzer used in a routine admitting procedure on different wards at Duke University Hospital, turned up over 100% more abnormalities than did the laboratory work selectively ordered by physicians for the same patients, according to Dr. Ralph E. Thiers, director of the clinical chemistry laboratory at Duke University Medical Center, Durham, N. C. [*J. Am. Med. Assoc.*, **189**, 31 (1964)].

Dr. Thiers' analyzer performs sodium, potassium, CO_2 content, chloride, phosphorus, uric acid, total protein, and albumin determinations and an albumin control. His equipment was pieced together from commercially available components, but it is not currently available as a unit.



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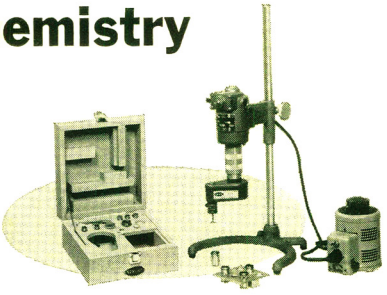

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DISSYMMETRIES

Browsing through the 1964 crop of papers on light scattering, we have prepared, along the way, a short list of the systems that have been studied by means of Brice-Phoenix Light Scattering Photometers (LSP) and Differential Refractometers (DR). Here, then, are our findings based on a somewhat less than thorough search of the papers published during the first eight months of 1964.

DETERGENTS AND MICELLAR COLLOIDS

Phosphatidylserine (Abramson, Katzman and Gregor, J. Biol. Chem., *239*, 70)—LSP
Sodium lauryl sulfate and dodecyltrimethylammonium bromide (Anacker, Rush and Johnson, J. Phys. Chem., *68*, 81)—LSP, DR
Sodium 2,6-di-n-alkylnaphthalene-1-sulfonates (Heilweil, J. Colloid Sci., *19*, 105)—LSP, DR
Dimethyldodecylamine oxide (Herrmann, J. Phys. Chem., *68*, 1540)—LSP, DR
Sodium dodecyl benzene sulfonate-nonionics mixed micelles (Mankowich, J. Am. Oil Chem. Soc., *41*, 449)—LSP

SYNTHETIC POLYMERS

Aromatic polysulfonates (Thomson and Ehlers, J. Polymer Sci., *A2*, 1051)—LSP, DR
Poly-n-alkyl acrylates (Burlant, Hinsch and Taylor, J. Polymer Sci., *A2*, 57)—LSP, DR
Polyhydroxy ether (Myers and Dagon, J. Polymer Sci., *A2*, 2631)—LSP, DR
Nylon 66 (Elias and Schumacher, Makromol. Chem., *76*, 23; Saunders, J. Polymer Sci., *A2*, 3755, 3765)—LSP, DR
Styrene-methyl methacrylate block copolymer (Krause, J. Phys. Chem., *68*, 1948)—LSP, DR
Polymers of higher olefins (Flowers, Hewett and Mullineaux, J. Polymer Sci., *A2*, 2305)—LSP
Polyisobutene (Turner, J. Phys. Chem., *68*, 1255)—LSP
Polystyrene (Graessley, J. Phys. Chem., *68*, 2258; Spitsbergen and Beachell, J. Polymer Sci., *A2*, 1205)—LSP
Polymethyl methacrylate (Krause and Cohn-Ginsberg, J. Polymer Sci., *A2*, 1393)—LSP
Styrene-acrylonitrile copolymer (Shimura, Mita and Kambe, J. Polymer Sci., *B2*, 403)—LSP
Polyethylene and polystyrene (Ehl, Loucheux, Reiss and Benoit, Makromol. Chem., *75*, 35)—DR
Polyethylene (Drott and Mendelson, J. Polymer Sci., *B2*, 187)—DR
Polyvinylpyrrolidone (Schnabel, Makromol. Chem., *77*, 51)—DR
Polydimethylsiloxane (Crescenzi and Flory, J. Am. Chem. Soc., *86*, 141)—DR
Poly-p-chlorostyrene (Greber, Tölle and Burchard, Makromolek. Chem., *71*, 47)—DR
Copolymers (Gallot, Franta, Rempp and Benoit, J. Polymer Sci., Pt. C, No. 4, 473)—DR

PROTEINS

Dog cardiac myosin (Mueller, Franzen, Rice and Olson, J. Biol. Chem., *239*, 1447)—LSP, DR
Gelatins from rat skin collagen (Piez and Carrillo, Biochemistry, *3*, 908)—LSP, DR
Contractile sheath protein of the tail of T2 bacteriophage (Sarkar Sarkar and Kozloff, Biochemistry, *3*, 511)—DR
Empty protein shells of turnip yellow mosaic virus (Kaper, Biochemistry, *3*, 486)—DR

POLYSACCHARIDES

Dextran (Antonini, Bellelli, Caputo, Chiancone and Rossi-Fanelli, Biopolymers, *2*, 27, 35)—LSP, DR

ELECTROLYTES

Alkaline niobium (V) solutions (Nelson and Tobias, Can. J. Chem., *42*, 731)—LSP

DISPERSIONS

Octanoic acid aerosols (Matijevic, Kitani and Kerker, J. Colloid Sci., *19*, 223)—LSP
Colloidal gold (Milligan and Morriss, J. Am. Chem. Soc., *86*, 3461)—LSP
Spinach chloroplasts (Dilley and Vernon, Biochemistry, *3*, 817)—LSP
Emulsions and polymer latexes (Graessley and Zufall, J. Colloid Sci., *19*, 516)—LSP, DR
Substituted styrene polymer latexes (Paoletti and Billmeyer, J. Polymer Sci., *A2*, 2049)—DR

If you are interested in light scattering and refractive index measurements on the systems listed above, or many others, from cellulose propionate plastic films (Sperling, TAPPI, *44*, 280) to spider fibers (Matijevic, Ottewill and Kerker, J. Opt. Soc. Am., *51*, 115), contact the **Phoenix Precision Instrument Company**, 3803 North 5th Street, Philadelphia, Pa., 19140, for detailed information on Light Scattering Photometers and Differential Refractometers.

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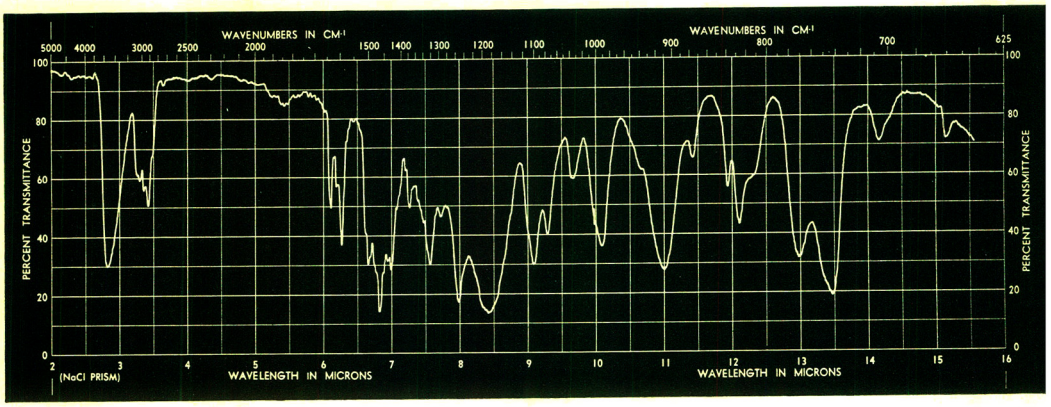

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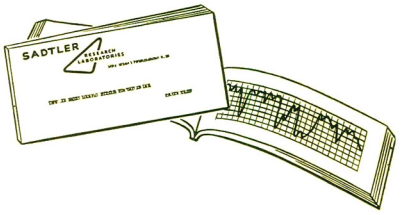

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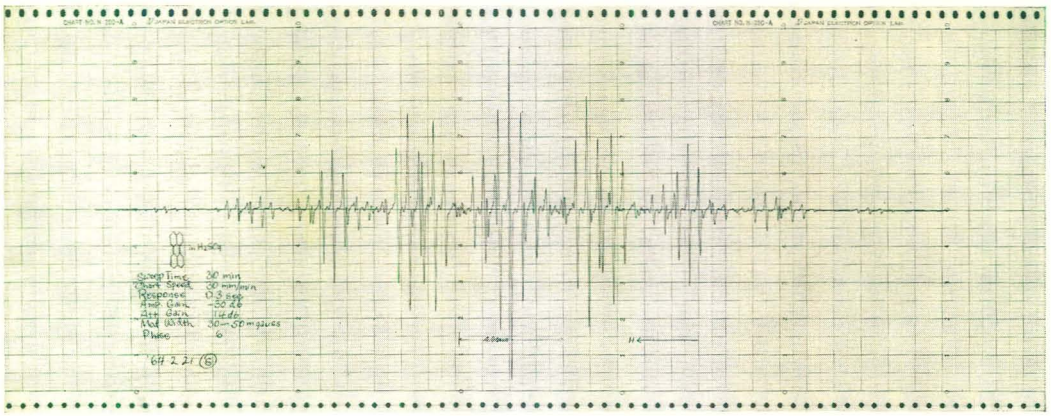

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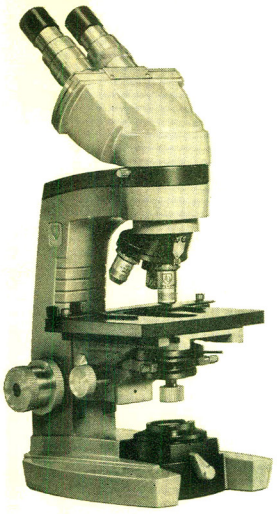

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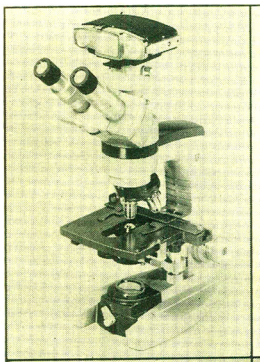

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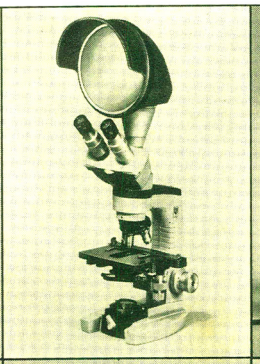

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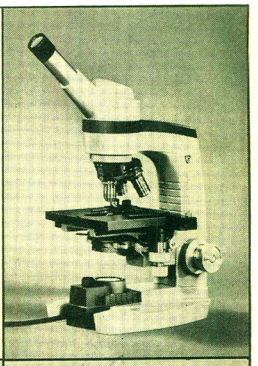

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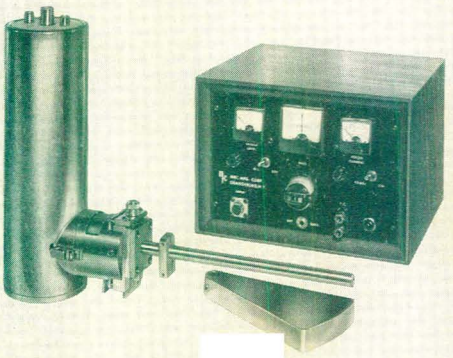

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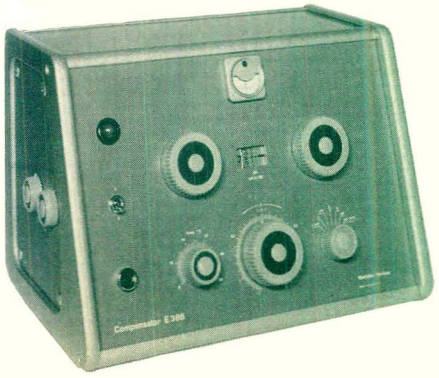

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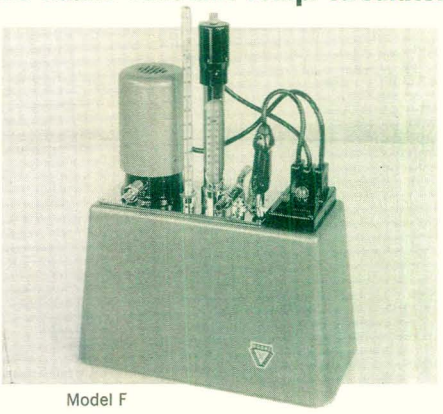

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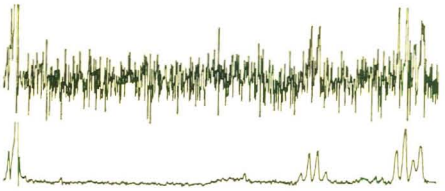

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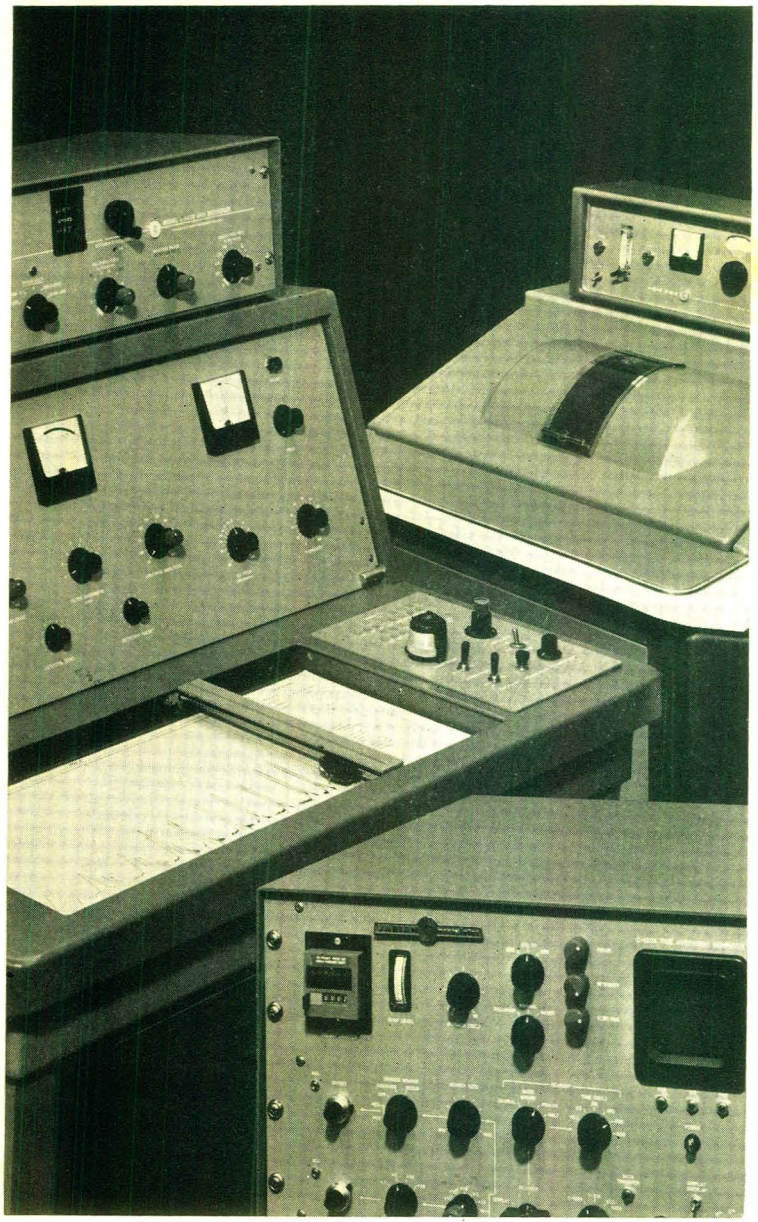

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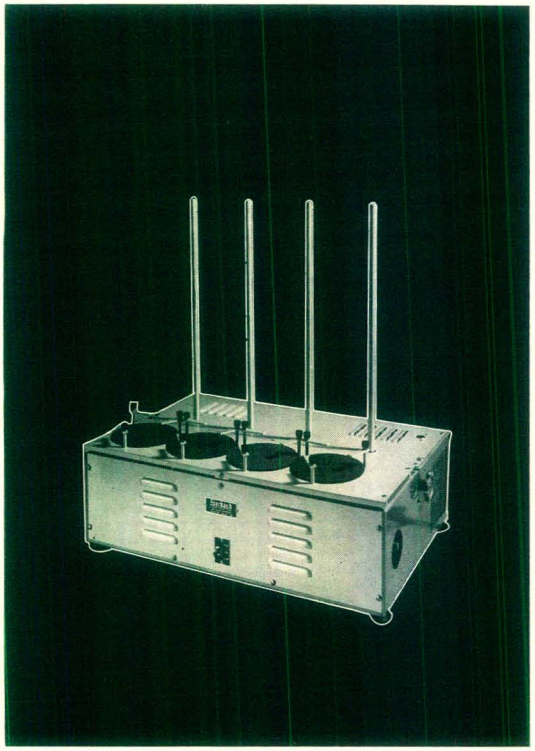

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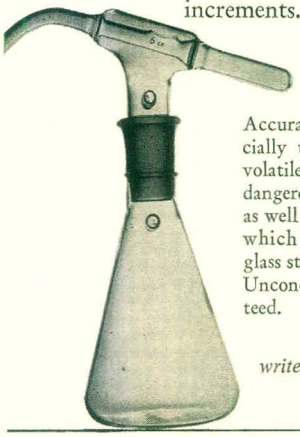

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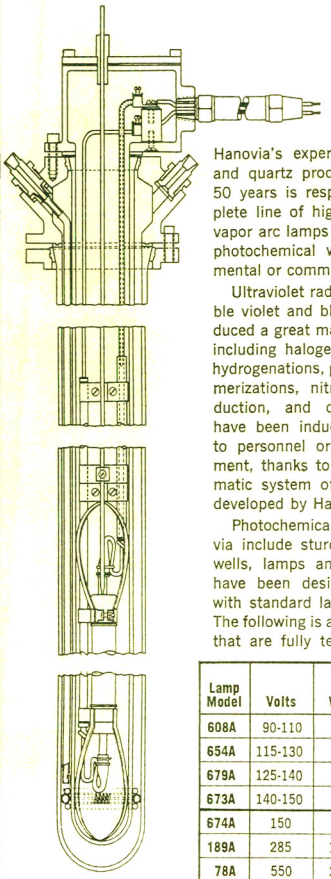

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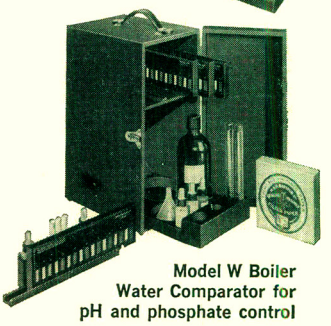

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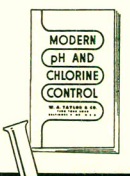

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These two runs of different peppermint oils were made under identical conditions of column, temperature, flow rate, program rate and duration. The "push-button" programming of the Model 226 made possible exact repetition of all conditions, without any chance of human error. The application of such automated analyses to incoming quality control, material inspection and product inspection with the Model 226 is one of its most unique features.

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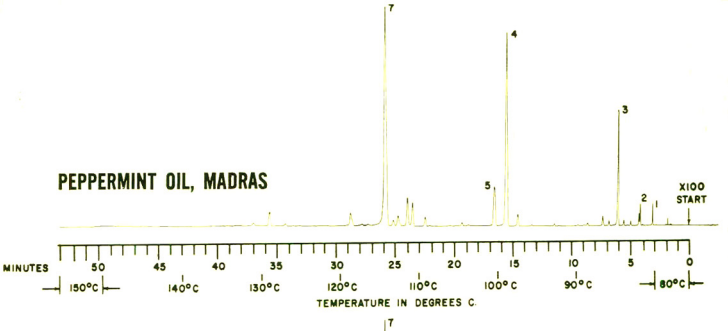
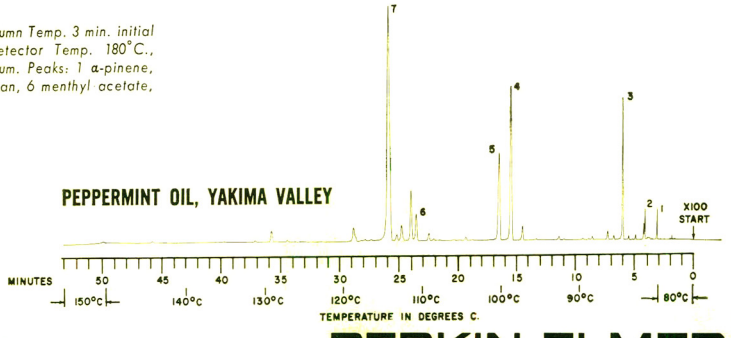


Column 150 ft. x 0.010 in. Ucon Oil 50-HB-2000, Column Temp. 3 min. initial at 80°C., program 80-150°C. at 1.5°C/min., Detector Temp. 180°C., Injector Temp. 250°C., Inlet Pressure 20 psig Helium. Peaks: 1 α-pinene, 2 β-pinene, 3 eucalyptol, 4 menthone, 5 menthofuran, 6 menthyl acetate, 7 menthol.



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New Freeport Sulphur Laboratory Consolidates Many Technical Operations

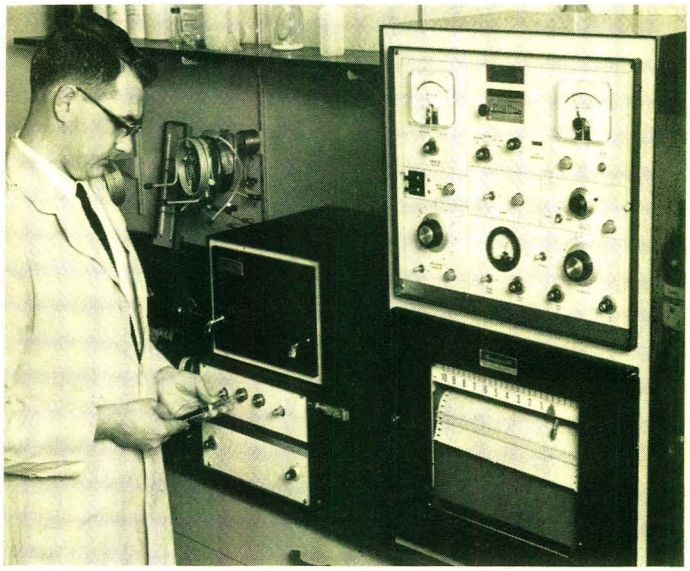
INCREASING STRESS on highly efficient sulfur production and quality, an expanding transportation system, and a drive for diversification have imposed heavier responsibilities on the technical personnel and facilities of Freeport Sulphur Company. In order to meet these demands and offer additional and expanded service to its customers, Freeport has consolidated many of its technical operations in a new Research and Development Laboratory at Belle Chasse, Louisiana.

The laboratory is very close to New Orleans, the location of the southern administrative offices for Freeport. An interlocking telephone and microwave system provides ready communication between New Orleans, the laboratory, and Freeport's various mines and shipping terminals.

The laboratory facilities at Belle Chasse are primarily devoted to research functions and to office accommodations which serve as home-base for the chemical engineering service group and development engineers. Large scale pilot studies are usually carried out at the operating properties, as are routine control analyses—though the latter are under overall supervision of the laboratory.

Because of the nature of the research activities, analytical requirements at the laboratory embrace both organic as well as inorganic materials. Emission spectral equipment, including photographic and direct reading instruments, is used extensively for the analysis of geological development samples, but probably plays its major role in evaluation and verification of alloys and in corrosion studies. Because of the nature and location of sulfur mining operations, equipment is subjected to severe corrosion conditions. Mining facilities are located over or near the Gulf of Mexico, and so are exposed to salt water corrosion as well as corrosion from sulfur products. A continued study of alloys and coatings is therefore necessary.

For the emission spectroscopic examination of most alloys, scales, and



Gas chromatographic techniques are used extensively for the analyses of gaseous reaction products such as sulfur dioxide, hydrogen sulfide, and mercaptans obtained during various sulfur studies

Process stream gas chromatographs are in use and under study at the Freeport Sulphur Belle Chasse Laboratory. Here a process stream gas chromatograph is being checked out in the laboratory and operating parameters are established

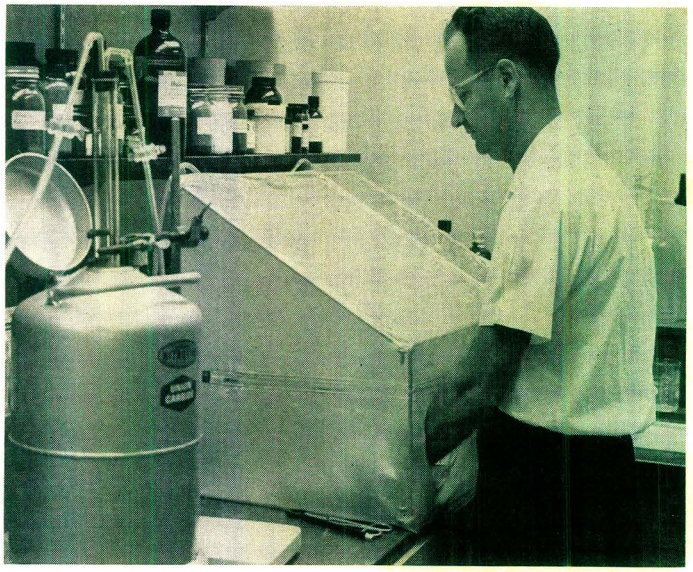
corrosion products, a solution technique is usually applied. This has greatly simplified preparation of standards and improved the quality of the quantitative measurements.

A unique emission application in use is the determination of carbon in sulfur. In this case the sulfur sample is mixed with a known amount of nickel metal powder and the mixture pressed, by use of a special mold, into a disk the shape and size of the conventional rotating disk electrode. The disk is then rotated and sparked as a sample.

Infrared absorption studies are playing an increasingly important role in Freeport's operations and research. Heated, thermostatically controlled infrared cells have been designed so that sulfur (which melts at about 115°C.) can be studied in the molten state. This actually permits the research scientist to study and follow reactions taking place in molten sulfur—the sulfur functioning either as the solvent or as a reactant. Sulfur is transparent in much of the infrared region. Facilities are also available for studying molten sulfur and sulfur solutions in the ultraviolet as well as visible regions of the spectra.

In many sulfur reactions and in mining and shipping operations it is important to follow the nature of the gaseous products, such as sulfur dioxide, hydrogen sulfide, mercaptans, etc. The study of these gases has been facilitated by the use of gas chromatography—but not without considerable development work. In many cases it has been necessary to concentrate the gases by freezing them out in liquid nitrogen in order to get sufficient quantities to examine by gas chromatography and by infrared spectrometry. Both the infrared spectrometer and gas chromatograph are being considered as process stream instruments.

The research studies at Belle Chasse involve long-range fundamental investigations, serving to expand knowledge of the physical and chemical properties of sulfur and to suggest potential new uses for the element. Immediate production problems are dealt with on a cooperative basis, with the research group providing assistance and technical advice to the chemical engineering service group which works out of the laboratory and under its administration.

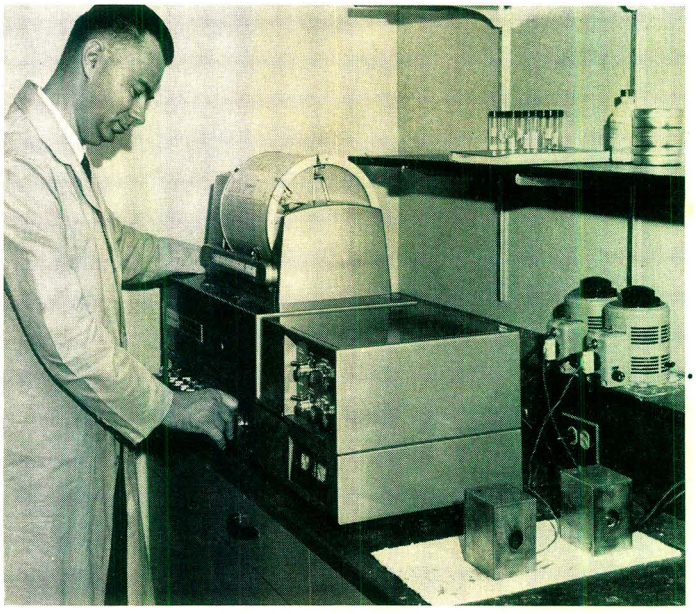


▲ **Low temperatures** and also inert atmospheres are required in order to study certain sulfur reactions. Many sulfur reactions are sensitive to oxygen and also to light

Freeport Sulphur's Research and Development Laboratory at Belle Chasse, La., is the site of studies to expand knowledge of the physical ▶ and chemical properties of sulfur and to suggest potential new uses for the element

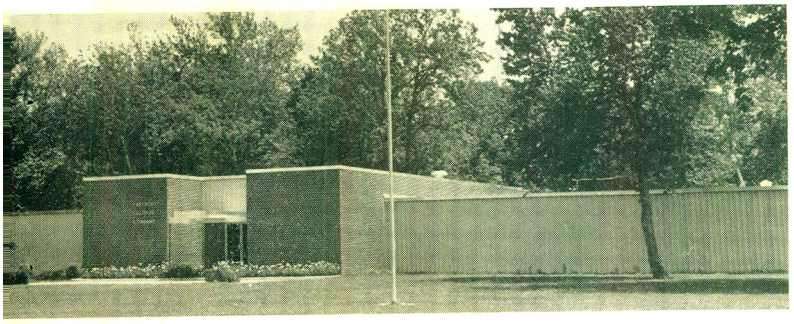
Infrared cells, heated and thermostatically controlled, are used for containing sulfur in the molten state, thus facilitating the study of sulfur as a solvent as well as a reactant

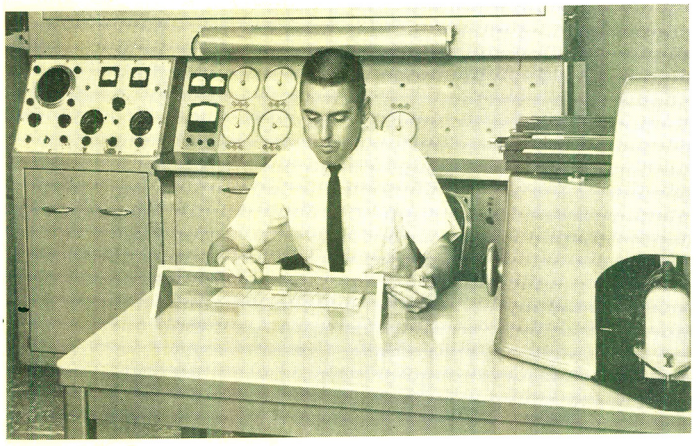
▼



▲

The Audigage is used in corrosion studies. The instrument provides a convenient test for metal thickness where conventional caliper-type equipment cannot be used





Emission spectrometry plays its major role in examining alloys and in corrosion studies. Rotating disk electrodes are often used as solid sample electrodes or for solutions. Some solid samples are pressed into a disk and used as the electrode. For solutions, the standard carbon disk is used

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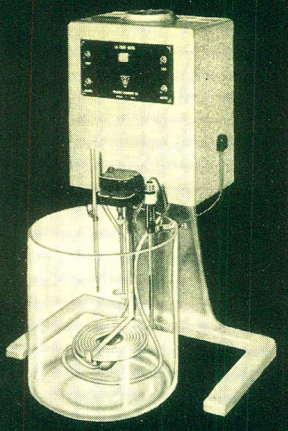

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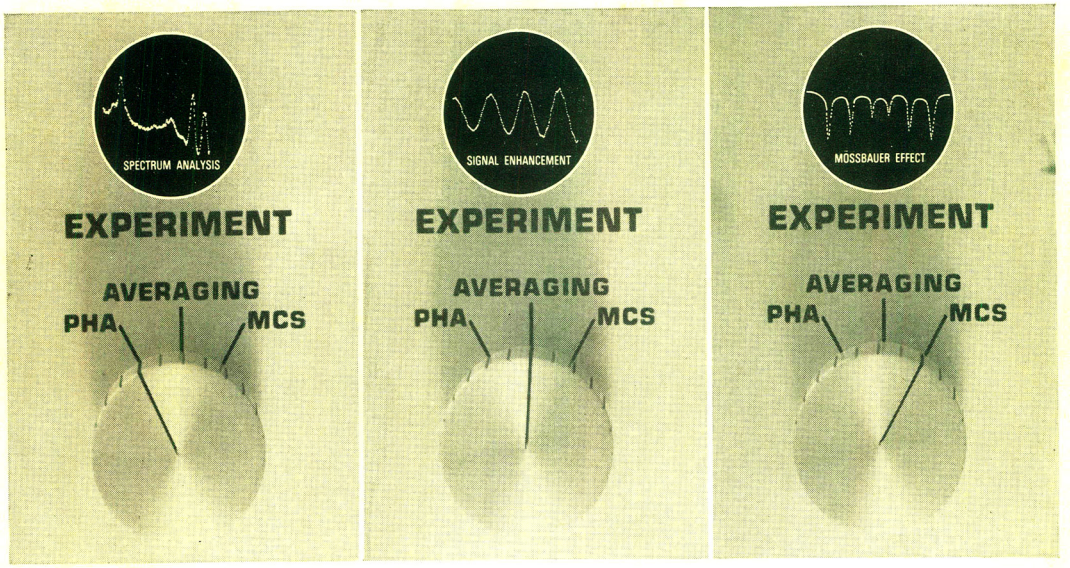

Pulse Height Analysis—In PHA operation, you can accumulate data on events per unit amplitude. Nuclear radiation spectral analysis is only one of many applications in the PHA mode. With suitable external programming the ND-180 and ND-181 systems can perform Mossbauer effect measurements, analog time-of-flight measurements for a time range of two nanoseconds to one microsecond per channel, and velocity modulated signal experiments.

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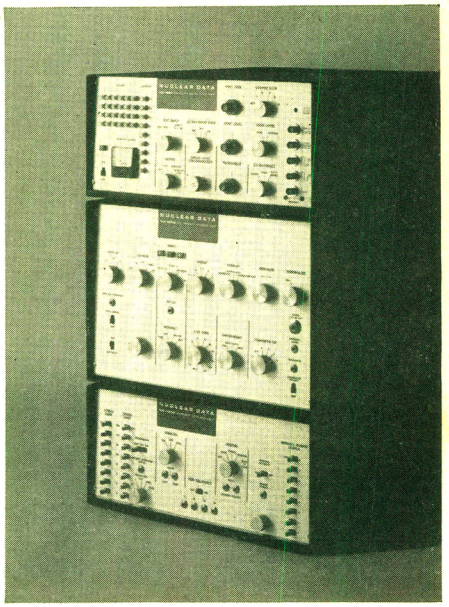

The Experiment Switch on the front panel of the ND-180 and ND-181 systems lets you select any one of three different modes of operation: PHA (pulse height analysis), AVERAGING (signal enhancement), and MCS (multichannel scaling).

For more information, please write for "Bulletin 180" . . . or a demonstration in your laboratory.

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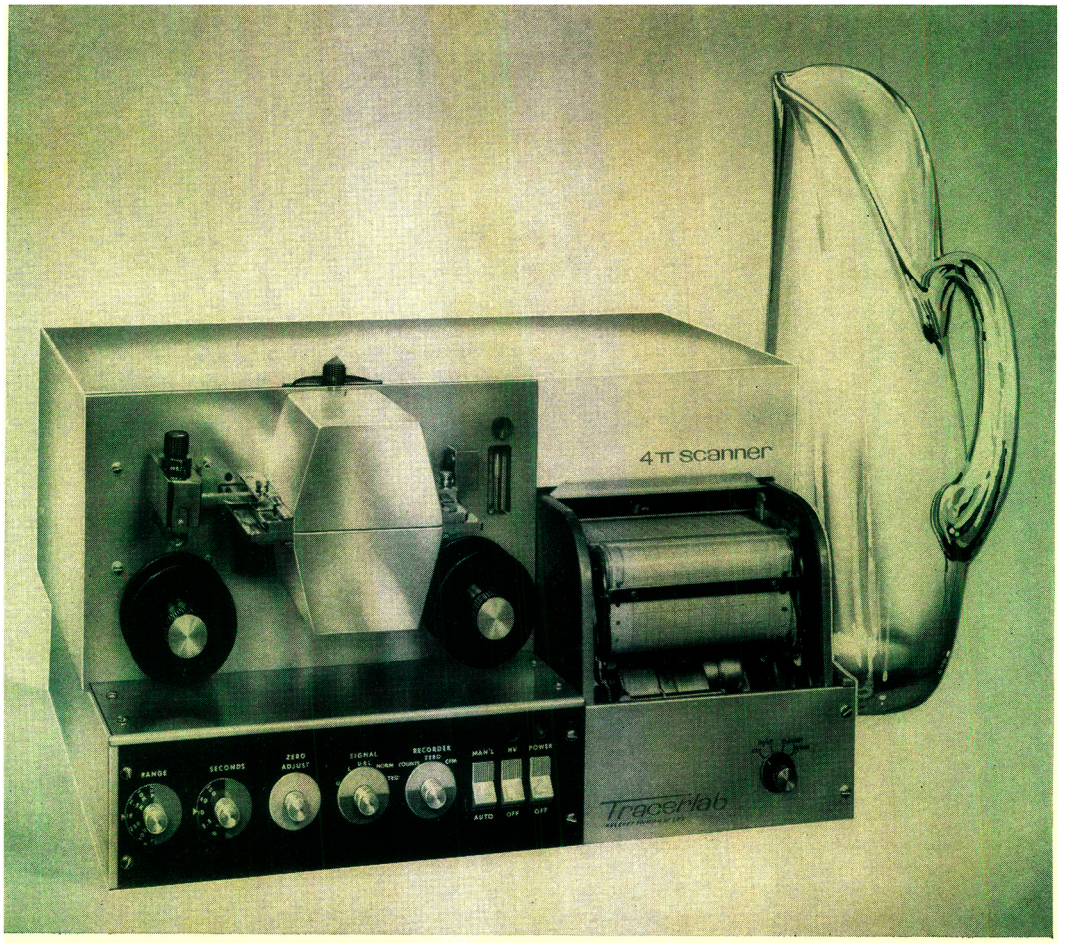

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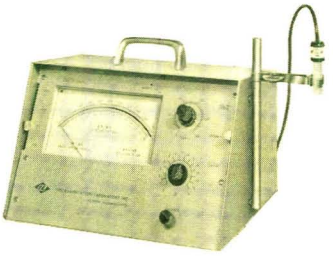
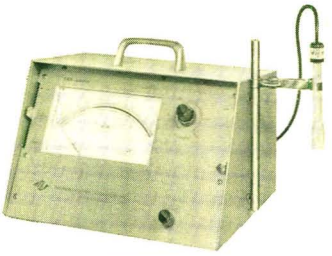


MODEL 145



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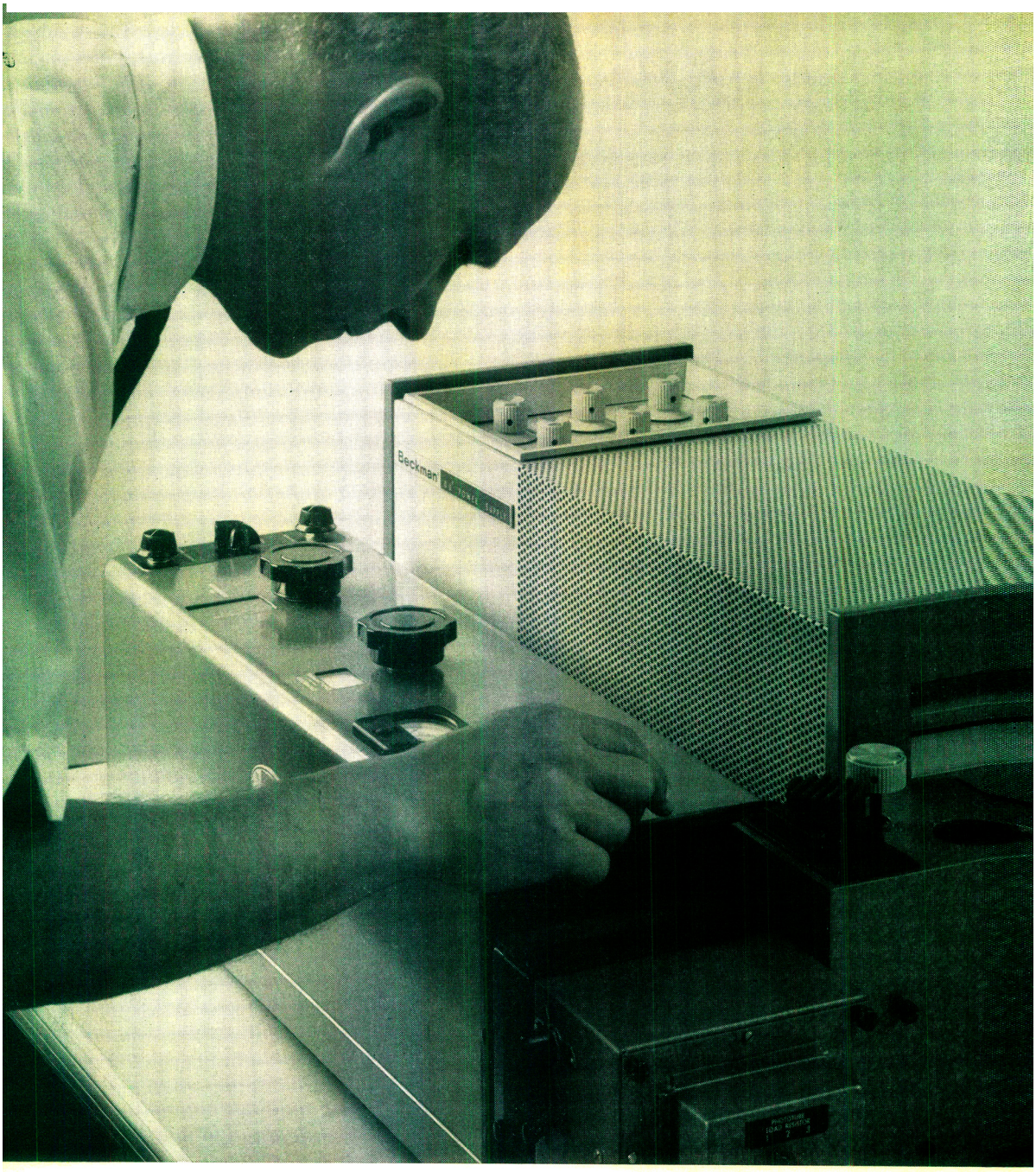

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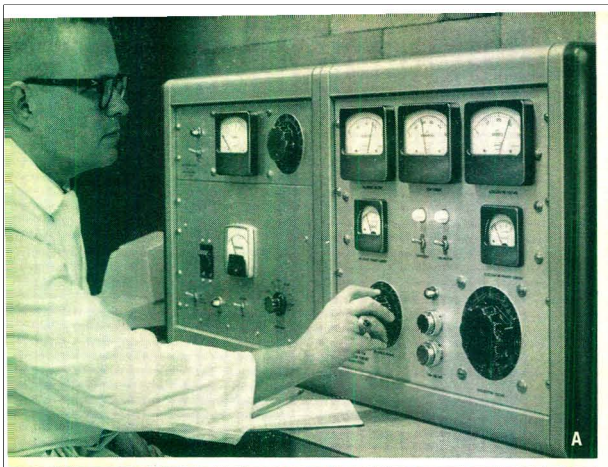

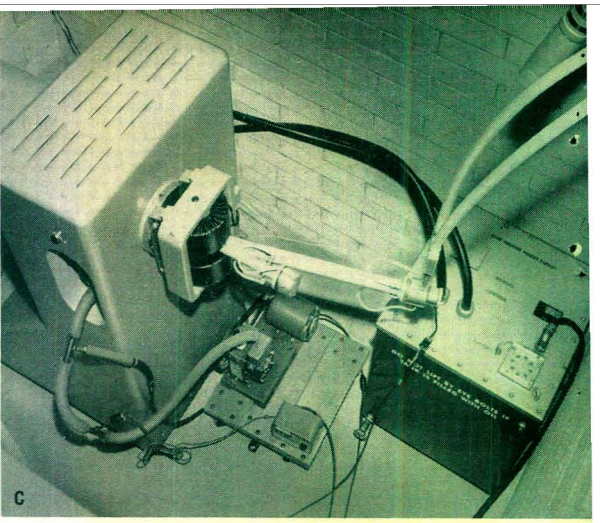

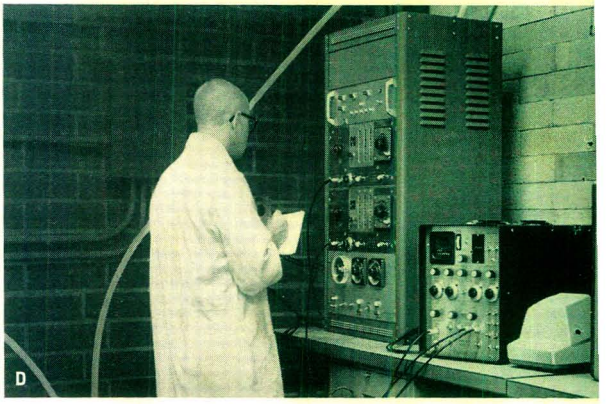

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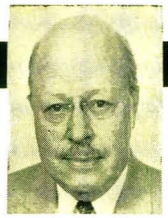

by Ralph H. Müller

The Role of Mathematics in Science

"It is a pleasant surprise to the mathematician and an added problem if he finds that the arts can use his calculations, or that the senses can verify them, much as if a composer found that the sailors could heave better when singing his songs."

—George Santayana

WHEN ERIC TEMPLE BELL speaks of "Mathematics—Queen and Servant of Science" we recognize the latter role the more easily; often the royal edict passes us unnoticed. For a long time scientists have heeded Lord Kelvin's injunction—"When you can express in numbers that, of which you speak, you have the beginning of a science. Until that time your knowledge is meager and unsatisfactory."

The long history of Science has witnessed the gradual assimilation and ordering of countless facts and observations. From time to time reasonably accurate mathematical equations were applied to give some semblance of order, regularity, and predictability to the several phenomena. Our present day insistence upon mathematical rigor and the mathematical approach to science and technology is not only commendable, it is the mark of an enlightened age. One fears, however, that in many instances it has engendered in our students the notion that most of the laws of Nature are directly predictable by mathematical reasoning, or were handed down by Moses.

We have long wished that someone would write a treatise putting the role of mathematics in science in its proper perspective. If the score were written down, we would note the countless routine examples of empirical formulas which lent some degree of respectability to hitherto poorly correlated data. The score would also contain some scintillating examples of mathematics in its Queenly role. We think of Planck's quantum theory, Einstein's equivalence of mass and energy, Bohr's model of the hydrogen atom, Fermi's prediction of the neutrino and Dirac postulating the existence of the positron. Our overenthusiastic student would note that Einstein and Dirac were engaged in speculations which led to new physical discoveries, and while the mathematical skill and genius of the others were of equal caliber, the original incentives were to explain poorly understood phenomena. Planck wished a precise description of the energy distribution in a black-body radiator, Bohr's quantitative model gave a precise prediction of the Balmer series of lines in the hydrogen spectrum. Fermi sought an explanation for the energy distribution among beta particles and his theoretical treatment, yielding perfect agreement, required the existence of a particle with no charge and negligible mass.

IMPLICATIONS OF TOPOLOGY

A recent discovery of considerable practical importance derives from the relatively queer subject of topology. "Topology is the geometry of distortion —it raises questions and propositions that are childishly obvious (until you try to prove them) or so difficult and abstract that not even a topologist can explain their intuitive meaning." (Newman). Much solemn and serious study has gone into linear figures, surfaces and solids, shapes like a pretzel, knots, networks, maps, etc. Is the hole "inside" or "outside" the doughnut? Can one construct a surface with just one side or make a bottle with no edges, no inside, and no outside?

The recent practical discovery is a direct consequence of one of the commonest topological examples—a surface with only one side, the Mobius strip or loop. This is formed by taking a long rectangular strip of paper and pasting its two ends together after giving one a half-twist. As Courant has said—"a bug crawling along this surface, keeping always to the middle of the strip, will return to its original position upside down."

Anyone who contracts to paint one side of a Mobius strip could do just as well by dipping the whole strip into a bucket of paint. The Mobius strip has only one edge; if it is cut down the center, it remains in one piece. If the resultant surface is once more cut down the middle, two separate but intertwined strips are formed.

Recently, physicist Richard L. Davis at Sandia Corporation in Albuquerque was seeking still newer and better methods of producing noninductive resistors. He constructed a Mobius loop using a metalized strip of plastic. When connections were made to opposite sides of the loop and pulses were applied, the current divided, flowed in both directions through the conducting foil, and passed itself twice. The observed inductance was extremely low. We like to think that this inspired experiment carries much greater impact than a possible improvement over bifilar windings and other well known techniques for minimizing self-inductance and distributed capacitance.

We like to ask what are the implications of topology and its queer systems as applied to optics, magnetic phenomena, and circuit networks. Is any chemist prepared to predict reaction kinetics in a Klein bottle which has no edges, no inside, or no outside? The question may be childish, but like many questions in pure topology or analysis situs, the answers are tough.

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The Du Pont Calorimeter permits the determination of heats of transition and the measurement of specific heats. This simple-to-use differential calorimeter has a temperature range of −100°C to +700°C.

For more information about the new Du Pont Calorimeter and other available modules, write to E. I. du Pont de Nemours & Co. (Inc.), Instrument Products Division, 2521 Nemours Bldg., AC-114, Wilmington, Delaware 19898.

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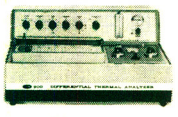

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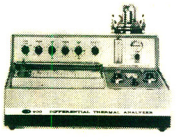
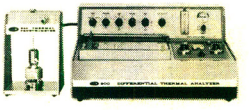


plug in cells for DTA from −150°C to 1200°C . . .



or plug in the 940 module for thermal penetrometry . . .

or plug in the 950 module for TGA to 1200°C.

See these thermal analysis systems in the Du Pont booth, #44, Eastern Analytical Symposium Nov. 11-13

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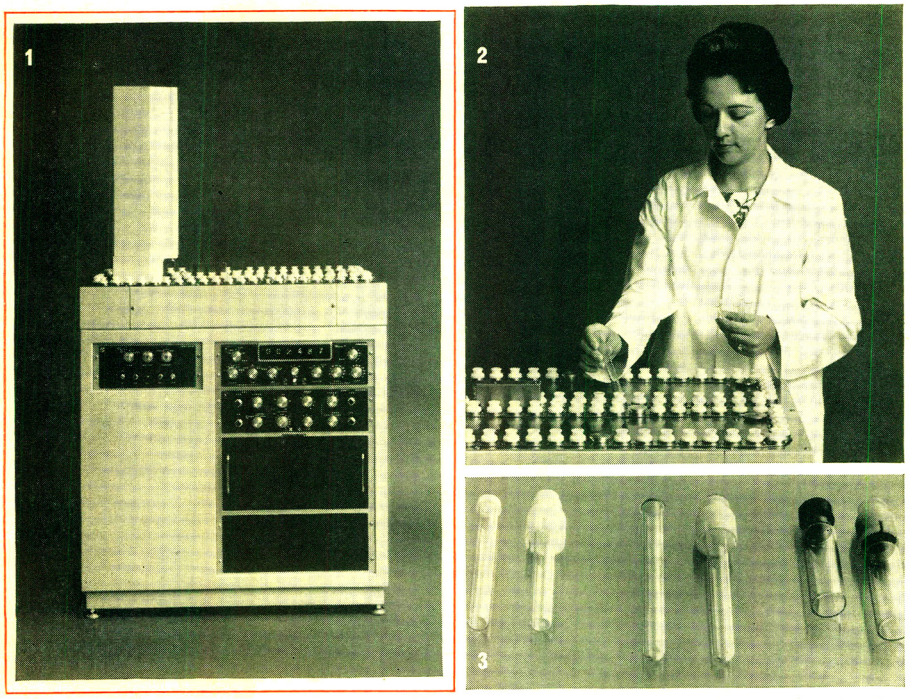

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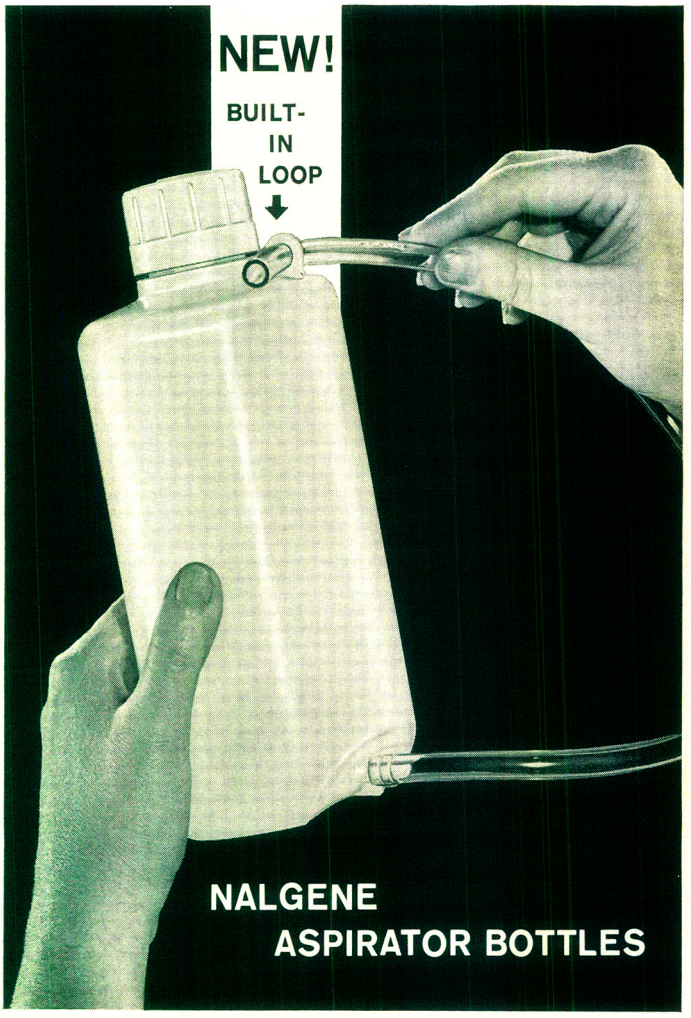

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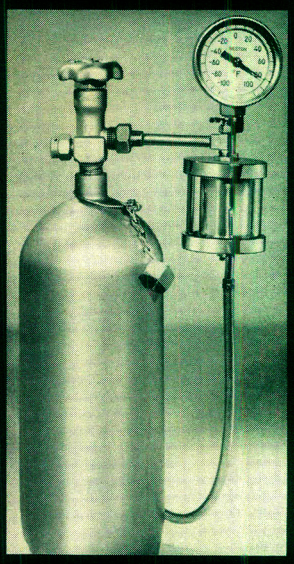

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5 B NEWS

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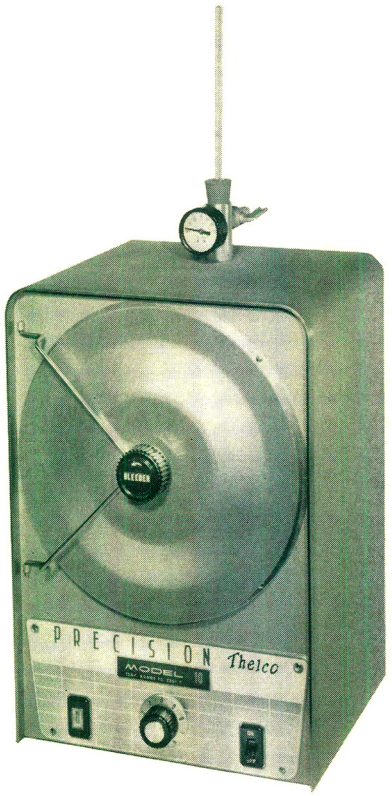

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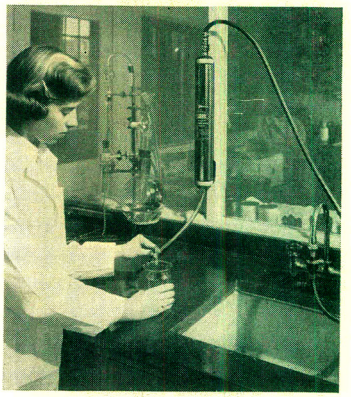

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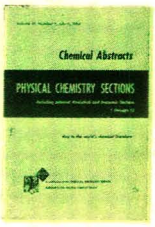

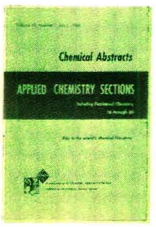

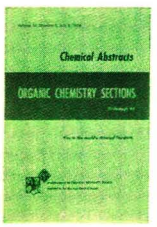

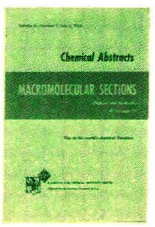

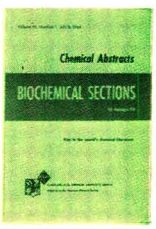

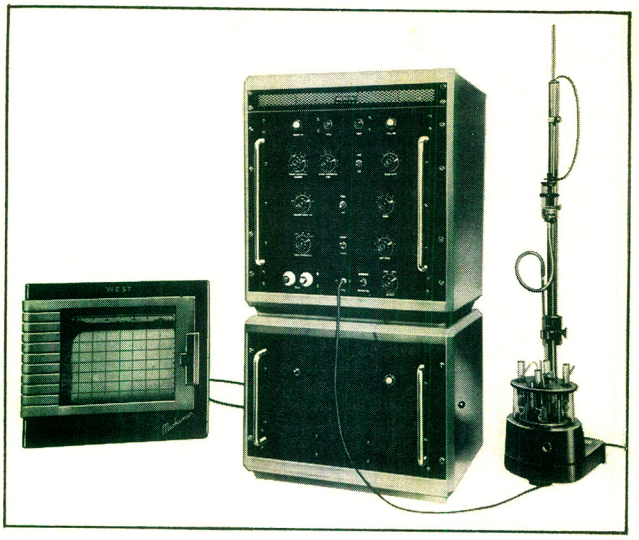

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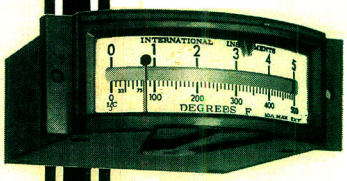

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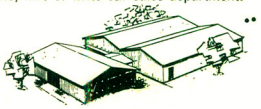

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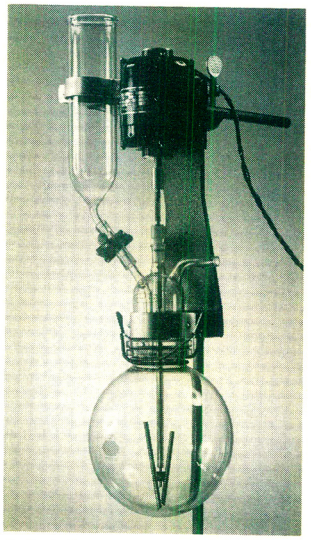

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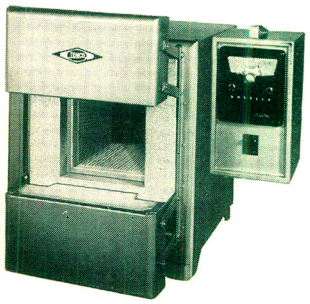

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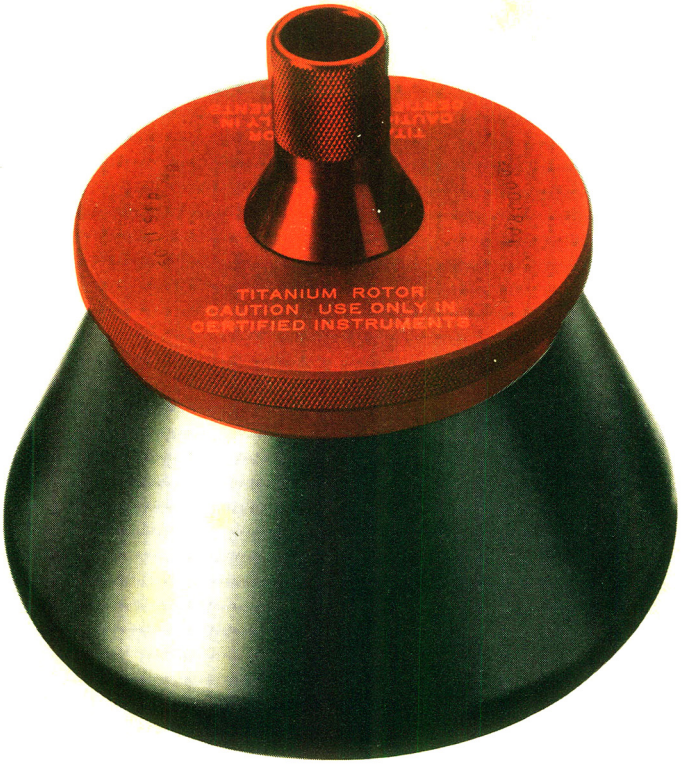

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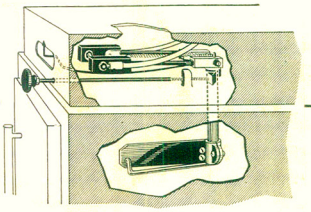

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THE ANALYTICAL CHEMIST is constantly aware of the importance of the precision and accuracy of his results. To those who receive his results, knowledge of the precision and accuracy of the values is equally important. Precision which relates to the variation among test results can now be treated statistically and a reasonably satisfactory answer can be given. However, accuracy measurements relate to the difference between a reported result and the true value. Here a primary standard is required. There is always some element of doubt even in primary standards so that the value given could vary depending on the final use of the standard. To establish validity it is best to use several unrelated methods to determine the true value and, of course, these results should agree within narrow limits.

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The Bureau is embarking on an expanded program of standard preparation which requires the help of all science, not only in the United States, but world-wide. Our Report this month, page 23 A, summarizes some of the problems which the Bureau faces in this endeavor. The Report also deals with the work of other national and international agencies in meeting the need for standards.

Porous Layer Glass Bead Column Packing in Gas Adsorption Layer Chromatography

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Institut für physikalische Chemie der Universität, Frankfurt am Main, Germany

▷ **The applicability of porous layer glass beads (PLGB) coated with highly disperse ferric oxide or zirconium oxide and impregnated with triethylene glycol (TEG) will be demonstrated for the separation of aliphatic and aromatic hydrocarbons and of aliphatic compounds containing oxygen or halogens. Variation of the impregnating liquid-to-active solid ratio causes the absolute and relative retentions of the sample components to vary, also. The higher permeability and lower capacity ratio of these columns (compared to conventional packed columns) result in shorter analysis times. A detailed description of the preparation of these columns is given.**

RECENTLY, we reported on the preparation and applications of porous layer glass beads (PLGB) in gas liquid (GLC) and gas solid (GSC) chromatography (*8*). Alumina had been the metal oxide almost exclusively used in gas chromatography (*6, 7, 12, 15*), either alone or combined with other metal oxides—e.g., ferric oxide (*5*). The oxides used to coat PLGB are obtained in the form of small spherical particles of uniform size (*3*), and the surface is pore-free. Columns packed with these beads were capable of separating low-boiling aliphatic hydrocarbons (up to C_6) at column temperatures below 100° C. (GSC). Halogenated hydrocarbons were also separated quickly on ferric oxide with PLGB at 60° C. Peaks were symmetrical; however, other polar substances showed a tailing effect and retention times were long. Results could be improved by moistening the carrier gas.

In this paper we should like to demonstrate the applicability of columns packed with PLGB to gas adsorption layer chromatography (GAC).

By impregnating the active solid—e.g., alumina, silica, ferric oxide, etc.—with a common partitioning liquid, a new stationary phase originates. The absolute (k) and the relative partitioning coefficients ($r_{1,2} = k_2/k_1$) of various substances in a sample normally do not correspond to the values obtained on an active solid, nor to those obtained on a partitioning liquid. This phenomenon generally is great with small amounts of liquid, especially when an active, polar solid is impregnated with a polar liquid (*11, 13*).

The properties of the stationary phase obtained in this way could be explained in several ways. One could assert that the "active centers" of the solid are blocked. Another possibility is that the physical properties of the liquid change in the force field of the solid. Finally, it is possible that the liquid is chemisorbed on the solid. None of these explanations gives us new knowledge about the character of the stationary phase.

When an active solid is impregnated with a small amount of liquid, one usually speaks of a "liquid-modified support." This points only to one of the above explanations. It is more correct to consider the active solid–liquid combination as a uniform stationary phase and, therefore, we will speak of gas adsorption layer chromatography. It should be mentioned that most of the so-called inactive supports have turned out to be more or less active, especially when used to separate polar substances. This effect becomes more evident when the "inactive" support is pulverized and loaded onto a column. The vapor pressure of a small quantity of liquid on an active support will always be smaller than the vapor pressure of the pure liquid in the bulk phase at the same temperature. The noise of the column is thus reduced.

EXPERIMENTAL

Apparatus. The apparatus is the same as that described previously (*2*). A flame ionization detector (FID) or a katharometer was used. Chromatograms were recorded with a fast recorder (full scale deflection, 0.3 second), and hydrogen was used for the carrier gas.

Preparation of Beads. PLGB No. 1. Highly disperse zirconium dioxide (DEGUSSA, Frankfurt am Main) with a specific surface area of 50 sq. meters per gram was heated to 300° C. overnight. Weight loss was 4%. Four grams of this pretreated zirconium dioxide were suspended in 150 ml. of petroleum ether (boiling range 40° to 70° C.) and 0.1 gram of triethylene glycol (TEG) was added with stirring. Stirring was continued for 5 minutes while cooling with ice. Sixty grams of glass beads (sieve fraction 0.09 to 0.10 mm.) were added to this suspension; the mixture was shaken for 10 minutes and sucked off. The moist product was rubbed in a mortar until it was dry. Then it was treated by rolling on a granulating plate. The product was sifted (0.09 to 0.10 mm.) and dried at 80° C. overnight. The beads were of the following composition (in % by wt.): glass beads, 93.60; ZrO_2, 6.24; TEG, 0.16.

PLGB No. 2. Three grams of highly disperse ferric oxide (E 7), with a specific surface area of 37 sq. meters per gram, and 0.3 gram of TEG were mixed with 10 ml. of methylene chloride. The paste was dried and the product was suspended while stirring rapidly in 150 ml. of petroleum ether (boiling point range, 40° to 70° C.). Fifty grams of glass beads (sieve fraction, 0.09 to 0.10 mm.) were added to this suspension, which then was shaken for 5 minutes. The product was sucked off and treated by rubbing in a mortar, 10 ml. of methanol having been added. The air-dry product then was treated for 20 minutes by rolling on a granulating plate. Thereafter the beads were sieved (particle size between 0.09 to 0.10 mm.) and the product was dried overnight at 80° C. The beads were of the following composition (in wt. %): glass beads, 93.81; β-ferric oxide, 5.63; TEG, 0.56.

PLGB No. 3. Five grams of ferric oxide (E 7), 0.5 gram of TEG, and 20.0 ml. of methanol were treated by rubbing in a mortar under an infrared lamp together with 45.0 grams of glass beads (sieve fraction, 0.12 to 0.15 mm.). After drying the product was sieved and dried at 120° C. The composition of the beads (in wt. %) was as follows: glass beads, 89.11; β-ferric oxide, 9.90; TEG, 0.99.

RESULTS AND DISCUSSION

Zirconium Oxide and TEG. The separations shown in Figures 1 to 3 were carried out with the same column, filled with PLGB No. 1. Methane was added to each of the samples. We assumed that the retention time of methane is identical with that of an inert gas, and that the solvents used during bead prep-

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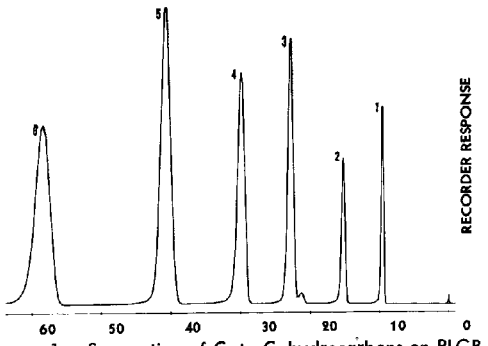

Figure 1. Separation of C_6 to C_7 hydrocarbons on PLGB No. 1

Coated with 97.56% highly disperse ZrO_2, and 2.44% TEG. Column data: L = 2 meters; i.d. = 2 mm.; packing, 7.31 grams of PLGB/meter; $K = 1.6 \times 10^{-7}$ sq. cm.; t_c = 100° C.; Δp = 3.0 atm.; F_c' = 50 ml./min.; s = 1.3 μg.; FID

1. Methane
2. n-Pentane
3. n-Hexane
4. Benzene
5. n-Heptane
6. Toluene

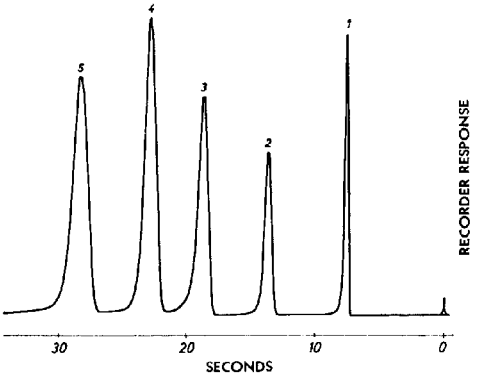

Figure 2. Separation of substances containing oxygen on PLGB No. 1

Conditions same as for Figure 1 except for the following: Δp = 4 atm.; F_c' = 90 ml./min.; s = 1.5 μg.; FID, full scale deflection 1×10^{-9} ampere

1. Methane
2. Diethyl ether
3. Acetone
4. Benzene
5. Ethyl acetate

aration—e.g., petroleum ether, methylene chloride, methanol—had been completely evaporated. The latter is an arbitrary assumption and is most probably incorrect. The solvents still sorbed will hardly vary the proportion by weight of the stationary phase, but can possibly influence its sorption properties.

Figure 1 illustrates the fast separation of a simple hydrocarbon mixture. As may be seen, this separation could have been carried out more quickly with an increased pressure drop.

The following chromatograms demonstrate the separation of polar substances in GAC. Figure 2 shows a quick separation (within a few seconds) of organic substances, most of them containing oxygen. Figure 3 illustrates a separation of halogenated hydrocarbons. The high gas permeability of the column and the fast equilibrium between the moving and stationary phases permit a carrier gas velocity of 90 ml. per minute (average linear velocity, 21 cm. per second) in a column with 2-mm. i.d. (Figure 2). In both cases a shorter analysis time could have been achieved. Despite the two components of the stationary phase (zirconium dioxide and TEG) and the polar character of the sample substances, the peaks are symmetrical. It is rather remarkable that saturated hydrocarbons are separated quite well on this "polar" phase (Figure 1).

Gas chromatographic practice often demands a single column to solve a great variety of problems. Figures 1 to 3 demonstrate that zirconium dioxide with 2.4% TEG is a versatile stationary phase indeed.

Ferric Oxide and TEG. A column packed with PLGB No. 2 can separate aromatic hydrocarbons at 100° C. within seconds (Figure 4). However, *meta*- and *para*-xylene are not separated.

The metal oxides impregnated with TEG can separate aromatic hydrocarbons. In Table I the C_6 to C_8 aromatic hydrocarbons are listed in the order of their boiling points. Column temperatures are much lower in GLC and GAC than in GSC (graphited carbon black).

Perhaps the most characteristic feature of the stationary phases in GAC is that the relative retentions ($r_{1,2}$) of many substances vary with the variation of the solid-to-liquid ratio (*10, 15*). The retentions of benzene relative to *n*-hexane against various compositions of the stationary phase are plotted in Figure 5. Column temperature is 80° C. A minimum appears at a composition of 2 grams of TEG and 100 grams of ferric oxide ($r_{1,2}$ = 2). The stationary phase in this composition has to be regarded as quite "apolar."

The separation of aliphatic compounds containing oxygen on a column filled with PLGB No. 3 at 100° C. is demonstrated in Figure 6. Sample size was 240 μg. and a katharometer was used as detector.

In general, one can assert that the charging capacity of PLGB columns is

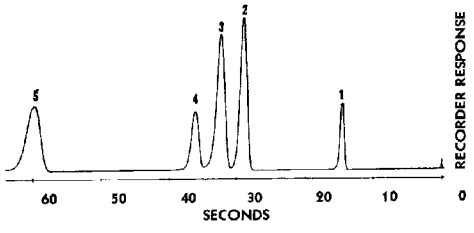

Figure 3. Separation of halogenated aliphatic hydrocarbons on PLGB No. 1

Conditions same as for Figure 1 except for the following: Δp = 2.0 atm.; F_c' = 27 ml./min.; s = 1.1 μg.; FID, full scale deflection 2×10^{-9} ampere

1. Methane
2. Trifluorotrichloroethane
3. Dichloromethane
4. Carbon tetrachloride
5. Chloroform

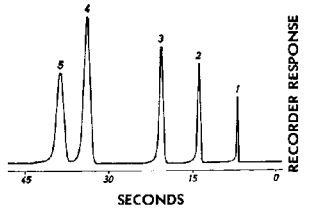

Figure 4. Separation of aromatic hydrocarbons on PLGB No. 2

Coated with 90.91% highly disperse β-ferric oxide and 9.09% TEG. Column data: L = 2 meters; i.d. = 2 mm.; packing, 7.08 grams of PLGB/meter; t_c = 100 °C.; Δp = 4.0 atm.; F_c' = 77 ml./min.; s = 0.5 μg.; FID

1. Methane
2. Benzene
3. Toluene
4. *m*- and *p*-Xylene
5. *o*-Xylene

Table I. Retentions of Aromatic Hydrocarbons Relative to Benzene

Stationary phase	Temp., °C.	Benzene	Toluene	Ethyl benzene	*p*-Xylene	*m*-Xylene	*o*-Xylene	Lit. ref.
Carbon black (CK 4) graph	292	1.00	3.30	5.42	8.61	7.94	8.61	(*9*)
Apiezon A oil	101	1.00	2.30	4.58	5.10	5.15	6.09	(*14*)
Paraffin oil	120	1.00	2.06	3.84	4.37	4.51	4.93	(*1*)
Benzyl diphenyl	100	1.00	2.05	3.93	4.14	4.27	5.25	(*16*)
Dinonyl phthalate	118	1.00	2.05	3.75	4.07	4.17	4.95	(*14*)
Polyethylene glycol 1000	78	1.00	1.89	3.27	3.42	3.59	4.71	(*14*)
7,8-Benzoquinoline	78.5	1.00	2.47	5.27	5.64	6.09	7.82	(*4*)
Fe_2O_3 + 9.1% TEG	100	1.00	1.99	...	3.94	3.94	4.63	...
ZrO_2 + 2.4% TEG	100	1.00	2.41	5.35	5.71	5.71	6.23	...

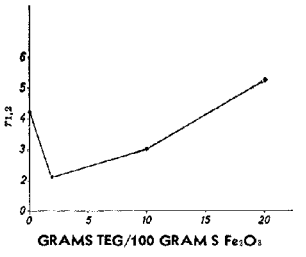

Figure 5. Variation of relative retention volumes of benzene on ferric oxide + TEG with varying composition of stationary phase

n-Hexane used as standard; retention volumes measured from methane peak

greater than that of classical micro glass bead columns, but smaller than that of the conventional packed columns.

Efficiency of PLGB Columns. To characterize the variation of the relative peak widths, h vs. $\bar{u}$ curves for *n*-pentane and *n*-heptane are shown in Figure 7. Column and operating conditions are the same as described in Figure 1. The h values are plotted in 0.1-mm. units. The capacity ratios for *n*-pentane and *n*-heptane are 0.53 and 2.9, respectively. At a capacity ratio of 2.9, the h values of the columns packed with PLGB can be compared with those of the classical packed columns. The h values obtained with PLGB columns correspond with those of a good classical packed column, but the minimum of the h values in PLGB columns is situated at higher linear carrier gas velocities. In addition, the minimum is flatter and the ascent of the curve at higher $\bar{u}$ values is less steep than in the case of the classical packed columns.

CONCLUSIONS

Porous layer technology makes it possible to use a great number of pulverized solids as support, independent of their mechanical properties. Peak widths are small, consequently the concentration and mass velocity of the sample are high at the peak maxima. In GAC the vapor pressure of the stationary phase is usually much lower than that of the impregnating liquid in the bulk phase. The charging capacity of PLGB columns is higher than that of the glass-bead-coated-with-liquid columns. Thus, it is not necessary to use the full sensitivity of an ionization detector, which again means that the base line will be practically noiseless. In some cases katharometers can be used (Figure 6). The capacity ratio (k') of the PLGB columns is variable within extended limits. This means that one is able to choose a favorable column temperature. PLGB can also help to study quickly surface properties of solids.

NOMENCLATURE

$h = \frac{L}{n}$	= height equivalent to a theoretical plate
k	= partition coefficient
$k' = k \cdot \frac{V_l}{V_g}$	= capacity ratio
$\Delta p = p_i - p_o$	= pressure drop in the column
$r_{1,2} = k_1/k_2 = k_1'/k_2'$	= relative retention

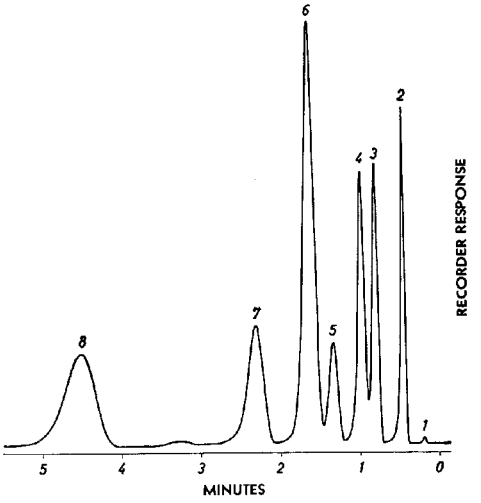

Figure 6. Separation of substances containing oxygen on PLGB No. 3

Coated with 90.91% ferric oxide and 9.09% TEG. Column data: L = 2 meters; i.d. = 4 mm.; packing, 22.75 grams PLGB/meter; t_c = 100° C.; Δp = 1.3 atm.; F_c' = 110 ml./min.; s = 240 μg.; katharometer

1. Air
2. Diethyl ether
3. Ethyl formate
4. Acetone
5. Ethyl acetate
6. Ethylmethyl ketone
7. Ethyl propionate
8. Ethyl butyrate

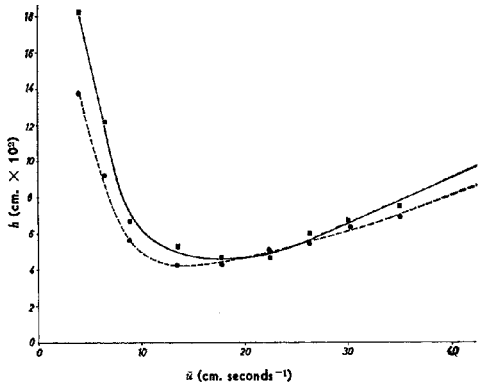

Figure 7. h vs. $\bar{u}$ for column packed with PLGB No. 1

Solid line *n*-heptane k' = 2.9. Dotted line, *n*-pentane, k' = 0.53. Column and conditions same as Figure 1, except for following: Δp = 0.4 atm. for F_c' = 11.4 ml./min.; Δp = 4 atm. for F_c' = 50 ml./min.; s = 1–2 μg.

s = sample size
t_c = temperature of the column
$\bar{u}$ = mean linear velocity of the gas
F_c' = volumetric flow rate of the carrier gas at 20° C. and 1 atm.
K = permeability constant
L = column length
V_l = liquid volume of the column
V_g = gas volume of the column

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It is a pleasure to thank E. E. Wegner for the results referred to in Figure 6, as well as for many helpful and fruitful discussions. The authors are grateful to DEGUSSA, Frankfurt am Main, Werk Rheinfelden, Germany, for presenting us with highly dispersek metal oxides.

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Vapor Pressure of Stationary Phases over Gas Chromatographic Supports

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▶ Several methods have been explored for measuring the vapor pressure of the stationary phase in GLC columns. The value is approximately equal to that of the bulk stationary phase when the latter is supported on Chromosorb P at loadings above 2%. At lower loadings the vapor pressure drops sharply, approximately in accordance with theory. The implications of these results are discussed.

VAPOR PRESSURE OF STATIONARY PHASES above the solid support in gas-liquid columns has been the subject of considerable speculation, but no quantitative documented report has yet dealt with the subject. A considerable amount of indirect evidence, summarized elsewhere (*2*, *3*), indicates that vapor pressures are reduced very little below bulk liquid values. The present report is designed to lessen the present uncertainty by measuring the vapor concentrations and losses directly.

A significant reduction of vapor pressure below bulk values would be important in several ways, the most obvious of which is a decreased bleed rate and thus longer column life. However, it is probably more important that such a reduction would reflect an attraction between the support and the stationary phase, strong enough also to enhance the retention of solutes; thus retention parameters would depend on the nature and loading of the support and would lose much of their value for identification. Moreover, so strong an attraction would influence the configuration of the liquid on the solid and thus strongly affect the column efficiency (*2*) and probably the retention parameters also.

Hence the effect of the support on the vapor pressure of a liquid is of considerable importance in gas-liquid chromatography. Such interactions are probably also important in liquid-liquid chromatography since the adsorption forces are much the same.

EXPERIMENTAL

The vapor pressures of ethylenediamine, ethylbenzene, *m*-cresol, and water supported on Chromosorb P were investigated by various methods.

A *m*-cresol column was weighed, eluted, and reweighed, and the vapor pressure of the stationary phase was calculated from loss in weight, elution time, and flow rate.

The retention time of toluene was measured on this column before and after elution, and the fractional loss of stationary phase, $\Delta V_l/V_l$, was calculated from the change in the adjusted retention time (peak minus air time) according to the formula

$$\Delta t'/t' = \Delta V_l/V_l \qquad (1)$$

A similar system was used with pentane on an ethylbenzene column, and ether on a water column. Pressure drop was negligible.

Nitrogen was passed through ethylenediamine at room temperature (ca. 25° C.) on Chromosorb P at various column loadings and was led into a gas cell; the absorbance at 3.4 microns (the —CH_2— band) was determined in each case.

Exactly 2 liters of nitrogen were passed through ethylbenzene columns at room-temperature (ca. 20° C.) with various loadings, and then into a $^1/_8$-inch o.d. copper column containing methylcyclohexane cooled in acetone–solid CO_2. The liquid was washed out of the tube with methylcyclohexane into a 25-ml. volumetric flask, made up to the mark, diluted 2 to 25, and the absorbance was determined at the maximum near 260 mμ.

RESULTS AND DISCUSSION

The results are shown in Tables I and II and Figures 1 and 2. In several cases it was not possible to reduce the precision to the desired level. These results show that at loadings above 1 or 2% the vapor pressure is approximately that of the bulk liquid. At lower loadings the vapor pressure drops sharply.

The specific surface area of Chromosorb P is given as 1.4 sq. meters per gram by Brandt (*9*) and as 4 sq. meters per gram by Ottenstein (*6*) and Pecsok (*7*). Martin (*5*) gives the surface area at various column loadings, and reports 2.8 sq. meters per gram for the lowest loading tried, indicating a higher figure for the naked support. Accordingly, 4 sq. meters per gram has been assumed for the calculation of the number of monolayers shown in Figures 1 and 2. Assuming that the molecule is cubic, it appears that about five monolayers are necessary to approach the bulk vapor pressure.

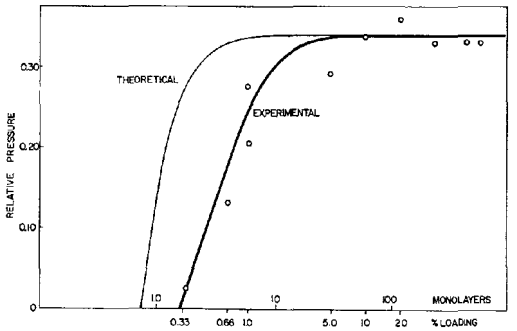

Figure 1. Volatility of ethylbenzene over Chromosorb P (arbitrary units)

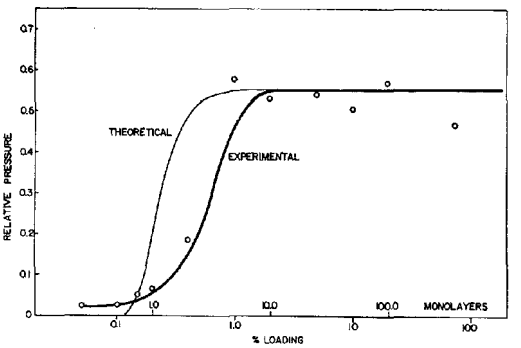

Figure 2. Volatility of ethylenediamine over Chromosorb P (arbitrary units)

The low apparent vapor pressure of ethylbenzene at 1% load, when determined by retention time, was caused by the adsorption of the sample on the Chromosorb, the retention time being the same with 1% load as when naked. Hence this method is unreliable.

The use of water as stationary phase with ether as sample proved unsatisfactory also, because the retention time increased with the elution of water, presumably because of increased adsorption on the support.

It is interesting to compare the reduction in vapor pressure at low loads with that predicted theoretically. An earlier treatment (*1*) showed that the thickness, d_s, of a liquid adsorbed on a flat surface should be given by

$$d_s^3 = \frac{V_m \Delta E}{NRT \ln p_o/p} \qquad (2)$$

Table I. Relative Volatilities by Absorbance Method

Stat. phase, g./100 g. Chromosorb P	Absorbance, mμ	Monolayers
ETHYLENEDIAMINE		
100	0.336	600
75	0.331	450
40	0.333	240
20	0.359	120
10	0.337	60
5	0.290	30
1	0.274	6
1	0.204[a]	6
2/3	0.130[a]	4
1/3	0.025[a]	2
ETHYLBENZENE		
∞[b]	0.568	∞[b]
75	0.468	350
20	0.568	100
10	0.505	50
5	0.538	25
2	0.530	10
1	0.576	5
0.4	0.184	2
0.2	0.063	1
0.1	0.025	0.5
0.05	0.025	0.25

[a] Determined at a later date, probably with a slight temperature difference.
[b] Unsupported free liquid.

if there are several (>3) monolayers. If the number of monolayers is given by $n = d_s/\delta$ where δ is the thickness of a monolayer, calculated as above, then

$$n = \frac{1}{\delta}\left\{\frac{V_m \Delta E}{NRT \ln P_o/p}\right\}^{1/3} \qquad (3)$$

This curve has been plotted to yield the theoretical curves in Figures 1 and 2, taking the value of ΔE as 1000 cal. per mole as estimated in the original paper. It has been extended to lower loadings than those to which the equation is properly applicable, but indicates the general shape and is in reasonable agreement with the experimental data.

The result is similar to the experimental plots although the predicted drop-off in vapor pressure occurs with several times less than the observed liquid load. This may be due in part to liquid tied up in very fine capillaries. The agreement is on the whole satisfactory and confirms the deduction (*1*) that stationary phase liquid approaches the bulk form, with attendant bulk properties, at most practical loadings.

NOMENCLATURE

d_s = thickness of liquid film
ΔE = difference in interaction energy per gram-atom between liquid-liquid and liquid-solid pairs
N = Avogadro number
p = vapor pressure of supported liquid
p_o = vapor pressure of bulk liquid
R = gas constant
t' = adjusted retention time (peak minus air)
T = absolute temperature
V_l = volume of stationary phase in column
V_m = molecular volume of stationary phase
δ = thickness of one monolayer

Table II. Vapor Pressures by Weighing and Retention Time

Stat. phase load, g./100 g. Chromosorb P	T, °C.	Expt. p, mm.	Literature p, mm. (*4*, *8*)	Monolayers
m-CRESOL BY WEIGHING				
12.5	52	1.4	0.9	51
12.5	84	6.1[a]	7.9	51
m-CRESOL (FROM RETENTION TIME OF TOLUENE)				
6	85	7.7	8.2	25
4.5	85	7.6	8.2	18
ETHYLBENZENE (FROM RETENTION TIME OF *n*-PENTANE)				
36	30[b]	14	11	180
4	32[b]	14	14	20
2	31[b]	8	12	10
1	30[b]	0	11	5

[a] Mean of six readings, $\sigma = 0.2$.
[b] There is some uncertainty in these temperatures.

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Zone Melting Considered as a Chromatographic Separation Technique

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▶ **Zone melting can be adapted to perform separations of the kind achieved in chromatography. A mixture of solutes is placed at a point in a long column of solid solvent, and molten zones are passed in one direction. The solutes separate into bands, each of which travels at a rate determined by the distribution coefficient of the solute. Idealized theory shows that the solute distribution in a band has the form of a modified Poisson distribution, and that the number of zone-passes required to separate two solutes depends only on the ratio of their distribution coefficients. Typically, some hundreds of zone-passes, and columns hundreds of zone-lengths long, are required. Since the permissible rate of zone-travel is relatively low, practical realization of zone chromatography requires techniques for producing very short and very closely-spaced molten zones.**

An aspect of zone melting (*6*, *8*) that has received little attention is its potential as a chromatographic separation technique. If a mixture of solutes is introduced at a point in a long charge, or column, of solid solvent, and if molten zones are passed along the column in one direction, the components of the mixture will become separated into individual "bands." We denote this technique "zone chromatography," or ZC, with the reminder to the reader that ZC is a technique of zone-melting, not of chromatography, a main difference from conventional zone refining being that longer charges and more zone-passes are required in ZC than in conventional zone refining.

In this paper we present elementary theory for ZC, compare it with theory for gas liquid chromatography (GLC), indicate requirements for the apparatus, and discuss variants of the basic technique. It appears, despite the relative slowness of ZC, that it has a useful place alongside conventional chromatographic techniques. We are not aware of any extensive experimentation with ZC; it is hoped that the present paper will lead to such effort.

In GLC (*1*, *3*) there is a column, or tube, of solid particles, coated with a liquid—the stationary phase. A sample of components to be separated is inserted at the beginning of the column. An inert gas, in which the components have a sensible vapor pressure, is passed through the column. By continuous repeated equilibrations of vapor and liquid, the components migrate along the column in bands, which travel at different rates, the component that most prefers the vapor traveling fastest. The rate of travel and the sharpness of a band depend on the vapor-liquid equilibrium constant and on features of the column, such as rate of gas flow, particle size, ratio of gas volume to liquid volume, dimensions and compositions of gas channels and liquid layers, diffusivities in gas and liquid.

In ZC, there is a column of solid solvent. A sample of components to be separated (soluble in the solid solvent) is introduced at the beginning of the column, or preferably, in certain cases, at a point farther along the column. A number of very short, closely-spaced, molten zones are caused to traverse the column. As in GLC, components migrate along the column in bands that travel at different rates. Components that prefer the liquid travel forward, at a rate in accord with their preference for the liquid; components that prefer the solid travel backward, at a rate in accord with their preference for the solid. The latter effect is why it may be appropriate to introduce the sample some distance along the column. The rate of travel and the sharpness of the bands depend on liquid-solid equilibrium constants, zone-length, zone-speed, zone-stirring, and little else.

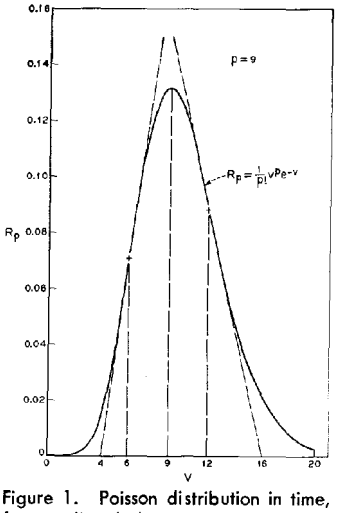

Figure 1. Poisson distribution in time, for gas liquid chromatography, showing relative solute concentration, R_p, at pth plate, as a function of the number, v, of relative plate volumes of carrier gas that have passed plate p

THEORY

Gas Liquid Chromatography. In this subsection we present an essential expression for the movement of a solute in ideal gas liquid chromatography. The expression presented represents plate theory, rather than differential theory. While we recognize that the latter may be regarded as more accurate, we nevertheless adhere to the former, because it is simpler in concept, because it is well known to chromatographers, and because exact expressions of identical form hold for ZC. Following Keulemans (*1*), the ratio, R_p, of the solute concentration in the vapor at the pth plate to that at the first plate is

$$R_p = \frac{e^{-v} v^p}{p!} \qquad (1)$$

where v is the number of effective plate volumes of carrier gas introduced.

Equation 1 represents a Poisson distribution, some important features of which are illustrated in Figure 1, which is a plot of R_p against v for $p = 9$. Note that Figure 1 is not a distribution in space. Rather, it is a plot of the concentration at plate p as a function of v, the number of effective plate volumes of gas that have passed plate p. It should be emphasized that, for a given volume of gas, v is different for each solute. In fact, this difference is the basis of the separating mechanism of the column.

Zone Chromatography. The basic equation underlying zone chromatography was derived by Reiss and Helfand (*9*), at the writer's suggestion. Their derivation is rigorous within the usual simplifying assumptions; namely that the distribution coefficient, k, de-

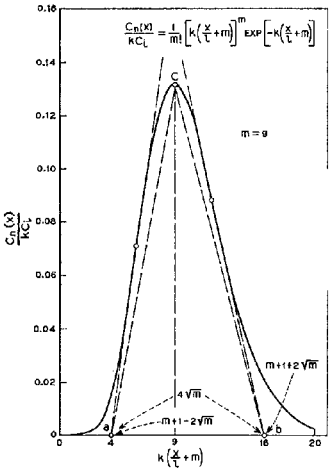

Figure 2. Poisson distribution in space, for zone-chromatography, showing relative solute concentration, after m zone-passes, as a function of reduced distance from the initial position of the solute

fined as the ratio of the solute concentration in the just-freezing solid to that in the molten zone, is constant; that there is no diffusion in the solid; and that there is infinitely rapid mixing in the liquid. The last assumption is not realized in practice, but this can be accounted for by using an effective value of k which is consistent with the freezing conditions (*8*). Concentrations may be in weight-fraction or atom-fraction, in which case the density change on freezing can be ignored, provided that the zone-length, l, is the length of solid that was melted to form the zone (*5*). If concentrations are expressed on a volume basis, then it is assumed that the density does not change on freezing.

Consider an infinite column of solid solvent extending in the x-direction from $x = -\infty$ to $x = +\infty$. The differential equation determining the distribution of solute in the solid after the nth pass is

$$(l/k)\ (dC_n(x)/dx) + C_n(x) = C_{n-1}\ (x + l) \quad (2)$$

where x denotes the position of the trailing end of the zone, $C_n(x)$ denotes the concentration in the solid, and the zone moves in the $(+x)$ direction.

Let the initial distribution of solute $C_0(x)$ be a delta (δ) function centered at $x = \xi$:

$$C_0(x) = K\delta(x - \xi), \quad (3)$$

$$\int_{-\infty}^{+\infty} \delta(x - \xi)dx = 1 \quad (4)$$

Then, for $x \geq \xi - nl$, Reiss and Helfand (*9*) showed that $C_n(x)$ is given by:

$$C_n(x) = \frac{Kk}{l(n-1)!}\left[\frac{k}{l}(x - \xi + nl)\right]^{n-1} \exp\left[-\frac{k}{l}(x - \xi + nl)\right] \quad (5)$$

In the remainder of this section we simplify Equation 5, show that it represents a Poisson distribution, and develop from it equations useful for the practice of zone chromatography.

Let the delta function be centered at $\xi = l$, and let $m = n - 1$. Then Equation 5 becomes:

$$\frac{lC_n(x)}{kK} = \frac{C_n(x)}{kC_i} = \frac{1}{m!}\left[k\left(\frac{x}{l} + m\right)\right]^m \exp\left[-k\left(\frac{x}{l} + m\right)\right] \quad (6)$$

where $C_i = K/l$ = the concentration in the zone at $x = 0$ in the first zone pass—i.e., when the front of the zone has just reached the delta function of solute at $x = l$. Equation 6 is a modified Poisson distribution. If m is held constant, it can be regarded as a true Poisson distribution.

Even though mathematically similar Poisson distributions are obtained in both GLC and ZC, the distributions are physically different and the comparable parameters have different physical meanings. Thus, by comparing Equations 1 and 6, it can be seen that a location, p, in GLC corresponds to a number, m, of zone-passes in ZC, and that a number, v, of plate volumes of inert gas in GLC corresponds to a location, $k[(x/l) + m]$, in ZC.

By differentiating Equation 6 and setting $d(C_n(x)/kC_i)/dx$ equal to zero, the maximum of the distribution is found to lie at:

$$(x/l)_{max} = m\left(\frac{1}{k} - 1\right) \quad (7)$$

The value of $C_n(x)/kC_i$ at $x = x_{max}$ is:

$$\frac{C_n(x)_{max}}{kC_i} = \frac{m^m e^{-m}}{m!}, \quad (8)$$

which, by Stirling's approximation, reduces to:

$$\frac{C_n(x)_{max}}{kC_i} = \frac{1}{\sqrt{2\pi m}} \quad (9)$$

The Poisson distribution defined by Equation 6 is plotted in Figure 2 for the value $m = 9$. The ordinates are in units of relative concentration, as in Figure 1. The abscissas are in units of $Z = k[(x/l) + m]$. The curve of Figure 2, in contrast with that of Figure 1, is a distribution in space. It represents the distribution of solute along the column after $n = m+1$ zone-passes. The peak width, in units of Z, is $4\sqrt{m}$. Figure 2 is a universal curve, representing the distributions of all solutes after 10 zone-passes. As such, it does not readily indicate the separating power of the column that arises from differences in k. For this, a plot having abscissas in units of (x/l) is more useful.

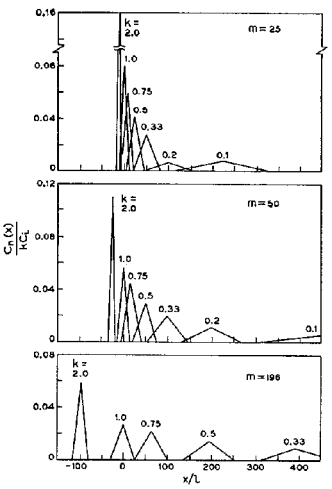

Figure 3. Schematic representation of height, location, and width of solute bands in zone chromatography, for various values of the distribution coefficient, k, after m = 25, 50, and 196 zone-passes

Such plots are shown in Figure 3 for various k's and for $m = 25$, 50, and 196. For simplicity, instead of the Poisson-curve for each k-value, triangles similar to abc in Figure 2 are plotted. Figure 3 illustrates the more rapid movement and more rapid increase of peak width with decrease in k, the stationary maximum for $k = 1$, and the reverse movement for $k > 1$.

It is useful to ask how many zone-passes, $n^* = m^*+1$ are required to separate two solutes. A useful approximate criterion for separation is that point a of triangle abc of the leading solute coincide with point b of triangle abc of the trailing solute. An expression for m^* is obtained as follows. On the Z-scale, let the coordinate of point a be $Z_a = m^* + 1 - 2\sqrt{m^*}$, and of point b be $Z_b = m^* + 1 + 2\sqrt{m^*}$. Let solute 2 be the faster moving, which means, for k's < 1, that $k_2 < k_1$. We require that, on the (x/l)-scale, point a for solute 2 coincide with point b for solute 1, in other words, that:

$$\left(\frac{x_2}{l}\right)_a = \frac{Z_a}{k_2} - m^* = \frac{m^* + 1 - 2\sqrt{m^*}}{k_2} - m^*, \quad (10)$$

$$\left(\frac{x_1}{l}\right)_b = \frac{Z_b}{k_1} - m^* = \frac{m^* + 1 + 2\sqrt{m^*}}{k_1} - m^*, \quad (11)$$

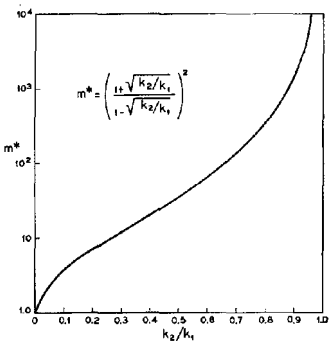

Figure 4. The number of zone- passes, m^*, required to separate two solute bands as a function of the ratio, k_2/k_1, of the distribution coefficients of the solutes

$$\left(\frac{x_2}{l}\right)_a = \left(\frac{x_1}{l}\right)_b \qquad (12)$$

Solving Equations 10, 11, and 12 for m^* results in:

$$m^* = \left[\frac{1+\sqrt{k_2/k_1}}{1-\sqrt{k_2/k_1}}\right]^2 \qquad (13)$$

Thus, the number of passes required depends only on the ratio of distribution coefficients. Equation 13 is illustrated in Figure 4. It is seen that m^* approaches infinity as (k_2/k_1) approaches unity.

It is also useful to have a feeling for the length, L^*, of column required to separate two solutes, for this determines the size of the column and the time for the separation. A rough measure of L^* is the value of $(x/l)_{max}$ for the faster moving solute after m^* passes, given by Equation 7, or, if $k_1 > 1$ and $k_2 < 1$, the difference between the values of $(x/l)_{max}$ for the two solutes. In Figure 5, L^* is plotted against k_2 with Δk as a parameter. Clearly L^* depends on many factors. The rise of all curves at small k_2 reflects the tendency, apparent in Equation 7, for L^* to approach infinity as k_2 approaches zero. The essentially constant regions to the left of $k_2 = 1.0$, occur in the range of k-values for which the solutes move in opposite directions. The rapid rise to the right of $k_2 = 1.0$ corresponds to both solutes moving backward.

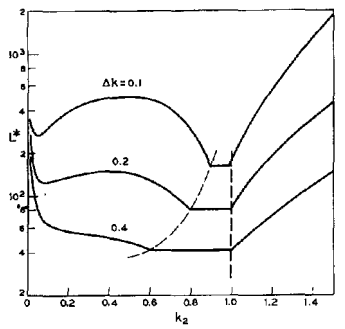

Figure 5. The length of column, L^*, in zone-lengths, required to separate two solute bands as a function of k_2, the smaller distribution coefficient, with Δk as a parameter

The calculations of L^* ignore the half peak-width beyond the maximum of the leading solute. This width can be quite large if k_2 is small. However, it is ignored because the solute will be "piled up" at the end of the column by the well-known zone refining effect; and this effect is strongest for the very range of k in which the half peak-width is large. In fact, a potentially useful variant of ZC, once a solute band has been isolated, is to concentrate the solute by a series of zone refining passes over the width of the band. For such concentrating action to be effective, k must differ substantially from unity.

We are now in a position to consider an important parameter in ZC, namely the time, t, required for a given separation. The time required to pass a series of n zones, of spacing, d, between zone fronts, through a charge of length L is (7):

$$t = \frac{L + (n-1)d}{v_z} \qquad (14)$$

where v_z is the velocity of the zones. Setting aside for the moment the value of v_z and the length of a zone, the primary consideration is the value of:

$$L^* + (n^* - 1)d = L^* + m^*d$$

Two cases are considered in Table I, for $d = 2$.

Despite the convolutions of the curves of Figure 5, it is clear from Table I, for Δk constant, that the separation time steadily decreases as k decreases. This, of course, is pertinent to selection of the inert solid solvent material of the column.

EXPERIMENTAL

Apparatus. One form that apparatus for zone chromatography might take is shown schematically in section in Figure 6. The charge,

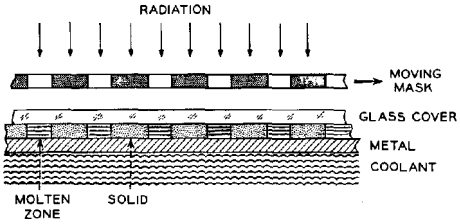

Figure 6. Schematic cross section of an apparatus for producing short molten zones for zone chromatography

Table I. Relative Time, $(L^* + 2m^*)$, Required to Separate Two Solutes Having Different k-Values.

Δk	k_2	m^*	L^*	$L^* + 2m^*$
0.10	0.1	34	306	370
0.10	0.5	480	480	1440
0.10	1.0	1760	176	3700
0.40	0.1	7	62	76
0.40	0.5	47	48	140
0.40	1.0	144	41	330

or column, is a long thin slab, perhaps ~0.1 cm. × 2.0 cm. × 50 cm., of a suitable solvent substance of fairly low melting point. It is contained between a clear glass or fused silica slide and a metal plate, which is cooled from the outside. Above the charge is a grid-like mask. Radiant energy from a projection lamp passes through the openings in the mask, and, by absorption in the charge or in the surface of the metal plate, heats the charge and forms a molten zone. The mask is moved at the desired zone velocity with either steady or reciprocating motion.

At this writing a zone-length, l, of 0.1 cm. appears quite feasible. A representative L^* may be ~500, which would mean a column 50 cm. long. A typical zone velocity, v_z, may be ~2 cm./hr.; and a typical value of $(L^* + 2m^*)$ may be ~1000 zone lengths. The time, t, would be ~50 hours for these values.

RESULTS

There are two ways in which reducing l can reduce the time. The first is by reducing the column length for a given value of $(L^* + 2m^*)$. The second is by permitting a greater zone velocity. If diffusion is the only mixing mechanism (as is likely in very short zones), v_z should be not more than $\sim D/l$, where D is diffusivity. Typically, $D \cong 3 \times 10^{-5}$ cm.^{2}/sec. Therefore, if l could be reduced to ~0.03 cm., v_z could be $\sim 10^{-3}$ cm./sec., or ~3.6 cm./hr. For the above values of L^* and $(L^* + 2m^*)$, the column would be ~15 cm. long and t would be ~4 hours. At this writing, however, it remains to be shown that l as small as ~0.03 cm. is feasible.

A major difference between ZC, in its simple form described above, and other chromatographic techniques, as described by Keulemans (*1*) is that no material moves through the column—there is no "percolation." In its fundamental aspect, however, the separation of solutes into bands, ZC resembles chromatography. Moreover, simulated or actual percolation of the solid solvent can be realized in ZC. If each time a molten zone is at one or the other end of the column it is removed and replaced by pure solvent, the effect will be to remove solutes just as in conventional chromatography, even though there is not a net flow of solvent through the column. Also, by using techniques of matter transport described in connection with continuous zone refining, (*8*) bulk flow of material along the column can be realized simultaneously with the zone-travels.

Another potentially useful group of procedures is to combine zone chromatography and paper chromatography by using a medium, such as a strip of filter paper or glass fiber, to contain the solid and liquid regions of the ZC column. Thus, percolation of solvent, (when liquid) can be realized, by gravity or capillarity, just as in paper chromatography, but modified by the motion of the molten zones. The net flow of solvent can be parallel to the direction of zone travel, with separation of solutes occurring both by the freezing process and by liquid-solid (medium) partition. Or, the net flow of solvent can be transverse to the direction of zone-travel, thereby enabling continuous separation of solutes as done, for example, by the use of a transverse electric field in electromigration chromatography. Transverse flows combined with zone-travels can also be realized in conventional, tray-shaped containers to achieve the same result without the need for a fibrous supporting medium.

Solid solvents suitable for zone chromatography fall into two main classes, both useful, depending on whether the solutes in the mixture to be separated have k's < 1 or k's > 1 in the solvent, or more properly, in the multicomponent solution. An example of the former is benzene as a solvent for polystyrene. A wide range of k's < 1 was found for certain growth conditions in this system by Loconti and Cahill (*2*). An example of the latter is xylene as a solvent for polyethylene. Bands of solutes having k's < 1 move forward, as mentioned above, and generally move more rapidly and spread out more rapidly than solutes having k's > 1. The latter move backward and tend to be more concentrated. It is also possible to select a solvent that will separate a mixture of solutes into two groups of bands, one moving forward, the other backward.

The only published experiments the writer is aware of that might fall in the class of ZC are those of Peaker and Robb (*4*) on the partial fractionation of polystyrene in naphthalene and those of Loconti and Cahill (*2*) on polystyrene in benzene. Because the distributions of k-values for their systems were continuous, and because short columns and few zone-passes were used, imited separations were achieved. Application of ZC to groups of distinct compounds, in apparatus utilizing an order-of-magnitude-greater number of zone-lengths per column and more zone-passes can be expected to result in the kind of separations associated with conventional chromatography.

While ZC is much slower than GLC, although perhaps comparable with some of the slower liquid-liquid chromatographic separations, it can be used for solutes of low volatility. It exploits a phase transformation hitherto unused for chromatography, and hence it may find application for entirely new classes of materials.

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Gradient Loaded Columns in Gas Chromatography

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▶ **The use of gradient loaded columns in gas chromatography is a new technique involving the systematic variation of the partition ratio, k, during the course of an analysis by varying the liquid loading from the beginning to the end of the column. The case of a continuous linear decrease in k down the column is considered theoretically and experimentally. Equations are derived describing solute retention behavior, column efficiency, and solute resolution on columns with a linear gradient in k. Good agreement is obtained between the theoretical predictions and the experimental results on a 16-stage step-wise approximation to a continuous linear gradient column. For linear gradient columns, the partition ratio is reduced to 50% of that which it would be on a regular column of liquid loading corresponding to the initial k on the gradient column. Column efficiency is improved for solutes of low or intermediate partition ratio on the gradient column. The combination of these effects results in resolution of solutes of low retention which is superior to that which could be obtained on a regular column.**

SEVERAL CHROMATOGRAPHIC TECHNIQUES have been developed which involve the systematic variation of a critical parameter during an analysis. Programmed temperature gas chromatography has provided a simple method for the analysis of wide-boiling mixtures in a minimum of time while enhancing resolution. Gradient elution liquid chromatography (*1*), which involves an increase in the eluting power of the mobile phase during the course of an analysis, has offered similar advantages to the column chromatographer. Porath (*14*) has described a step-graded adsorption column constructed of six sections, each successive section down the column containing charcoal deactivated with stearic acid to a lesser extent than the preceeding section. Satisfactory results were claimed for the analysis of pea-root exudate.

It has been suggested, notably by Purnell (*15*), that a gas chromatographic column in which the partition ratio, k, was varied down the column, might exhibit capabilities similar to those

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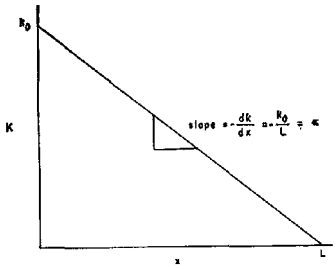

Figure 1. Schematic diagram of gradient loaded gas chromatographic column

offered by programmed temperature gas chromatography. This technique, involving a gradient liquid loading (for which the anacronym GLGC is used), has been considered theoretically and experimentally in this work.

In GLGC, the partition ratio is varied continuously (or discontinuously) from the beginning to the end of the column by a continuous (or discontinuous) variation in the liquid loading on each (infinitesimal) increment of column packing. Columns possessing a linear variation in k from the beginning (where the initial k is k_o) to the end of the column (where k is 0) have been treated theoretically from the points of view of solute retention, column efficiency, and resolution. These equations have been verified experimentally on a column which closely approximates a linear gradient—a 16-stage step-wise gradient.

In linear GLGC, the partition ratio is reduced by 50% to a value characteristic of the mean liquid loading on the gradient column. For solutes of low or intermediate retention, column efficiency is improved to a level matching that of a column constructed of the mean quantity of stationary phase on the gradient column. Most important is the improvement in resolution, which is superior for solutes of low or intermediate partition ratio on the gradient column to that on a regular column containing the average liquid loading on the gradient column. The gain in resolution results from the combination of the reduced partition ratio and the improved efficiency.

THEORETICAL

..Solute Retention Behavior in GLGC. Solute retention time, t_r, may be defined by

$$t_r = \int_0^L \frac{dx}{v_s} \qquad (1)$$

where v_s is the solute velocity and x is its position down the column of length L. From the fundamental theorems of chromatography, solute velocity is related to the partition ratio, k, by

$$v_s = v_o R_f = u(x) R_f = u(x)\left(\frac{1}{1+k}\right) \qquad (2)$$

where $v_o = u(x)$ is the velocity of an unsorbed substance—i.e., the carrier gas velocity—and R_f is the ratio of solute velocity to carrier gas velocity. u is given as a function of x, $u(x)$, to emphasize that the carrier gas velocity will vary down the column because of the compressibility of the mobile phase.

Using ordinary gas chromatographic columns, an expression for retention time can be derived from Equations 1 and 2:

$$t_r = \int_0^L \frac{1+k}{u(x)}\,dx = \frac{L}{\bar{u}}(1+k) = t_m(1+k) \qquad (3)$$

where $\bar{u}$ is the time average carrier gas velocity and t_m is the retention time of an unsorbed component.

In GLGC, k is a function of x and hence changes as the solute moves down the column. Many relationships can be written to describe an x-dependence of k. The case to be considered in this paper is a linear decrease in k with x, as described in Figure 1.

For a linear gradient, the partition ratio at any point down the column is

$$k = k_o + \alpha z \qquad (4)$$

where k_o is the initial partition ratio and $\alpha = dk/dx$.
Thus Equation 2 becomes

$$v_s = u(x)\,R_f = u(x) \times \left(\frac{1}{1+k_o+\alpha x}\right) \qquad (5)$$

Retention time is now

$$t_r = \int_0^L \frac{dx}{u(x)\,R_f} = \int_0^L \frac{1+k_o+\alpha x}{u(x)}\,dx = (1+k_o)\int_0^L \frac{dx}{u(x)} + \int_0^L \frac{\alpha x}{u(x)}\,dx \qquad (6)$$

To evaluate the first integral in this equation, the general derivation of the Martin and James compressibility factor is followed, as detailed in reference (3). We find:

$$\int_0^L \frac{dx}{u(x)} = \frac{2L}{3u_o}\left(\frac{a^3-1}{a^2-1}\right) = \frac{L}{u_o j} = \frac{L}{\bar{u}} = t_m \qquad (7)$$

where a is the ratio of inlet to outlet pressures, p_i/p_o, and j is the gas compressibility factor. To arrive at this result, we note first that the carrier gas velocity is related in a general way to the pressure drop across the gradient column by

$$u = -c(dp/dx) \qquad (8)$$

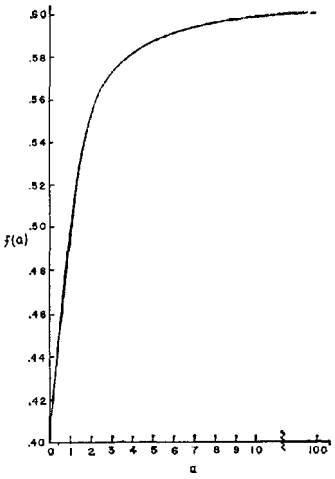

Figure 2. Dependence of partition ratio on $a = p_i/p_o$ on GLGC column

$f(a)$ is defined by Equation 16

where c is the permeability constant. Second, from Boyle's law, $pu = p_o u_o$ = constant. From these equations, it is readily derived that

$$x = L - \frac{c}{2p_o u_o}(p^2 - p_o^2) \qquad (9)$$

Combining these equations, we arrive at a manageable form for the second integral in Equation 6:

$$\int_0^L \frac{\alpha x}{u(x)}\,dx = \frac{\alpha c^2}{2(p_o u_o)^3}\int_{p_i}^{p_o}(p^4 - p_o^2 p^2)\,dp - \frac{\alpha L c}{(p_o u_o)^2}\int_{p_i}^{p_o} p^2 dp$$

whose solution is

$$\int_0^L \frac{\alpha x}{u(x)}\,dx = \frac{\alpha c^2 p_o^2}{2u_o^3}\left(\frac{a^3-1}{3} - \frac{a_5-1}{5}\right) + \frac{\alpha L^2}{u_o j} \qquad (10)$$

Thus retention time is given by

$$t_r = t_m(1+k_o) + \frac{\alpha c^2 p_o^2}{2u_o^3}\left(\frac{a^3-1}{3} - \frac{a^5-1}{5}\right) + \frac{\alpha L^2}{u_o j} \qquad (11)$$

In terms of the partition ratio,

$$k = k_o + \frac{\alpha c^2 p_o^2}{2t_m u_o^3} \times \left(\frac{a^3-1}{3} - \frac{a^5-1}{5}\right) + \frac{\alpha L^2}{u_o j t_m} = k_o + \frac{\alpha c^2 p_o^2 j}{2u_o^2 L}\left(\frac{a^3-1}{3} - \frac{a^5-1}{5}\right) + \alpha L \qquad (12)$$

From Equation 9, it is readily shown that

$$c^2 = \frac{4L^2 u_o^2}{p_o^2(a^2-1)^2} \qquad (13)$$

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Making substitution for jc^2 in Equation 12, and recognizing that for a linear gradient column, $\alpha = -k_o/L$,

$$k = k_o\left[\frac{3a^5 - 5a^3 + 2}{5(a^2 - 1)\,(a^3 - 1)}\right] \quad (14)$$

Note that when $\alpha = 0$—i.e., when no gradient exists, $t_r = t_m\,(1 + k_o)$ as usual.

Equation 14 predicts that the partition ratio on the GLGC column is a function only of the initial partition ratio, k_o, and the inlet/outlet pressure ratio, a (or p_i, when $p_o = 1$ atm.). Figure 2 presents a plot of the coefficient of k_o in Equation 14,

$$f(a) = \left[\frac{3a^5 - 5a^3 + 2}{5(a^2 - 1)\,(a^3 - 1)}\right],$$

as a function of a. As a increases, solute retention on the more heavily loaded end of the column must be disproportionately weighted. In their recent study of combination columns, Hildebrand and Reilley (*9*) observed such behavior with a column consisting of two stages in series, the simplest case (and worst approximation) of a gradient column. Equation 14 provides some theoretical basis for their observations.

Although a situation where $a < 1$ is physically impossible, the curve in Figure 2 is drawn to $a = 0$ to show the mathematical form of Equation 14. Of course, if the column was used with the heavily loaded end at the outlet, that portion of the curve in Figure 2 for $a < 1$ would be relevent—i.e., the theory is applicable to situations involving both a linear decrease and a linear increase in k.

Using the GLGC column, at least a 50% decrease in partition ratio is predicted by Equation 14. In terms of retention time, this corresponds to a minimum decrease given by

$$t_r = t_m(1 + k_o) - t_m(1 + k_o/2) = 0.5\,t_m k_o$$

The limit of $f(a)$ as a becomes very large is 0.4, indicating that the maximum decrease in partition ratio is 60%, corresponding to a retention time difference of $0.6\,t_m\,k_o$.

For purposes of predicting retention values from a knowledge of k_o and Equation 14, the value of $f(a)$ at $a = 1$ is used. This represents an extrapolation to zero pressure drop across the column, and yields a static value for k. A quite simplified derivation of a retention equation in GLGC lends support to this view:

From Equation 6, for a gradient column,

$$t_r = \int_0^L \frac{1 + k_o + \alpha x}{u(x)}\,dx$$

Extracting the mean value of $u(x)$ over the interval $0<x<L$, $\bar{u}$, integrating, using $\alpha = -k_o/L$, and solving for k,

$$k = \frac{k_o}{2} \quad (15)$$

This is the same result as Equation 14 with $a = 1$.

Column Efficiency in GLGC. To arrive at a suitable formulation for plate height in GLGC, we must first recognize that the local plate height, H, will change with position down the gradient column because of the k-dependence of the mass transfer resistance contributions. Furthermore, as has been stressed in detail by Giddings (*6*), experimentally one does not measure the local plate height, but rather the apparent plate height, $\hat{H}$. These two quantities, H and $\hat{H}$, cannot be equated because of the existence of nonuniform conditions (in most cases, of pressure, and in this work, of pressure and k) down the column.

To evaluate the effect of these column nonuniformities on $\hat{H}$, Giddings (*5*) recommends use of the formula (his Equation 10)

$$\hat{H} = L\,\frac{\left[\int_0^L \frac{H\,dx}{R_f{}^2u^2}\right]}{\left[\int_0^L \frac{dx}{R_f u}\right]^2} \quad (16)$$

However; in GLGC, H, R_f, and u all vary with x; which leads to an overly complicated integral to evaluate. We have thus adopted an approximate procedure which is somewhat different than that of Giddings.

Following a general derivation of the classical (noncoupling) plate height equation, such as has been outlined in part by Dal Nogare and Juvet (*3*), for the gradient column we arrive at

$$H = A + \frac{B}{u} + C_l u + C_g u = A + \frac{B}{u} + c_1\frac{d_l{}^2}{D_l}\frac{k_o + \alpha x}{(1 + k_o + \alpha x)^2}\,u + c_2'\frac{d_g{}^2}{D_g}\frac{(k_o + \alpha x)^2}{(1 + k_o + \alpha x)^2}\,u \quad (17)$$

where A, B, c_1, and c_2' are constants, D_g and D_l are solute diffusion coefficients in the gas and liquid phases, respectively, and d_g and d_l are the respective gas and liquid film thicknesses. The C_g term in this equation is due to Jones (*10*). More recent work by Giddings (*4*) and Perrett and Purnell (*13*) has shown the inadequacy of such a k-dependence of the C_g term. They suggest that the gas phase mass transfer resistance contribution to H is rather given by an equation of the form

$$C_g = \left[\left(0.5 - \frac{0.1}{1 + k} + f(V_l)\right]\frac{d_p{}^2}{D_g} \quad (18)$$

where d_p is the mean solid support particle diameter and $f(V_l)$ represents a liquid phase maldistribution function. For the sake of completeness, in this work we will study the effect of gradient liquid loading on both the Jones and the Giddings–Purnell C_g terms.

With the gradient column, d_l, d_g, c_2', $f(V_l)$, and u all vary with x. To simplify Equation 17, we employ mean values for these parameters, $\bar{d}_l$, $\bar{d}_g$, $c_2 = \bar{c}_2'$, and $f'(V_l)$, some average value for the maldistribution function. Furthermore, we assume that velocity gradients in the column are negligible such that $u \neq u(x)$. Incorporating these approximations into Equation 17 and multiplying through by dx, we have

$$H\,dx = (A + B/x)dx + \frac{c_1\bar{d}_l{}^2u}{D_l}\frac{k_o + \alpha x}{(1 + k_o + \alpha x)^2}\,dx + \frac{c_2\bar{d}_g{}^2u}{D_g}\frac{(k_o + \alpha x)^2}{(1 + k_o + \alpha x)^2}\,dx$$

or

$$+\left[\left(0.5 - \frac{0.1}{1 + k_o + \alpha x}\right) + f'(V_l)\right]\frac{d_p{}^2}{D_g}\,u\,dx \quad (19)$$

where the "or" emphasizes the alternative expressions for the C_g terms.

Integration of Equation 19 and algebraic simplification of the result leads to an expression for the apparent (observed) plate height:

$$\hat{H} = A + B/u + \frac{c_1\bar{d}_l{}^2u}{D_l}\left[\frac{1}{\alpha L}\ln\left(\frac{\alpha L + k_o + 1}{k_o + 1}\right) - \frac{1}{(\alpha L + k_o + 1)\,(k_o + 1)}\right] + \frac{c_2\bar{d}_g{}^2u}{D_g}\left\{\frac{1}{\alpha L}\left[\frac{(\alpha L + k_o + 1)^2 - 1}{\alpha L + k_o + 1} - \frac{k_o(k_o + 2)}{k_o + 1} - 2\ln\left(\frac{\alpha L + k_o + 1}{k_o + 1}\right)\right]\right\}$$

or

$$+\frac{d_p{}^2u}{D_g}\left[0.5 - \frac{0.1}{\alpha L}\ln\left(\frac{1 + k_o + \alpha L}{1 + k_o}\right) + f'(V_l)\right] \quad (20)$$

For a linear gradient, $\alpha = -k_o/L$, and

$$\hat{H} = A + B/u + \frac{c_1\bar{d}_l{}^2u}{D_l}\left[\frac{\ln(1 + k_o)}{k_o} - \frac{1}{k_o + 1}\right] + \frac{c_2\bar{d}_g{}^2u}{D_g}\left[\frac{k_o + 2}{k_o + 1} - \frac{2}{k_o}\ln(1 + k_o)\right]$$

or

$$+\frac{d_p{}^2u}{D_g}\left[0.5 - \frac{0.1}{k_o}\ln(1 + k_o) + f'(V_l)\right] \quad (21)$$

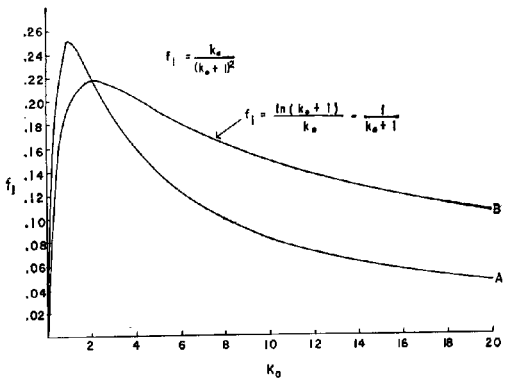


Figure 3. Comparison of liquid phase mass transfer resistance on GLGC column and regular column

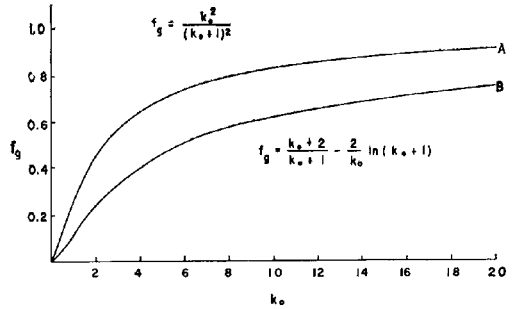


Figure 4. Comparison of Jones-type gas phase mass transfer resistance on GLGC column and regular column

Giddings-Purnell term similar, but varies between 0.4 and 0.5

It should be pointed out that when no gradient exists—i.e., when $\alpha = 0$—application of l'Hopital's rule (*12*) to Equation 20 reduces it to the familiar form

$$H = A + B/u + \frac{c_1 d_i^2 u}{D_l}\frac{k_o}{(1+k_o)^2} + \frac{c_2 d_c^2 u}{D_g}\frac{k_o^2}{(1+k_o)^2}$$

or

$$+ \frac{d_p^2 u}{D_g}\left[\left(0.5 - \frac{0.1}{1+k_o}\right) + f(V_l)\right] \quad (22)$$

Equations 21 and 22 are compared graphically in Figures 3, 4, and 5. In Figure 3, the retention dependence of the regular and gradient column liquid phase mass transfer resistance terms are displayed as a function of k_o. The term for the GLGC column exhibits a broader maximum at a higher k_o value but decreases less sharply than the ordinary column with increasing k_o. This result is not unexpected for initially heavily loaded columns. Two effects are working to counteract each other. Because the amount of liquid decreases from the beginning to the end of the column, the front of a peak is always moving faster than its tail. This results in a broader peak and lower efficiencies. However, the peak is always moving into a region of the column where the liquid mass transfer resistance term is less significant. The latter effect wins out for the peaks of low retention; the first effect predominates for compounds of higher k.

In Figure 4, the corresponding Jones-type gas phase mass transfer resistance terms are plotted *vs.* k_o. These curves indicate that a gradient column will have less contribution to the overall plate height from the gas phase term than would a regular column coated with an amount of stationary liquid corresponding to k_o. The physical significance of this result is not obvious. For a gradient column of overall low liquid loading, the curves indicate that for all solutes the gradient column would perform more efficiently than a regular column corresponding to k_o. The analogous plot of the Giddings-Purnell type C_g term is quite similar in shape to the Jones-type plot except $f_g(k)$ varies between 0.4 and 0.5 instead of 0 to 0.5. For any k_o such that $0 < k_o < \infty$, the curve for the gradient column is below that for the regular column, again indicating more efficient performance of C_g-controlled gradient columns.

The overall dependence of the apparent GLGC plate height on k_o for a wide range of liquid loadings is presented in Figure 5. The ordinate for the curve with the ratio of liquid to gas mass transfer resistance term coefficients, $r = 100$, is $\times 10^{-1}$. These curves pass through the same general sequence as the mass transfer terms on ordinary columns as liquid or gas mass transfer resistance begins to predominate. As the liquid phase term overpowers the gas phase term (as r increases), a maximum begins to appear which shifts to progressively lower k_o values until it stops at $k_o = 2.2$ (at $k = 1$ for regular columns).

The above considerations are ultimately based on manipulations with the rate equation itself. Giddings' treatment (*5*) is based on the observation that

$$H = L\frac{\sigma^2}{t_r^2} \quad (23)$$

where σ is the standard deviation of the peak under consideration (expressed in the same units as t_r). Equation 16, which is readily derived from Equation 23, is most often used to generate the correction factors ("*f*" factors) which account for the discrepancy between the observed and the local plate height. However, the effect of the k gradient on plate height should not be considered as a correction. The local plate height changes with position; Equation 21 gives the observed plate height.

One of the simplifying assumptions invoked above involved the neglect of velocity gradients down the column. In reality, of course, pressure gradients do exist in all gas chromatographic columns. An exact description of their effect could be obtained if the complete Equation 16, where H, R_f, and u all vary with x, was integrated. An approximate measure of these corrections can be achieved by analogy with regular columns; thus,

$$\bar{H} = A + \left\{\frac{B_*}{p_o \bar{u}_o} + \frac{c_2 \bar{d}_g^2 p_o \bar{u}_o}{D_g^\circ}\left[\frac{k_o+2}{k_o+1} - \frac{2}{k_o}\ln(1+k_o)\right]\right.$$

or

$$\left. + \frac{d_p^2 p_o \bar{u}_o}{D_g^\circ}\left[0.5 - \frac{0.1}{k_o}\ln(1+k_o) + f'(V_l)\right]\right\} f_1 + \left\{\frac{c_1 \bar{d}_l^2 u_o}{D_l}\left[\frac{\ln(1+k_o)}{k_o} - \frac{1}{1+k_o}\right]\right\} f_2 \quad (24)$$

where $f_1 = \frac{(a^2+1)f_2}{2} = \frac{9}{8}\frac{(a^4-1)(a^2-1)}{(a^3-1)^2}$

and $f_2 = \frac{3}{2}\frac{a^2-1}{a^3-1} = j$

Resolution in GLGC. Resolution, R, of two closely-spaced peaks can be defined (*8*) by

$$R = \frac{t_2 - t_1}{\sigma} \quad (25)$$

where t_i is the retention value and σ is the standard deviation (in units of t_i) of the peaks under consideration, assuming $\sigma_1 = \sigma_2 = \sigma$. When $R = 4$, resolution is 97.7% complete; 99.9% resolution is indicated by $R = 6$. For the second (later) peak under considera-

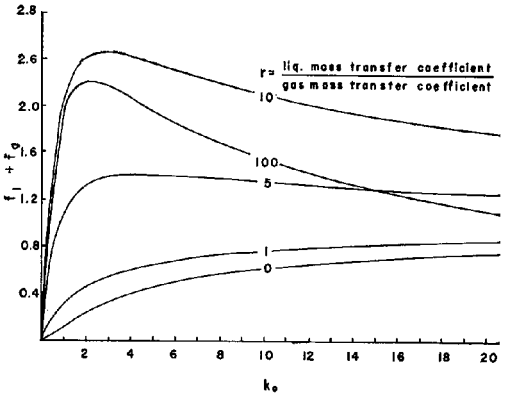


Figure 5. Dependence of GLGC theoretical plate height on partition ratio

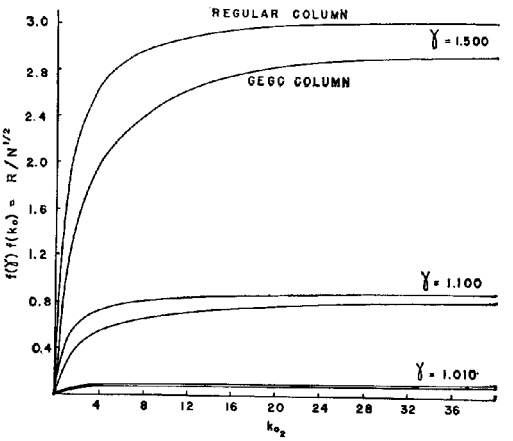


Figure 6. Dependence of resolution on partition ratio on GLGC and regular columns of same efficiency

tion, the observed number of theoretical plates, $\hat{N}$, is

$$\hat{N}_2 = \hat{N} = \frac{L}{\hat{H}_2} = 16\left(\frac{t_r}{w}\right)^2 = \left(\frac{t_2}{\sigma}\right)^2 \quad (26)$$

From Equation 3,

$$t_i = t_m(1 + k_i) \quad (27)$$

At any point down the gradient column,

$$t_r = t_m(1 + k_o + \alpha x) \quad (28)$$

Rearranging Equation 26, using the retention time for the second peak,

$$\sigma = \frac{t_m(1 + k_{o_2} + \alpha_2 x)}{\sqrt{\hat{N}}} \quad (29)$$

Substituting Equation 29 into Equation 25,

$$R = \sqrt{\hat{N}}\left(1 - \frac{1 + k_{o_1} + \alpha_1 x}{1 + k_{o_1} + \alpha_2 x}\right) \quad (30)$$

Multiplying through by $(1 + k_{o_1} + \alpha_2 x)\, dx$, we have

$$\int_0^L \frac{R}{\sqrt{\hat{N}}}\, dx = \int_0^L \frac{(k_{o_2} - k_{o_1}) + (\alpha_2 - \alpha_1)x}{(1 + k_{o_2} + \alpha_2 x)}\, dx \quad (31)$$

On integration and evaluation,

$$R = \frac{\sqrt{\hat{N}}}{\alpha_2 L}\left[L(\alpha_2 - \alpha_1) + \frac{(\alpha_2 - \alpha_1) + \alpha_1 k_{o_2} - \alpha_2 k_{o_1}}{\alpha_2} \ln \times \left(\frac{1 + k_{o_2} + \alpha_2 L}{1 + k_{o_2}}\right)\right] \quad (32)$$

Again, for a linear gradient $\alpha_i = -k_{o_i}/L$. Thus

$$R = \sqrt{\hat{N}}\left[\left(1 - \frac{k_{o_1}}{k_{o_2}}\right)\left(1 - \frac{\ln (1 + k_{o_2})}{k_{o_2}}\right)\right] \quad (33)$$

Recognizing that the relative volatility (relative retention), γ, is

$$\gamma = k_{o_2}/k_{o_1},$$

$$R = \sqrt{\hat{N}}\left(\frac{\gamma - 1}{\gamma}\right)\left(1 - \frac{\ln (1 + k_{o_2})}{k_{o_2}}\right) \quad (34)$$

For ordinary columns (*2*),

$$R = \sqrt{\hat{N}}\left(\frac{\gamma - 1}{\gamma}\right)\left(\frac{1 + k_{o_2}}{k_{o_2}}\right) \quad (35)$$

Application of l'Hopital's rule to Equation 32 allows evaluation of R in the limit as $\alpha_2 \rightarrow \alpha_1 \rightarrow 0$:

$$R = \sqrt{\hat{N}}\left(\frac{k_{o_2} - k_{o_1}}{1 + k_{o_2}}\right)$$

which is equivalent to Equation 35.

Figure 6 shows the variation of R with k_{o_2} for two peaks of relative retention γ. In this plot, resolution in GLGC which is proportional to

$$\left(\frac{\gamma - 1}{\gamma}\right)\left(1 - \frac{\ln (1 + k_{o_2})}{k_{o_2}}\right) = f(\gamma)\, f(k_o)$$

For a given $\sqrt{\hat{N}}$ constant in Equation 34, is compared with resolution on an ordinary column of k_{o_2} and the same $\sqrt{\hat{N}}$, which is proportional to

$$\left(\frac{\gamma - 1}{\gamma}\right)\left(\frac{k_{o_2}}{1 + k_{o_2}}\right) = f(\gamma)\, f(k_o)$$

Figure 6 reveals that for two components of some relative retention γ, a larger number of theoretical plates is needed on the GLGC column to achieve the same resolution as obtained on an ordinary column. Conversely, for two columns of equal efficiency, the gradient column will offer poorer resolution than the ordinary column. In general, more efficient operation will be realized on the GLGC column than on a heavily loaded regular column, at least for components of not-too-large partition ratio, because, as discussed above, the components will spend most of their time in regions of progressively lesser liquid loading. The increase in efficiency thus obtained will, in general, overcome the opposing effect brought about by the velocity differential between peak front and tail. Thus the GLGC column will provide resolution better than, or about the same as, the regular column of k_{o2}.

The curves also show that as the difficulty of separation increases (γ decreases to 1.0000), the gradient column performance will approach that of the ordinary column for the same efficiency.

EXPERIMENTAL

A gas chromatograph assembled in this laboratory was used for all measurements. A glass vapor jacket was used as a thermostat, through which was circulated water from a constant temperature bath. The column and detector temperature was maintained at 45.0 ± 0.1° C. The injection port temperature was independently heated to 120° C.

The flow-through thermistor thermal conductivity cell used has been described previously (*11*). All measurements were made with a Leeds and Northrup Speedomax H recorder with a 2 inch/minute chart speed.

Inlet pressures were measured in psig with a calibrated U. S. pressure gauge. Column outlet pressure was always atmospheric. Helium carrier gas flow rates were measured with a soap bubble flow meter.

Phillips Hydrocarbon Blend No. 42 was used in all experiments. Generally, 5 μl. of vapor was sufficient sample. The minor components of the standard blend (total present in 0.23 wt. %) are at a nondetectable level. The major components are propane (hereafter abbreviated C_3, comprising 2.2 wt. % of the blend), isobutane (iC_4, 8.2%),

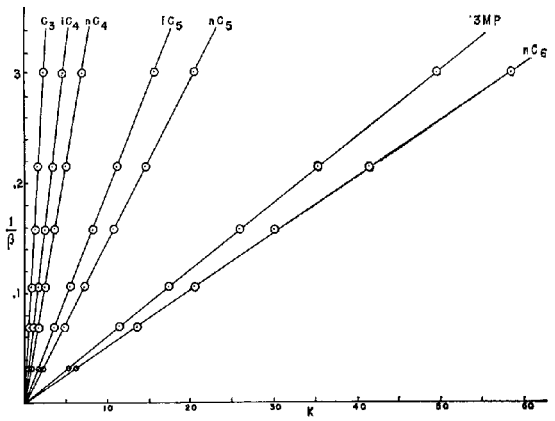


Figure 7. Dependence of $1/\beta = V_l/V_m$ on partition ratio

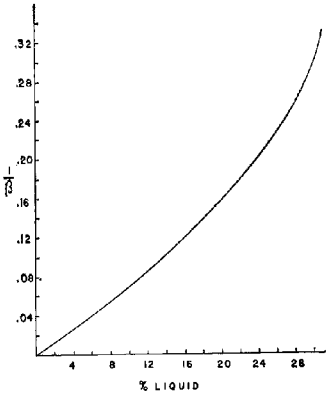


Figure 8. Dependence of $1/\beta = V_l/V_m$ on liquid loading

n-butane (nC_4, 20.7%), isopentane (iC_5, 13.0%), *n*-pentane (nC_5, 15.0%), 3-methylpentane (3MP, 9.6%), *n*-hexane (nC_6, 12.0%), and *n*-heptane (nC_7, 19.2%). Measurements were made on all detectable components except nC_7.

The columns used in this work (see below) were all prepared from squalane (Eastman No. 7311) and 80/100 mesh Chromosorb P, and packed by vertical tapping into 0.25-inch o.d. copper tubes. Minimal size glass wool plugs held the packing in place. All columns were conditioned at 45.0° C. for at least 12 hours under a high flow of helium.

Packing materials were prepared by the addition from a buret of a standard squalane–CH_2Cl_2 solution to a weighed amount of Chromosorb P in a CH_2Cl_2 slurry, with constant stirring. The solvent was evaporated with stirring to apparent dryness at room temperature, and the packing was completely dried on a steam bath until the odor of the CH_2Cl_2 solvent could no longer be detected. The final packing was checked by weighing to obtain the exact composition.

Several ordinary squalane columns were evaluated to establish operating conditions and obtain retention and resolution values and column efficiencies for comparison with the gradient columns. Columns 112 cm. long containing 0, 5.0, 10.0, 15.0, 20.0, 25.0, and 30.0 wt. % squalane on 80/100 mesh Chromosorb P were prepared.

Two gradient columns were studied. Because of experimental difficulties in making a truly continuous gradient column, the best approximation to a continuous gradient was employed—a step function consisting of a large number of steps. The first gradient column containined 0.700 gram of each packing, in 2.0 wt. % increments ranging from 0 to 30% (i.e., 0, 2.0, 4.0, . . . , 28.0, and 30.0 wt. %). These packings were prepared in small quantities as described above. Each was weighed out (0.700 gram) and packed one by one into a 0.25-inch o.d. copper tube somewhat longer than necessary, with considerable vertical tapping after each addition. The column was then trimmed down to a position sufficiently above the top of the packing to allow a minimal size glass wool plug to be inserted; the final length was 114 cm. As discussed below, this column provided a nonlinear gradient in k (see Figure 9).

After subsequent experiments and calculations, a second approximation to a linear gradient column was prepared. In this column, 0.700 gram of each of the following packings were placed one after another into the column, which ended up being 110 cm. long: 30.6, 30.0, 29.4, 28.5, 27.3, 25.9, 24.5, 22.8, 20.8, 19.0, 16.8, 14.3, 11.4, 8.1., 4.9, and 0 wt. % squalane (see Figure 15).

RESULTS AND DISCUSSION

Regular Columns. The regular columns studied behaved normally. A plot of $\beta = V_m/V_l$ *vs.* % liquid was quite similar to that of Dal Nogare and Chiu (*2*) (and thus not reproduced here), who studied Nujol–Chromosorb P columns.

With a column at 45.0° C. containing only Chromosorb P (straight from the bottle), an unexpectedly large amount of adsorption was observed: in specific retention values, C_3 and C_4's, 0.41 cc./gram of Chromosorb P; C_5's, 1.16 cc./gram; 3MP, 3.20 cc./gram; nC_6, 3.59 cc./gram. Whatever the nature of the adsorption sites, they are rendered completely innocuous by coating with squalane. Plots of partition ratio, k, *vs.* % liquid passed through the origin for all compounds studied, which is as good a test as any for verifying the absence of adsorption. Further, linear plots of ln V_g^0 (ln of the specific retention volume) *vs.* the number of carbon atoms for the *n*-hydrocarbons were identical on the gradient column and on the regular columns, indicating that the gradient columns were entirely free from adsorption. It is apparent that a vapor phase liquid transfer mechanism such as described by Hildebrand and Reilley (*7*) is occurring to a slight extent on the gradient columns.

Figure 7 presents k as a function of $1/\beta = V_l/V_m$. This quantity was used as ordinate rather than % liquid or V_l since these latter two quantities are not linearly related to k when V_m and/or the packing weights and densities in the different columns are unequal. k can be related to a % liquid value using Figure 8. These two curves show why % liquid or V_l are not linearly proportional to k. Two plots were used rather than merely one involving k and β because they could be used to obtain a % liquid value from a k value with greater accuracy, especially at low β and high k.

Measurements of column efficiency and resolution of three pairs of compounds were made on these columns for comparison purposes, as discussed below (see Figures 11 and 13). The efficiency measurements can be summarized in a plot of H_{min} *vs.* k. These curves were very similar to those obtained by Dal Nogare and Chiu (*2*) and are therefore not reproduced here. In passing from high to low liquid loadings, the curves pass through a deformation from a curve similar to curve *A* in Figure 3 to one similar to curve *A* in Figure 4, as in the transformation displayed in Figure 5.

Gradient Columns. The first gradient column studied was constructed early in this work on the assumptions that the packing densities of a wide range of liquid loadings were more or less equal, and that all V_m were the same, such that k was linearly related to V_l. Equal weights of packings from 0 to 30.0 wt. % squalane, in 2.0% increments, were used to prepare the column.

In reality, the difference in packing densities of the component packings leads to a plot of V_l (or % liquid) *vs.* x, the distance down the column, which is slightly concave toward the x-axis.

The second, and far more serious incorrect assumption, causes a nonlinear gradient in k, as shown in Figure 9.

Table I. Nonlinear Gradient Column

Compd.	k_o	$k_{theor.}$	$k_{exptl.}$
C_3	2.69	1.35	0.95
iC_4	5.02	2.51	2.00
nC_4	7.35	3.68	2.97
iC_5	17.8	8.90	6.72
nC_5	21.9	11.0	8.81
3MP	53.7	26.9	21.2
nC_6	66.5	33.3	25.2

Table II. Nonlinear Gradient Column

Compd.	k	H_{min}	Equivalent % liquid
C_3	0.95	1.88 mm	14.1
iC_4	2.00	1.99	16.5
nC_4	2.97	1.84	16.4
iC_5	6.72	1.67	18.0
nC_5	8.81	1.49	17.7
3MP	21.2	1.36	25.4
nC_6	25.2	1.27	25.7
			19.1

In this plot, as in Figure 15 to follow, a smooth curve is drawn through the midpoints of the x-increments. It should be remembered, however, that the column only approximates this smooth curve, describing actually a step-function.

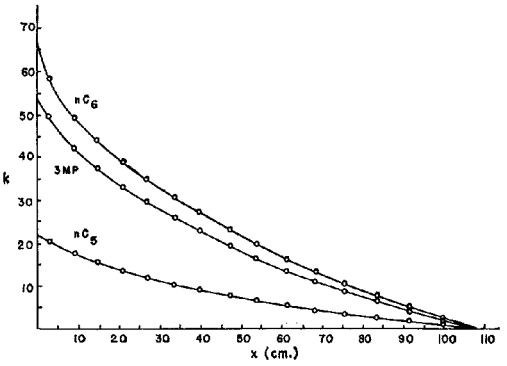
No theoretical development was undertaken for $k - x$ curves of the shape in Figure 9. However, the data obtained on this column are useful at least in so far as it is demonstrated that the equations for a truly linear gradient do have power to discriminate between linear and nonlinear gradients.

Table I lists the partition ratios extrapolated to $x = 0$ in Figure 9 (k_o values), along with the k predicted from Equation 14 and the experimental value of k. The experimental values are in clear disagreement with those predicted for a linear gradient column of initial partition ratios k_o. As anticipated from inspection of the shapes of the curves in Figure 9, the measured k values are about 30% lower than would be found on a linear gradient column.

From Figures 7 and 8, these k values correspond to those on a regular 16.9% squalane column. The mean % squalane on the nonlinear gradient column is 15.0%.

Comparison of the efficiency results on the gradient column with theory (Equation 21) is achieved through a plot of H_{min} *vs.* k_o, Figure 10. The same general shape is obtained as with the linear gradient column (see Figure 16). However, the position of the maximum is shifted to higher k_o values. Further, at high k_o the curve levels out more rapidly than with the linear gradient. This is apparently related to the fact that on the gradient columns, the column acts toward compounds of higher k_o as if it were more heavily loaded. A more quantitative measure of this can be determined as described below.

From the aforementioned plot of H_{min} *vs.* k for the regular columns, values of H_{min} were taken at each % liquid at several k's of interest. These values were then plotted *vs.* % liquid, as exemplified in Figure 11. To compare the gradient with the regular columns, the measured values of H_{min} and k on the GLGC column are used with Figure 11 to determine the equivalent % liquid



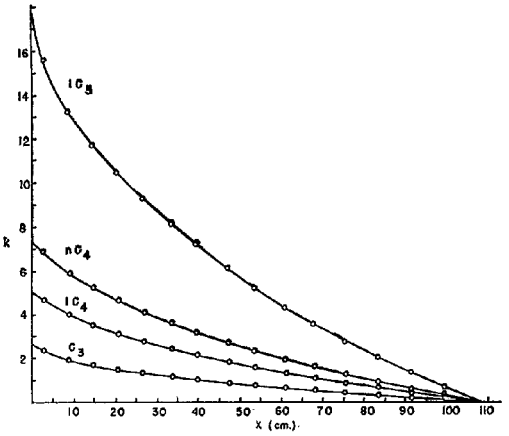


Figure 9. Schematic diagram of partition ratio on the nonlinear GLGC column

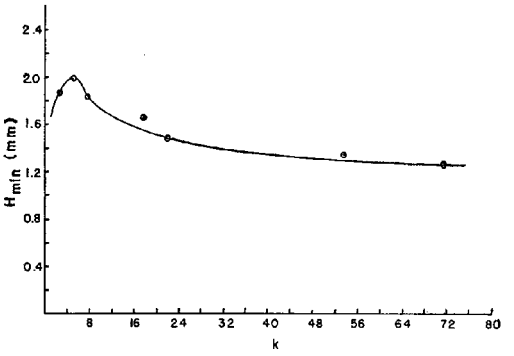


Figure 10. Dependence of theoretical plate height on partition ratio on the nonlinear GLGC column

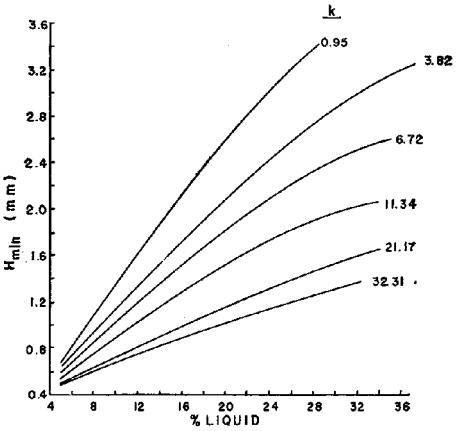


Figure 11. Dependence of theoretical plate height on liquid loading

A: $R = \sqrt{N}\left(\frac{\gamma-1}{\gamma}\right)\left(\frac{k_2}{k_2+1}\right)$

B: $R = \sqrt{N}\left(\frac{\gamma-1}{\gamma}\right)\left(1-\frac{\ln(k_2+1)}{k_{e_2}}\right)$

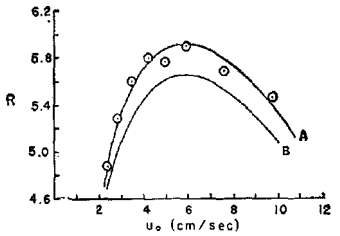


Figure 12. Resolution on nonlinear GLGC column

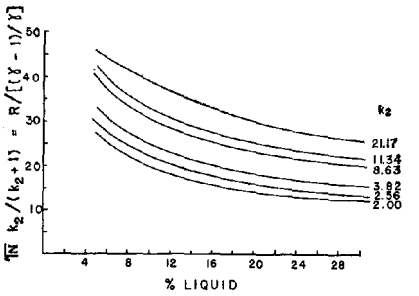


Figure 13. Dependence of resolution on liquid loading

corresponding to H_{min}. The results are given in Table II.

From these data it is apparent that as k increases, the column acts with respect to efficiency as though it were of progressively higher liquid loading. This explains the shape of Figure 10. The source of this apparent increase in equivalent liquid loading is the mechanisms discussed above.

Similar results were obtained with the resolution measurements. As expected, agreement on the nonlinear gradient column is not found with theory (Equation 34). However, as will be seen below, neither is good agreement always obtained with the linear gradient column. In Figure 12, resolution R of iC_4 and nC_4 is presented as a function of carrier gas outlet velocity, u_o. Curve A is a plot of Equation 34 using measured values of $\sqrt{N}$ (i.e., of $\sqrt{\bar{N}}$) and γ, and a value of k_{e_2} from Figure 9. Curve B is a plot of Equation 35, which was derived for regular columns, using the same $\sqrt{N}$ and γ, but the k_2 measured on the gradient column.

Comparable results were obtained for all three compound pairs (iC_4–nC_4, iC_5–nC_5, and 3MP–nC_6). In each case, Equation 34 gave too conservative a prediction of resolution and Equation 35 agreed with experiment. As discussed below, this is probably accounted for by the difference in the true number of theoretical plates, N, and the measured (apparent) number, $\hat{N}$, on the gradient columns.

To determine equivalent liquid loadings on the gradient columns, a plot of $\sqrt{\hat{N}}[k_2/(k_2+1)]$ *vs.* % liquid at several k_2's of interest was constructed from data extracted from Figure 11. A family of curves was obtained, as in Figure 13. To use these curves, $R/[(\gamma-1)/\gamma]$, which is equal to $\sqrt{\hat{N}}[k_2/(k_2+1)]$, is calculated from the experimental values of R and γ. This value is then used with the curve for the appropriate k_2 in Figure 13 to determine the equivalent % liquid. Table III lists the results. As with the efficiency measurements, as k increases, the column acts as though it were of increasingly higher liquid loading.

The form of the curves in Figure 13 is easily rationalized when they are broken down into their components: $\sqrt{\hat{N}}$ will decrease with increasing V_l, somewhat more rapidly at first. Since $k\beta = K$, the partition coefficient, $k_2/(k_2+1) = K_2/(K_2+\beta)$. As V_l increases, β decreases and the whole term will increase; but the increase is less rapid than the decrease in $\sqrt{\hat{N}}$. The product of the two curves is therefore as in Figure 13.

The second gradient column was designed to have a linear gradient in k. Again, for experimental reasons, a step-wise approximation to a continuous linear gradient was employed. First, a k_o value was arbitrarily chosen, and a straight line drawn on Figure 9 from this k_o to $k = 0$ at $x = L$. At the midpoint of each x-increment (taking differences in packing density into account), the k value was read off. With the aid of Figures 7 and 8, these k values were converted into % liquid values, and then into V_l's, knowing that 0.700 gram of each was to be used.

The V_l values correspond to the weight per cents of squalane noted above. The column is diagrammed in Figures 14 and 15. While it is decidedly nonlinear in V_l, k does vary linearly with x.

Using the linear GLGC column, the experimental results are in good agreement with theory. Table IV demonstrates the prediction of partition ratios using Equation 14, with the coefficient equal to 0.500 ($a = 1$) (or Equation 15). These partition ratios correspond to an equivalent regular column containing 20.6 wt. % squalane. The true mean % squalane on the linear gradient column is 21.0%.

A 50% decrease in partition ratio is highly desirable if it is not accompanied by a comparable loss in column efficiency and resolving power. Figures 16 and 17 show the variation of efficiency with partition ratio. This linear gradient column has a ratio of liquid to

Table III. Equivalent Liquid Loadings on Nonlinear GLGC Column

Compound pair	R_{max}	γ	Equivalent % liquid	Eq. % − 15.0%
iC_4–nC_4	6.10	1.485	15.8%	+0.8%
iC_5–nC_5	5.90	1.311	18.5	+3.5
3MP–nC_6	4.44	1.185	25.6	+10.6

Table IV. Prediction of k on the Linear GLGC Column

Compd.	k_o	$k_{theor.}$	$k_{exptl.}$
C_3	2.47	1.24	1.21
iC_4	5.10	2.55	2.56
nC_4	7.55	3.78	3.82
iC_5	17.1	8.55	8.63
nC_5	22.5	11.3	11.3
3MP	54.8	27.4	27.3
nC_6	64.3	32.2	32.3

Table V. Linear Gradient Column

Compd.	k	H_{min}	Equivalent % liquid
C_3	1.21	2.06 mm	15.9
iC_4	2.56	2.18	19.2
nC_4	3.82	1.92	18.2
iC_5	8.63	1.62	19.2
nC_5	11.3	1.42	23.3
3MP	27.3	1.19	23.9
nC_6	32.3	1.08	22.1
			20.9

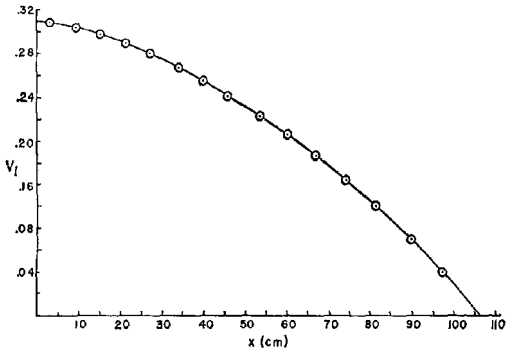


Figure 14. Schematic diagram of liquid loading on linear GLGC column

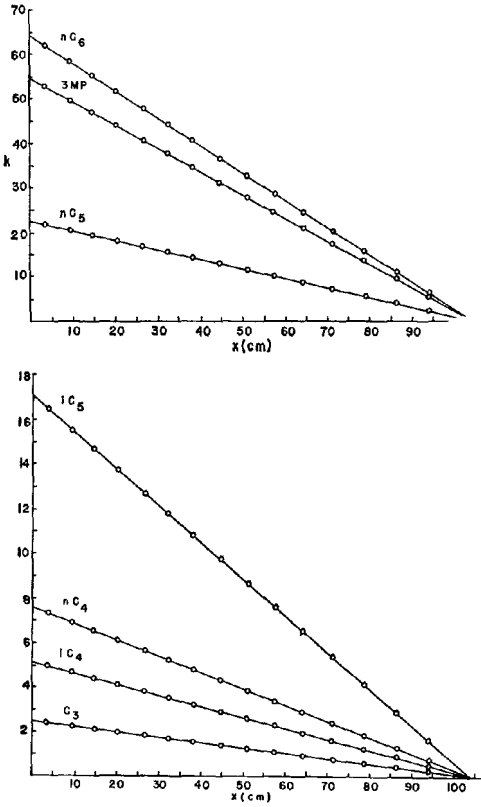


Figure 15. Schematic diagram of partition ration on linear GLGC column

gas mass transfer resistance coefficients of about 8 or 9, as a comparison of the two figures indicates. This corresponds to an overall equivalent column containing about 20 wt. % squalane. The experimental follows the theoretical curve quite well. From Figure 11, it is seen that on the average the column acts equivalently to a regular column composed of 20.9% squalane, which nearly coincides with the true mean wt. %. Table V gives the data.

It has now been demonstrated, theoretically and experimentally, that the partition ratio is decreased by 50%; i.e., the retention of the linear gradient column with an initial 30.6 wt. % squalane has been reduced to that corresponding to an overall regular 20.6% column. Further, column efficiency (which of itself has little utilitarian significance) on the GLGC column is comparable to that on the regular 21% column. The obvious question now is, why not use a regular 21% column to achieve the separation?

If resolution on the gradient column were equivalent to that on a regular column constructed of its mean liquid loading (21% in this case), there would be no point to the gradient column. However, resolution on the GLGC column is superior to that on a regular 21% column.

The three pairs of compounds, iC_4–nC_4, iC_5–nC_5, and 3MP– nC_6, were used to test Equation 34 and to compare it with Equation 35. Figure 18 presents R as a function of u_o. It is apparent that agreement with Equation 34 improves as k_o increases. Table VI presents the equivalent liquid loadings determined using Figure 14 with the experimental R and γ values.

On this gradient column, for compounds of k_2 < about 24, resolution is superior to that on a regular 21% column. This is shown graphically in Figure 19, which is a plot of the data in Table VI. The trend of the results shown here and the ultimate justification for linear GLGC. Better resolution can be obtained in shorter time on the linear gradient column.

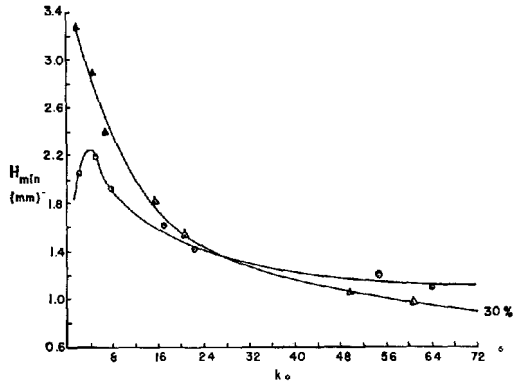


Figure 16. Theoretical plate height on linear GLGC column, compared with that on regular 30% column

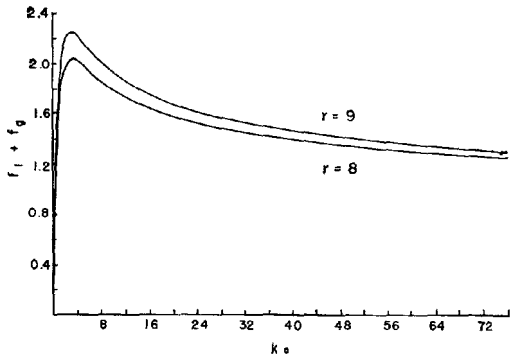


Figure 17. Resolution on linear GLGC column

A: $R = \sqrt{N}\left(\frac{\gamma - 1}{\gamma}\right)\left(\frac{k_2}{k_2 + 1}\right)$

B: $R = \sqrt{N}\left(\frac{\gamma - 1}{\gamma}\right)\left(1 - \frac{\ln(k_{o2} + 1)}{k_{o2}}\right)$

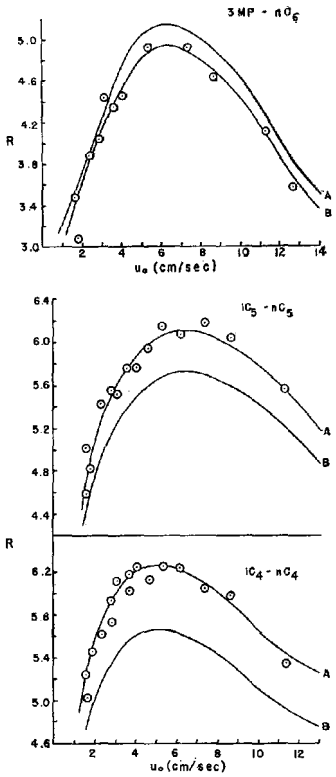


Figure 18. Justification of GLGC

Refer to Table VI

Physically, as the components of the blend move down the column, their resolution as well as their relative velocities increases as they move onto ever more lightly loaded regions of column packing. For compounds of large retention, the resolution does not improve as fast as the relative velocity. This can be visualized through Equation 35 and Figure 11. For a linear gradient and a regular column of the same efficiency, Equation 35 predicts that resolution will always be inferior on the gradient column. This is true. However, in Figure 18, experimental agreement with theory is found only with compounds a of large retention, 3MP and nC_6. As seen in Figure 16, for $k_o <$ about 25, the efficiency of the gradient column is better than that on the regular column.

Another consideration is also relevent. As noted above, the observed plate height is always greater than the actual local plate height because of systematic column homogeneities. This is translated into a difference between the apparent and actual number of theoretical plates. This presumably accounts for the discrepancy between the resolution of the butanes and pentanes predicted on the basis of the measured number of plates and the experimental resolution. If values of N could be used instead of $\hat{N}$, the theoretical curves would be displaced upward and bring the experimental points closer to curve B. It is apparent that as k_o increases, $\hat{N}$ approaches N.

It is fully realized that the resolution gains achieved here are not phenomenal. However, the trends shown in the experimental data are the justification for further study of GLGC.

Another advantage of GLGC should also be pointed out. Because the inlet end of the column is heavily loaded, and since overall solute retention on the gradient column is comparable to that which it would be on a regular column corresponding to the mean liquid loading on the GLGC column, it would seem that at least a two-fold greater sample size and feed volume could be accomodated on the gradient column than on a regular column of liquid loading corresponding to $k_o/2$. This fact should have important consequences in preparative scale gas chromatography.

Certain comparisons can be made with programmed temperature gas chromatography (PTGC). In that technique, solute retention is decreased, column efficiency increased, and resolution correspondingly improved. Strict analogy cannot be drawn because in the gradient loading technique, all solutes experience the same column under the same conditions; in PTGC, the sample components are not all subjected to the same conditions over the course of the whole analysis. The result in PTGC is to provide a mechanism for equally spacing the peaks; GLGC does not do this. Thus, although PTGC is a more powerful technique, GLGC would be more applicable in cases of severe substrate bleeding with increasing temperatures, with temperature-sensitive solutes, and, of course, where one does not have a gas chromatograph equipped for temperature programming.

Table VI. Equivalent Liquid Loadings on Linear Gradient Column

Compd. pair	R_{max}	γ	Equivalent % liquid	Eq. % − 21.0%
iC_4–nC_4	6.25	1.485	17.8%	−3.2%
iC_5–nC_5	6.10	1.311	19.0	−2.0
3MP–nC_6	4.94	1.185	22.3	+1.3

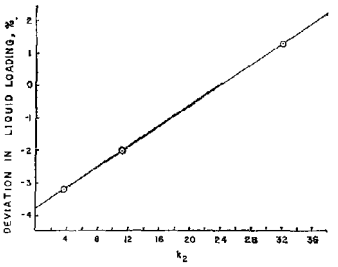


Figure 19. Resolution of GLGC column compared to a regular 21% column

ACKNOWLEDGMENT

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Gas Chromatography of Free Fatty Acids

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▶ **Most free fatty acid homologs and isomers from C_2 through C_{13} can be completely separated with little or no peak tailing on columns made with a polar liquid phase and an acidic additive coated on acid-washed glass microbeads. Washing the glass microbeads with dilute acid and using isophthalic acid in the liquid phase reduces or eliminates the adsorption and dimerization of the fatty acids. The columns can be operated isothermally or with temperature programming up to 180° to 190° C.**

SEPARATIONS of unesterified fatty acids by gas chromatography have been limited by the relatively high boiling points of the acids and by peak tailing which is caused mostly by adsorption on the solid support (*7, 14*). This is especially serious for the higher molecular weight acids which are of biological importance. Consequently, gas chromatographic procedures commonly require the conversion of the fatty acids to methyl esters but the esterification step makes the analytical procedure longer, more tedious, and in some cases it may alter the analytical results (*20*).

Several techniques have been used to reduce or eliminate tailing of free fatty acids. Four main approaches may be discerned. In the first of these, the liquid phase is chosen for its polar or (as in the more successful cases) for its acidic nature. Smith described the separation of the lower fatty acids, up to C_4, using a column of 5% Tween-8 or Carbowax on Celite 545 (*2, 19*), while Hunter, Ortegren, and Pence report separations up to C_8 using 1.5% diethylene glycol adipate on C-22 firebrick (*6*); however, peak tailing remained a serious disadvantage. Recently, McKinney demonstrated a successful separation through C_6 on a column of 20% benzylamine adipate on Chromosorb W (*13*), the maximum column temperature being limited to 125° C. because of liquid phase decomposition.

The second approach, following the suggestion of Martin (*5, 7, 14*), involves the use of a nonvolatile acidic substance as an additive to the liquid phase (*14, 18*). The acidic additive deactivates the adsorptive sites on the solid support and prevents dimerization of the fatty acids. Some of the additives which have been used are the acids stearic, terephthalic, phosphoric, sebasic, and mixtures of long-chain dicarboxylic and tricarboxylic acids (usually known as dimer and trimer acids).

In the third approach, a volatile acidic or polar substance is continuously passed through the column with the carrier gas. Formic acid vapor was used for this purpose and also for the elimination of ghost peaks in subsequent runs (*1*). Water vapor has also been used to prevent tailing of polar substances in general; a steam generator specifically designed for this purpose is commercially available (Wilkens Instrument and Research Co., Walnut Creek, Calif.).

In the fourth approach, the solid support is chosen or modified so that it is less adsorptive. With respect to fatty acids, very little has been reported in this area. Jowett and Horrocks have used 100-micron glass beads coated with 1% polyethylene glycol succinate and 0.4% phosphoric acid (*8*) but the separations were incomplete because of tailing. Kirkland has used Teflon-6 coated with 10% Carbowax 400 to separate formic and acetic acid from an aqueous solution (*11*).

In the present work, a study was made to find a suitable column by using a nonvolatile acid additive with a polar liquid phase and a solid support specifically modified for fatty acids. Several acidic additives, liquid phases, and solid supports were tested. These included (ethylenedinitrilo)tetraacetic acid (EDTA), isophthalic acid, diethylene glycol succinate, Carbowax 20M, and glass microbeads with and without pretreatment. The best column found, based on convenience of preparation, stability, operating temperature range, efficiency, and selectivity was 0.25% Carbowax 20M and 0.4% isophthalic acid coated on 200-micron glass microbeads which were prewashed with dilute acid.

EXPERIMENTAL

Apparatus and Materials. A flame ionization gas chromatograph was used (Model 609, F. & M. Scientific Co., Avondale, Pa.) with a recorder of 1-mv. full scale sensitivity and 1-second pen response. The chromatograph was modified by reducing the volume of the sample vaporization space so that the injected sample was introduced into the column over a shorter time. This was accomplished by inserting a $^1/_8$- × $4^1/_4$-inch copper rod through the exit port of the sample splitter which was then sealed with a silicone gum rubber septum.

Most of the reagents and chemicals used were supplied commercially except for the glass microbeads which were supplied courtesy of Microbeads, Inc., Jackson, Miss. Also some of the 99% pure fatty acids were furnished through the courtesy of the Eastern Regional Utilization Laboratory, USDA, and by Lachat Chemicals, Chicago 43, Ill.

Procedure. A very large number of columns were screened by comparing their performance at optimum operating temperature and carrier gas flow rate. For this initial screening, it was experimentally convenient to use a single column length, 60 cm., and a single test sample, approximately 0.1 μl. of a C_{12} to C_{18} fatty acid mixture, while varying the nature of the column packing. Once a packing was found to be satisfactory or worthy of further testing, the column length was increased depending on the desired analysis time and degree of separation.

The column packings were usually prepared in the standard procedure by dissolving the liquid phase and acidic substance in a volatile solvent, adding the resulting solution to the solid support, and evaporating the volatile solvent with frequent stirring of the mixture and mild heating. The columns were made from $^1/_4$-inch aluminum tubing to which the packing was added in the conventional manner with vigorous tapping along the side of the tube until no more packing was accepted. Most columns were made with glass microbeads, about 52 grams being required for a 2-meter column. In the cases where the glass microbead packing was sticky—i.e., not free flowing—it was introduced in small portions, each portion being pressed with a $^1/_8$-inch stainless steel rod. The ends were plugged with glass wool and the columns were coiled appropriately to fit into the column compartment.

All samples were injected with a 10-μl. Hamilton syringe through the injector port maintained at 250° C. Since most of the injected samples were only a few tenths of a microliter, the injected volume was only approximately known and the peak areas were normalized for quantitative results. On the other hand, the injected samples were quite reproducible as ascertained by the magnitude of the absolute peak areas.

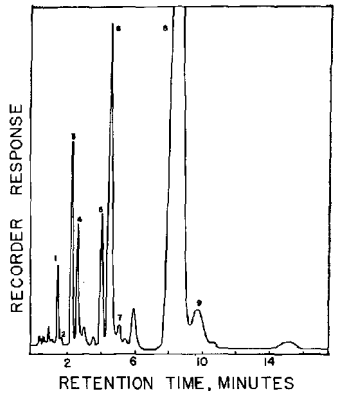

Figure 1. Chromatogram of C_{12} to C_{18} fatty acids

Column, 3 meters, 0.05% DEGS and 0.2% isophthalic acid on 200-micron glass microbeads (acid-washed). Temp. 175° C., He flow rate 80 cc. per minute, sample size 0.1 μl.

Identification of peaks:

1. Lauric
2. Dodecenoic
3. Myristic
4. Tetradecenoic
5. Palmitic
6. Palmitoleic
7. Palmitolenic
8. Oleic
9. Linoleic

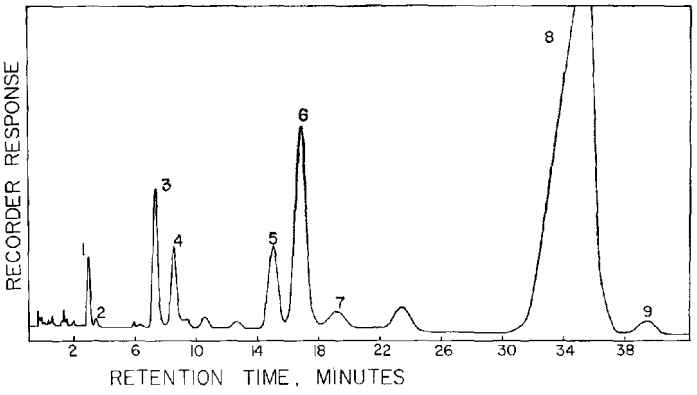

Figure 2. Chromatogram of C_{12} to C_{18} fatty acids

Column, 2 meters, 0.25% Carbowax and 0.4% isophthalic acid on 200-micron glass microbeads (acid-washed). Temp. 180° C., He flow rate 80 cc. per minute, sample size 0.1 μl. Identification of peaks as in Figure 1

RESULTS AND DISCUSSION

The Solid Support. Because of their low surface area and relative inertness, glass microbeads appeared to be the most suitable solid support for fatty acids, especially for those in the higher molecular weight range (*3, 16*); however, the superiority of microbeads over Celite and Firebrick was not easily demonstrated. A valid comparison requires a large number of tests to establish the optimum conditions such as liquid film thickness, column temperature, and column length using each support. Nevertheless, as best as could be determined by using 60-cm. columns of Celite and Firebrick supports coated with nearly optimum amounts of liquid phase and acidic additive, glass microbeads were superior; at operating temperatures below 190° C., the minimum amount of liquid phase which was required to prevent tailing, permitted the elution of acids up to C_{18} in a reasonable time with essentially complete homolog and isomer separation. The Celite and Firebrick columns required higher operating temperatures which were deleterious to the stability of the acidic additive in the liquid phase.

Although the role of glass bead particle size was not clearcut, the optimum particle size based on the successful separation of the higher molecular weight acids was estimated to be about 200 microns (average diameter). The estimate was made by comparing separations on columns which were made with 58-, 200-, and 460-micron glass microbeads, each packing being coated with an amount of liquid phase calculated to result in equal film thickness. These columns which were equivalent in length so that the amount of liquid phase was constant, showed somewhat poorer separations than the 200-micron size. The optimum particle size of glass microbeads is probably determined by the number of contact points between the beads which decreases with bead size and on the total void volume of the column which increases with bead size.

Surface treatments of glass microbead supports for the purpose of decreasing tailing are often ineffective (*3, 17*) or deleterious (*16*). Following the work of Macdonell who reduced tailing of hydrocarbons on porous glass supports (*12*), glass microbeads were treated by refluxing in decanol for several hours. Following this treatment, some of the microbeads were acid-washed (see next paragraph), but the resulting columns showed worse adsorption effects than untreated microbeads. Waterproofing the glass microbeads by treatment with a 1% solution of soluble silicone (Siliclad, Clay Adams, N. Y.) had no effect on column characteristics.

As the microbeads are made from ordinary glass which contains soluble alkali, it seemed important that their surface be made neutral or preferably acidic. Since alkali and basic oxides would be expected to be selectively leached from glass by an acid or neutral solution while the silica component would resist attack, experiments were carried out in which glass beads were rinsed with distilled water or first washed with 1% nitric acid and then rinsed with distilled water. The pH of each rinsing was then determined and used as an indication of washing efficiency and surface pH. It was found that the water rinsings of untreated microbeads had a pH above 9 even after several rinsings over a period of 1 hour. On the other hand, acid washing for a few minutes followed by several water rinsings gave a pH of 6 to 7. The results support the desirability and effectiveness of acid washing —i.e., glass beads are very alkaline and the alkalinity is not easily removable by water.

However, it was difficult to assess quantitatively the effect of acid washing on column life or on the minimum amount of added acidic substance which is required in the liquid phase to prevent tailing; it was merely observed, that unless the microbeads were acid-washed, most preliminary column packings showed tailing of acid peaks.

The Liquid Phase. Several polar liquid phases can be used for the separation of free fatty acids. The two important requirements are high temperature stability, which is desirable for the elution of the higher fatty acids, and polarity, which is desirable for the efficient shielding of adsorption sites on the solid support and for selectivity to fatty acid isomers. In the present study two liquid phases were tested: Carbowax 20M which is a solid at room temperature (a fact that facilitated the packing of thicker liquid film columns) and diethyleneglycol succinate (DEGS) which is typical of the polyester phases recommended for fatty acids.

Both liquids gave similar results, although a somewhat lower amount of DEGS may be used without tailing of the acid peaks. This advantage of DEGS which permits a lower operating temperature is offset, however, by its slightly higher bleed rate near 180° C. and by the difficulty associated with

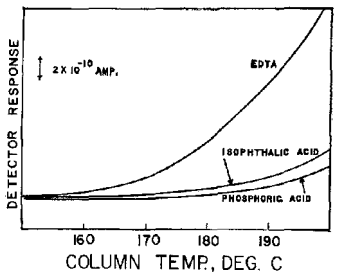

Figure 3. Base lines obtained with different acidic additives

He flow rate 60 cc. per minute. Columns' 60 cm., 0.2% acidic additive and 0.1% Carbowax 20M on acid-washed glass microbeads

packing a sticky material into the column tubing.

In choosing the amount of liquid phase to be used, it was first considered that the optimum would be the lowest amount that could be used without causing adsorption (*3*). This is particularly desirable since it allows a decrease in operating temperature, which is an important consideration for packings containing thermally unstable or sublimable substances such as EDTA and isophthalic acid. This minimum amount was 0.02 to 0.05% by weight depending on the amount and nature of acidic substance added to the liquid phase. A chromatogram typical of such a lightly coated column is shown in Figure 1 obtained with a 3-meter column of 0.05% DEGS and 0.2% isophthalic acid operated at 175° C. In less than 10 minutes there is a fairly good separation of the fatty acid isomers from C_{12} through C_{18}. Similar results were also obtained with columns using Carbowax with isophthalic acid and Carbowax with EDTA. The capacity of these columns was sufficient so that no serious overloading occurred when the sample size was a few tenths of a microliter. This was ascertained by the symmetrical peak shapes—e.g., only the major component (oleic acid) in Figure 2 shows evidence of column overloading.

These very thinly coated packings were short-lived presumably because the liquid phase accumulated at the contact sites between the beads (*4, 9, 10*) thus exposing some uncoated surface which causes tailing. Thus, when the amount of liquid phase was increased to about 0.3–0.4%, and provided a sufficient amount of acidic additive was used, no column deterioration was observed even after operating such columns for more than one month; the increased retention time for C_{18} acids was a reasonable $^1/_2$ hour and the optimum operating temperature was 175° to 185° C., well below the point where column deterioration becomes a problem. Figure 2 shows the chromatogram obtained on such a column with the same sample used in Figure 1.

The Acidic Additive. Several acidic additives were tested for their ability to reduce peak tailing. These included sulfuric, arsenic, phosphoric, phthalic, isophthalic, and (ethylenedinitrilo) tetraacetic acids which were selected for testing either because they have been used previously for this purpose or simply because they appeared promising on the basis of their reported stabilities.

Arsenic acid failed to reduce tailing; phthalic acid was too volatile, producing severe base line noise; and sulfuric acid resulted in unstable and low efficiency columns—i.e., tailing appeared after a few hours' operation. Of the remaining acids, isophthalic was the most satisfactory from the standpoint of column life, followed by EDTA (1–2 weeks' column life) and phosphoric acid (2–3 days' column life). Column life depended largely on the operating temperature. In most cases the operating temperature was 180° C. which is sufficiently high for satisfactory elution of the C_{18} acids while permitting a long column life.

Temperature-programmed base line recordings of EDTA, isophthalic, and phosphoric acid columns are shown in Figure 3. The phosphoric acid–containing column gives a good base line with low bleeding and at the same time such columns are unstable. This may indicate that the instability of phosphoric acid columns is caused by an interaction with the glass microbead surface, rather than by degradation.

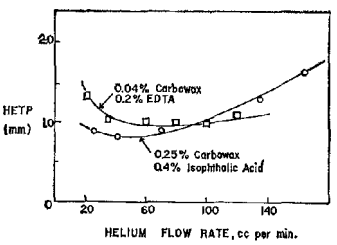

Figure 4. Column efficiency (HETP) vs. flow rate

Columns, 2 meters, temp. 175° C., sample 0.2 μl. of 10% palmitic acid

The optimum amount of isophthalic acid was found to be 0.3 to 0.5% by weight. Although peak tailing was eliminated with as little as 0.05% isophthalic acid, such columns had a relatively short life, 2 to 3 days of operation at 180° C., before peak tailing

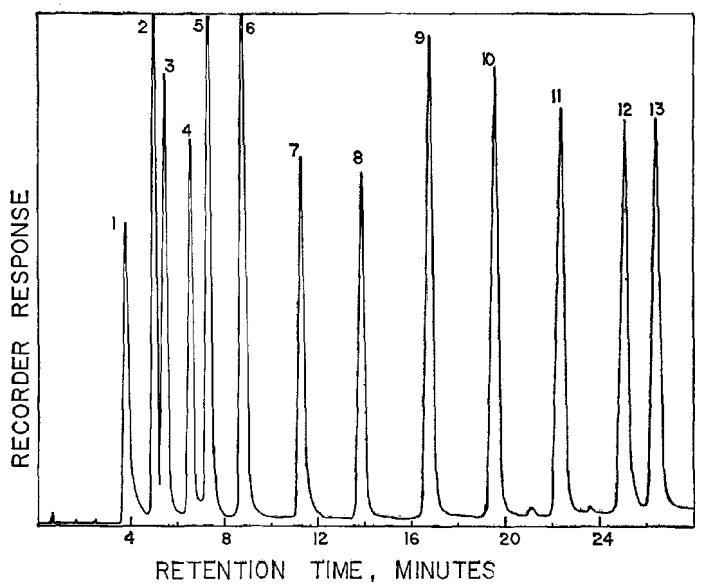

Figure 5. Synthetic mixture of C_2 to C_{11} fatty acids

Column as in Figure 2. Temperature-programmed from 90° to 175° C. at 3.3° C. per minute. Sample 0.2 μl., flow rate 80 cc. per minute

Identification of peaks:

1. Acetic
2. Propionic
3. *iso*-Butyric
4. Butyric
5. *iso*-Pentanoic
6. Pentanoic
7. Hexanoic
8. 2-Ethylhexanoic
9. Octanoic
10. Nonanoic
11. Decanoic
12. Undecanoic
13. Undecenoic

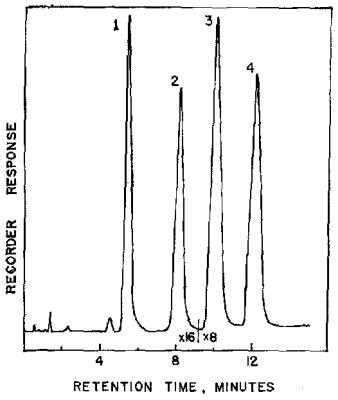

Figure 6. Synthetic mixture of C_{10} to C_{12} fatty acids

Columns as in Figure 2. Flow rate 60 cc. per minute, temperature 150° C., sample 0.1 μl.

Identification of peaks:

1. Decanoic
2. Undecanoic
3. Undecenoic
4. Dodecanoic

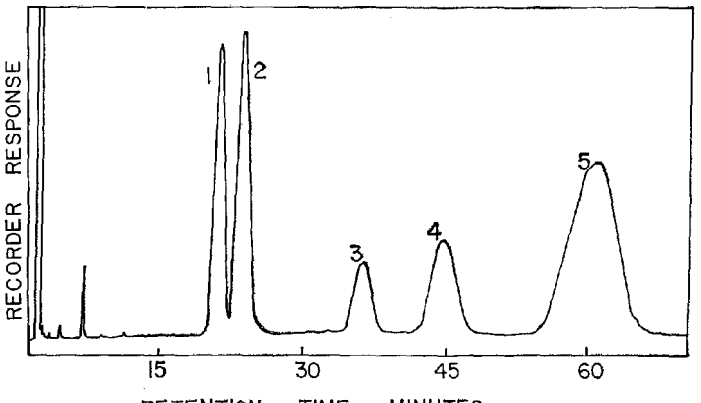

Figure 7. Synthetic mixture of C_{16} to C_{18} fatty acids

Column as in Figure 2. Flow rate 70 cc. per minute, temperature 180° C., sample 0.2 μl. of 50% acetone solution

Identification of peaks:

1. Palmitic
2. Palmitoleic
3. Stearic
4. Linoleic
5. Linolenic

occurred. As in the case for the liquid phase discussed above, this is probably caused by the accumulation of the isophthalic acid at the contact points, with consequent exposure of adsorption sites on the glass microbeads. On the other hand, if more than 0.5% isophthalic acid was used, column efficiencies were somewhat lower, presumably because of increased liquid phase thickness. As much as 1% isophthalic acid was used in one column with only a small decrease in column efficiency.

The acidic additive and the liquid phase were added together as a solution to the solid support, followed by evaporation of the solvent. Isophthalic acid was added as a methanol solution, while EDTA was added in the form of NaH_3EDTA dissolved in hot water. (A 100-ml. volume of hot water dissolves approximately 1 gram of NAH_3-EDTA or its equivalent: 0.5 gram each of Na_2H_2EDTA and H_4EDTA.) In the case of columns containing EDTA, a high conditioning temperature was required, (about 200° C. rather than 170° to 180° C.) to accelerate the redistribution of liquid phase and EDTA on the support (*10*). Most other columns required little or no conditioning indicating that the liquid phase and acidic additive were uniformly distributed. In most cases of stable columns—i.e., columns containing isophthalic acid—once a column was conditioned it did not require reconditioning.

No indication of instrument corrosion was found over a period of several months' continuous use of acid-containing columns.

Column Efficiency. Typical column efficiencies for these columns is equivalent to about 1 mm. of HETP as shown in Figure 4. This is approximately the same value reported by Cooke who worked with glass microbead columns coated with thinner liquid phase films (*8*). The curves in Figure 4 are less flat than those reported by Cooke apparently because of the thicker film of liquid phase. This is also supported by the somewhat higher curvature for the column containing the thicker film (0.5% Carbowax and 0.4% isophthalic acid). Generally, the optimum flow rate was approximately 80 cc. per minute which was chosen for short analysis time with near maximum efficiency.

Typical Separations. In addition to the mixture of C_{12} to C_{18} fatty acids shown in Figures 1 and 2, other separations were made of various synthetic samples prepared from 98 or 99% pure fatty acids. Figure 5 shows a single-run separation of 13 different acids in the range of C_2 through C_{11}, including some unsaturated and branched isomers. Because of the wide molecular weight range of this sample, the run was temperature-programmed. Heptanoic acid was not included in this homologous series because it overlapped with 2-ethylhexanoic acid. Formic acid was also excluded from the mixture since it would not be detectable by the flame ionization detector. Because of the relatively higher polarity and water solubility, the acetic acid peak shows some tailing.

Figures 6 and 7 show the separations of a C_{10} to C_{12} mixture and a C_{16} to C_{18} mixture, respectively. These mixtures were prepared quantitatively. The per cent area of each peak is approximately proportional to the weight per cent composition as shown in Table I which also includes data on a C_{12} to C_{16} mixture; however, the number of runs made were not sufficient to permit calculation of the standard deviation.

In addition to the fatty acids, several carboxylic acids of relatively low molecular weight were tested for separation. These included benzoic, salicylic, acetylsalicylic, lactic, succinic, oxalic, citric, and tartaric acids. As described elsewhere (*15*), only the first three of these acids were eluted from the column, the others being irreversibly adsorbed. Furthermore, the salicylic acid peak showed severe tailing because of the interaction of the hydroxyl group with the liquid phase and solid support.

Other compound types such as ketones and hydrocarbons were also

Table I. Quantitative Results

Components	Wt. % composition by synthesis	Composition as % area
Decanoic acid	24.1	23.3
Undecanoic acid	28.6	28.5
Undecenoic acid	25.8	25.9
Dodecanoic acid	21.5	22.4
Lauric acid	45.3	44.4
Myristic acid	29.3	29.6
Palmitic acid	25.4	26.0
Palmitic acid	15.1	16.2
Palmitoleic acid	16.0	16.9
Stearic acid	10.7	9.8
Linoleic acid	13.7	13.3
Linolenic acid	44.5	42.9
Impurities	...	0.9

chromatographed on the isophthalic acid–Carbowax columns. With most of the compounds tested, this column behaved as an ordinary Carbowax column, the isophthalic acid having no apparent effect on the elution of such compounds. There was, however, one notable exception involving the nitrophenols which may possibly apply to other compound types as well: both *ortho-* and *para*-nitrophenol could not be eluted at any temperature on commonly used columns such as Apiezon or Carbowax on glass microbeads. But on the isophthalic acid columns, it was possible to elute only *o*-nitrophenol. Apparently, intramolecular hydrogen bonding allows the ortho isomer to be eluted on an acidic column.

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Gas Chromatographic Determination of Acetylsalicylic Acid

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▶ Acetylsalicylic acid can be separated quantitatively on a 1- to 2-meter column of 0.25% Carbowax 20M and 0.4% isophthalic acid coated on acid-washed glass microbeads of 200-micron particle size. The column is operated at 125° C. A calibration curve is necessary because of detector nonlinearity but the analysis requires only about 10 minutes and has a precision of 1% or better. The limit of detectability is about 50 p.p.m. or 10^{-11} gram.

ACETYLSALICYLIC ACID is usually determined by volumetric titration methods (*1*, *5*, *8*) or by spectrophotometric methods (*7*). In all cases the analysis is time-consuming because some preliminary separation steps are usually required even when relatively pure acetylsalicylic acid is being analyzed. For example in the official USP method (*8*) for the assay of aspirin tablets, three acidimetric titrations are required because of the interference of acetic acid which is usually present with acetylsalicylic acid. Furthermore, the above methods are not sensitive for low concentrations or small samples.

The separation of acetylsalicylic acid by gas chromatography is difficult because of its low vapor pressure and its carboxylic acid functional group which interacts with the solid support causing adsorption and tailing. However, two gas chromatographic procedures have been reported recently. In the procedure by Crippen and Freimuth (*2*), the acid is first converted to the methyl ester by refluxing with boron trifluoride and then chromatographed on a column of 30% Carbowax 20M at a temperature of 175° C. In the other procedure (*3*), Hoffman and Mitchell have demonstrated the separation and determination of acetophenetidin, acetylsalicylic acid, and caffeine in APC tablets by using a column of 2% Dow Corning 200 Fluid on tetrafluoroethylene polymer (Haloport F) with temperature programming.

In the present method, acetylsalicylic acid in the presence of other compounds dissolved in an anhydrous volatile solvent such as chloroform can be separated in a few minutes on a column which was developed for the separation of unesterified fatty acids (*6*). The column, operated at 125° C., is 1 to 2 meters long packed with 0.25% Carbowax 20M and 0.4% isophthalic acid coated on acid-washed glass microbeads of 200-micron particle size. Also, in the same run, the amount of acetic and salicylic acids which are usually present because of the hydrolysis of aspirin can be estimated.

EXPERIMENTAL

Apparatus and Materials. A flame ionization gas chromatograph was used (F & M Scientific Co., Model 609) with a recorder of 1-mv. full scale sensitivity.

The glass microbeads used as the solid support were supplied through the courtesy of Microbeads, Inc., Jackson, Miss. The microbeads were pretreated by washing for a few minutes with 1% HNO_3 followed by several rinsings, first with water and then with acetone. The choice of acetone for the final rinsings permits the rapid removal of solvent in the next step. Hot methanol was used to dissolve both the 0.4 wt. % isophthalic acid (Fisher Scientific Co., Pittsburgh, Pa. 15219) and the 0.25 wt. % Carbowax 20M which were then added together to the glass microbeads. The packing was then heated and stirred until the solvent was completely volatilized.

The dry and free-flowing packing was packed into a 2-meter column of $\frac{1}{4}$-inch aluminum tubing with vigorous tapping along the side of the tube until no more packing was accepted. About 52 grams of packing are required for a 2-meter column. The ends were plugged with glass wool.

Procedure. A stock solution of acetylsalicylic acid in anhydrous chloroform was prepared from commercial 5-grain aspirin tablets which were pulverized in a mortar. Anhydrous chloroform was a suitable solvent because of the favorable solubility of aspirin (1 gram in 17 ml.). Aspirin is less soluble in other solvents such as acetone and methanol; furthermore, these cannot easily be kept anhydrous so that some hydrolysis of aspirin takes place, particularly in the heated injection port. This was evident by the appearance of the acetic and salicylic acid peaks when these solutions were chromatographed.

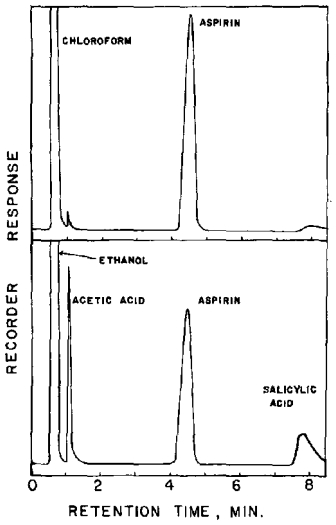

Figure 1. Chromatograms of aspirin in different solvents

2-Meter column packed with acid-washed 200-micron glass microbeads coated with 0.25% Carbowax 20M and 0.4% isophthalic acid. Column temp., 125° C. Injection port temp., 250° C. He flow rate, 60 ml. per minute. Sensitivity, 8×10^{-11} ampere full scale. Sample, 1 μl. of 2 mg. per ml. The peaks labelled aspirin are acetylsalicylic acid

The above stock solution was standardized with the official USP method (*8*). A series of standard solutions was then made by successive volumetric dilutions of the stock solution, using anhydrous chloroform.

One-microliter volumes of the standard solutions were injected with a Hamilton 10-μl. syringe (without a Chaney adapter). In order to obtain reproducibility data, the runs were made over a period of six days, the instrument being turned off overnight and reset with the same conditions the next day. The height of the acetylsalicylic acid peaks was measured to the nearest millimeter and normalized by using the height of the chloroform peak as an internal standard. The use of chloroform solvent as an internal standard was an acceptable alternative which eliminated the quantitative steps of adding an internal standard having a concentration and retention time similar to acetylsalicylic acid.

The above procedure may be summarized as follows. Prepare and standardize volumetrically a stock solution containing about 30 mg. of acetylsalicylic acid per milliliter of anhydrous solvent. Prepare a series of standard solutions by volumetric dilution of the standard stock solution.

Inject equal volumes of each of the standard solutions using the instrument conditions described in Figure 1 and determine the height or area of the solvent and acetylsalicylic acid peaks (retention time of acetylsalicylic acid, 4 to 5 minutes).

Table I. Peak Height Measurements of Standard Acetylsalicylic Acid Solutions

Concentration, mg./ml.	33.86	13.55	5.424	2.210	0.900
Attenuation factor	4	2	1	1	1
Peak height,[a] mm.					
1.	1216	596	254	107	44
2.	1242	588	253	106	43
3.	1232	604	257	107	43
4.	1238	610	255	108	44
Mean	1232	600	255	107	43.5
Std. error	20.3	6.9	1.6	1.2	0.5
% Std. error	1.6	1.2	0.6	1.1	1.1

[a] Computed from the actual peak height multiplied by the attenuation factor.

Prepare a calibration curve by plotting per cent area or per cent height of the peaks *vs.* the concentration. Inject an equal volume of the unknown solution and determine the concentration from the calibration curve.

RESULTS AND DISCUSSION

Typical Chromatograms. Typical chromatograms appear in Figure 1 in which the acetylsalicylic acid peaks are labelled aspirin. Although the column used is undoubtedly overloaded with respect to the solvent, the acetylsalicylic acid peaks are symmetrical and well resolved. In fact, it is apparent that a shorter column may be used to give adequate separation with a shorter analysis time, particularly if it is not necessary to estimate the acetic acid present in the sample; a shorter column would be even more susceptible to overloading by the solvent so that the solvent peak would obscure the acetic acid peak.

The lower recording in Figure 1 shows the formation and separation of the acetylsalicylic acid hydrolysis products, acetic and salicylic acids. These are formed from the presence of water in the ethanol solvent. Both peaks show tailing; typically, acetic acid tails more than other fatty acids (*6*), while salicylic acid tails presumably because of the interaction of the hydroxy group with the column packing. As a result of tailing, it was difficult to determine quantitatively the amount of acetic and salicylic acids in these solutions, especially at the low concentration levels at which they are normally expected. It is possible however to estimate the relative concentrations of these acids in different samples by comparing their relative areas as shown in Figure 1.

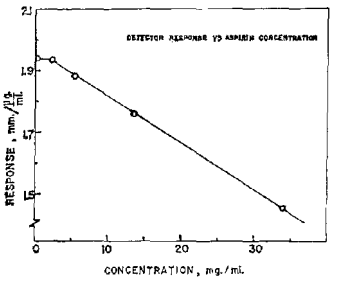

Figure 2. Calibration curve for acetylsalicylic acid

The detector response is defined here as peak height in millimeters divided by concentration in milligrams per milliliter. In the concentration range of interest, the response decreases with increasing concentration—i.e., the detector is nonlinear. The instrument conditions are as in Figure 1, with chloroform as the solvent

Precision and Accuracy. The precision in the determination of acetylsalicylic acid was about 1%, based either on peak height or peak area measurements. The results for peak height measurements shown in Table I were obtained over a period of 6 days so that they may reflect the repeatability of instrument conditions.

For accurate results, a calibration procedure is required because of nonlinearity in the detector signal for the concentration range used, 0 to 34 mg. per milliliter. This is shown in Figure 2. For 1-μl. samples in the concentration range 2 to 34 mg. per milliliter—i.e., up to the solubility limit of aspirin in chloroform, the detector response, peak height per mass, is not independent of the mass injected. Below 2 mg. per milliliter the response is apparently independent of the injected mass,—i.e., the signal is linear. However, this concentration range is near the lower concentration limit of detector sensitivity for 1-μl. samples. Larger sample volumes were not tested.

Under the conditions used in this work the point at which the detector departs from linearity corresponds to about 10^{-8} gram. This amount is considerably lower than the corresponding amount reported for propane in propane-nitrogen mixtures for which the detector is linear up to 10^{-4} or 10^{-3} gram (*4*). However, this difference may be caused by column overloading as well as by differences in molecular weight and ionization efficiency.

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Sulfonation and Dehydrogenation as an Aid to Gas Chromatography in Evaluating 90° to 150° C. Petroleum Fractions

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▷ A combination of sulfonation, catalytic dehydrogenation, and gas chromatography is used to analyze petroleum fractions through about C_{10}. For a 90° to 150° C. fraction, procedures are described to determine most of the individual components through *n*-heptane, individual aromatics through C_8 compounds, ethylcyclohexane and the four isomers of dimethylcyclohexane (cis and trans structure combined), combined total of C_9 and C_{10} aromatics, individual *n*-paraffins, and an approximate carbon number distribution of the remaining paraffins and naphthenes above C_7 compounds. A portion of the original sample is sulfonated to remove aromatics, dehydrogenated to convert ethylcyclohexane and the disubstituted cyclohexanes to aromatics, and again sulfonated to determine the amount of ethylcyclohexane. Chromatograms are obtained at each step using a capillary gas chromatography column. Calculations are made by comparing peak areas on these chromatograms to the peak areas on a chromatogram of the original sample. This combination of techniques is used to obtain both qualitative and quantitative analyses of the samples of this type.

THE VALUE of gas chromatography as a means of analyzing petroleum fractions has been adequately demonstrated in the literature. Examples of this application of gas chromatography are given in the reviews of Le Tourneau (*7*), and Dal Nogare and Juvet (*2*). However, the large number of components present in even relatively narrow boiling ranges of petroleum has caused difficulties in obtaining quantitative data for specific components in the C_7 and C_8 boiling range.

Several techniques for the analysis of petroleum fractions were investigated. Sulfonation has long been a standard procedure in determining aromatics in petroleum fractions. Rampton (*11*) and Polishuk, Donnel, and Wood (*10*) have described the selective dehydrogenation of cyclohexyl rings to aromatics. This was successfully used by Howard and Ferguson (*6*) and Cousins and Chaney (*1*) in developing mass spectroscopic methods to differentiate between cyclopentyl and cyclohexyl naphthenes. Polgar, Holst, and Groennings (*9*)e mployed long capillary gas chromatography columns to resolve the cyclohexanes in the C_8 range.

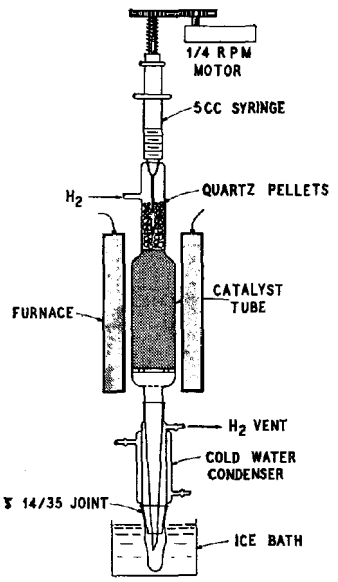


Figure 1. Dehydrogenation apparatus

This paper reports the results of combining sulfonation and dehydrogenation with gas chromatography to increase the utility of the latter technique in the analysis of petroleum fractions boiling in the range of 90° to 150° C.

EXPERIMENTAL

Apparatus. A Perkin-Elmer Model 154B equipped with a flame ionization kit and a 150-foot × 0.01-inch i.d. stainless steel column coated with squalane was used for this study. The sample splitter was of concentric tube design and was controlled by an Ideal valve with a micrometer handle. The injection port and inlet line to the splitting chamber were heated to 200° C. and the column was operated at 35° C.

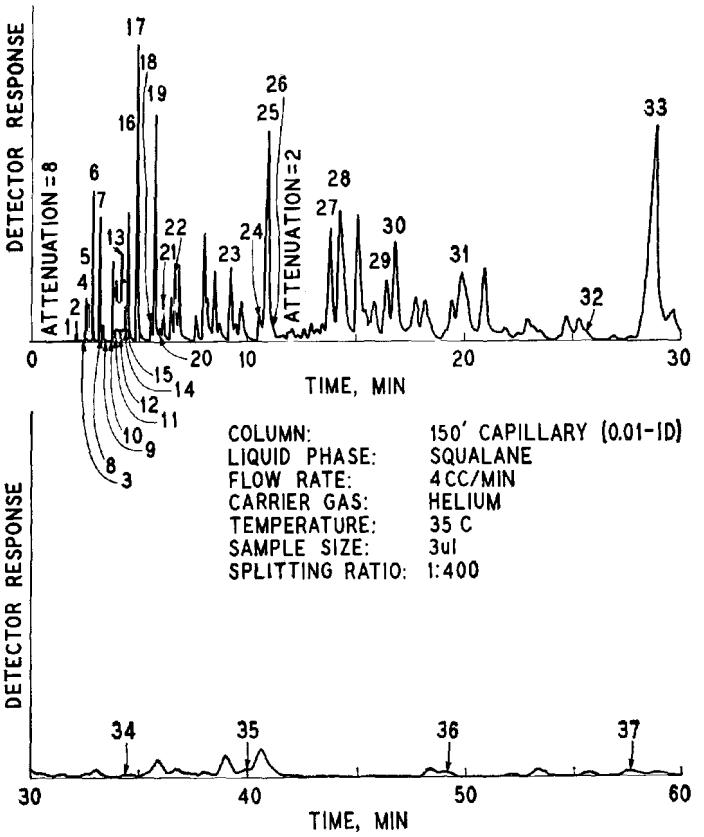
The hydrogen flame ionization detector had a polarizing voltage of 300 volts across the electrodes. The detector response was coupled to an ionization detector amplifier. The output of the amplifier was fed in parallel to a Brown 5-mv. recorder with a 1-second full scale pen speed and a digital chromatograph readout system, Model CRS-1, Infotronics Corporation.

Figure 1 is a block diagram of the dehydrogenation apparatus. It was equipped with a motor driven syringe-type charging device and a cold collection trap. A 500-watt single-wound furnace drawing 5.6 amperes was used. A borosilicate tube with a 10-cc. catalyst chamber was modified so the effluent vapors were carried directly into the collection trap which was cooled in an ice bath. This modification minimized entrainment of hydrocarbon vapors in the vented hydrogen stream.

Reagents. The sulfonation acid was prepared as described in test method ASTM (D 1019). Platinum(ic) chloride was obtained from Fisher Scientific Co. The catalyst support was Columbia activated carbon, Grade L, 20 to 30 mesh. Products of sulfonation were removed from the samples by

Figure 2. Reduced tracing of 90° to 150° C. natural petroleum fraction

Peak No.	Component
1	iC_5
2	n-C_5
3	CyC_5 + 2,3-DMB
4	2-MeC_5
5	3-MeC_5
6	n-C_6
7	MCP + 2,2-DMP
8	2,4-DMP
9	B_Z
10	CyC_6 + 3,3-DMP
11	2-MeC_6
12	1,1-DMCP + 2,3-DMP
13	3-MeC_6
14	*cis*-1,3-DMCP
15	*trans*-1,3-DMCP
16	*trans*-1,2-DMCP + $EthCyC_5$
17	n-C_7 (key peak No. 1)
18	*cis*-1,2-DMCP
19	MCH + 2,2-DMH + 1,1,3-TMCP
20	2,5-DMH
21	2,4-DMH + ECP
22	Tol. + 3,3-DMH
23	1,1-DMCH + 1-*trans*-4-DMCH + 1-*cis*-3-DMCH
24	*cis*-2-*cis*-4-TMCP + 1-*trans*-4-DMCH
25	n-C_8
26	1-*trans*-3-DMCH + 1-*cis*-4-DMCH
27	C_8 Isoparaffin (key peak No. 2)
28	ECH + $EthB_Z$ + C_9 paraffin-naphthene
29	1,4-DMB_Z + C_9 paraffin-naphthene
30	1,3-DMB_Z
31	1,2-DMB_Z + C_9 paraffin-naphthene
32	Isopropylbenzene
33	n-C_9
34	C_9-C_{10} aromatics
35	C_9-C_{10} aromatics
36	C_9-C_{10} aromatics
37	C_9-C_{10} aromatics



percolation through Davidson 923 silica gel.

Procedure. SULFONATION. Fifty milliliters of sulfonation acid was placed in a 250-ml. glass-stoppered Erlenmeyer flask and chilled in an ice bath for 10 minutes. Chilling the sample to near 0° C. is necessary to prevent oversulfonation of the sample. The work of Mills, Kurtz, Heyn, and Lipkin (*8*) reports that there is virtually no sulfonation of saturated hydrocarbons at 0° C. and 20 minutes of contact with the sulfonation acid. Twenty-five milliliters of sample were pipetted slowly down the inside of the flask. The flask was shaken according to the procedure outlined in ASTM (D 1019), Appendix III, except the time was extended from 10 minutes to 20 minutes. The cold mixture was poured into a chilled glass-stoppered separatory funnel and the sulfonation acid layer was drawn off and discarded. The hydrocarbon layer was washed three times with 50-ml. portions of cold water and percolated twice through 10 ml. of silica gel in a glass column to remove sulfur and oxygen compounds. Washing reduced the volume of silica gel needed and the double percolation minimized the selective retention of paraffins and naphthenes on the silica gel.

DEHYDROGENATION. The activated carbon was impregnated with 15% platinum(ic) chloride by dissolving the catalyst in water and forming a slurry of the carbon and catalyst solution. Excess water was evaporated on a hot plate and the supported catalyst was dried in a muffle furnace at 200° C. for 4 hours. The catalyst tube was filled with 10 ml. of dried catalyst; approximately 2 ml. of quartz pellets were added to provide heat capacity for rapid vaporization of the sample. Hydrogen (15 cc. per minute) and the sample were charged to the catalyst tube through a glass tee-joint at the top of the catalyst tube. A 6-inch hypodermic needle (19 gauge) with a Lur-O-Lock valve was inserted into the catalyst tube through the tee-joint with the exit end below the top level of the quartz pellets. The freshly charged catalyst was conditioned for 24 hours at the operating temperature of 305° C. Approximately 4 ml. of sample were charged to a 5-ml. syringe and the syringe was mounted in a motor driven metering device that charged 2 ml. per hour to the catalyst tube. The initial 1 ml. of product was discarded and the next 2 ml. were collected for analysis.

CHROMATOGRAPHY. The capillary column was mounted in the chromatograph and heated to 35° C. Helium inlet pressure was 30 p.s.i.g. with an exit flow of 4 ml. per minute. The optimum sensitivity of the flame was obtained at inlet pressures of 10 p.s.i.g. for hydrogen and 40 p.s.i.g. for air. The gas chromatography unit and its accessory equipment were stabilized for 1 to 2 hours with all power switches on, the ionization voltage on, and the flame ignited. Samples of 3 μl. were injected into the chromatograph using a splitting ratio of 1 to 400. Chromatograms and their respective digital tapes were obtained on the original sample, the sulfonated portion, the sulfonated portion after dehydrogenation, and the dehydrogenated portion after sulfonation.

RESULTS AND DISCUSSION

The complete chromatogram of the original sample was measured. The remaining chromatograms were measured only in the areas where interferences or additional components were resolved. Two peaks were selected to compare resolved interferences or components on any one chromatogram to the chromatogram of the original sample. Two peaks were chosen because the sulfonated and dehydrogenated portion of the sample lost 5 to 10% of the material in the n-heptane range by vaporization and 10 to 15% in the C_9 range by selective retention of the heavier components on the silica gel. To minimize the effects of these losses,

key peaks were selected in the areas where corrections for resolved interferences or components were made. Peak No. 17, key peak No. 1 in Figure 2, *n*-heptane, was used for the portion eluting before *n*-octane and peak No. 27, key peak No. 2 in Figure 2, a C_9 isoparaffin, was used for the portion eluting after *n*-octane. A typical example of the use of individual chromatograms to obtain the analyses shown in Table I is the C_8 aromatic portion in the simulated drawings of Figure 3. Figure 3*B* shows the C_8 aromatic portion after sulfonation. Since 1,3-dimethylbenzene (peak No. 10) shows no interferences it can be measured on the original chromatogram (Figure 3*A*). 1,4-Dimethylbenzene (peak No. 8) shows a small interference of C_9 paraffin or naphthene (peak No. 9) which was compared to the original chromatogram and subtracted from the 1,4-dimethylbenzene and added to the C_9 paraffin-naphthene total. Similar measurements were made for ethylbenzene (peak No. 5) and 1,2-dimethylbenzene (peak No. 11). Figure 3*C* shows the C_8 aromatic portion after dehydrogenation of the sulfonated portion. 1,3-Dimethylcyclohexanes (*cis* and *trans*) (peak No. 14) were converted to 1,3-dimethylbenzene and were compared to the original chromatogram. The 1,4-dimethylcyclohexanes (*cis* and *trans*) (peak No. 13) were converted to 1,4-dimethylbenzene and were compared to the original chromatogram and corrected for the C_9 paraffin or naphthene previously shown to be present. Similar measurements were made for the 1,2-dimethylcyclohexanes (peak No. 15). Figure 3*D* shows the dehydrogenated portion after sulfonation. When the ethylcyclohexane that was converted to ethylbenzene (peak No. 16) by dehydrogenation was removed by sulfonation, a C_9 paraffin or naphthene interference (peak No. 7) was present. This interference was compared to the original chromatogram and subtracted from the total area of ethylcyclohexane, ethylbenzene, and C_9 interference. The ethylcyclohexane area was obtained by subtracting the previously determined ethylbenzene area from the combined area of ethylcyclohexane and ethylbenzene. The C_9 interference was added to the C_9 paraffin-naphthene total. Procedures used to determine components in the C_8 aromatic portion were used to determine interferences or additional components on other portions of the original chromatogram. Sulfonation revealed an interference in the toluene peak and also removed the C_9 and C_{10} aromatic peaks. Dehydrogenation revealed a doublet interference in the MCH peak. 1,1-Dimethylcyclohexane was sufficiently resolved to calculate its concentration.

After corrections for interferences and additional components were made on the chromatogram of the original sample, the areas of the individual components and groups of components were totaled and their area percentage was determined by dividing the individual areas by the total area multiplied by one hundred. Ettre (*4*) found that equating area response to weight response was valid above a carbon range of about C_6 to C_7. Durret, Simmons, and Dvoretzky (*3*) found that the area response of the flame ionization detector to hydrocarbons in the boiling range described in this method was within 5% of the weight response for

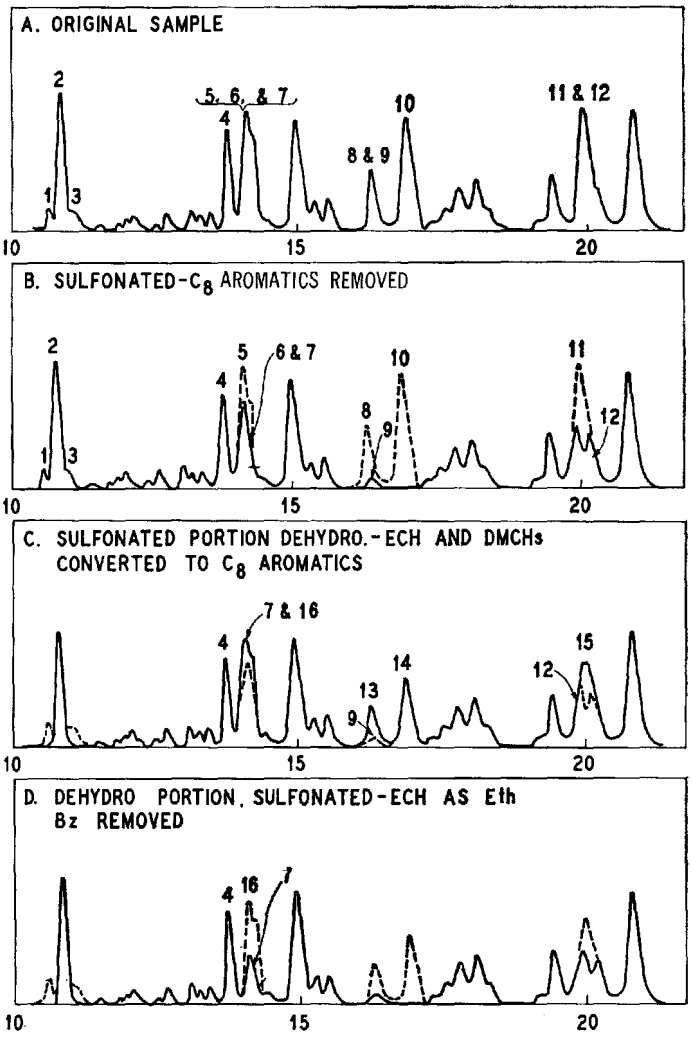


Figure 3. Simulated drawing of C_8 aromatic portion depicting the stepwise analysis

Peak No.	Component
1	*trans*-1,2-DMCH
2	*n*-Octane
3	*cis* and *trans*-DMCH's
4	C_9 isoparaffin (key peak No. 2)
5	$EthB_z$
6	ECH
7	C_9 paraffin-naphthene
8	$1,4\text{-}DMB_z$
9	C_9 paraffin-naphthene
10	$1,3\text{-}DMB_z$
11	$1,2\text{-}DMB_z$
12	C_9 paraffin-naphthene
13	1,4-DMCH's as $1,4\text{-}DMB_z$
14	1,3-DMCH's as $1,3\text{-}DMB_z$
15	1,2-DMCH's as $1,2\text{-}DMB_z$
16	ECH as $EthB_z$

Table I. Replicate Analyses of Two Samples of 90° to 150° C. Petroleum Fractions, Area Per Cent

Components	Abbreviations Figures 2 and 3	Sample I Run 1	Sample I Run 2	Sample I Run 3	Sample I Average	Sample II Run 1	Sample II Run 2	Sample II Run 3	Sample II Average
Isopentane	IC_5	0.04	0.04	0.05	0.04	0.05	0.04	0.07	0.05
n-Pentane	*n*-C_5	0.12	0.11	0.11	0.11	0.11	0.10	0.13	0.11
Cyclopentane	CYC_5	0.11	0.11	0.11	0.11	0.08	0.06	0.09	0.08
2,3-Dimethylbutane	2,3-DMB								
2-Methylpentane	2-MeC_5	0.34	0.35	0.35	0.35	0.39	0.38	0.41	0.39
3-Methylpentane	3-MeC_5	0.32	0.31	0.32	0.32	0.26	0.24	0.25	0.25
n-Hexane	*n*-C_6	1.35	1.34	1.33	1.34	0.91	0.90	0.92	0.91
2,2-Dimethylpentane	2,2-DMP	1.40	1.40	1.38	1.39	0.73	0.76	0.74	0.74
Methylcyclopentane	MCP								
2,4-Dimethylpentane	2,4-DMP	<0.01	<0.01	<0.01	<0.01	0.09	0.08	0.09	0.09
Benzene	BZ	0.24	0.25	0.25	0.25	2.07	2.10	2.12	2.10
Cyclohexane	CyC_6	1.14	1.15	1.14	1.14	1.30	1.29	1.27	1.29
3,3-Dimethylpentane	3,3-DMP								
2-Methylhexane	2-MeC_6	0.87	0.86	0.87	0.87	0.76	0.70	0.78	0.75
1,1-Dimethylcyclopentane	1,1-DMCP	0.62	0.64	0.64	0.63	0.43	0.40	0.46	0.43
2,3-Dimethylpentane	2,3-DMP								
3-Methylhexane	3-MeC_6	1.35	1.33	1.34	1.34	0.89	0.90	0.94	0.91
n-Heptane	*n*-C_7	5.20	5.28	5.32	5.27	3.36	3.39	3.36	3.37
Dimethylcyclopentanes	DMCP's	4.17	4.29	4.25	4.24	1.34	1.31	1.47	1.37
3-Ethylpentane	3-$EthC_6$								
Methylcyclohexane	MCH	4.29	4.47	4.47	4.41	5.96	6.05	5.71	5.91
Toluene	Tol.	1.76	1.76	1.74	1.75	16.14	16.57	16.30	16.34
n-Octane	*n*-C_8	10.66	10.58	10.84	10.69	7.66	7.59	7.82	7.69
Ethylcyclohexane	ECH	1.76	1.80	1.80	1.79	1.31	1.33	1.13	1.26
1,4-Dimethylcyclohexane (*cis* & *trans*)	1,4-DMCH	0.54	0.57	0.58	0.56	0.82	0.85	0.70	0.79
1,3-Dimethylcyclohexane (*cis* & *trans*)	1,3-DMCH	2.61	2.58	2.58	2.59	2.56	2.57	2.55	2.56
1,2-Dimethylcyclohexane (*cis* & *trans*)	1,2-DMCH	1.55	1.58	1.50	1.54	1.27	1.26	1.39	1.31
1,1-Dimethylcyclohexane	1,1-DMCH	0.59	0.61	0.54	0.58	0.33	0.32	0.39	0.35
C_8 paraffins and naphthenes		17.42	17.09	17.51	17.34	8.17	8.26	8.52	8.32
Ethylbenzene	$EthB_z$	0.54	0.57	0.65	0.59	1.95	2.00	1.84	1.93
1,4-Dimethylbenzene	1,4-DMB_z	0.40	0.36	0.32	0.36	2.94	2.99	2.91	2.95
1,3-Dimethylbenzene	1,3-DMB_z	1.94	1.97	1.96	1.96	12.07	12.26	11.42	11.92
1,2-Dimethylbenzene	1,2-DMB_z	0.91	0.86	0.66	0.81	3.49	3.58	3.60	3.56
n-Nonane	*n*-C_9	7.56	7.64	7.49	7.56	4.75	4.62	4.51	4.63
C_9 paraffins and naphthenes		18.35	18.16	18.19	18.23	9.83	9.46	10.30	9.86
C_{10} paraffins and naphthenes		9.11	8.59	8.90	8.87	4.74	4.64	4.07	4.48
C_9 and C_{10} aromatics		2.74	3.35	2.82	2.97	3.20	3.14	3.81	3.38

paraffins and naphthenes and within approximately 10% for the aromatics. Work in this laboratory with a limited number of components indicated the area response of the flame ionization detector closely approximated weight response. Toluene showed 8% less area response than *n*-heptane. When the total aromatic values were corrected by this amount for each of the samples, they agreed to within 5% of the weight values obtained by mass spectrometer methods.

Replicate analyses of the two samples shown in Table I illustrate the repeatability of the data. Coefficient of variation, $C = S/\bar{X}$ was used to characterize the variability of the *n*-paraffins, aromatics, and C_8 sub-

Table II. Dehydrogenation of Dimethylcyclopentanes (DMCP's) and Trimethylcyclopentanes (TMCP's), Per Cent by Weight

Component	Original blend	Dehydrogenated blend
1,*cis*-3-Dimethylcyclopentane	<0.1	0.9
1,*trans*-3-Dimethylcyclopentane	1.8	1.0
1,*trans*-2-Dimethylcyclopentane	2.0	1.4
1,*cis*-2-Dimethylcyclopentane	0.0	0.3
1,1,3-Trimethylcyclopentane	1.7	1.7
1,*trans*-2,*cis*-4-Trimethylcyclopentane	0.0	2.1
1,*cis*-2,*cis*-4-Trimethylcyclopentane	2.0	1.0
1,*cis*-2,*cis*-3-Trimethylcyclopentane	2.0	0.2
Olefin	0.0	0.7
Aromatics	0.0	0.0
	9.5	9.3
Normal nonane	90.5	88.2
Isomerization and dehydrogenation products of *n*-nonane	0.0	2.5
	100.0	100.0

Table III. Dehydrogenation of Dimethylcyclohexanes (DMCH's), Per Cent by Weight

Component	Original blend	Component	Dehydrogenated blend
1,1-Dimethylcyclohexane	2.63	1,1-Dimethylcyclohexane	2.61
1,*cis*-4-Dimethylcyclohexane	2.45	1,4-Dimethylbenzene	2.52
1,*cis*-3-Dimethylcyclohexane	2.54	1,3-Dimethylbenzene	2.63
1,*trans*-2-Dimethylcyclohexane	2.91	1,2-Dimethylbenzene	2.47
Normal nonane	89.47	Normal nonane	86.97
		Isomerization and dehydrogenation products of *n*-nonane	2.80
	100.00		100.00

Table IV. Dehydrogenation of 1,1,3-Trimethylcyclohexane, Methylcyclopentane, Ethylcyclopentane and Tetramethylcyclopentane, Per Cent by Weight

Component	Original blend	Dehydrogenated blend
Methylcyclopentane	5.76	5.79
Ethylcyclopentane	6.67	6.58
1-*trans*-2,*cis*-3,*trans*-4-Tetramethylcyclopentane	6.47	4.60
1,1,3-Trimethylcyclohexane	3.22	3.10
Toluene	0.00	0.29
1,4-Dimethylbenzene	0.00	0.12
1,3-Dimethylbenzene	0.00	0.22
1,2-Dimethylbenzene	0.00	0.09
Olefin	0.00	1.53
Normal nonane	77.88	75.08
Isomerization and dehydrogenation products of *n*-nonane	0.00	2.60
	100.00	100.00

stituted cyclohexanes in each of the samples, where:

C = coefficient of variation
S = standard deviation
$\bar{X}$ = mean of experimental values

The coefficients of variation at the 90% confidence level were: aromatics, 0.16 and 0.06; C_8 substituted cyclohexanes, 0.06 and 0.13; and *n*-paraffins, 0.02 and 0.02 for samples 1 and 2. Except for cases where components were present in concentrations of 0.11 area % or less, the remaining components or types had coefficients of variation less than 0.13. These data indicate precisions at the 90% confidence level of ±2% of the amount present for *n*-paraffins, ±16% for aromatics, ±13% for C_8 substituted cyclohexanes, and approximately ±10% for the remaining components.

The dehydrogenation procedure was checked with several blends of known concentration. Table II shows the results of dehydrogenation of trimethylcyclopentanes and dimethylcyclopentanes. No aromatics were formed; however, it is apparent that some dehydrogenation to olefin and considerable isomerization occurred. Table III shows the complete conversion of a mixture of dimethylcyclohexanes to their respective C_8 aromatics except the gem-substituted 1,1-dimethylcyclohexane which was not affected by dehydrogenation. Table IV shows methylcyclopentane, ethylcyclopentane, and the gem-substituted 1,1,3-trimethylcyclohexane not affected by dehydrogenation. The tetramethylcyclopentane showed appreciable dehydrogenation to olefin and approximately 11% conversion to aromatics. A small amount of material, most of it in the C_9 boiling range, was evident in each of the blends dehydrogenated. Because the retention times of these peaks were identical in all the blends, they were assumed to be isomerization and dehydrogenation products of the *n*-nonane used as a diluent in the blends. A blend of 20% cyclohexane, 5% methylcyclohexane, and 5% ethylcyclohexane in *n*-nonane, used to check catalyst activity periodically, showed conversion levels of 90% or better for cyclohexane to benzene and essentially 100% for methylcyclohexane and ethylcyclohexane to toluene and ethylbenzene. A conversion level of approximately 90% for cyclohexane is necessary to ensure complete conversion of the mono- and disubstituted cyclohexanes.

The dehydrogenation step was first tried using 1% platinum catalyst. However, the activity level dropped so rapidly that only one or two samples could be run before regeneration was necessary. A 15% platinum catalyst has been used for up to 10 months without regeneration.

To determine a carbon number distribution of the paraffins and naphthenes, other than those determined individually, the C_8, C_9, and C_{10} *n*-paraffins were taken as the highest boiling components in their respective carbon range. A survey of hydrocarbons [Ferris, (5)] that could be present in olefin-free naphtha showed 43 out of 57 C_8 paraffins and naphthenes boiling below *n*-octane and 102 out of 129 C_9 paraffins and naphthenes boiling below *n*-nonane. Although some overlapping of carbon ranges occurs, 70 to 75% of the total number of compounds possible in each carbon range will boil lower than the *n*-paraffin. A survey of the components most likely to be present in the largest concentrations is even more favorable for this procedure. In the C_8 range, 90 to 95% of the components occurring in the highest concentrations boil lower than *n*-nonane. The survey indicated that in the absence of aromatics and olefins a reasonable approximation of the carbon number distribution of the paraffins and naphthenes can be obtained. Figure 2, a tracing of a reduced chromatogram, shows the range of components beginning with isopentane and extending into the decanes. Identifications of the individual components were established using pure compounds. Because of reduction the depicted resolution is less than actually obtained.

The electronic integrator reduces the tedious nature of this method. The response of the integrator was excellent on narrow peaks; however, on the broad peaks in the C_{10} paraffin and naphthene range the slope detector quite often failed to detect either positive or negative changes in slope. Because all the C_9 and C_{10} aromatics, except isopropylbenzene, were determined by comparing the total area beyond *n*-nonane on the chromatogram of the sulfonated portion to the same area on the chromatogram of the original sample, individual peak areas on this portion of the chromatograms were not obtained.

Although the procedures given here have been applied primarily to 90° to 150° C. fractions from a wide variety of crude oils, they are applicable to other complex mixtures where the identification and measurement of C_6 to C_8 aromatics and cyclohexanes is desired. Extension to the C_9 and C_{10} range is possible, although the large number of possible isomers and the lack of pure reference compounds may limit the completeness of the analysis.

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Gas Chromatographic Separation of 2,4-Dinitrophenylhydrazone Derivatives of Carbonyl Compounds

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▶ Direct gas liquid chromatography of the 2,4-dinitrophenylhydrazone derivatives of a variety of carbonyl compounds has been accomplished using SF-96 (100) silicone oil as a liquid phase at temperatures from 200° to 250° C. The compounds include alkyl aldehydes and ketones up to C_{12}, alkyl phenyl ketones, some terpene aldehydes and ketones, and aromatic aldehydes. The reagent, itself, does not interfere and recrystallization of the derivatives is not necessary.

IDENTIFICATION of carbonyl compounds as their 2,4-dinitrophenylhydrazone (2,4-DNP) derivatives has been accomplished by paper (*2, 10, 15*), column (*4, 12, 17*), and thin layer (*5, 16*) chromatography. Some 2,4-DNP derivatives have been analyzed by gas liquid chromatography (GLC) using an exchange procedure with alpha keto acids (*6, 13, 19*). In this case, liberated carbonyls and not the derivatives themselves are actually chromatographed. The oxime derivatives of carbonyls have been directly analyzed by GLC (*3, 9*). This paper deals with the direct analysis of the 2,4-DNP derivatives by GLC.

EXPERIMENTAL

Apparatus. The gas chromatograph used was a Hy-Fi, Model 600 (Wilkins Research, Walnut Creek, Calif.) equipped with a flame ionization detector. The instrument was modified by a ThermisTemp temperature controller, Model 63 RA (Yellow Springs Instrument Co., Yellow Springs, Ohio) and a glass insert (Wilkens) for the injector chamber. The recorder was a 1-mv. Leeds & Northrup Speedomax Type G, Model S, 60,000 series with a paper feed of $^1/_2$ inch/min. The column was 10% w./w. General Electric silicone SF-96 (100) coated on chromosorb W, acid washed (Wilkens), 60- to 80-mesh, packed in a 2 meter, $^1/_8$-inch o.d., 0.085-inch i.d., stainless steel tube. The usual conditions of operation were column temperature 250° C., injection temperature 275° C., and helium flow 86 ml./min.

Because of the high temperature used, a silicone residue from column bleed built up on the flame jet tip causing base line and peak distortion. Frequent cleaning of the flame tip minimized this problem. It was also necessary to replace the flame tip O-ring seals at least once a week to keep base line noise at a minimum.

Methods. The 2,4-DNP derivatives of the carbonyl compounds were prepared by standard methods (*11, 18*) except for the mono-2,4-DNP derivative of diacetyl, which was prepared according to Reich and Hefle (*14*), and all were recrystallized until constant melting points were obtained.

The melting points of the prepared derivatives agreed closely with the literature values (*7, 8, 14*) except for the derivative of caprylophenone which melted at 118° C. The reported melting point (*1*) of this compound is 103° C.

The derivatives were dissolved in benzene at a 0.5% concentration for testing in the gas chromatograph. Those not soluble in benzene were dissolved or suspended in dimethylformamide.

Ten microliters was the usual injection sample size. This relatively large amount of injected solvent extinguished the hydrogen flame which was then reignited after the solvent had passed through.

Detectability of these derivatives, limited by the column background, was in the range of 10^{-8} to 10^{-5} mg.

RESULTS AND DISCUSSION

Chromatographic responses were obtained for the 2,4-DNP derivatives of *n*-alkyl aldehydes, C_1–C_{12}, methyl alkyl ketones, C_3–C_{11}, several members of the alkyl phenyl ketone series, and miscellaneous carbonyl compounds. The separation of the even carbon chain members of the *n*-alkyl aldehyde series is shown, Figure 1. A separation of *n*-butyraldehyde, isobutyraldehyde, 2-butanone, *n*-valeraldehyde, isovaleraldehyde, and 2-pentanone compounds is shown, Figure 2. Table I lists the retention times of all 2,4-DNP compounds tested.

The reagent used to prepare the derivatives, 2,4-dinitrophenylhydrazine, does not produce a chromatographic peak. Therefore, liquid and solid

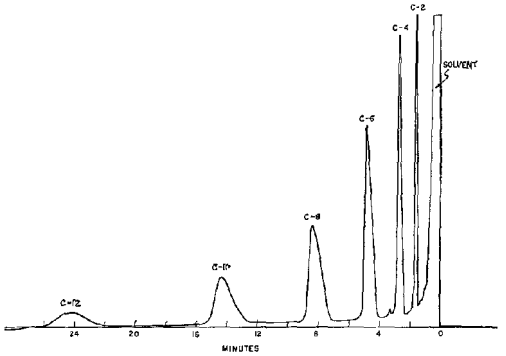

Figure 1. Gas chromatographic separation of the DNP derivatives of *n*-alkylaldehydes

Sample size, 3 μl. containing 1% of each derivative in benzene; column temperature, 250° C.; injector temperature, 267° C.; attenuation, 64X; helium flow, 86 ml./min.

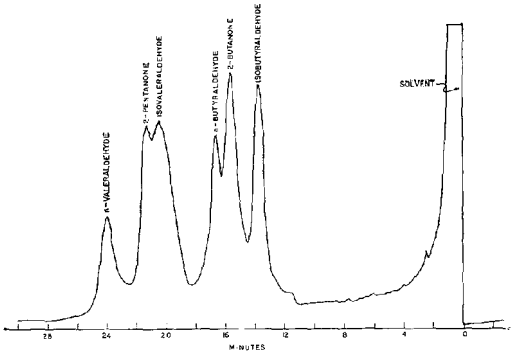

Figure 2. Gas chromatographic separation of the DNP derivatives of closely related carbonyl compounds

Sample size, 10 μl. containing 0.1% of each derivative in benzene; column temperature, 201° C.; injector temperature, 274° C.; attenuation, 8X; helium flow, 57 ml./min.

Table I. Retention Times of 2,4-DNP Derivatives of Various Carbonyl Compounds[a]

Parent compound	Retention time, min.	Parent compound	Retention time, min.
Formaldehyde	1.3	Propiophenone	10.6
Acetaldehyde	1.7	Nonanal	10.9
Acetone	2.2	Acetophenone	11.4
Propionaldehyde	2.3	*d*-Citronellal	11.6
Isobutyraldehyde	2.5	*dl*-Menthone	11.9
2-Butanone	2.8	Butyrophenone	12.6
Butyraldehyde	3.0	Hydrocinnamaldehyde	13.8
Diacetyl	3.0 (mono)	Decanal	14.4
Isovaleraldehyde	3.3	Valerophenone	16.2
Crotonaldehyde	3.4	*l*-Carvone	16.3
2-Pentanone	3.5	2-Undecanone	16.6
Valeraldehyde	3.6	Undecanal	19.4
2-Hexanone	4.4	*p*-Anisaldehyde	22.8
Hexaldehyde	4.9	Dodecanal	24.4
2-Heptanone	5.7	Caprylophenone	36.6
Furfural	5.8	*o*-,*m*-,*p*-hydroxybenzaldehydes	N.R.[b]
Phenylacetaldehyde	5.8	Cinnamic aldehyde	N.R.
Heptaldehyde	6.4	Citral	N.R.
2-Octanone	7.4		
Octanal	8.4		
2-Nonanone	9.5		
Benzaldehyde	10.5		

[a] Conditions as given in Experimental Section.
[b] N.R.—No response.

derivatives can be analyzed directly without further purification. This is especially useful for the identification of trace amounts of aldehydes and ketones separated by other gas chromatographic methods. In this laboratory, an unknown aldehyde or ketone, separated from other compounds on a thermal conductivity–equipped gas chromatograph, is bubbled into 2,4-DNPH reagent as it emerges from the column The resulting solid precipitate or oil is separated, taken up in an appropriate solvent, and injected into a chromatograph under the conditions described in this paper. This has proven to be a good supplementary tool for identification. It is simple, rapid, and has fewer limitations than any single column or paper chromatographic method.

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Quantitative Determination of Parts-per-Million Quantities of Nitrogen Dioxide in Nitrogen and Oxygen by Electron-Capture Detection in Gas Chromatography

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▷ An electron-capture detector was used in a gas chromatograph to measure parts-per-million quantities of nitrogen dioxide in a ternary mixture of nitrogen, oxygen, and nitrogen dioxide. For concentrations of nitrogen dioxide from 5 to 150 p.p.m. and for oxygen present to the extent of 9% by volume in nitrogen, the standard deviation of the best curve through the points showing response vs. concentration was 2 p.p.m. compared to about 3 p.p.m. for chemical techniques. The main advantages of gas chromatography are the short time for analysis and the small samples (1/2 cc.) required.

USE OF GAS CHROMATOGRAPHY for analysis of nitrogen dioxide at concentrations between 10 and 1000 p.p.m. has not been described in the literature. Greene and Pust (*1*) used a wetted molecular sieve column to analyze for nitrogen dioxide at relatively high concentrations. Currently small concentrations of nitrogen dioxide in air are usually measured by means of the Saltzman (*4*) technique which requires much larger samples than gas chromatography.

EXPERIMENTAL

Apparatus. A Loenco 15A gas chromatograph with a Loenco 15B electrometer was used in the study. The electron-capture detector was a Barber-Colman Model A 5042 with a 220-mc. tritium source. High purity dry nitrogen and commercial grade oxygen, both obtained from Linde, were the diluent gases. They were dried by passage through a 4-foot length of 5/16-inch i.d. copper tubing packed with 13-X molecular sieve and mounted in a dry ice–acetone bath.

Several column materials were tested for their ability to separate oxygen and nitrogen dioxide. They were 5% by weight of 710 silicone oil on Chromosorb W (HMDS), 5% Apiezon L on Chromosorb W (HMDS), an unpacked column with a coating of aluminum oxide, and a glass capillary column. These materials did not effect a satisfactory separation, and at the suggestion of

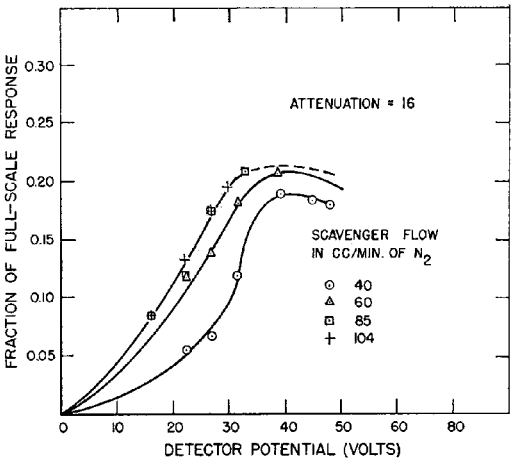

Figure 1. Effect of detector potential on relative response to nitrogen dioxide with a nitrogen carrier flow of 10 cc. per minute

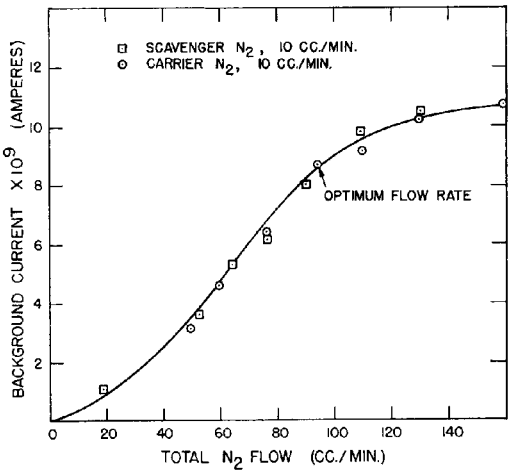

Figure 2. Background current as a function of total nitrogen flow at a detector potential of 33 volts

I. H. Williams of the British Research Council, 10% SF 96 (a methyl silicone oil) on Fluoropak 80 was tried and gave a reasonable separation. It was used in the present study.

Special care was required in the preparation of the column with 10% SF 96 on Fluoropak 80. The SF 96 was placed on the solid phase, which was 20- to 80-mesh, by use of standard evaporation procedures with diethyl ether as the solvent for the methyl silicone oil. The coated packing was then placed into a 15-foot length of a 304 stainless steel tube having an inside diameter of $^3/_{32}$ inch. Three grams of material were used to pack the 15-foot column which was then coiled into a diameter of approximately 4 inches and conditioned at 200° C. for 30 hours by flowing dry nitrogen through it at a rate of 10 cc. per minute as measured at 1 atm. and 22° C. Then the column was cooled to 22° C. while the nitrogen flow was maintained. Next, 20 3-cc. samples of nitrogen, each containing 300 p.p.m. of nitrogen dioxide, were injected into the column at approximately 5-minute intervals. After that treatment, the column quantitatively separated oxygen and nitrogen dioxide. In continuous use, three to four $^1/_2$-cc. samples of nitrogen containing 100 p.p.m. of nitrogen dioxide were injected into the column each day before beginning the quantitative analysis.

Nitrogen Dioxide. Nitrogen dioxide was obtained from a mixture furnished by Matheson containing nominally 1500 p.p.m. of nitrogen dioxide in nitrogen. Analysis of the gas in the cylinder by the phenoldisulfonic acid method (ASTM D 1608-60) showed that the concentration of nitrogen dioxide was 1627 p.p.m., based on moles of nitrogen dioxide per mole of gas, with a standard deviation of 70 p.p.m. Standard mixtures used to calibrate the chromatograph were made by evacuation of a 6000-cc. vessel followed by addition of the appropriate gases. Changes in pressure combined with compressibility factors and the assumption that Dalton's law prevailed were used to calculate the concentrations of the gases in the 6000-cc. vessel. For very low concentrations of nitrogen dioxide, successive dilution procedures were used.

Procedure. The conditioned Fluoropak 80 column was operated at 22° C. (room temperature) to determine the optimum conditions for determination of the nitrogen dioxide. Preliminary work showed that a flow rate of 10 cc. per minute of carrier gas provided the best separation of the nitrogen dioxide. That flow rate then received special interest in studies of detector response as a function of detector potential and flow rate of scavenger gas. In the study of the optimum conditions of operation, $^1/_2$-cc. samples of nitrogen containing 100 p.p.m. of nitrogen dioxide were used.

RESULTS AND DISCUSSION

Figure 1 presents information on the response obtained as the detector potential was varied for constant values of total nitrogen flow. Within the limits of experimental error for the case of a carrier flow of 10 cc. per minute, a scavenger flow of 85 cc. per minute of nitrogen and a detector potential of 33 volts gave the most sensitive response.

The background current was then studied as a function of total nitrogen flow and detector potential for comparison with the results presented in Figure 1. Figure 2 shows the background current as a function of the total flow rate of

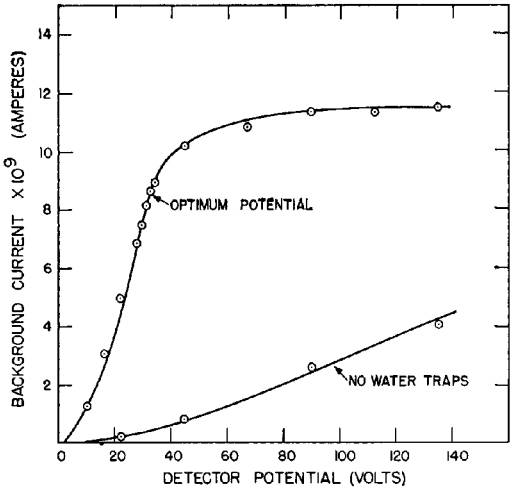

Figure 3. Background current as a function of detector potential for a total nitrogen flow of 95 cc. per minute

nitrogen. The data were obtained at a constant potential of 33 volts and flow of scavenger gas or carrier gas of 10 cc. per minute. Figure 3 shows the background current as a function of detector potential for a constant flow rate of 85 cc. per minute of scavenger gas and 10 cc. per minute of carrier gas. In Figure 3 the lower curve is the background current as a function of detector potential in the absence of water traps on the nitrogen and oxygen streams. The need for removal of water by the molecular sieves is shown to be very important. The optimum conditions for the operation of the electron-capture cell were then selected as 33 volts, 10 cc. per minute of nitrogen as the carrier gas and 85 cc. per minute as scavenger gas, and a background current of 8.6×10^{-9} ampere.

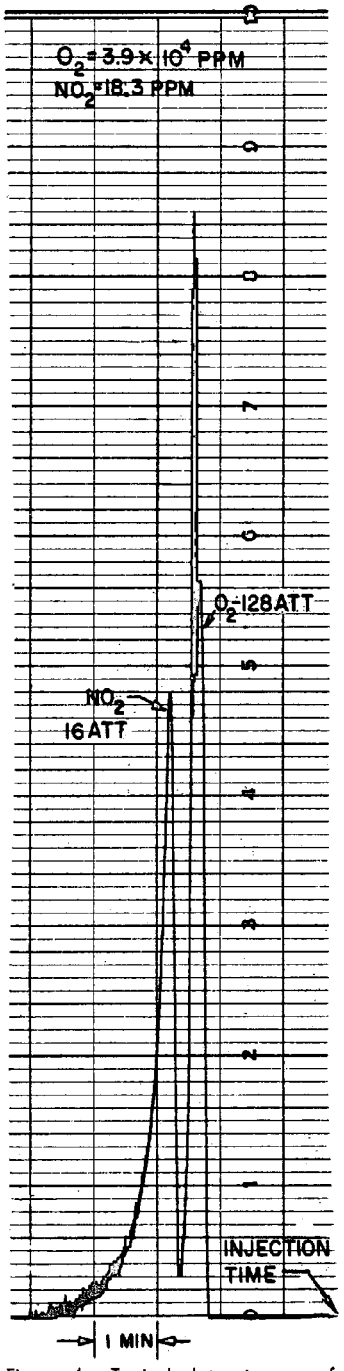

Figure 4. Typical chromatogram of nitrogen dioxide in nitrogen with added oxygen

A chromatogram for the optimum conditions of analysis is shown in Figure 4. Nitrogen was the carrier. The concentration of nitrogen dioxide was 18.3 p.p.m. and that of oxygen was 3.9×10^4 p.p.m. Oxygen was present just to check separation, and the multiple oxygen peak was developed merely by decreasing the attenuation by factors of two from a value of 128 to 16 during the course of the oxygen peak. The sample volume was $1/2$ cc.

Lovelock (*2*) noted that the electron capture detector should obey the following equation:

$$I = I_s e^{-BC} \qquad (1)$$

in which I is the measured current in the presence of the test substance at a concentration C, I_s is the background current or current measured with no electron-capturing material in the detector cell, and B is a constant. Rearrangement of the equation gives

$$C = A - D \ln I \qquad (2)$$

in which A and D are constants. I is obtained by use of the following relation:

$$I = I_s - I_p \qquad (3)$$

where I_p is a decrease in current effected by the presence of the electron-capture substance and is obtained as the product in appropriate units of the peak height measured for that substance and the prevailing attenuation. A semilog plot of I as a function of the concentration of nitrogen dioxide in parts per million in the presence of nitrogen is given in Figure 5. Over the range of 5 to 150 p.p.m. of nitrogen dioxide the experimental data do not exactly follow Lovelock's proposed relationship as expressed by Equation 2. A least-squares analysis of the data using Equation 2 gave the dashed line with a standard deviation of 7.3 p.p.m. while the best curve through the averaged experimental points is the solid line with a standard deviation of 2 p.p.m. of nitrogen dioxide. Although no data for day-to-day variability of the standard sample are yet available, it is estimated that the within-day standard deviation would prevail at the level of 2 p.p.m. of nitrogen dioxide. The lower limit of concentration of about 5 p.p.m. was set by the noise in the detector circuit.

Subsequent to the experiments reported in detail here, the noise has been significantly reduced by use of a pulsed voltage (*3*) and a detector with concurrent flow. The change in flow pattern reduced the noise level by a factor of two, and an additional reduction by a factor of two was obtained with the pulsed voltage. In this later work, argon was used as both carrier and scavenger gas for increased sensitivity of signal from the detector. The best performance in the pulsed operation was found for a total flow of argon of 40 cc. per minute, a 50-volt output, an on-time of 4 μseconds, and a period of 150 μseconds. To minimize the effect of

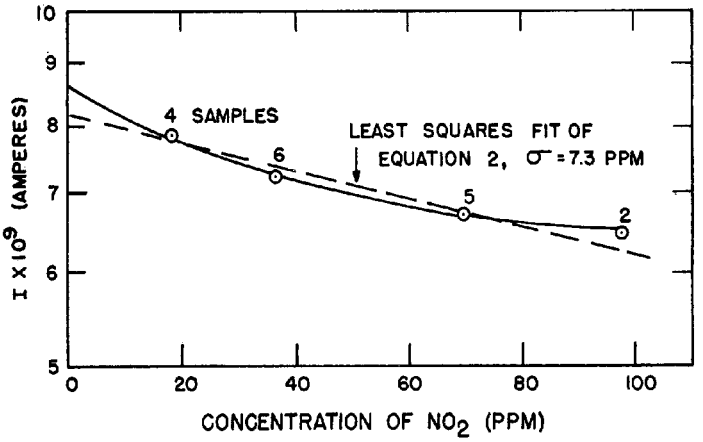

Figure 5. Concentration of nitrogen dioxide as related to detector current for 1/2-cc. samples containing nitrogen and up to 9% oxygen

column bleed on the tritium foil in the detector, the temperature of the detector was held at 200° C. A noise level of 4×10^{-12} ampere was observed with a background current of 2.6×10^{-9} ampere which suggests a limit of detection of 1 p.p.m. of nitrogen dioxide for this particular pulsed system.

In this laboratory, experience with the ASTM D 1608–60 analysis for nitrogen dioxide showed a standard deviation of about 3 p.p.m. at very low concentrations of nitrogen dioxide in comparison with the 2 p.p.m. reported here for the electron-capture unit. In consideration of the analysis time of 5 minutes for the gas chromatography *vs.* 3 to 4 days with the ASTM method and a sample size of $^1/_2$ cc. *vs.* nominally 1 liter, the gas chromatographic analysis shows advantages for the particular conditions studied. Similarly the advantage of sample size would prevail relative to the Saltzman (*4*) procedure. Special care must be exercised to eliminate water or any other impurity that has electron affinity. Where nitrogen is used as a carrier and scavenger gas, water apparently is the main impurity, and it may be relatively easily removed by means of molecular sieves at the temperature of a dry ice–acetone bath.

ACKNOWLEDGMENT

The advice on column packing given by I. H. Williams of the British Research Council is appreciated.

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Investigation of Trace Impurities in Solids by Electron Paramagnetic Resonance

Distribution of Manganese in Calcium Carbonate

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▶ **Electron paramagnetic resonance techniques were utilized for the analysis of the state of microcomponents of solids. The dipolar interactions among Mn^{+2} ions substituted in calcium carbonate were calculated and compared with the line widths of hyperfine lines from the viewpoint of whether or not the Mn^{+2} ions will make homogeneously random distribution. It was found that the existence of free and coagulated Mn^{+2} ions can be confirmed in synthesized calcium carbonate doped with Mn^{+2} ions.**

CONSIDERABLE INTEREST exists in processes for analyzing solid substances for microcomponents and for the determination of their distribution, structure, and valence states. It would be very desirable to know whether trace components of solids form homogeneous or inhomogeneous mixtures. The experimental difficulties involved have previously precluded a thorough investigation of this problem. However, through the use of electron paramagnetic resonance (EPR) techniques, precise information concerning these phenomena are attainable. The use of EPR lines to study the distribution of transition element impurities in solid substances should be a very helpful approach to this problem. In the present study, EPR spectra were measured for Mn^{+2} ions in synthesized calcium carbonate as well as in natural calcite and other related compounds. Synthesized samples were used to avoid interference by other impurities, and evidence was obtained to show that one cannot assume a random distribution of Mn^{+2} ions substituting for Ca^{+2} ions. Several articles have appeared (*2*, *6*, *7*) which indicate that both coagulated and free Mn^{+2} ions exist simultaneously in host lattices such as MgO and NaCl. However, a thorough study of this phenomenon has never been made. A detailed study of the EPR spectra of Mn^{+2} ions in calcium carbonate has been carried out in this laboratory and it was found that a trace amount of Mn^{+2} ions in calcium carbonate is not randomly distributed. This finding establishes further information concerning the understanding of the contamination of solids by trace impurities. It has definitely been shown that trace impurities are not distributed on the basis of homogeneous probability when mutual interaction among atoms of the impurity occurs.

EXPERIMENTAL

Apparatus. Electron paramagnetic resonance spectrometer, Type JES-118, Japan Electron Optics Co.

Preparation of Samples. Natural samples were collected from various mines in Japan. Serial samples of calcium carbonate containing Mn^{+2} ions in concentrations from 0.0001 to 8.00% were prepared by adding ammonium carbonate and an excess of ammonium hydroxide to aqueous solutions of calcium chloride containing varying amounts of manganous chloride and a small amount of hydroxylamine to prevent oxidation of Mn^{+2} ions. The precipitates were then filtered off and dried. It was confirmed by analysis that all of the manganese added was contained in the precipitates.

RESULTS AND DISCUSSION

Divalent manganese is an S-state ion. Its 3*d* shell consists of five unpaired electrons and, as a result of low spin-orbit coupling, long relaxation times and relatively narrow line spectra may be expected.

Fifty-four species of calcite and limestone were analyzed; the manganese contents varied from 0.001 to about 0.3%, mostly ranging less than 50 p.p.m.

The EPR spectra of natural calcite, aragonite, and limestone exhibit the characteristic spectrum of Mn^{+2} ions with hyperfine structures. The hyperfine structure is that of isolated Mn^{+2} ions and does not indicate the presence of manganese carbonate as a coagulate. Manganese carbonate gives a spectrum of very broad line width where either fine or hyperfine structures are smeared out. It is thus shown that minor constituents of manganese are randomly distributed in all samples investigated. With regard to the randomness of distribution, more detailed investigation can be accomplished by the use of

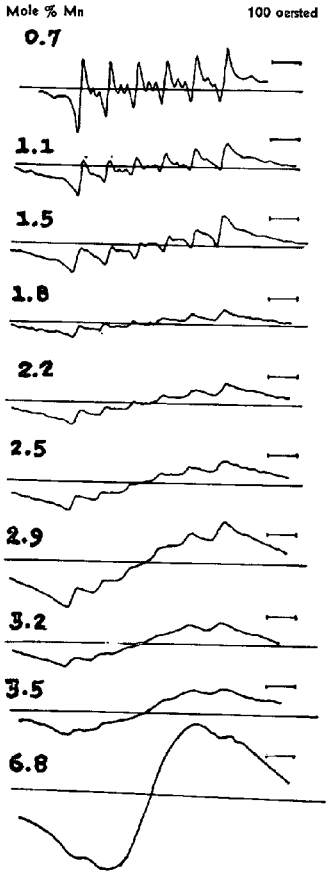

Figure 1. Derivatives of observed EPR spectra for Mn^{+2} in synthesized calcium carbonate

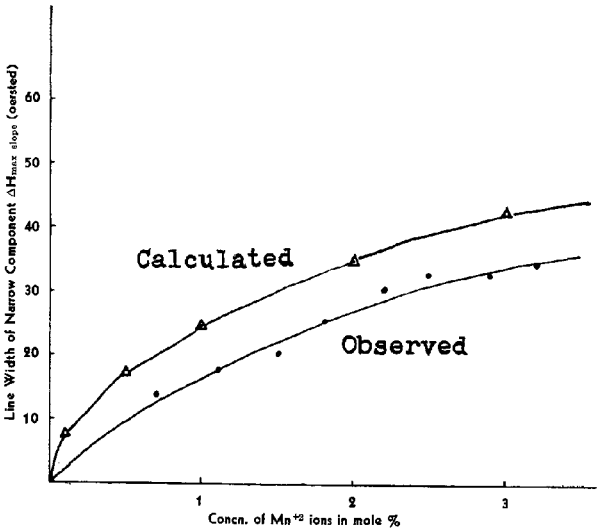

Figure 2. Line width of hyperfine component as function of concentration of Mn^{+2} ions

synthesized calcium carbonate doped with Mn^{+2} ions.

Synthesized samples containing manganese in concentrations of 1 p.p.m. to about 0.7% gave EPR spectra with the hyperfine structure of isolated Mn^{+2} ions. The intensities of the spectra showed an almost linear correlation with manganese contents from 1 to about 20 p.p.m. Spectra for samples containing more than about 0.7% manganese are as shown in Figure 1. They are divided into three types: (a) hyperfine structure composed of six main peaks, (b) a single broad line, and (c) superposition of (a) and (b).

Synthesized calcium carbonate containing less than about 0.7% manganese gave the spectra of type (a) and samples containing more than about 7% manganese gave the spectra of type (b). Samples containing concentrations between 0.7 and 7% manganese show spectra of type (c). Additional synthesized calcite samples containing 0.1 to 8% manganese showed excellent reproducibility with the above types of spectra. In these materials manganese atoms evidently replace calcium in the calcite crystal. In Figure 1, the broad signal is evident, as are hyperfine lines in samples containing more than about 1 mole per cent of manganese, while with samples containing more than about 7% manganese, the hyperfine structure is almost completely smeared out by the broadening of the absorption line.

Samples containing 7% manganese have 1.134×10^{21} Mn^{+2} ions per cubic centimeter of calcium carbonate and the average distance between adjacent Mn^{+2} ions is about 9.6 A., which is approximately twice the distance between the nearest Ca^{+2} ion sites in the calcite structure.

The line width of the EPR spectrum is principally determined by the magnetic dipolar interactions of Mn^{+2} ions. The dipolar interactions between Mn^{+2} ions separated by 5, 10, and 15 A. are 150, 20, and 6 oersteds, respectively. The line width of each component of the hyperfine spectrum ranges from a few oersteds to about 50 oersteds with variation in concentration as shown in Figure 2. The states of Mn^{+2} ions which exhibit hyperfine structure may be defined as free ions. Spectra of type (c) could then be interpreted either as a mixture of free and coagulated Mn^{+2} ions or in terms of the broadening of the components of hyperfine structure. The former case may be considered the superposition of hyperfine structure on a broad line and would be expected to be observed in an inhomogeneous mixture of free and coagulated Mn^{+2} ions, while in the latter case, the character of the hyperfine structure of six main peaks is maintained until each component is smeared out by broadening as the Mn^{+2} ion concentration is increased.

To determine which condition applies to the samples of synthesized calcium carbonate, we may assume that Mn^{+2} ions have a homogeneous probability of occupying any of the lattice sites of Ca^{+2} ions in the calcite structure and that the calcite structure is formed of rectangular cubes with a lattice constant of 5 A. where each lattice point is occupied by either Ca^{+2} or Mn^{+2}. By considering an Mn^{+2} ion placed at a corner of a cube, the probability of another Mn^{+2} ion at the lattice sites of the same and adjacent cubes can be calculated, and the second moment of the width produced by the dipolar interactions of all Mn^{+2} ions which are statistically distributed in the sites outside of the original cube can also be calculated. The square root of this second moment can be taken as the line width of the component of the hyperfine spectrum. This calculation shows that the dipolar contribution to line width produced by Mn^{+2} ions outside of the original cube ranges from 0 to about 50 oersteds for Mn^{+2} ion concentrations of less than 4% as shown in Figure 2 and in the second column of Table I, where the line width thus calculated is referred to as (ΔH) narrow. Comparison of the calculated (ΔH) narrow to the observed line width of the hyperfine lines is made as shown in Figure 2, and it is found that the latter is slightly smaller than the width calculated with the assumption of homogeneous probability of distribution. This difference can be inter-

preted either in terms of exchange narrowing as was proposed in the case of Mn^{+2} ions in MgO and other systems (*2*, *3*) or in terms of the reduction of numbers of Mn^{+2} ions in free states. The latter is inferred by inhomogeneous distribution of Mn^{+2} ions.

Dipolar interactions of Mn^{+2} ions sited within the original cube give six principal broadened lines to form a smooth integrated line with widths from about 500 to more than 1000 oersteds as shown in the third column of Table I.

According to the results of Table I, the free ions defined as before can be referred to as those outside of the original cube as long as Mn^{+2} concentrations are not so high, say up to 4% at the highest. Therefore, the analysis of the line widths of hyperfine component is now related to the distribution of free ions determined either by homogeneous or inhomogeneous probabilities of distribution.

Further consideration of this problem favors the view of inhomogeneous distribution of Mn^{+2} ions.

First, if the exchange interactions among Mn^{+2} ions outside of the original cube are the main reason for line width narrowing of hyperfine lines, a dominant effect would be observed in kutnahorite, a mineral of calcium and manganese carbonate with a formula of $CaMn(CO_3)_2$. The structure of this mineral is well established by x-ray analysis which shows that Ca^{+2} ions are replaced in a regular pattern one after another by Mn^{+2} ions in the calcite structure. The second moment of the EPR absorption line width to be produced by magnetic dipolar interactions among Mn^{+2} ions in kutnahorite has been calculated theoretically (*4*, *5*) as 87,600 ± 150 oersteds^2 through the use of the reported structural data (*1*), and its value for the observed spectrum was found to be about 66,700 ± 1000 oersteds^2. The experimental value of the second moment is crude, since the line shape of the observed spectrum is of the Lorentzian type and the second moment cannot be rigorously obtained. Keeping this in mind, we may assume that the observed line width is comparable to the theoretical width to be produced by dipolar interactions. The line width measured at the points of slope maxima and at half maximum intensity for kutnahorite is 250 ± 2, and 430 ± 10 oersteds, respectively, and the square root of the average of the second moments is 259 ± 10 oersteds. These results do not suggest the existence of appreciable line width narrowing due to exchange interactions in kutnahorite.

Second, if we evaluate the per cent of the area of the broad component with regard to the total area of the absorption spectrum, it is found that the values obtained for the observed spectra shown in Figure 1 are much larger than the values calculated in terms of the contributions of the dipolar interactions among Mn^{+2} ions in the original cube. For example, the value obtained for the observed spectrum of the sample with $Mn/(Mn + Ca) = 3\%$ is about 80%, whereas the calculated value is only 50%. This discrepancy in the weight per cent of the areas of the broad component can be seen throughout the samples to give spectra of type (c). These two results suggest that the narrowness of the hyperfine components is not caused by the exchange interactions among Mn^{+2} ions outside of the original cube, but to the reduction of the number of these ions. The reduction of these ions occurs as a result of the fact that a higher concentration of Mn^{+2} causes coagulation or ion pair formation according to inhomogeneous statistical probability of distribution.

Table I. Results of Calculation of the Dipolar Interactions among Mn^{+2} Ions Homogeneously Distributed in Calcium Carbonate

Concn. of Mn^{+2}, %	$(\Delta H)^a$ narrow, oersteds	$(\Delta H)^b$ broad, oersteds	$(\Delta H)^c$ integrated, oersteds	Fractional wt. of broad line, %
0				
0.1	7.7	225.4	562	2.0
0.5	17.3	234.4	572	10.9
1.0	24.6	245.2	570	20.0
2.0	34.8	265.4	576	36.0
3.0	42.5	285.2	582	49.8
4.0	49.0	302.6	590	59.2
100.0	277	1046.6	1180	100

[a] Line width of a component of the six main hyperfine lines produced by dipolar interactions of Mn^{+2} ions sited outside original cube with homogeneous probability of distribution. [b] Line width of a component of six main hyperfine lines produced by dipolar interactions of Mn^{+2} ions sited within original cube with homogeneous probability of distribution. [c] Half maximum line width of broad line which is obtained as integrated sum of the six main lines of Mn^{+2} ions sited within original cube.

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Kinetics and Mechanism of Extraction of Zinc, Nickel, Cobalt, and Cadmium with Diphenylthiocarbazone, Di-o-Tolylthiocarbazone, and Di-α-Naphthylthiocarbazone

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▷The kinetics of extraction of zinc, nickel, cobalt, and cadmium with diphenylthiocarbazone, di-o-tolylthiocarbazone, and di-α-naphthylthiocarbazone were studied. Each of these reactions were first order in metal ion and, with one exception, first order in reagent anion. The reaction of zinc with di-α-naphthylthiocarbazone was second order in reagent anion. The rate constants for each metal ion paralleled the rate at which water dissociates from the hydrated metal ion. In every case sterically hindering substituents on the phenyl rings of the reagents increased the rate of the reaction. A mechanism is proposed in which the rate-controlling step is the reaction involving the change in configuration of the monodithizonate complex from six- to four-coordinate metal ion, accompanied by the dissociation of water. Values of the distribution coefficients, $K_{D,r}$, of the reagents between $CHCl_3$ and water are reported.

In addition to the use of solvent extraction as a means of studying chelate formation equilibria, in favorable cases it provides a simple technique for the determination of rate constants of chelation reactions which are quite rapid. This is made possible by maintaining the concentration of ligand low by virtue of high reagent distribution coefficient ($K_{D,r}$) and pH control. Thus, when a dithizone solution in chloroform of $10^{-4}M$ is equilibrated with an aqueous phase, the aqueous dithizone concentration is lower by a factor of about 10^6, the value of the $K_{D,r}$. The ligand, dithizonate anion, concentration would be still lower at pH values less than the pK_a for dithizone. The significance of the ability to control ligand concentration at such low levels is, of course, that reactions have rate constants as large as $10^7 M^{-1}$sec.$^{-1}$ and can be observed at reasonable time intervals (2–60 minutes) without elaborate apparatus.

In an earlier paper (*4*), the course of the reaction of zinc(II) with dithizone was studied. The results indicated the probable importance of the role of rupture of zinc-water bonds in the rate-determining step. This suggested further study along two lines: first, to extend the zinc study to other dithizones, in which substituents are so situated as to make steric hindrance a factor in the overall chelate structure (the effect of steric hindrance on chelate formation thermodynamics has been previously investigated but rarely its effect on kinetics); second, to extend the study to other transition metal dithizonate extractions to learn whether the kinetics of these reactions could be correlated with the rate of water loss from the respective metal cations (*2, 3*).

EXPERIMENTAL

Apparatus. All extractions were performed in 50-ml. vials fitted with polyethylene liners and plastic caps. The samples were agitated on an Eberbach box type shaker at the low speed setting. The sample agitation was somewhat more vigorous than the maximum attainable using the Burrell shaker (*4*). The insulated shaker box was kept at constant temperature (±1° C.) by means of a copper coil through which water from a constant temperature bath was circulated. The coil was welded to a copper plate which served as the base of the shaker box. Measurements of radioactivity were made with a Nuclear-Chicago Model DS5-5 well-type scintillation detector whose output was registered on a Model 192A scaler. A Beckman Model G pH meter was used for all pH measurements. This meter was standardized against Beckman pH 7 buffer before each set of measurements. Spectrophotometric measurements were made with Beckman Model DU and DB spectrophotometers.

Materials. Specially processed, high activity zinc-65 in the form of $ZnCl_2$ was obtained from the Oak Ridge National Laboratory. The active zinc solution was diluted so that the final solution for extraction contained a total zinc concentration of $2.5 \times 10^{-6}M$ and a chloride concentration of $1 \times 10^{-7}M$. Reagent grade nickel perchlorate, cobalt perchlorate, and cadmium perchlorate obtained from G. F. Smith Chemical Co. were used to prepare $1 \times 10^{-3}M$ solutions of the metal ions. The isotopes Co^{60} and Cd^{115} were obtained from the Oak Ridge National Laboratory. Reagent grade dithizone was further purified by the method cited by Welcher (*9*). The 2,2′-dimethyl and di-α-naphthyl derivatives of dithizone were prepared and purified by standard methods in this laboratory by K. S. Math. The reagent solutions were prepared by direct weighing of the carefully purified and dried reagents. The stability of the solutions was checked at regular intervals by spectrophotometric methods using the following data:

Dithizone λ max. = 606 mμ, $\epsilon = 4.06 \times 10^4$

2,2′-Dimethyl derivative λ max. = 610 mμ, $\epsilon = 4.95 \times 10^4$

Di-α-naphthyl derivative λ max. = 685 mμ, $\epsilon = 2.15 \times 10^4$

Dithizone solutions were stable for only about a week, while the 2,2′-dimethyl derivative solutions showed no evidence of decomposition even after a month. The di-α-naphthyl derivative solutions were very unstable, and had to be prepared each day. All other chemicals were reagent grade. Water was purified by passing it through a mixed bed ion exchange column supplied by Crystal Research Laboratories, Inc., Hartford, Conn.

Partition of Reagent. Equal volumes of a solution of the reagent in chloroform and an aqueous phase consisting of phosphate buffer and sufficient sodium perchlorate to give an ionic strength of 0.25 were shaken for 15 minutes. The solutions were allowed to stand for 10 minutes to ensure complete phase separation. The pH of the aqueous phase was measured. A portion of the organic phase was then transferred by pipet to a spectrophotometric cell and the absorbance, A, was measured.

From a plot of

$$\frac{A_{orig.} - A_{final}}{A_{final}} \text{ vs. } \frac{1}{[H^+]}$$

values for K_a/K_{D_r} were obtained (*3*).

Determination of Kinetics of Reaction. The extraction procedure was altered somewhat from that of Honaker and Freiser (*4*). Their method involved taking micro aliquots, at definite time intervals, on a single sample for a kinetic run. The standing time after agitation affected the results of the kinetic study. Since at least a 5-minute standing period is necessary for phase separation, their method leads to large variations in the standing time following agitation. Therefore the procedure was altered so that a separate sample was used for each time interval. This allowed each sample to stand the same length of time following agitation. The detailed procedure for zinc follows.

All extractions were made from aqueous solutions having an ionic strength of 0.25 produced by the addition of sufficient sodium perchlorate to the buffered solutions. Acetate buffers were used for all the kinetic studies with zinc, but phosphate buffers were sometimes used for the other metal ions. All extractions were performed at 25° ± 1° C. The initial aqueous zinc concentration in all cases was $2.5 \times 10^{-6} M$. This zinc solution contained enough Zn^{65} to give a count of about 5000 c.p.m. per ml. Similar concentrations and count rates were used with Co and Cd extractions. With Ni, $2.0 \times 10^{-4} M$ solutions were used, since the Ni in the aqueous phase after extraction was spectrophotometrically determined using dimethylglyoxime (*3*). The pH of the aqueous phase was adjusted to the desired value by addition of the appropriate buffer solution, and its value was checked with the pH meter. A 10-ml. aliquot was shaken for a definite time interval (from 2 to 60 minutes) with 10 ml. of a chloroform solution of the reagent. The time of reaction, measured with an electric timer, was taken from the time agitation was begun until it was stopped. Each sample was then allowed to stand 5 minutes to ensure complete phase separation. A 5-ml. aliquot was transferred to a plastic tube for counting. The sample was then counted for a length of time necessary to obtain a total count of at least 10,000. The ratio of the count rate of the sample to the count rate of the same volume of the original metal solution gave the metal concentration in the aqueous phase. A typical set of extraction data is shown in Table I.

Table I. Kinetic Data for Extraction of Zinc with Dithizone

$[HDz]_o \times 10^4$	$[H^+] \times 10^4$	Slope[a]	k'[b]
0.97	2.82	0.0018	0.012
1.94	2.82	0.0040	0.013
3.00	2.82	0.0078	0.017
5.00	2.82	0.0160	0.021
1.00	1.26	0.0082	0.024
3.00	1.26	0.0280	0.027
3.00	0.49	0.0630	0.024
5.00	0.49	0.1220	0.028
5.00	0.71	0.0750	0.024
2.00	1.32	0.0196	0.030
2.00	1.32	0.0160	0.024
2.00	4.90	0.0022	0.012
2.00	2.57	0.0048	0.014
2.00	1.26	0.0134	0.019
2.00	0.74	0.0258	0.022
2.00	0.45	0.0366	0.019
0.10	0.16	0.0090	0.033
0.10	0.06	0.0104	0.015

$k'_{av.} = 0.021$
$\sigma = 6.3 \times 10^{-3}$

[a] Slope of a plot of $\log \frac{[Zn]_{t=0}}{[Zn]_t}$ *vs.* time.

[b] $k' = 2.303 \times \text{slope} \times \frac{[H^+]}{[HDz]_o}$

RESULTS AND DISCUSSION

Distribution of Reagent. The distribution of dithizone and its derivatives between an aqueous and an organic phase involves two equilibria according to the Nernst distribution law

$$HDz_{(o)} \overset{K_{D_r}}{\rightleftharpoons} HDz_{(w)}; \quad K_{D_r} = \frac{[HDz]_o}{[HDz]_w}$$

$$HDz_{(w)} \overset{K_a}{\rightleftharpoons} H^+ + Dz^-; \quad K_a = \frac{[H^+]\,[Dz^-]}{[HDz]_w}$$

The expression for the distribution of the reagent, D_r, or distribution ratio, is

$$D_r = \frac{[HDz]_o}{[HDz]_w + [Dz^-]_w}$$

from which it can be shown that

$$\frac{1}{D_r} = \frac{1}{K_{D_r}} + \frac{K_a}{K_{D_r}[H^+]}$$

Although very high values of D_r, requiring very sensitive spectrophotometric assay of the low reagent concentration in the aqueous phase, would be needed to determine K_{D_r}, a series of intermediate values of D_r as a function of pH is more readily accessible and permits the determination of Ka/K_{D_r} (the slope of a plot of $1/D_r$ *vs.* $1/[H^+]$).

The values of Ka/K_{D_r} obtained in this manner for dithizone, the 2,2′-dimethyl, and the di-α-naphthyl derivatives of dithizone are shown in Table II. Values of K_{D_r} that have been calculated from this data with the aid of independently measured K_a values (*6*) are also included. The distribution coefficient of dithizone is quite high. The effect of methyl substitution is to increase the value of log K_{D_r} by 0.7 unit per carbon atom which is similar to that (0.6) found for a number of reagents. As expected, when the substituent is part of an aromatic ring, the rise in log K_{D_r} per additional carbon atom is smaller (0.34) in the naphthyl derivative.

Table II. Distribution Characteristics of Dithizones between $CHCl_3$ and Water at 25° C.

Compound	[a]log Ka/K_{D_r}	pK_a[b]	log K_{D_r}
Dithizone	10.18	4.3	5.9
2,2′-Dimethyldithizone	12.00	4.7	7.3
Di-α-naphthyldithiocarbazone	12.30	3.7	8.6

[a] Ionic strength = 0.25.
[b] Values of (*6*) lowered by 1.5 units to correct the observed value obtained in dioxane-water mixture to aqueous medium. This correction is approximate but permits a valid comparison of these three related reagents.

Kinetics of Extraction. The reaction orders with respect to the metal ion were determined from plots of log

$$\frac{[Me^{+2}]_t = 0}{[Me^{+2}]_t}$$

vs. time. This yielded straight lines, indicative of a first-order reaction with respect to metal ion in all cases. The change in the values of the slopes of these lines obtained at various pH and $[HR]_o$ values were used to obtain reaction orders with respect to $[HR]_o$ and $[H^+]$ (Table III).

Although the reaction orders of these extractions with respect to metal ion concentrations were exactly unity, the orders in reagent and hydrogen ion concentrations deviate from this value. The reason for this deviation is considered to arise from the greater uncertainty of the determination of these orders in all but the reaction of zinc with the di-α-naphthyl derivative where the orders are +2 in reagent and −2 in $[H^+]$.

The steps involved in the reaction for the extraction of zinc with dithizone are as follows.

Table III. Reaction Orders for Metal Dithizonates

Metal	Reagent[a]	Reaction order in $[HR]_o$	Reaction order in $[H^+]$
Zinc	A	1.15	−1.17
	B	1.30	−1.13
	C	1.91	−1.70
Nickel	A	1.10	−0.82
	B	0.80	−1.04
	C	1.35	−0.78
Cobalt	A	0.96	−0.72
	C	1.53	−0.75

[a] A, B, and C refer to dithizone, its di-2-methyl, and di-α-naphthyl derivatives, respectively.

$$HDz_{(o)} \rightleftharpoons HDz_{(w)} \quad (1)$$

$$HDz_{(w)} \rightleftharpoons H^+ + Dz^- \quad (2)$$

$$Zn^{+2} + Dz^- \rightleftharpoons ZnDz^+ \quad (3)$$

$$ZnDz^+ + Dz^- \rightleftharpoons ZnDz_{2(w)} \quad (4)$$

$$ZnDz_{2(w)} \rightleftharpoons ZnDz_{2(o)} \quad (5)$$

Honaker and Freiser (*4*) reported the forward reaction of step 3 to be the rate-controlling reaction. Substituting the equilibrium expression for steps 1 and 2 in

$$\frac{d[Zn^{+2}]}{dt} = k[Zn^{+2}]\cdot[Dz^-] \text{ or} \quad (6)$$

$$\frac{-d[Zn^{+2}]}{dt} = \frac{k'[Zn^{+2}]\ [HDz]_o}{H^+} \text{ yields} \quad (7)$$

$$\frac{-d[Zn^{+2}]}{dt} = k\frac{K_a}{K_{D_r}} \times \frac{[Zn^{+2}]\ [HDz]_o}{[H^+]} \quad (8)$$

Hence, dividing the value of k' by K_a/K_{D_r} yields the rate constant, k, for the reaction. The values for k are 3.7 $\times$ $10^8 M^{-1}$minute^{-1} for dithizone, 4.5 $\times$ $10^8 M^{-1}$minute^{-1} for 2,2′-dimethyl diphenylthiocarbazone, and would be still larger for di-α-naphthylthiocarbazone if the kinetic order were the same as for the other two. Although the zinc dithizone is considerably more stable (log K_{f_1} = 4.7) (these K_f values are 1.5 log units lower than observed in dioxane-water mixture to make them more applicable to aqueous equilibria) than the methyl-substituted zinc chelate (log K_{f_1} = 3.0) (*6*), the zinc dithizonate does not form more rapidly than does the 2,2′-dimethyl diphenylthiocarbazone chelate. In this case, the expected relationship between the stability of the chelate and the rate of formation is reversed. Bulky groups substituted on the phenyl rings in dithizone increased the rate of formation of the zinc chelates.

The failure of the thermodynamic disadvantage of the presence of the sterically hindering substituents to be reflected in the rate of chelate formation indicates that step 3 might be more complex than first envisioned. Several steps are involved in the formation of the chelate: loss of water molecules from the octahedral zinc hexahydrate, addition of the first and second ligands, and change of structure from the octahedral hexahydrate to the tetrahedral zinc dithizonate. In aqueous solution, zinc exists as the octahedral hexahydrate (*7*). Coordination reactions of metal ions would involve either loss of coordinated water or expansion of the coordination sphere (*1*). The former alternative seems more likely in the case of zinc. Eigen (*3*) reports the rate of removal of water molecules from the zinc ion to be greater than 10^8 minute^{-1}. The rate at which water molecules can be removed from the zinc ion would be expected to be the limiting rate of formation of the zinc chelates.

The following mechanism for the formation of the zinc dithizonates is presented as a modification of that given by Honaker and Freiser (*4*):

$$Zn(H_2O)_6^{+2} + Dz^- \xrightleftharpoons{K_{f_1}} Zn(H_2O)_4Dz^+ + 2H_2O \quad (9)$$

$$Zn(H_2O)_4Dz^+ \xrightarrow{k_1} Zn(H_2O)_2Dz^+ + 2H_2O \quad (10)$$

$$Zn(H_2O)_2Dz^+ + Dz^- \xrightarrow{k_2} Zn(Dz)_2 + 2H_2O \quad (11)$$

This alternative mechanism better explains the experimental results. First, the substituted dithizone derivatives show an increased reaction rate with zinc. The explanation for this might be that the bulky groups facilitate the removal of water molecules after the addition of the first ligand. Also, steric strain is relieved in changing from the octahedral to the tetrahedral structure. As k_1 increased, k_2 might be expected to become more significant in the overall rate expression. This would explain what has happened in the case of the di-α-naphthyl derivative. The rate equations for this mechanism are as follows:

$$\frac{-d\ [Zn^{+2}]}{dt} = k_1[Zn(H_2O)_4Dz^+]$$

or, upon substitution from Equation 9:

$$\frac{-d[Zn^{+2}]}{dt} = \frac{k_1K_aK_{f1}[Zn^{+2}]\ [HDz]_o}{K_{D_r}[H^+]}$$

and, when k_1 is sufficiently high to make Equation 11 rather than Equation 10, rate determining:

$$\frac{-d[Zn^{+2}]}{dt} = k_2[Zn(H_2O)_2Dz^+]\ [Dz^-]$$

which upon substitution gives:

$$\frac{-d[Zn^{+2}]}{dt} = K_TK_{f_1}k_2\ [Zn^{+2}]\frac{K_a^2}{K_{D_r}^2}\frac{[HDz]_o^2}{[H^+]^2}$$

where

$$K_T = \frac{[Zn(H_2O)_2Dz^+]}{[Zn(H_2O)_4Dz^+]}$$

The values for k_1, calculated for the reaction of zinc with dithizone and its 2,2′-dimethyl derivative based upon this mechanism, are $10^{+3.9}$ minute^{-1} for dithizone and $10^{+5.65}$ minute^{-1} for 2,2′-dimethyl derivative. The value of k_2K_T is 2.6 $\times$ $10^{16} M^{-1}$minute^{-1} for di-α-naphthyl derivative. The value for K_T is not known at the present, therefore k_2 cannot be calculated. The value for K_T would be expected to be quite large. This explains the abnormally high value that would be obtained for k_2 if the mechanism given by Honaker and Freiser (*4*) were used, since there the K_T does not enter into the rate equation.

It is rather unusual to find that the first formation step in metal chelation is slower than the successive steps in view of the natural advantage of greater charge neutralization. Our results would seem to indicate that the change in coordination number of zinc ion is responsible. In this connection, an attempt was made to observe the rate of reaction of zinc with diphenylcarbazone and with 8-hydroxyquinoline. In both cases, where zinc remains six coordinate, the reactions occurred too rapidly to study the kinetics by the extraction method. Further work with other sulfur-containing ligands is under way to test the generality of this conclusion.

A further implication of the zinc study is that water removal from the metal ion appears to play a key role in the rate-determining step. In this case, the reaction kinetics of other metal dithizonates might be expected to follow a course related to the rate of water loss from the respective metal cations (*2, 3*). As seen in Table III, the reaction orders observed with Ni and Co were the same as those for zinc. The rate constants, k, based on equations analogous to Equation 8 are listed in Table IV.

An attempt was made to study the

Table IV. Comparison of Rate Constants for Formation of Metal Chelates with Dithizone and Related Compounds with Rate of H_2O Substitution in Metal Ions

Metal ion	Rate of H_2O substitution, k(minute^{-1})	Rate constant (kM^{-1}minute^{-1})		
		HDz	HMeDz	α-NHDz
Cd^{+2}	2.4×10^{10}	10^9	...	$>10^{10}$
Zn^{+2}	3.0×10^9	3.7×10^8	4.5×10^8	5.8×10^{9a}
Co^{+2}	3.0×10^7	5.2×10^6	...	4.8×10^8
Ni^{+2}	1.2×10^6	8.0×10^4	3.1×10^5	7.6×10^6

[a] Arbitrarily calculated in same manner as others for purposes of comparison.

kinetics of extraction of cadmium with dithizone and its di-α-naphthyl derivative. In both cases, the reaction occurred too rapidly to be studied by the solvent extraction method. Equilibration was attained in less than two minutes in every run. The data indicated the rate constant to be greater than $10^9 M^{-1}$minute^{-1} in the case of dithizone and greater than $10^{10} M^{-1}$minute^{-1} in the case of the α-naphthylthiocarbazone.

From Table IV, the importance of the lability of the metal ion–water bond in the overall reaction kinetics may be seen. The rate of metal dithizonate formation increases in an approximately linear fashion with the rate of dissociation of water from the various metal ions. Thus, it would seem reasonable to postulate that loss of coordinated water is involved in the rate-determining step in each of the reaction systems studied. This view is supported by the effect of steric hindering substituents on the reagent molecules on the rates observed. These substituents can be expected to facilitate the removal of coordinated water molecules.

Math *et al.* (*6*) have shown that the chelate formation constants of nickel(II) dithizonates do not decrease, as do those of zinc and cadmium with the presence of steric hindering substituents, probably because the nickel dithizonate involves an N—N (rather than N—S) structure. The rates observed here are of the same order of magnitude and display the same reaction order as those obtained in the polyamine nickel complexes (*5*).

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Study of Kinetics of Iridium(III)–Chlorate Reaction by Steady-State Controlled-Potential Coulometry

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▶ **The use of steady-state controlled-potential electrolysis in the investigation of kinetics of redox reactions has been examined with regard to types of systems amenable to study. The kinetics of the iridium(III)–chlorate redox system have been investigated by this method. The rate law has the form**

$$\frac{d(IrCl_6^{-3})}{dt} = -k(IrCl_6^{-3})\,(ClO_3^-)$$

at a constant hydrogen ion concentration of 0.2M with $k = (3.2 \pm 0.1) \times 10^{-4} M^{-1}$second^{-1} at 45° C. and $\mu = 1.0$. The effects of various reactants and products on the rate of the reaction were investigated over the concentration ranges $(H^+) = 0.05$ to 0.8M; $(ClO_3^-) = 0.02$ to 0.15M; $(Cl^-) = 0.0$ to 0.2M; $(IrCl_6^{-3}) = 8 \times 10^{-4}$ to 0.01M; and initial $(IrCl_6^{-2}) = 0.0$ to 2.8×10^{-3}M. The rate constant is in good agreement with that determined polarographically ($3.0 \times 10^{-4} M^{-1}$second^{-1}). The Arrhenius activation energy, determined over a temperature range of 35° to 50° C., is 30 kcal. The overall reaction is thought to proceed through the rate-determining step $IrCl_6^{-3} + ClO_3^- \rightarrow IrCl_6^{-2} + ClO_3^{-2}$. Aquation of $IrCl_6^{-3}$ during the rate measurement was considered, and it was shown that $IrCl_6^{-3}$ and $IrCl_5(H_2O)^{-2}$ react with ClO_3^- at the same rate.

INFORMATION ABOUT KINETICS of a reaction can be useful in choosing optimum experimental conditions for carrying out that reaction. Application of controlled-potential electrolysis in the investigation of kinetics of homogeneous solution reactions has been approached through the relationship between kinetic parameters and the apparent extent of oxidation or reduction during electrolysis (*2*, *3*, *6*, *7*), and through the relationship between kinetic parameters and the steady-state current obtained during an electrolysis opposed by a chemical regeneration of the electroactive material in the bulk of the solution (*9*, *11*). This paper discusses some of the limitations of the latter approach and illustrates it by application of the method to an investigation of the kinetics of the iridium(III)–chlorate redox system.

THEORY

In the following discussion, *B*, *C*, and *D* are not electroactive at the potential at which *A* undergoes an electrode reaction.

If a bulk electrolysis is carried out on a substance, *A*, to yield a product, B, at an electrode whose potential is maintained constant and under limiting current conditions, the current will decay exponentially with time according to $i = i_0 e^{-\lambda t}$ where i_0 is the current at time zero and λ is a constant depending upon prevailing mass transfer conditions, cell geometry, solution volume, electrode area, and stirring (*1*).

If, however, the electroactive species, *A*, is regenerated by a chemical reaction between the electrolysis product and some species, *C*, in the bulk of the solution ($B + C \xrightarrow{k_1} A + D$), the current, after an initial decay, will attain some steady-state value. This steady-state current, which results when the rates of the electrochemical process and chemical reaction in the bulk of the solution become equal, can be used to obtain information about the kinetic parameters of the chemical reaction. The relationship between the steady-state current, i_{ss}, and the rate of the chemical reaction is shown by the following.

The rate of the electrode reaction is given by

$$-\left[\frac{d(A)}{dt}\right]_{elec.\ rxn.} = \lambda(A) = \frac{i}{nFV} \quad (1)$$

where *A* is the concentration of the electroactive species, *i* the electrolysis current, *n* the electron change, *F* the faraday, and *V* the volume of solution in the electrolysis cell. The rate of the chemical reaction, for simple kinetics, is given by

$$-\left[\frac{d(B)}{dt}\right]_{chem.\ rxn.} = k(B)^x(C)^y \quad (2)$$

If electrolysis is begun with only A and C present, the rate of the electrolysis reaction will decrease as time passes, as a result of a decrease in the bulk concentration of A, and the rate of the chemical reaction will increase as a result of increase in the bulk concentration of B. Eventually, a situation will be reached in which the rates of the two reactions become equal—i.e.,

$$\left[\frac{d(A)}{dt}\right]_{\text{elec. rxn.}} = \left[\frac{d(B)}{dt}\right]_{\text{chem. rxn.}}, \text{ and}$$

the electrolysis current, now a steady-state current, attains a constant value.

Before steady state is reached, $\frac{d(B)}{dt}$ the overall rate of change of B, is given by

$$\frac{d(B)}{dt} = -k_1(B)^x(C)^y + \lambda(A)$$

where k_1 is the forward rate constant for the chemical reaction taking place in the bulk of the solution. At steady state, $\frac{d(B)}{dt} = 0$; therefore, we have

$$k_1(B)^x(C)^y = \lambda(A) \qquad (3)$$

and from Equations 1, 2, and 3,

$$\frac{i_{ss}}{nFV} = k_1(B)^x(C)^y = -\left[\frac{d(B)}{dt}\right]_{\text{chem. rxn.}}$$

a relationship between the steady-state current and the rate of the chemical reaction. The effect of the various reactants and products, A, B, C, and D, on the rate of the chemical reaction can be tested by varying their steady-state concentrations and observing the corresponding variation in steady-state current.

Steady-state controlled-potential electrolysis should be applicable to the investigation of kinetics of any redox reaction which is part of a cycle involving regeneration of the electroactive species by chemical reaction provided that the system meets certain electrochemical requirements, and the rate constant does not exceed a certain value.

The main electrochemical requirement is that only one species be electroactive at the controlled potential. This species, of course, will be that which is regenerated by the chemical reaction in the bulk of the solution. If this condition is not met, species C, which reacts with the electrolysis product B, regenerating A, will also be consumed at the electrode. The electrolysis current will continue to fall as both A and C are consumed and a steady-state situation will not be reached. When one considers the standard potentials of the redox couples involved in a chemical reaction, it is obvious that, if both couples are reversible, more than one species will be electroactive at the controlled potential. That is, if C is capable of oxidizing B ($C + B \rightarrow A + D$), the electrolysis product of A, the standard potential of the couple $C + ne^- \rightarrow D$ must be more positive than that of $A + ne^- \rightarrow B$, so that C will also be reduced at the controlled potential where A is reduced. Thus, the couple involving the species which regenerates the electroactive species must be irreversible. This requirement is obviously a limitation on the number of reactions which can be investigated by the controlled-potential electrolysis method.

The smallest rate constant which can be investigated by this method is probably limited by the experimenter's ability to distinguish between background and steady-state currents. The maximum rate constant which can be measured is limited by the requirement that there be an initial decay of current before the steady-state is attained. This condition ensures that the chemical reaction is taking place homogeneously in the bulk of the solution, not just in the region of the electrode surface, and that the current is a measure of the rate of the chemical reaction. This condition may or may not be attainable for a given reaction depending on mass transfer conditions and reactant concentrations. A large mass transfer coefficient, λ, is desirable when studying fast reactions. With optimum cell geometry and good stirring, λ values as high as 0.1 second^{-1} can be attained (*1*). Reactant concentrations should be such that measurable values of i_0 and i_{ss} are obtained, and, if a colorimetric method is to be used to measure steady-state concentration, high enough to give a measurable absorbance. The concentration of C, which is consumed as it regenerates the electroactive species, should be high enough not to change significantly—e. g., not more than 1%—during the steady-state measurement. If the consumption of C is rapid, the rate of the regeneration reaction will decrease with time, and a steady-state situation will obviously never be reached. The per cent change allowed is somewhat arbitrary, depending on the accuracy desired. A relationship is given below for the maximum rate constant which can be investigated for a given set of mass transfer and reactan concentration conditions.

At steady state for a second-order reaction,

$$\frac{i_{ss}}{nFV} = \left[\frac{d(B)}{dt}\right]_{\text{chem. rxn.}} = \left[\frac{d(A)}{dt}\right]_{\text{elec. rxn.}} = \lambda(A) = k(B)(C)$$

or

$$k = \frac{\lambda(A)}{(B)(C)}$$

Recalling the requirement that the current must decay before steady state is reached and that this decay be at least 1% of the initial current,

$$\frac{(A)}{(B)} = \frac{0.99\,(A)_0}{0.01\,(A)_0} = 10^2,$$

and

$$k = \frac{\lambda\,(100)}{(C)}$$

λ and C should be chosen so that the conditions outlined above (measurable current and concentration and no change in concentration during the steady-state measurement) are met. The maximum rate constant which can be investigated by this method is $\simeq 10^5\ M^{-1}$ second^{-1}, corresponding to a situation where λ = 0.1 second^{-1}, cell volume = 5 ml., n = 1, $(A)_0 = 10^{-6}\ F$, and $(C) = 10^{-4}\ F$. Under these conditions, assuming i_{ss} = 99% i_0, i_{ss} will be about 50 μ $A[nFV\lambda(A)]$. Steady state should be reached in about 0.1 second $\left(\frac{i}{i_0} = e^{-0.1t} = \frac{99}{100}\right)$, and (C) should decrease less than 1% in 10 seconds

$$\left(\frac{d(C)}{dt} \times dt = 10^5 \times 10^{-8} \times 10^{-4} \times 10 = 10^{-6}\right)$$

This method has been shown to give rate constants with a precision of ± 3% (this paper). More rigid control of such variables as cell temperature and reactant concentrations should result in even better precision. This method may be especially useful in the investigation of systems in which one of the reactants is unstable and can be generated at an electrode.

EXPERIMENTAL

Reagents. All materials were of reagent grade. G. F. Smith reagent grade $NaClO_4 \cdot H_2O$ was used without further purification. G. F. Smith reagent grade $HClO_4$ was standardized against Na_2CO_3. Baker Analyzed Reagent grade $NaClO_3$ was used without standardization. Na_2IrCl_6, obtained from A. D. Mackay (198 Broadway, New York 38, N. Y.) was standardized by Mohr's salt titration with potentiometric end point, by spectrophotometry using Poulsen's ϵ values (*10*), and by coulometry. The three independent determinations agreed within 2% (relative). Na_2IrCl_6, obtained from K and K Labs (177-10 93rd Avenue, Jamaica 33, N. Y.), was standardized by titration with $KMnO_4$, using a photometric end point, and by spectrophotometrically measuring the $IrCl_6^{-2}$ produced by bubbling chlorine gas through a solution of $IrCl_6^{-3}$. Relative agreement between the two independent determinations was 2%. The absorbance of $IrCl_6^{-3}$ could not be used for standardization because of an interference in the absorbance measurement from insoluble particles.

Apparatus. A Duffers Model 600 potentiostat was used to maintain the potential of the working electrode

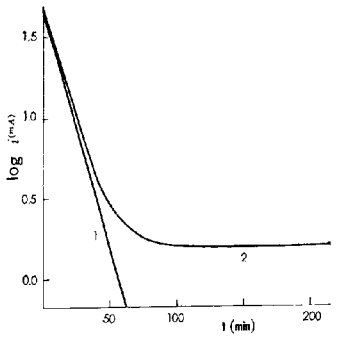

Figure 1. (1) Reduction of $IrCl_6^{-2}$ in absence of ClO_3^-. (2) Reduction of $IrCl_6^{-2}$ in presence of ClO_3^-

constant. The control potential was continuously monitored with a Houston Model HV-160 d.c. voltmeter. The electrolysis current was followed by measuring the iR drop across a precision resistor with a Photovolt Model 43 recorder. A voltage-to-frequency converter was employed for integration of the current. The electrolysis cell was similar to that described by Meites (*8*). The working electrode was a mercury pool cathode with an area of 50 sq. cm.; the reference electrode was a Leeds & Northrup S.C.E. separated by a salt bridge and agar plug from the working electrode compartment; and the counter electrode was a platinum gauze electrode separated from the working electrode compartment by two frits to minimize diffusion between the two compartments. The cell was immersed in a constant temperature bath held at 45° C. ± 0.1° in all experiments, except those in which the effect of temperature on the reaction rate was tested.

All solutions were pre-electrolyzed to a constant background current, which was subtracted to determine the steady-state current due to the regeneration reaction. $IrCl_6^{-2}$ was added to the cell from a pipet after removing an equal volume of solution to maintain constant cell volume (130 ml. in all experiments). $NaClO_3$, $NaClO_4$, and $HClO_4$ were present during the pre-electrolysis. The ionic strength was held constant at 1.0 by addition of $NaClO_4$. The mass transfer coefficient (λ) for the above conditions was 6×10^{-4} second^{-1}.

Polarograms were recorded on a Sargent Model XXI polarograph. A Perkin Elmer Model 202 UV-visible recording spectrophotometer was used for absorbance measurements.

RESULTS

The current-time behavior of the iridium–chlorate system is shown in Figure 1. When $IrCl_6^{-2}$ is reduced to $IrCl_6^{-3}$ in the absence of ClO_3^- at a potential of 0.00 volt *vs.* S.C.E. (limiting current conditions), the current decays exponentially with time. In the presence of ClO_3^-, however, the current, after an initial decay, levels out to some steady-state value, owing to a regeneration of the electroactive species, $IrCl_6^{-2}$, by reaction of the electrolysis product, $IrCl_6^{-3}$, with ClO_3^- in the bulk of the solution.

This steady-state current, i_{ss}, is related to the rate of the $IrCl_6^{-3}$–ClO_3^- reaction by

$$\frac{i_{ss}}{nFV} = -\left[\frac{d(IrCl_6^{-3})}{dt}\right]_{chem.\ rxn.} = k(IrCl_6^{-3})^x(ClO_3^-)^y.$$

The effect of various reactants and products on the rate of this reaction was tested by varying their steady-state concentrations and observing the corresponding variation in steady-state current.

A plot of i_{ss}/nFV *vs.* $(IrCl_6^{-3})_{ss}$ gives a straight line indicating that the rate law is first order in $IrCl_6^{-3}$ (Figure 2 and Table I). The steady-state $IrCl_6^{-3}$ concentration was estimated by making use of the relationship between electrolysis current and concentration of electroactive species: at any time, $i = k'(IrCl_6^{-2})$, where k' may be estimated by dividing i_0, the initial current obtained by extrapolating to time zero, by $(IrCl_6^{-2})_0$ which is known from the amount of $IrCl_6^{-2}$ added to the cell and the cell solution volume. The steady-state concentration of $IrCl_6^{-2}$ is then i_{ss}/k', and, since all of the iridium is in the +3 and +4 oxidation states, $(IrCl_6^{-3})_{ss} = (IrCl_6^{-2})_0 - (IrCl_6^{-2})_{ss}$. $(IrCl_6^{-2})_{ss}$, calculated by measuring the iridium(IV) absorbance [using ϵ values of Poulsen (*10*)] at steady state, agreed with the concentration calculated by the above method within 2%. In the optical method, $(IrCl_6^{-2})_{ss}$ was measured by removing

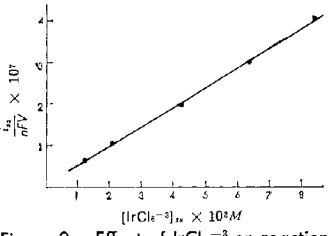

Figure 2. Effect of $IrCl_6^{-3}$ on reaction rate

0.15*M* ClO_3^-, 0.2*M* $HClO_4$, μ = 1.0, *V* is in liters, *i* is in amperes

solution from the cell and placing it in a spectrophotometer cell. The total time for sampling and running the spectrum was 4 minutes. It can be shown (based on the rate of the chemical reaction) that the $IrCl_6^{-2}$ concentration changes only about 1% during this time.

The effect of ClO_3^- on the rate of the reaction is shown in Figure 3 (see also Table II). The straight-line plot indicates that the rate law is first order in ClO_3^-. The steady-state concentration was calculated from the amount of $NaClO_3$ added to the cell before pre-electrolysis. It can be shown, from current values and electrolysis time, that the ClO_3^- concentration remains essentially constant (within 1%) during the electrolysis.

The effect of Cl^- and H^+ on the reaction rate is shown in Figures 4 and 5 (see also Tables III and IV). Chloride ion apparently does not affect the reaction rate until its concentration reaches a value of 0.06*M*, about 25 times the steady-state $IrCl_6^{-3}$ con-

Table I. Effect of $IrCl_6^{-3}$ on Reaction Rate

ClO_3^- = 0.150*M*, $HClO_4$ = 0.20*M*

i_{ss},[a] ma.	$i_{residual}$, ma.	$(IrCl_6^{-3})_{ss}$	$k = \frac{i_{ss}}{nFV(IrCl_6^{-3})(ClO_3^-)}$
0.790	0.38	1.25×10^{-3}	3.36×10^{-4}
1.35	0.28	2.11×15^{-3}	3.40×10^{-4}
2.48	0.39	4.25×10^{-3}	3.10×10^{-4}
3.76	0.42	6.35×10^{-3}	3.15×10^{-4}
5.05	0.48	8.40×10^{-3}	3.20×10^{-4}

[a] After subtracting residual current.

Table II. Effect of ClO_3^- on Reaction Rate

$HClO_4$ = 0.20*M*

i_{ss},[a] ma.	$i_{residual}$, ma.	$(IrCl_6^{-3})_{ss}$	$(ClO_3^-)_{ss}$	$k = \frac{i_{ss}}{nFV(IrCl_6^{-3})(ClO_3^-)}$
0.360	0.182	4.39×10^{-3}	0.0200	3.27×10^{-4}
0.533	0.230	4.35×10^{-3}	0.0300	3.26×10^{-4}
0.900	0.296	4.33×10^{-3}	0.0500	3.31×10^{-4}
0.847	0.202	2.12×10^{-3}	0.100	3.18×10^{-4}
			0.150	3.24×10^{-4}[b]

[a] After subtracting residual current.
[b] Av. k from Table I.

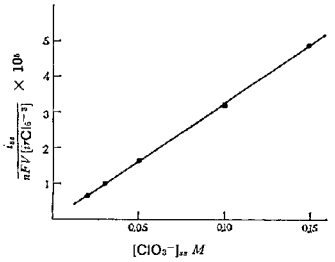

Figure 3. Effect of ClO_3^- on reaction rate

0.2M $HClO_4$, μ = 1.0. Concentrations are in moles per liter

centration. The chloride ion concentration was not varied (see Table III) under conditions of a constant ratio of $(Cl^-)/Ir(III)$. Therefore, it is difficult to say which effect, the total (Cl^-) or the ratio $(Cl^-)/(IrCl_6^{-3})$, is the important one in causing an apparent increase in the reaction rate. This apparent increase in rate of reaction with increase in chloride ion concentration may be due, at least in part, to an interference from the reaction

$$ClO_3^- + 2H^+ + Cl^- \rightarrow ClO_2 + {}^1/_2\,Cl_2 + H_2O \quad (4)$$

The products would react rapidly with $IrCl_6^{-3}$, producing $IrCl_6^{-2}$, causing the $IrCl_6^{-3}$–ClO_3^- reaction to appear to proceed more rapidly than it actually does. Kinetic data for the ClO_3^-–Cl^- reaction (*5*) indicate that at Cl^- = 0.2*M*, H^+ = 0.2*M*, ClO_3^- = 0.2*M*, and μ = 8.0, this reaction could increase the apparent rate of the $IrCl_6^{-3}$–ClO_3^- reaction by 8%. The observed apparent increase in rate was 38% at Cl^- = 0.2*M*, and μ = 1.0.

The reaction rate is apparently insensitive to hydrogen ion until its concentration reaches a value of about 100 times the steady-state concentration of iridium(III). Calculations show that a contribution from Reaction 4 should be negligible for conditions under which the effect of hydrogen ion was tested. The rapid increase in reaction rate with increase in H^+ beyond 0.25*M* may be due to a change in the nature of the iridium(III) species reacting with ClO_3^-. It is possible that an equilibrium exists between iridium(III) and a protonated form of iridium(III). The latter species, with its lower charge, may react more rapidly with ClO_3^- because of decreased coulombic repulsion. Another possibility is that the proton associates with ClO_3^-. This would also lead to less coulombic repulsion. At higher hydrogen ion concentration (for a given ClO_3^- concentration), greater association would occur and would increase the reaction rate in the direction observed (see Table IV). Figure 5 indicates that there may be a second-order dependence on H^+ at higher hydrogen ion concentrations. This effect may be related to the formation of ClO_2^+, which, in terms of coulombic effects, would be expected to undergo reaction with $IrCl_6^{-3}$ even more favorably than does $HClO_3$.

No evidence has been obtained which would distinguish among the above possibilities offered to explain the hydrogen ion function. The last mechanism suggests that ClO_2 may be a product. Detection of this species in the reaction mixture may be possible unless it reacts too rapidly with additional $IrCl_6^{-3}$ in solution.

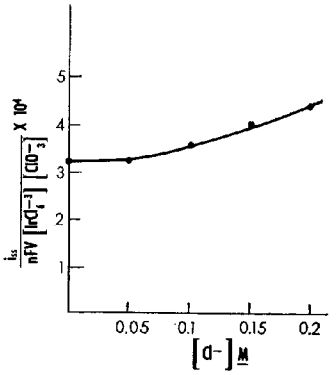

Figure 4. Effect of Cl^- on reaction rate

0.2M ClO_3^-, 0.2M $HClO_4$, μ = 1.0

The effect of $IrCl_6^{-2}$ on the rate of the $IrCl_6^{-3}$–ClO_3^- reaction cannot be unambiguously tested by the controlled-potential electrolysis method, since the steady-state concentration of $IrCl_5^{-2}$ cannot be varied independently of either $IrCl_6^{-3}$ or ClO_3^-. Therefore, its effect was tested by following the rate of the reaction spectrophotometrically. The reaction rate was followed by observing the appearance of iridium (IV). Since both $IrCl_6^{-2}$ and $IrCl_5(H_2O)^-$ are produced as a result of aquation of $IrCl_6^{-3}$ before oxidation, it was necessary to follow the reaction at a wavelength where the molar absorptivities of both species are the same

Table III. Effect of Cl^- on Reaction Rate

ClO_3^- = 0.20*M*, $HClO_4$ = 0.20*M*

i_{ss},[a] ma.	$i_{residual}$, ma.	$(IrCl_6^{-3})_{ss}$	$(Cl^-)_{ss}$	$k = \frac{i_{ss}}{nFV(IrCl_6^{-3})(ClO_3^-)}$
			0.00	3.25×10^{-4}[b]
1.75	0.41	2.14×10^{-3}	0.05	3.26×10^{-4}
1.77	0.43	2.18×10^{-3}	0.05	3.23×10^{-4}
2.23	0.38	2.33×10^{-3}	0.10	3.82×10^{-4}
2.18	0.41	2.13×10^{-3}	0.15	4.08×10^{-4}
2.27	0.40	2.05×10^{-3}	0.20	4.42×10^{-4}

[a] After subtracting residual current.
[b] Av. *k* from Tables I and II.

Table IV. Effect of H^+ on Reaction Rate

ClO_3^- = 0.20 *M*

i_{ss},[a] ma.	$i_{residual}$, ma.	$(IrCl_6^{-3})_{ss}$	$(H^+)_{ss}$	$k(M^{-1}\,sec.^{-1}) = \frac{i_{ss}}{nFV(IrCl_6^{-3})(ClO_3^-)}$
1.80	0.14	2.11×10^{-3}	0.050	3.40×10^{-4}
1.70	0.39	2.10×10^{-3}	0.20	3.25×10^{-4}
2.04	0.51	2.14×10^{-3}	0.30	3.80×10^{-4}
2.36	0.54	2.04×10^{-3}	0.438	4.60×10^{-4}
3.50	0.77	2.00×10^{-3}	0.60	6.98×10^{-4}
5.51	0.61	1.92×10^{-3}	0.80	11.4×10^{-4}

[a] After subtracting residual current.

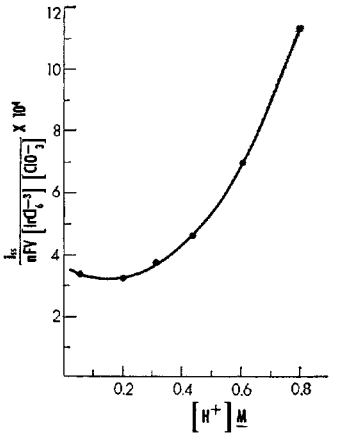

Figure 5. Effect of H^+ on reaction rate

0.2M ClO_3^-, μ = 1.0

(isosbestic point). An isosbestic point for this system occurs at 471 mμ. The reaction of iridium(III) with excess chlorate, at 45° C., followed at this wavelength gave the results listed in Table V.

Because the redox reaction is so slow, it was followed to only 15% of completion. To show that the reaction obeys a first-order rate law over 15% of completion, it was necessary to vary the initial $IrCl_6^{-3}$ concentration. Over a fourfold concentration range of initial $IrCl_6^{-3}$, the experimentally determined rate constants agreed with each other within 2%, indicating that the redox reaction is pseudo-first order under these conditions. These data suggest that the iridium(III)–chlorate reaction is not sensitive to iridium(IV). The second-order rate constant, k, calculated from $k'' = k[ClO_3^-]$ was $1.5 \times 10^{-4} M^{-1}$ second^{-1} which is in fair agreement with that obtained by the controlled-potential electrolysis method ($3.2 \times 10^{-4} M^{-1}$ second^{-1}).

The rate constant was also determined by monitoring the appearance of iridium(IV) polarographically. A solution, $10^{-2}M$ in $IrCl_6^{-3}$, $0.15M$ ClO_3^-, $0.2M$ H^+, and $\mu = 1.0$ was prepared at 45° C. The reaction rate was followed by measuring the iridium(IV) diffusion current at 0.00 volt *vs.* S. C. E. The first-order rate constant obtained from a plot of log $[IrCl_6^{-3}]$ *vs.* t, where $[IrCl_6^{-3}]_t = [IrCl_6^{-3}]_0 - [IrCl_6^{-2}]_t$, was 4.5×10^{-5} second^{-1}. The second-order rate constant, using $ClO_3^- = 0.15M$, was $3.0 \times 10^{-4} M^{-1}$ second^{-1} which is in good agreement with that obtained by the controlled-potential electrolysis method ($3.2 \times 10^{-4} M^{-1}$ second^{-1}).

At constant H^+ ($0.2M$), $\mu = 1.0$, and $T = 45°$ C., the rate law has the form

$$-\left[\frac{d(IrCl_6^{-3})}{dt}\right]_{\text{chem. rxn.}} = k(IrCl_6^{-3})(ClO_3^-)$$

with $k = (3.2 \pm 0.1) \times 10^{-4} M^{-1}$ second^{-1}.

Arrhenius Activation Energy. The rate constant, determined over a temperature range of 35° to 50° C., gave an Arrhenius activation energy of 30 kcal. for the $IrCl_6^{-3}$–ClO_3^- reaction (see Table VI).

Stoichiometry. The stoichiometry of the iridium(III)–chlorate reaction was tested by adding a known amount of chlorate to an excess of iridium(III) and determining the amount of iridium(IV) produced after the reaction had gone to completion. The mixture, $3.5 \times 10^{-3} M$ in iridium(III), $4.5 \times 10^{-4} M$ or $2.7 \times 10^{-3} F$ ClO_3^-, and $2.5M$ H^+, was heated to 75° C. to cause the reaction to proceed at a practical rate. After 12 hours at this temperature ($t_{1/2} \simeq 1$ hour), the iridium(IV) absorbance reached a constant value indicating that the reaction had gone to completion. The iridium(IV) concentration could not be estimated from its absorbance, however, because of the uncertainty in the molar absorptivity to be used [several aquated iridium(IV) species may be present in this system]. Controlled-potential electrolysis was used to estimate the iridium(IV) concentration because it gives a measure of the total concentration of all iridium (IV) species.

Table V. Effect of $IrCl_6^{-2}$ on Reaction Rate

$HClO_4 = 0.2$, $\mu = 1.0$ (adjusted with $NaClO_4$)

Initial $[IrCl_6^{-3}]$, M	Initial $[IrCl_6^{-2}]$, M	First-order rate constant, sec.$^{-1}$	$[ClO_3^-]$	Second-order rate constant, M^{-1} sec.$^{-1}$
5.04×10^{-3}	0.00	2.26×10^{-6}	0.150	1.5×10^{-4}
4.90×10^{-3}	1.16×10^{-3}	2.24×10^{-5}	0.147	1.5×10^{-4}
4.84×10^{-3}	2.81×10^{-3}	2.13×10^{-5}	0.143	1.5×10^{-4}

For a reaction in which 6 moles of iridium(III) react with 1 mole of chlorate, the iridium(IV) concentration in the above mixture at completion of the reaction should be 2.7×10^{-3}. A controlled-potential electrolysis of a 2-ml. aliquot of the test solution indicated that the iridium(IV) concentration was 2.7×10^{-3}. This indicates that the iridium(III)–chlorate reaction has the following stoichiometry.

$$6IrCl_6^{-3} + ClO_3^- + 6H^+ \rightarrow 6IrCl_6^{-2} + Cl^- + 3H_2O$$

The possibility was considered that iridium(IV) might also be produced in the above experiment via the chlorate–chloride reaction, which produces chlorine dioxide and chlorine, capable of oxidizing iridium(III). Calculations based on kinetic information (*5*) for the chlorate–chloride reaction show, however, that its half time under the above conditions is $\simeq 150$ hours, and, therefore, its contribution to the oxidation of iridium(III) should be negligible.

Approach to Steady State Starting with $IrCl_6^{-3}$ and ClO_3^- Only. In the above experiments, the steady state was approached by reduction of $IrCl_6^{-2}$ until the rate of the back reaction, increasing as a result of a build-up of $IrCl_6^{-3}$, became equal to the rate of the electrolysis reaction. An alternative means of approaching steady state was afforded by the following procedure. A solution, $0.15M$ in ClO_3^-, 0.2 H^+, $\mu = 1.0$ (adjusted with $NaClO_4$), was pre-electrolyzed to a constant background current. A known amount of $IrCl_6^{-3}$ was pipetted into the electrolysis cell after removal of an equal volume of the pre-electrolyzed solution (changes in salt concentration due to this last step were taken into consideration). The electrolysis current increased as iridium(IV) was produced by oxidation of iridium(III) with ClO_3^-, until the rate of the electrochemical reaction became equal to the rate of the chemical reaction. The rate constant (3.1×10^{-4}) calculated from the steady-state current obtained was in good agreement with that calculated from experiments in which $IrCl_6^{-2}$ was initially in excess ($3.2 \times 10^{-4} M^{-1}$ second^{-1}).

Table VI. Effect of Temperature on Reaction Rate

Temperature, °C.	$k(M^{-1}$ sec.$^{-1})$
35.0	8.25×10^{-5}
40.0	1.92×10^{-4}
45.0	3.2×10^{-4}
50.0	8.4×10^{-4}

Aquation of $IrCl_6^{-3}$. A mixture of $IrCl_6^{-2}$ and $IrCl_5(H_2O)^-$ was obtained by chlorine oxidation of an aliquot of the cell solution, withdrawn at the time when the steady-state situation was first reached. The spectrum of this solution indicated that about 70% of the iridium(III) was in the aquated form. This value is consistent with the time required to reach steady state (during which the aquation process takes place) and with kinetic data for the aquation reaction as given by Poulsen (*10*). The fact that most of the iridium(III) reacting with ClO_3^- at steady state is of the aquated form raised the question as to whether $IrCl_6^{-3}$ reacts with ClO_3^- at the same rate as $IrCl_5(H_2O)^{-2}$. This was tested by approaching steady state starting with only $IrCl_6^{-3}$ and ClO_3^-. Under these conditions, when steady state was reached, only about 40% of the iridium(III) was in the aquated form. The electrolysis was allowed to continue until $\simeq 94\%$ of the iridium(III) was in the aquated form. During this time, the steady-state current did not change significantly, indicating that $IrCl_6^{-3}$ and $IrCl_6(H_2O)^{-2}$ react with ClO_3^- at the same rate. A slight drop in i_d ($\sim 8\%$) observed may be due to a decrease in the diffusion coefficient of iridium(IV) as the aquated form becomes predominant. Polarographic measurements indicate that the diffusion coefficient of $IrCl_5(H_2O)^-$ is about 10% smaller than that of $IrCl_5^{-2}$. Another controlled-potential electrolysis was carried out beginning with concentrations of $IrCl_6^{-2}$ and $IrCl_6^{-3}$ approximately corresponding to concentrations

for a steady-state situation. Steady state was reached in 9 minutes. At this time, about 25% of the iridium (III) was in the aquated form. The electrolysis was continued until about 75% of the iridium(III) was aquated. During this time the current decreased by 10%.

DISCUSSION

The most probable rate-determining step for the $IrCl_6^{-3}$–ClO_3^- reaction at lower hydrogen ion concentration is thought to be

$$IrCl_6^{-3} + ClO_3^- \rightarrow IrCl_6^{-2} + ClO_3^{-2}$$

For higher hydrogen ion concentrations, corresponding to a region where the reaction becomes sensitive to H^+, the slow step could be

$$IrCl_6^{-3} + HClO_3 \rightarrow IrCl_6^{-2} + HClO_3^-$$

or

$$IrCl_6^{-3} + ClO_2^+ \rightarrow IrCl_6^{-2} + ClO_2$$

where

$$ClO_3^- + 2H^+ \xrightarrow{\text{fast}} ClO_2^+ + H_2O$$

The possibility of reduction products of ClO_3^- being reduced at the controlled-potential (0.00 volt *vs.* S.C.E.) was considered. This was shown not to occur by comparing the concentration of $IrCl_6^{-2}$ calculated from the $i_{ss} = k'(IrCl_6^{-2})_{ss}$ relationship with that calculated from the absorbance of the solution at steady state. Both concentrations agreed within 2%, indicating that the current observed at steady state is due to the reduction of iridium(IV) only.

Because of the unsymmetrical geometric relationship of the counter electrode with respect to the working electrode, it was thought that sizable potential gradients might exist across the surface of the working electrode. To make certain that there was no potential anywhere on the electrode which would cause an interfering electrochemical reaction to occur, it was necessary to measure the potential gradients at the current levels used for consideration in the light of known polarization curves for the $IrCl_6^{-2}$ system. The potential gradients were measured by moving a probe across the surface of the working electrode (mercury pool) while current was flowing and measuring the potential difference between the probe and a fixed reference electrode. The maximum potential gradient (at ≃2.5 ma.) was 13 mv., which is in reasonable agreement with the values determined by Booman (*4*) for a cell with slightly different geometry. Gradients of this magnitude are seen to be unimportant in this study in view of the fact that the current-voltage curve for $IrCl_6^{-2}$ has a plateau extending from +0.15 to −0.6 volt *vs.* S.C.E. at a D.M.E.

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Analysis of Mixtures of Hydroxyl Compounds Using Differential Reaction Rates

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▶ A rapid method has been developed for the analysis of binary and ternary mixtures of alcohols, based on the reaction of the hydroxyl group with phenyl isocyanate. The reaction is followed by the disappearance of the NCO band at 4.42 microns in the infrared spectrum. Rate constants of the reactions between phenyl isocyanate and the propyl alcohols and butyl alcohols are reported. A correlative equation between the concentrations of hydroxyl species and catalyst species confirms the mechanism of the organotin-catalyzed formation reaction of urethanes.

WITHIN the last few years considerable use has been made of kinetic methods for resolving mixtures of organic compounds which contain the same functional group. In this investigation, the dissimilarity in reaction rates constitutes the basis for a method of analysis which differentiates between hydroxyl compounds in an organic system. Recently, a number of analytical methods have been developed to determine the primary hydroxyl content in mixtures of isomeric primary and secondary alcohols and in polyalkylene glycols (*3–6, 9, 11*). Reed, Critchfield, and Elder (*8*) showed that phenyl isocyanate reacts with most hydroxyl compounds including sterically hindered and tertiary alcohols. Hanna and Siggia (*4*) investigated a titrimetric method based on the triethylenediamine-catalyzed reaction between a hydroxyl compound and phenyl isocyanate but reported the method to be inaccurate and inconvenient. The present method is also based upon the reaction of hydroxyl compounds with phenyl isocyanate. The reaction is followed by the disappearance of the NCO band at 4.42 microns in the infrared spectrum. A special solvent system is used which eliminates a blank determination. The method is applicable to the resolution of mixtures of primary, secondary, and tertiary alcohols. Another basic reason for the employment of this method is its convenience as an aid in understanding the kinetics of the reactions which occur during the manufacture of urethane flexible and rigid foams.

EXPERIMENTAL

Reagents and Apparatus. DIMETHYLFORMAMIDE, redistilled or dried with Linde Molecular Sieve, Type 5A, until the water content is less than 0.01%. Stored in a capped bottle.

TOLUENE, redistilled from stannous octoate catalyst (100 grams per gallon toluene). Water content should be

less than 0.005%. Stored in a capped bottle.

PHENYL ISOCYANATE, reagent grade, boiling point 60° to 62° C./20 mm. (Matheson Coleman & Bell). Add 10.0 ml. (10.95 grams) of phenyl isocyanate to 50 ml. of dry toluene, dilute to 100 ml. with additional toluene, and mix thoroughly. Store in the volumetric flask. If any crystalline precipitate is formed the reagent is discarded.

ALCOHOLS used as standards were reagent grade chemicals.

CATALYST. Add 0.404 gram of stannous octoate (catalyst T-9 from M & T. Corp.) to 50 ml. of dry toluene, dilute to 100 ml. with additional toluene, and mix thoroughly. The concentration of this solution is $1.00 \times 10^{-2}M$ Sn^{+2}. Stannous content was determined by polarographic analysis. Prepare fresh catalyst solution daily, in particular for reaction rate experiments.

INFRARED SPECTROPHOTOMETER. Beckman Model IR 5A or equivalent can be used. The absorption cells are 0.10-mm. calcium fluoride cells. CaF_2 cells are preferred rather than NaCl cells because of the elimination of possible complications due to the water content in polypropylene glycols.

Calibration. Prepare standard solutions of phenyl isocyanate in 90/10 (v./v.) anhydrous toluene–dimethylformamide in the concentration range from 1 to 5 mmoles per 50 ml. of solution. Determine the absorbance value of the 4.42-micron peak and plot this value *vs.* isocyanate concentration. The graph should be a straight line.

Procedure. A sample containing 5 mmoles of hydroxyl is transferred to a 50-ml. volumetric flask, using toluene, and is diluted to almost 30 ml. with toluene. Five milliliters of dimethylformamide are pipetted into the flask, and then 10 ml. of the catalyst solution is added. The time is noted as soon as 5 ml. of the phenyl isocyanate solution (4.60 mmoles) are added, and the mixture is rapidly diluted to volume with toluene. The volumetric flask is kept in a constant-temperature water bath, maintained at 25° C. At intervals of 5 minutes, small aliquots (±1 ml.) are withdrawn with a hypodermic syringe, injected into the cell, and the absorbance is measured at 4.42 microns. The isocyanate concentration values during the course of the analysis are calculated from the absorbance data with the aid of the calibration curve.

In accordance with the conventional graphical method (*11*), extrapolation to zero time of the line representing the slope of the less reactive alcohol yields the amount of more reactive alcohol. If the double-point method (*7*, *9*) is employed, the initial concentration of the faster reacting hydroxyl compound can be calculated directly from the isocyanate concentration values at two different times, t and t'. The factors which have to be considered in choosing appropriate values for t and t' are reported in Reilley's publication (*9*). In this particular case, t and t' can be chosen after 30 minutes reaction time for the determination of primary hydroxyl content in polyether polyols because the primary hydroxyl is essentially depleted before this time.

DISCUSSION AND RESULTS

As the first step in this investigation, the feasibility of the infrared determination following the decrease of the isocyanate absorption peak was established. A number of factors can cause consumption of phenyl isocyanate, hence a decrease in the isocyanate absorption peak, apart from the basic hydroxyl–isocyanate reaction. Impurities in the solvent, in phenyl isocyanate and/or in the catalyst (in particular water) will effect consumption of the isocyanate. In addition, phenyl isocyanate undergoes, in toluene solution, a dimerization reaction that is catalyzed by stannous octoate, and would thus necessitate a correction for the rate of reaction between hydroxyl and isocyanate. The first source of isocyanate consumption can be eliminated by excluding water from the solvent system; dimerization of the isocyanate was experimentally found to be completely suppressed, even at relatively high catalyst concentrations, by the presence of 10% (v./v.) of dimethylformamide in the toluene solvent. As a result, a rate study on a blank along with the sample is not required to correct for isocyanate consumption other than that by hydroxyl groups.

Catalyst Activity. The catalytic activity of stannous octoate decreased with respect to the time of dissolution in toluene. The catalyst activity decreased about 1% after 30 minutes, 3% after 3½ hours, and 6% after 72 hours. This does not affect the determinations based on differential kinetics because of the relatively short analysis times (always less than 1 hour). However, results for absolute rate values are inaccurate unless a fresh solution of stannous octoate in toluene is employed to catalyze the hydroxyl–isocyanate reaction.

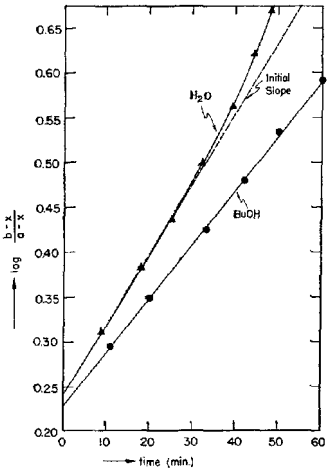

Figure 1. Graphical representation of the second-order reactions between phenyl isocyanate and either water or 1-butanol

Table I. Specific Rate Constants for Alcohol–Isocyanate Reactions and Water–Isocyanate Reaction

a = Concentration of alcohol or water = 80 to 160 mmoles/liter
b = Concentration of phenyl isocyanate = 92.0 mmoles/liter

Stannous octoate concentration = $\frac{a}{200}$

Temperature: 25° C.

Alcohol	$k \times 10^2$, liter mole^{-1} minute^{-1}
1-Propanol	11.1
2-Propanol	5.07
1-Butanol	14.7
2-Butanol	5.64
2-Methyl-2-propanol	0.139
2-Ethylhexanol	3.22
Water	31.4

Reaction Rates of Aliphatic Alcohols. By use of the conventional method (*11*) of analyzing second-order reactions, the rate constants of some simple aliphatic alcohols in their reaction with phenyl isocyanate at 25° C. for a catalyst–alcohol molar concentration ratio of 1:200 were obtained; they are reported in Table I. Both the primary and secondary butanols react faster than the corresponding propanols.

Reaction Rate of Water. If the data representing a second-order reaction between water and phenyl isocyanate are plotted, a straight line is initially obtained (Figure 1) indicating the occurrence of a mole for mole reaction pattern, and the relative stability of phenyl carbamic acid. The rate constant for the water–isocyanate reaction is calculated from the slope value of this straight line (Table I). After an induction period, the data points start to diverge from the straight line. The decomposition of the carbamic acid is apparently very slow, but the amine formed—i.e., aniline—reacts instantaneously with a second molecule of phenyl isocyanate, and the reaction thus appears to proceed faster than expected from a second-order reaction pattern.

Dependence of Reaction Rates on Stannous Octoate Concentration. Variance in the stannous octoate catalyst concentration markedly affects the rate of reaction between hydroxyl and isocyanate. The calculated second-order rate constant is not a linear function of the catalyst concentration for the reaction between the propanols and phenyl isocyanate.

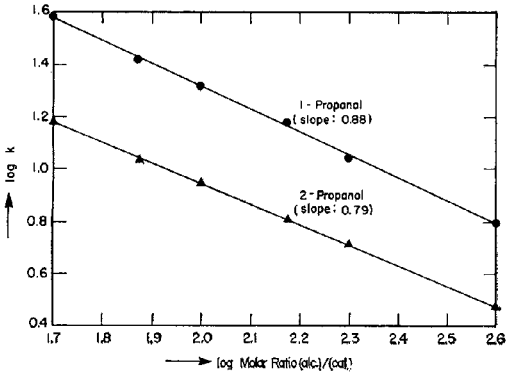

Figure 2. Dependence of the specific rate constant on the ratio of alcohol to catalyst concentrations

This is in agreement with data on the triethylamine-catalyzed reaction between 1-butanol and phenyl isocyanate in toluene (*2*) but contrary to the observations of this reaction in di-*n*-butyl ether as solvent (*1*).

The dependence of the rate constants of 1-propanol and 2-propanol on catalyst concentration is presented in Figure 2. Doubling the catalyst concentration nearly doubled the specific rate constants in both cases, but the catalyst concentration level per se did not effect a constant reaction rate if the concentrations of the reactants were varied. Instead, the ratio of alcohol concentration to stannous octoate concentration, both expressed in moles/liter, proved to be the deciding factor. The data plotted in Figure 2 suggest the following general expression for the dependence of specific rate constant upon R, the molar ratio (alcohol)/(catalyst)

$$\log k = C + n \log R \qquad (1)$$

in which k is the over-all catalytic rate constant, n the slope of the curve, and C an equation constant, expressing the extrapolated value of $\log k$ at equal concentrations of alcohol and catalyst.

For the reaction between 1-propanol and phenyl isocyanate, Equation 1 becomes

$$\log k_1 = 3.08 - 0.88 \log R$$

The rate constant for the 2-propanol–phenyl isocyanate reaction is obtained in a similar way

$$\log k_2 = 2.53 - 0.79 \log R$$

Thus these equations express a simple relationship between specific rate constant and catalyst level with reference to hydroxyl concentration. This observation must be considered as an independent confirmation of the mode of catalysis postulated by Smith (*12*). Because of their very high, selective catalyst activity, organotin compounds appear to activate both reagents, alcohol and isocyanate. This activation must be accomplished first by the formation of a binary complex between the catalyst and the alcohol, and then by the joining of the isocyanate to form a ternary complex of the catalyst and both the reactants.

Determination of Primary, Secondary, and Tertiary Hydroxyl Content in Various Mixtures of Alcohols. The slope intercept method (*11*) and double-point method (*7,9*) were used for the analysis of binary mixtures of alcohols with hydroxyl groups of different reactivity. Mixtures of primary and secondary alcohols, of primary and tertiary alcohols, and of secondary and tertiary alcohols (Table II) can be accurately determined. The data obtained are the average values of two determinations, one with a higher concentration of total hydroxyl (>4.60 meq.) than that of isocyanate, the second one with a lesser amount of total hydroxyl (<4.60 meq.) than isocyanate. The latter type of determination generally showed a slightly lower value (by 0.2 to 0.7%) for the hydroxyl content of the more reactive alcohol. This would imply that the consumption of phenyl isocyanate is slightly greater than normally expected in the less reactive alcohol–isocyanate reaction region. Apparently a very small amount of isocyanate is still consumed in a side reaction in the case of excess isocyanate over total hydroxyl.

If more than 50% of the faster reacting alcohol is present in the mixture, it becomes hardly possible to plot the second part of the rate curve. As the reaction nears completion, the upper portion of the rate plot becomes inaccurate because of relatively rapid change in the ratio of concentration values of alcohol and isocyanate. The data points are in this case less suitable for a linear plot representing the less reactive component of the mixture. This difficulty is illustrated by the results of some of the propanol–isopropanol mixtures in Table II. A way to overcome this divergence is to add a known amount of the slower reacting

Table II. Analysis of Binary Mixtures of Primary, Secondary, and Tertiary Alcohols

Constituents		Faster reacting alcohol, %	
Faster reacting alcohols	Slower reacting alcohols	Calcd.	Found
1-Propanol	2-Propanol	12.8	12.9
		25.6	25.5
		38.3	37.9
		50.7	48.8[a]
		63.1	59.6[a]
1-Butanol	2-Butanol	12.5	12.4
		25.0	24.8
		37.5	37.0
1-Propanol	2-Butanol	20.1	20.0
		40.0	39.4
1-Butanol	2-Propanol	15.7	15.4
		32.8	32.5
1-Propanol	2-Methyl-2-propanol	13.1	13.0
		26.4	26.2
		39.7	39.3
1-Butanol	2-Methyl-2-propanol	12.5	12.6
		25.0	25.0
2-Propanol	2-Methyl-2-propanol	12.1	11.8
		24.0	23.3
2-Butanol	2-Methyl-2-propanol	12.5	12.3
		25.0	24.7
		37.5	36.9
1-Propanol	2-Ethylhexanol	13.1	13.3
		26.4	26.8
		39.7	40.6
1-Butanol	2-Ethylhexanol	12.5	13.0
		25.0	25.9

[a] Amount of primary alcohol relative to secondary alcohol is too large for an accurate representation of the secondary alcohol rate curve since this is near end of the reaction.

alcohol to the mixture prior to the determination, and the final result corrected for the amount added.

The differential reaction rate method is generally limited to binary mixtures. However, the equations worked out by Schmalz and Geiseler (*10*) provide a convenient means of calculating the composition of ternary mixtures if all of the components react with a common reagent. If the rate constants are known, only two data points are required. A successful attempt to resolve a mixture of primary, secondary, and tertiary butanol in this fashion is depicted in Table III. The agreement with the theoretical contents is very good in concentration ranges consisting of 0 to 15% of the most reactive alcohol, 25 to 45% of the intermediately reactive alcohol, and 40 to 70% of the least reactive alcohol.

Analysis of Mixtures of Primary Alcohols. Whenever alcohols with the same type of hydroxyl function show noticeably different specific rate constants, an analysis of a binary mixture should be possible. To show that the differential reaction rate method applies to such a system, mixtures of primary alcohols were chosen for this purpose. The last two series of data presented in Table II show good agreement, in particular when the amount of more reactive alcohol is relatively small.

Determination of Primary Hydroxyl Content in Polyoxypropylene Glycols. Results on known mixtures of NIAX polyol LG-56 and Carbowax polyethylene glycol PEG-200 are summarized in Table IV. LG-56 is a 3000 molecular weight propylene oxide adduct of glycerine with a primary hydroxyl content of 1 to 6%, whereas PEG-200 is a 200 molecular weight oxyethylene diol with a primary hydroxyl group content of nearly 100%. Six blends of these polyols cover a primary hydroxyl content region from about 10 to 60% which is completely satisfactory for all practical purposes. Good agreement is obtained between this method and the acetic anhydride method of Siggia and Hanna (*11*) for the primary hydroxyl content in the synthetic samples. However, the phenyl isocyanate method yields somewhat lower primary hydroxyl values than the acetic anhydride method if the primary hydroxyl content is lower than 17%, whereas a somewhat higher value is obtained if the content is higher than 20%. The reason for these differences is not considered to be caused by a possibly different response of primary and secondary hydroxyl groups in polyloxypropylene glycols with respect to either phenyl isocyanate or acetic anhydride as reagent since this discrepancy does not appear to exist for mixtures of simple alcohols. The variance between the two methods applied to polyols, however, is generally considered insignificant. Results on commercially available polymeric diols and triols (Table V) substantiate the accuracy equivalence of the two methods.

Interferences. Since water reacts with phenyl isocyanate under the conditions of the method, a correction has to be made if water is present in the sample to be determined. In the case of polyglycols, this is particularly relevant since they invariably contain a small amount of water. Water reacts faster with phenyl isocyanate than a primary hydroxyl group does (Table I), and the primary hydroxyl content of polyols has thus to be corrected for the water content by subtracting the latter. It was experimentally found that the correction is effected by assuming that 1 mole of isocyanate is consumed by 1 mole of water. The decomposition of carbamic acid occurs very slowly under the conditions of the method.

Primary and secondary amines interfere in this determination because of their comparable reaction rates with

Table III. Ternary Mixtures of Primary, Secondary, and Tertiary Alcohols

	Constituents	Alcohol, % Calcd.	Found	Calcd.	Found
Most reactive	1-Butanol	8.3	8.9	12.5	12.9
Intermediately reactive	2-Butanol	41.6	41.5	27.0	26.4
Least reactive	2-Methyl-2-propanol	50.1	49.6	60.5	60.7

Table IV. Primary Hydroxyl Content of Synthetic Samples

Sample code	Composition wt. ratio NIAX polyol LB-56/ Carbowax PEG-200	$\overline{OH}$ No.[a] (NCO, corr.)	Wt. %	Primary hydroxyl, % Found Calcd.[b]	Ac$_2$O method[c]	PhNCO method
LG-56	NIAX polyol LG-56	56.3	0.043	...	3.0	1.8
P-15	80:1	62.6	0.045	13.4	9.1	8.7
P-30	40:1	67.8	0.046	19.8	16.7	16.5
P-45	80:3	73.8	0.048	25.9	22.3	23.1
P-60	20:1	80.6	0.049	32.6	29.8	30.3
P-120	10:1	103.6	0.054	47.6	45.7	46.9
P-180	20:3	122.7	0.061	55.5	54.0	57.1

[a] Hydroxyl equivalent weight, determined by the phenyl isocyanate method and corrected for water content (*8*).
[b] Based on the assumption that the increase in hydroxyl equivalent weight is solely due to primary hydroxyl groups.
[c] Differential kinetic method with acetic anhydride as reagent (*11*).

Table V. Primary Hydroxyl Content of Propoxylated and Ethoxylated Polymers of Propylene Glycol, Glycerine, and Trimethylolpropane

Sample	$\overline{OH}$ No. (NCO, corr.)	H$_2$O, wt. %	Primary hydroxyl, % Ac$_2$O method	PhNCO method
NIAX polyol PPG 425[a]	255	0.038	1.3	0
NIAX polyol PPG 2025[a]	55.9	0.043	5.6	4.9
Pluronic L61[b]	47.2	0.042	37.0	33.4
NIAX polyol PPG 3025[a]	36.9	0.033	8.1	8.7
NIAX polyol LG-56 ONE[a]	58.3	0.086	10.4	6.7
Voranol CP 3000[c]	57.2	0.032	7.0	5.8
NIAX polyol LC-60[a]	57.1	0.024	43.2	45.0
Poly-G 3030 PG[d]	55.6	0.044	4.7	3.0
Actol 31-56[e]	55.5	0.023	6.9	6.3
NIAX polyol 11-48[a]	47.8	0.031	36.2	38.1
Voranol CP-3500[c]	47.7	0.022	38.6	39.8
Poly-G 4031 PG[d]	44.2	0.098	39.1	37.3
NIAX polyol LC-45[a]	42.7	0.040	52.3	54.9
Pluracol TPE 4542[b]	35.9	0.043	31.5	31.3

[a] Union Carbide Corp.
[b] Wyandotte Chemicals Co.
[c] Dow Chemical Co.
[d] Olin Mathieson Chemical Corp.
[e] Allied Chemical Co.

phenyl isocyanate. Tertiary amines do not interfere; neither do carbonyl compounds, carboxylic acids, or acetals. Most aromatic hydroxyl compounds do not react with phenyl isocyanate, or react with a rate less than that of tertiary butanol—e.g., the rate of reaction between 2,6-di-*tert*-butyl-*p*-cresol and phenyl isocyanate is approximately 5×10^{-4} liter mole^{-1} minute^{-1} under the reaction conditions, about three times slower than the *tert*-butanol reaction.

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Identification of 2-Quinolones in a California Crude Oil

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▷ **The discovery and identification of 2-quinolones in a California crude oil are described. This is the first time that 2-quinolones have been reported in any crude oil. Infrared spectra of heavy gas oils vacuum distilled from a few crude oils sampled from wells in the Ventura Basin of California showed a unique spectral absorption band at 6.07 microns. From the particular gas oil showing the most intense 6.07-micron band, a fraction containing the substances causing this band was isolated by chemical and chromatographic methods. This fraction was analyzed by elemental analysis, nonaqueous titration, nuclear magnetic resonance and mass spectrometry, and infrared and ultraviolet spectrophotometry. The 6.07-micron band was identified as being predominantly caused by the amide carbonyl group of 2-quinolones. They comprise 0.4 weight % of the gas oil and 0.05 weight % of the crude oil.**

MODERN ANALYTICAL METHODS and separation techniques are making it possible to better understand the chemistry of the nonbasic nitrogen compounds in petroleum. The definition of nonbasic nitrogen compounds proposed by Richter and coworkers (*10*) as those nitrogen compounds having a $pK_a \leqq 2$ is used in this paper. Amides constitute one of these nitrogen types currently being studied. Bezinger, Abdurakhamanov, and Gal'pern (*3*) reported the presence of 3,4-dihydro-2-quinolones in a Russian crude oil, while Jewell and Hartung (*6*) described the identification of benz-2-quinolones in a heavy gas oil. In both cases, there was no direct evidence of the amide functional group in the original stock, whereas the work reported here was performed to identify the cause of a band at 6.07 microns in the infrared spectra of some heavy gas oils. This band was caused by the amide carbonyl functional group of 2-quinolones. The gas oils were vacuum distilled from crude oils sampled from wells located in the Ventura Basin of California.

EXPERIMENTAL

The particular crude oil whose heavy gas oil showed the most intense 6.07-micron band was selected for study. Crude oil obtained directly from the well was dewatered by centrifuging. Preliminary small scale distillation studies showed that the 6.07-micron band first appeared in the infrared spectra of fractions boiling above 300° C. This suggested that the compounds responsible for the band would be rather large molecules. About 250 ml. of heavy gas oil with a boiling range between 343° and 454° C. were vacuum distilled from the crude oil by an ASTM method (*2*). This cut represented 14.2 weight % of the crude oil. Figure 1 shows separation steps and analytical data. Nonaqueous extracts or solutions were dried over potassium hydroxide pellets whenever possible. Removal of solvents was carried out below 100° C. under nitrogen at about 0.5 atm.

Hydrogen Chloride Gas Treatment of Gas Oil. A 100.0-gram portion of the heavy gas oil was dewaxed with 750 ml. of *n*-pentane at 0° C. The brown, waxy precipitate weighed 0.52 gram. Dry hydrogen chloride gas was bubbled through the pentane filtrate for 45 minutes. After removing the supernatant liquid by

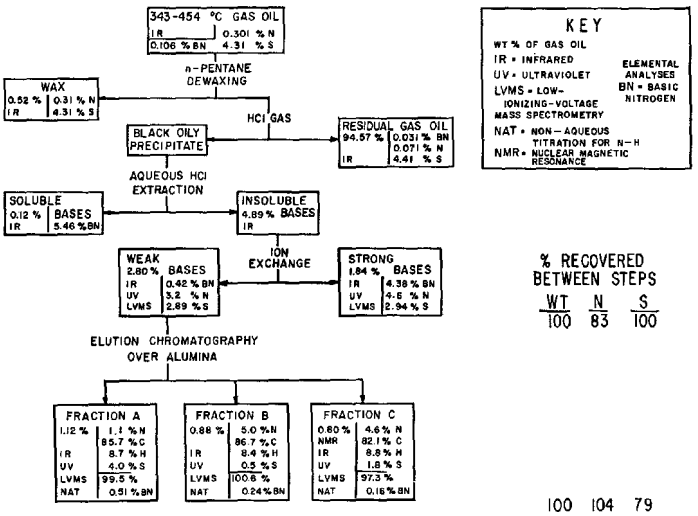

Figure 1. Flow diagram and material balance of fractions separated from 343–454° C. gas oil

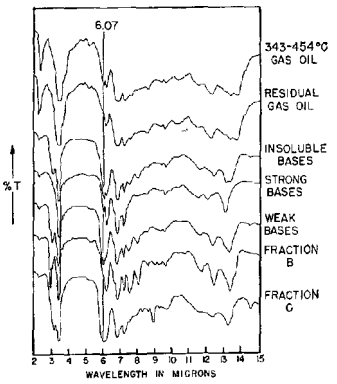

Figure 2. Infrared spectra of 343–454° C. gas oil and fractions separated from it

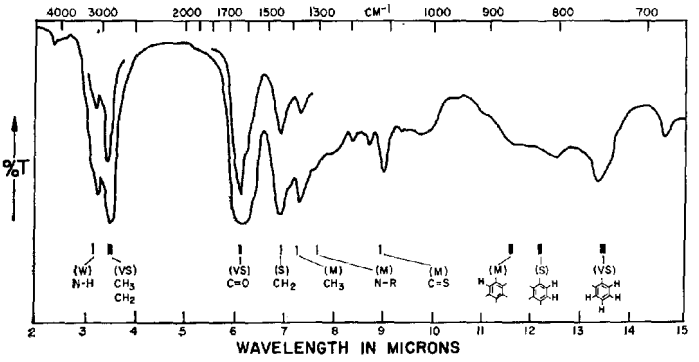

Figure 3. Comparison of infrared spectral absorption bands shown by fraction C with those exhibited by 2-quinolones

filtration, the black, oily precipitate adhering to the apparatus was washed into a separatory funnel with 150 ml. of chloroform. The chloroform solution was extracted with four 80-ml. portions of 10% hydrochloric acid and two 80-ml. portions of water, in that order. After the extracts were combined and made alkaline, they were, in turn, extracted with three 60-ml. portions of chloroform. The chloroform extracts yielded 0.12 gram of material labeled soluble bases.

The chloroform solution remaining after the acid extraction was washed with three 70-ml. portions of 3% sodium hydroxide, followed by four 100-ml. portions of water. The chloroform was removed, and 4.89 grams of a fraction labeled insoluble bases was obtained.

The pentane filtrate from the hydrogen chloride gas treatment was processed like the chloroform solution discussed immediately above and 94.57 grams of residual gas oil were recovered from it.

Ion Exchange of Insoluble Bases Fraction. A Duolite C-10 cation exchange method developed by Snyder and Buell (*11*) was used to separate the insoluble bases fraction into two parts. The part adsorbed on the resin weighed 1.84 grams and was labeled strong bases. The part not absorbed on the resin weighed 2.80 grams and was labeled weak bases.

Elution Chromatographic Separation of Weak Bases Fraction. To a 4-foot by 0.75-inch diameter column of 2.5% H_2O–Al_2O_3 (Alcoa F-20) was charged 0.883 gram of the weak bases fraction. Elution of the sample was started with benzene, and fraction A was collected. Fraction B was obtained using ether as the eluent. Fraction C was obtained using a 1:1 mixture of methanol and benzene as eluent. The retention volume of fraction C agreed with that of model 2-quinolones. After the solvents were removed, fraction A weighed 0.353 gram; fraction B, 0.276 gram; and fraction C, 0.250 gram.

Analysis of Fractions Separated from Heavy Gas Oil. Elemental analyses of the original gas oil and the fractions separated from it appear in Figure 1. Total nitrogen content was determined by either the Kjeldahl or the Dumas method, the latter being used on samples containing more than 1 weight % nitrogen. Potentiometric titration with perchloric acid of samples dissolved in glacial acetic acid was used to measure their basic nitrogen contents. Total sulfur was determined by the peroxide bomb method. Carbon and hydrogen were determined by micro combustion methods.

The spectral data were obtained by conventional infrared, ultraviolet, nuclear magnetic resonance, and low ionizing voltage mass spectrometric techniques. Because the intent of this paper is to describe the isolation and identification of 2-quinolones, the compositional analysis of the other fractions is omitted, except to state that fraction B was a mixture of carbazoles and benzcarbazoles.

Fractions A, B, and C were titrated in pyridine with tetrabutylammonium hydroxide. This system will titrate the N—H functional group of carbazoles, benzcarbazoles, and 2-quinolones and will not titrate their *N*-alkyl derivatives. Fraction A contained no titratable material. Fraction B, the carbazole-benzcarbazole fraction, contained titratable material equivalent to 4.9 weight % nitrogen. Since the nitrogen in fraction B was found by elemental analysis to be 5.0 weight %, essentially all of the nitrogen appears to be present as N—H. About 75% of the total nitrogen in fraction C could be titrated, and if it is assumed that only 2-quinolones are present, then about 25% must contain *N*-alkyl groups.

DISCUSSION

Material Balance of Fractions Separated from Gas Oil. The weight % of material recovered after each separation step is included in Figure 1. Only 83% of the total nitrogen originally present in the gas oil was found in the wax, residual gas oil, soluble bases, strong bases, and weak bases fractions. The fate of the remaining 17% nitrogen is presently unknown. The cause of the 21% loss of total sulfur in the elution chromatographic step is likewise presently unknown.

Separation of 2-Quinolones from Original Gas Oil. Infrared spectrophotometry was used to trace the presence of 2-quinolones during the separation process. Figure 2 contains the infrared spectra of the original gas oil and some of the fractions separated from it. Those fractions not appearing in Figure 2 do not show the 6.07-micron band. The top two curves are spectra of 0.20-mm. thick films, while the bottom five curves are spectra of films approximately 0.025 mm. thick.

The absence of the 6.07-micron band in the spectrum of the residual gas oil fraction and its presence in the insoluble bases fraction shows that precipitation of 2-quinolones from a pentane solution of the gas oil is efficient. A similar result was obtained by chromatographing some of the original gas oil over alumina. This demonstrates that 2-quinolones were not generated by the hydrogen chloride gas treatment. After the ion exchange separation, a negligible amount of 2-quinolones was found in the strong bases fraction. Elution chromatography of the weak bases fraction over alumina further concentrated the 2-quinolones into fraction C.

Infrared Spectrophotometric Analysis of Fraction C. The infrared spectrum of fraction C shown in Figure 3 agrees with infrared spectra of 2-quinolones obtained in this laboratory and from the literature (*4, 7, 9, 12*). The weak band at 3.14 microns is the N—H stretching band of 2-quinolones. At 6.07 microns is the strong amide carbonyl band of 2-quinolones. The shoulder at 7.7 microns indicates that there may be some *N*-alkyl-2-quinolones present. The 25% of nontitratable nitrogen in fraction C may at least in part be due to these compounds.

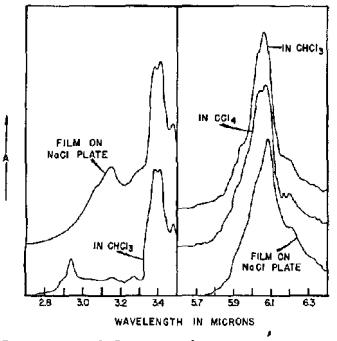

Figure 4. Influence of environment on N—H and C=O stretching bands in infrared spectra of fraction C

The relative intensity of the 13.4-micron C—H out-of-plane bending band compared to the other bands at 11.7 and 12.4 microns indicates that most of the 2-quinolones are unsubstituted on the benzene ring. The weak band at 14.7 microns appears to be typical of 2-quinolones but could not be correlated with any particular functional group. An unusual band shows up at 8.95 microns. Tentatively, this has been assigned to the moderately intense C=S stretching band of 2-thioquinolones (*12*), the sulfur analogs of 2-quinolones. The presence of 2-thioquinolones may account for the 1.8 weight % sulfur found in fraction C.

An additional problem in the identification of the molecular species causing the band at 6.07 microns was that the infrared spectra of 2- and 4-quinolones are practically identical (*9*). Therefore it was necessary to determine how much of each was in fraction C. For this reason, infrared spectra of fraction C in solution were recorded and are shown in Figure 4. The N—H stretching band appears at 3.14 microns for the film and at 2.94 microns in chloroform solution. According to Katritzky and Ambler (*8*), this shift is typical of 2-quinolones. In contrast, Price and Willis (*9*) found 4-quinolones to exhibit a broad, weak N—H band, between 3 and 4 microns, which is not greatly influenced by environment.

Another criterion used in this work to differentiate between 2- and 4-quinolones was the comparison of average molecular weights of fraction C determined by independent methods. Assuming one nitrogen atom per molecule, 4.6 weight % total nitrogen in fraction C is equivalent to an average molecular weight of 304. The 6.07-micron carbonyl band of fraction C in chloroform shown in Figure 4 was integrated from 5.8 to 6.2 microns and compared to the integrated absorbance of the amide carbonyl group in a reference compound, *N*-ethyl-2-quinolone. By this technique the average molecular weight of fraction C was 285, which is in good agreement with the previous value of 304. The average molar absorptivity of 4-quinolones is about half that of 2-quinolones (*8*). If fraction C were assumed to be 4-quinolones, then its average molecular weight would be about 150, which is much too low.

Ultraviolet Spectrophotometric Analysis of Fraction C. The ultraviolet spectrum of fraction C shown in Figure 5 is almost identical to those of 2-quinolones (*5*), whereas the spectra of 4-quinolones do not have a band at 277 mμ (*13*). In addition, the molar absorptivities of 4-quinolones at 327 mμ are about twice those of 2-quinolones. Using the 2-quinolone average molar absorptivity of 6170 liter per mole-cm., at 327 mμ an average molecular weight of 308 was calculated for fraction C. This is in good agreement with 304 and 285 determined earlier. Therefore, it appears that 4-quinolones, if present, comprise less than 10% of fraction C. 2-Thioquinolones which have a band at 376 mμ (*1*) were not detectable. It is probable that such a band would be masked by the spectra of 2-quinolones.

Nuclear Magnetic Resonance Spectrometric Analysis of Fraction C. Semiquantitative nuclear magnetic resonance spectrometric data are in good agreement with the previously described spectral data. Fraction C contains little, if any, *N*-alkyl-2-quinolones. Aromatic rings are predominantly unsubstituted, and heterocyclic rings are highly substituted.

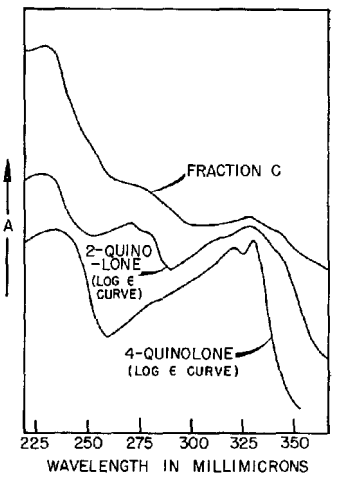

Figure 5. Ultraviolet spectra of fraction C and two reference compounds

The alkyl groups on the hetero rings average C_5 in length.

Low Ionizing Voltage Mass Spectrometric Analysis of Fraction C. Figure 6 shows the low ionizing voltage mass spectrometric (LVMS) data obtained for fraction C. The LVMS data have been deisotoped, and the sensitivities of all homologous series have been assumed equal. The *Z* numbers ($C_nH_{2n+z}N$) and structural formulas of the compound types that best fit the chemical and spectral data are shown in Figure 6. For example, the mass peaks for the −9 series started low at 145 (the molecular weight of 2-quinolone), reached a maximum at 215, and formed

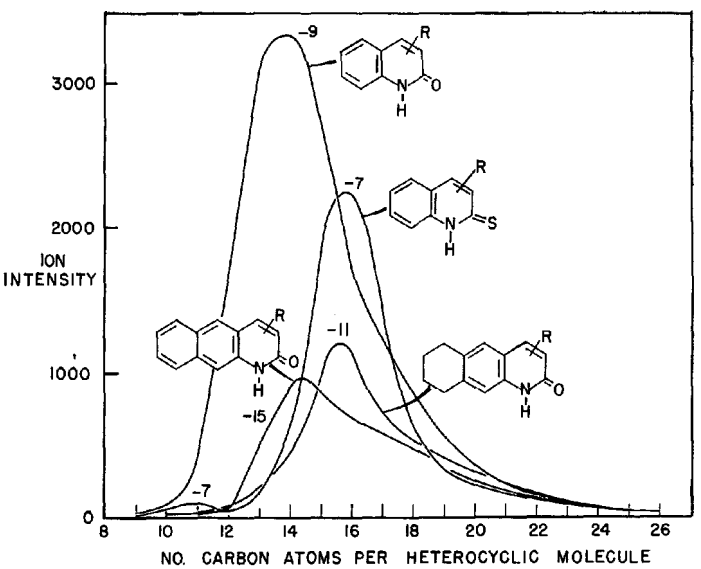

Figure 6. Distribution of thioquinolones, quinolones, and benzquinolones in fraction C as determined by low ionizing voltage mass spectrometry

a smooth distribution curve. If another −9 homologous series were present in a significant amount, excluding 4-quinolones, it is quite likely that the distribution curve would show either a shoulder or another peak.

Each curve in Figure 6 represents a homologous series present to more than 5%, and all four curves together represent 75% of fraction C. The remaining 25% of the total peak intensities was uniformly divided throughout the rest of the mass data. Fraction C contained 47 weight % 2-quinolones, 11 weight % benz-2-quinolones, and 17 weight % 2-thioquinolones. The identification of the latter two compound types must remain tentative until additional information is gathered. However, this concentration of 2-thioquinolones is equivalent to 2.1 weight % sulfur, which is in good agreement with 1.8 weight % total sulfur found by elemental analysis. Using all of the mass spectral peak intensities, an average molecular weight of 277 was calculated for fraction C. This is in reasonably good agreement with the values of 304, 285, and 308 determined from total nitrogen, infrared, and ultraviolet spectrophotometry, respectively.

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Thickness Measurement of Polymer Films for Infrared Spectrometry by Beta-Ray Absorption

Analysis of Ethene-Propene Copolymers

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▶ **Determination of the thickness of films for infrared spectrometric examination may be accomplished in several ways. In the method described here, use is made of β-ray absorption. The method has several advantages over the conventional procedures for thickness determination. Since there is no mechanical contact between the measuring device and the sample, the thickness of rubber films can be measured without difficulty. The effective optical thickness is determined, so that the method is applicable to films having a rough surface; knowledge of the density of the film material is superfluous. The relative error in the determination of the thickness does not exceed 1%.**

QUANTITATIVE ANALYSIS of polymers by means of infrared spectrometric methods requires knowledge of the sample thickness. In general, infrared spectrometric examination of a polymer is carried out on a film pressed from the polymer or on films cast from solutions.

Determination of the film thickness normally presents a number of problems. Many spectrometrists therefore prefer to work with an absorption band which can be used as an internal standard. This does away with the need for sample thickness determination.

In many cases, however, internal standards are useless owing to crystallinity or orientation effects.

The film thickness can be measured in two fundamentally different ways—with a simple or modified thickness gauge or by means of β-ray absorption.

The second method for determining the thickness (*2*) was subjected to a more detailed study. The advantages and the accuracy of this method are emphasized.

EXPERIMENTAL

Apparatus. A recess constructed in the top of a perspex block contains a radioactive source, consisting of a ^{60}Co or a ^{14}C derivative. The dimensions of the source are about 5 × 18 sq. mm.

The ^{60}Co source consists of a thin layer of $CoCO_3$ enriched with $^{60}CoCO_3$, deposited on a piece of filter paper. The activity of the source is about 0.5 μc. The source is covered with a thin aluminum film (4 mg. cm.$^{-2}$) stuck on the perspex block with araldite.

The ^{14}C source consists of polymethylmethacrylate, thickness 0.3 mm., enriched with ^{14}C. The activity is about 3 μc.

A sample holder can be placed in the above mentioned block. This sample holder can also be used in the infrared spectrophotometer. The dimensions of the sample, a film of the polymer, are 5 × 17 sq. mm. At about 10 mm. above the source an adjustable Geiger-Muller counter, provided with a mica window (2 mg. cm.$^{-2}$) is placed. The auxiliary equipment consists of a power supply, a preset count selector, and an electronic counter.

Procedure. The isotope ^{60}Co disintegrates via a β^--decay to the second excited state of ^{60}Ni at 0.312 m.e.v. This excited state deactivates immediately via two γ-quants, with 1.17 and 1.33 m.e.v. of energy, respectively, to the stable ^{60}Ni isotope.

The sensitivity of the employed G.M. tube is about 2% for the γ-quants, the sensitivity for the β's absorbed by the tube being 100%. With a very thin layer of a ^{60}Co preparation the count rate observed by the detector will be determined mainly by the β-particles. The absorption curve varies nearly exponentially with the absorber thickness under the influence of the energy distribution and scattering. The range of the β-particles is about 80 mg. cm.$^{-2}$ for ^{60}Co. Deviations from the exponential curve occur above 30 mg. cm.$^{-2}$ In practice, the film thickness needed for infrared spectroscopic work never exceeds 200 microns.

This means that at an assumed material density equal to 1, the film thickness never exceeds 20 mg. cm.$^{-2}$

A semilog plot of the measured activity *vs.* the thickness traversed gives a straight line. The following equation is applicable.

$$N = N_0 e^{-\alpha s} \qquad (1)$$

where N_0 is the count rate of incident β-particles, N the count rate of transmitted β-particles, α the mass absorption coefficient, and s the thickness of the film in mg. cm.$^{-2}$

The expected relative error of a measured film thickness is given by

$$\sigma_s = \frac{ds}{s} = \frac{dN}{N} \cdot \frac{1}{\ln N_0/N}$$

In practice it is easier not to determine the number of transmitted β's per unit time, but to determine the time needed for 10^5 counts. Hence:

$$\sigma_s = \pm 0.32 \frac{1}{\ln N_0/N} \% \qquad (2)$$

When we consider 1% as an acceptable relative error, it follows that N should not exceed 0.7 N_0. In practice this means that the ^{60}Co source is useful for measuring film thicknesses in the range 4.5 to 20 mg. cm.$^{-2}$

For film thicknesses smaller than 45 microns (4.5 mg. cm.$^{-2}$) a ^{14}C source can be used successfully. ^{14}C emits β-particles with $E_{max} = 0.155$ m.e.v. The range is about 28 mg. cm.$^{-2}$ This source is very convenient for use in measuring film thicknesses exceeding 1 mg. cm.$^{-2}$

Equation 1 is now modified to:

$$t_0 = te^{-\alpha s}$$

because $t_0 = 10^5/N_0$ and $t = 10^5/N$. So,

$$s = \frac{1}{\alpha} \ln t/t_0 \text{ or } s = a \log t/t_0 \qquad (3)$$

After calibration of the apparatus only the times t and t_0 are measured to find the thickness s.

Calibration of the Apparatus. For calibrating the ^{60}Co equipment use is made of thin polyethylene films of homogeneous thickness. Determination of the surface area and weight of the films give the desired thickness in mg. cm.$^{-2}$

For calibrating the ^{14}C equipment use was made of films whose thickness was measured by interference. The procedure is as follows. An infrared spectrum was run of a film of about 5 mg. cm.$^{-2}$ thickness, as determined with the ^{60}Co meter. Application of

$$s = 10^3 \rho d = \frac{10^3 p \rho \lambda_k \lambda_{k+p}}{4 n_k(\lambda_k - \lambda_{k+p})} \qquad (4)$$

where s is the thickness in mg. cm.$^{-2}$, d is the thickness in centimeters, ρ is the density in gcm.$^{-3}$, p is the number of extremes in the interference pattern between λ_k and λ_{k+p}, n_k is the index of refraction at λ_k, and λ_k and λ_{k+p} are wavelengths at an extreme, gives n_k. In the derivation of this formula it is assumed that n_k equals n_{k+p}. It was found, that at a wavelength of 8 microns, n_k is 1.514; n_k being known now, it is possible to determine the thickness, s, of thin films, when p, λ_k, λ_{k+p} and ρ have been measured.

The term a in Equation 3 can now be derived. With a given arrangement of the equipment, a is nearly constant. However, the count rate decreases with time owing to the decreasing intensity of the source. The influence of the dead time of the detector (about 100 μ seconds) also decreases with time (*1*). The half life of ^{60}Co being 5.25 years, a must be periodically redetermined (once in three months) for measurements with ^{60}Co.

DISCUSSION AND RESULTS

The advantages of measuring thicknesses by means of β-ray absorption are: there being no mechanical contact between the measuring device and the sample, the thickness of rubber films can be measured without difficulty. As the surface of polymer films—especially of films prepared in the laboratory—is seldom ideally flat, an average thickness (effective optical thickness) is required. This average thickness is determined with the method described. If a gravimetric method is used, the density of the material must be known. In the method described knowledge of the density is superfluous.

The method will be illustrated by an actual problem: the determination of the propene content of an ethene-propene copolymer.

A film is pressed from the polymer under investigation. The infrared spectrum is run from 1420 to 1370 cm.$^{-1}$ The extinction is determined of the band with maximum at 1380 cm.$^{-1}$ (methyl symmetrical bending). A horizontal base line is drawn at the inflection at about 1410 cm.$^{-1}$

Application of Beer's law leads to

$$E = 10 \epsilon x \rho d \text{ or}$$

$$E = 10^{-2} \epsilon xa \log t_1/t_0 \text{ or}$$

$$E = \epsilon' x \log t_1/t_0$$

where E is the extinction, ϵ is the specific extinction coefficient, d is the film thickness in cm., and x is the weight percentage of propene in the copolymer.

The modified extinction coefficient ϵ' was determined on copolymers of known propene content. This content was determined by comparing solutions of the copolymers in carbon tetrachloride with solutions of amorphous isotactic polypropene.

The outlined procedure is illustrated by the results found for six experimental copolymers, *A*–*F*. These results are summarized in Table I.

Table I. Analysis of Copolymer Films

Sample	E 1378 cm.$^{-1}$	t_1, minutes	x	$10^2 E / x \log t_1/t_0$
A	0.592	13.706	57	4.4
B	0.579	12.425	67	4.4
C	0.420	11.149	61	4.6
D	0.505	12.937	50	4.7
E	0.569	12.695	56	4.9
F	0.492	13.209	48	4.7
				av. 4.6

In these experiments t_0 was 7.94′. The formula to be used for analysis of copolymers thus changes into:

$$\text{weight \% propene} = \frac{21.7 E}{\log t_1/t_0}$$

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Correction

Determination of Diethyl Sulfate, Ethyl Hydrogen Sulfate, and Sulfuric Acid in Mixtures

In this article by D. K. Banerjee *et al.* [ANAL. CHEM. **36**, 2016 (1964)] the captions for the two figures on page 2017 are reversed. The caption for the figure at the top of the page should read "Figure 2. Titration curve of typical plant sample" and that at the bottom of the page should read "Figure 1. Titration curve of synthetic mixture 11 (see Table IV)."

Diffusion Method for the Determination of Silicon in Inorganic Materials

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▶ A rapid and accurate method was developed for the determination of silicon in copper-, aluminum-, and iron-base alloys; fluoride-bearing ores; and other types of materials including phosphoric acid, titanium dioxide, and dolomite. The method consists of the decomposition of the sample in a plastic Petri dish, formation of H_2SiF_6 with the addition of hydrofluoric acid, and the diffusion of SiF_4 from the sample by using elevated temperatures. The SiF_4 is absorbed in a layer of sodium hydroxide which is placed on the inside of the Petri dish lid. The sodium hydroxide portion is then analyzed for silicon by an ordinary spectrophotometric procedure using the reduced molybdenum blue color complex formation. The absorbance is measured at 815 mμ wavelength using 1-cm. cells. The concentration range studied in this investigation is between 0.003 and 2.7% Si. The elimination of most interfering cations and anions in the analysis of silicon was accomplished by this procedure.

THERE are many accurate methods for the spectrophotometric determination of silicon in the literature. This method supplements most of them and is, in addition, more expedient, and by the volatilization step, speeds the separation and the quantitative collection of small quantities of silicon.

Various methods have been proposed for the separation of silicon from different alloys, including steels. Fowler (*4*) employs an acid dehydration, followed by volatilization of the excess iron by passing a dry stream of HCl gas over the sample at 400° to 700° C.; while Honda (*7*) uses ion exchange techniques for the determination of silicon in steel to remove the interferences caused by iron. Hill (*5*), in steel analysis, employs sodium fluoride to remove the iron (as FeF_6^{-3} from the color system. Dozinel (*3*) uses a modified ASTM procedure (*1*), which is direct and requires no separation, for the determination of silicon in copper-base alloys. Its use is limited by impurities in the alloy, such as phosphorus in large amounts, arsenic, and other elements that interfere with colorimetric silicon analysis. Various colorimetric methods have been employed for the determination of silicon in aluminum-base alloys; most of these require the decomposition of the material with NaOH in nickel beakers and are invalid if certain interfering ions are present (*9, 16*). Several procedures have been suggested for the determination of silicon in fluoride-bearing materials (*2, 6, 12–14*); but, time-consuming fusions and/or complexing of the fluoride ion are required.

Titrimetric procedures have been employed in some instances (*15*); but, experience in the titration is necessary to ascertain the exact end point, and interfering substances such as calcium, borates, and phosphates must be absent.

A multitude of colorimetric procedures for the development of the yellow silico-12-molybdate or the reduced heteropolic blue color may be found in the literature as demonstrated by the lengthy bibliography on the subject by King *et al.* (*8*). However, these procedures for the colorimetric determination of silicon in various types of alloys and/or ores usually involve tedious decomposition of the material for conversion of the silicon to its monomeric form.

Many gravimetric procedures using acids HCl, H_2SO_4, $HClO_4$, or HNO_3 for the dehydration of silicon are given by Lundell and Hoffman (*10*). In many instances, alloys containing low silicon (0.01 to 1.0%) are analyzed by using these techniques with a large sample size (3.0 to 10.0 grams). A few of the serious disadvantages of these procedures include the following (*4*) precipitation is rarely complete, even when two dehydrations are made; boron causes high results by partial coprecipitation with SiO_2 because it is weighed with the silicon dioxide and volatilized as BF_3; and niobium, tantalum, and tungsten are largely precipitated with silicon.

These disadvantages do not include, of course, the tremendous amount of the analyst's time involved for decomposition of the sample and a minimum of two dehydrations, nor the possible error encountered in filtrations, evaporations, and volatilization of the SiO_2 with HF.

Rowley and Farrah (*11*) proposed a method for the determination of fluoride using a diffusion technique which was both accurate and rapid. Applying this principle, the following method was evolved and applied to the determination of silicon in various alloys and ores. Because the diffusion method for fluoride was quantitative, the possibility arose that other determinations involving volatile compounds might also be adaptable to a quantitative procedure. We knew from silicon chemistry that the following two reactions in the presence of either sulfuric or perchloric acid were valid:

$$SiO_2 + HF \rightarrow H_2SiF_6 + H_2O$$

$$H_2SiF_6 \xrightarrow{\Delta} SiF_4 + 2\ HF$$

With this information it was probable that SiO_2 could be determined by such a diffusion procedure. Experimentation with various materials verified this. The possibilities of applying this procedure to other types of alloys and ores in addition to those used in this investigation could prove equally successful and could be of aid to the analyst for some of the more difficult wet analyses for silicon.

This method covers the determination of silicon in various alloys or ores in concentrations of 0.003 to 3.0% based on a 0.05- to 2.0-gram sample weight. The sample size taken should be adjusted so as to give 10 to 250 μg. of silicon in a final dilution of 250 ml. The color developed by this procedure follows Beer's law for at least 250 μg. of silicon in a 250-ml. dilution for final color development. The method may be extended by using different dilutions and/or changing the size of the cells in which the developed color can be read. This is customarily done by the experienced colorimetric analyst.

EXPERIMENTAL

Apparatus. Plastic Petri dishes, 100 mm. × 15 mm., polystyrene available from Fisher Scientific Co.; Teflon or polystyrene beakers, 250-ml. capacity; polystyrene graduated cylinders for dispensing all reagents; drying oven, capable of maintaining constant temperature of 70° to 72° C. for extended periods of time; Beckman

Model DU spectrophotometer or equivalent; heating lamps; pH meter.

Reagents. All reagents are stored in plastic containers.

Molybdic Acid Solution, 10%. Dissolve 25.0 grams of ammonium molybdate in 230 ml. of water. Add 20.0 ml. of concentrated sulfuric acid. Mix and cool.

Tartaric Acid. Aqueous solution, 20%.

Reducing Solution. Dissolve 27.0 grams of sodium bisulfite 2.0 grams of sodium hydroxide, and 0.50 gram of 1-amino-2-naphthol-4-sulfonic acid in 250 ml. of water. Prepare fresh weekly.

Sodium Hydroxide. Alcoholic solution, 4%. Dissolve 4.0 grams of sodium hydroxide in 10 ml. of water and, after cooling, add 90.0 ml. of denatured ethyl alcohol. Mix.

Perchloric Acid Solution. Aqueous solution, 2–1 by volume with 70% $HClO_4$. Cool before using.

Nitric Acid Solution, 1:1 by volume.

Sulfuric Acid Solution, 1:1 by volume.

Sodium Hydroxide Solution, 20% aqueous.

Mercuric Nitrate Solution, 5%. Dissolve 5.0 grams of A.R. mercuric nitrate in 100 ml. of water containing 1 ml. of concentrated HNO_3.

Boric Acid Solution. Saturated.

Hydrofluoric Acid Solution. Twenty milliliters of A.R. reagent grade 48% hydrofluoric acid is mixed with 80.0 ml. of water.

Standard Silicon Solution. Ten micrograms Si per ml. Weigh 1.0779 grams of NBS glass sand No. 165 into a platinum crucible and fuse thoroughly at 1000° to 1100° C. with 5.0 grams of sodium carbonate for 1 hour. Dissolve the melt in 50 ml. of water containing 10 ml. of concentrated HNO_3. Dilute to 1 liter in a volumetric flask with water (Si = 500 μg. per ml.). Pipet 10.0 ml. of this solution into a 500-ml. volumetric flask, dilute to the mark, and mix. (Si = 10 μg. per ml.). Store the 500 μg. standard solution in a plastic bottle. We have kept this solution for 6 months with no signs of decomposition. The 10 μg. per ml. solution should be prepared fresh each day it is used.

Preparation of Standard Calibration Curve. Pipet 0 (blank), 1.0, 3.0, 5.0, 8.0, 10.0, 15.0, 20.0, and 25.0 ml. of standard silicon solution (10 μg. per ml.) into plastic beakers (250-ml. capacity). Add 50 ml. of saturated boric acid solution followed by exactly 5.0 ml. of 10% molybdic acid solution. After 5 minutes, adjust the pH of the solution to 1.2 to 1.3, using either 1:1 sulfuric acid or 20% aqueous solution of sodium hydroxide. After 8 minutes, but no longer than 12 minutes, add 5 ml. of 20% tartaric acid solution and immediately add 4 ml. of reducing solution. Mix thoroughly and dilute the solution to 250 ml. in volumetric flasks. After 1 hour (which is necessary for full color development) read the blue color on a photometer with a light band set at approximately 815 mμ, using water in the reference cell. The readings are made in 1.0-cm. cells. Correct for the blank and plot the photometer readings of the calibration solutions against micrograms of silicon in 250 ml. of solution.

Preparation of Coating of the Petri Lid. Four milliliters ± 0.01 ml. of the alcoholic sodium hydroxide is placed on the inside portion of the Petri lid. This is done with a pipet, and after the addition of the sodium hydroxide, the lid is carefully swirled to obtain an even coating over the inside of the lid. The solution is air dried for about 20 minutes and placed under a heat lamp and dried thoroughly. Care must be taken at this point that the temperature does not become too hot or the lid will warp out of shape and not fit the bottom portion of the Petri dish containing the sample. After drying, the lid is placed over the decomposed sample and the lid and dish are placed in the drying oven as soon as possible to prevent the absorption of moisture by the dried sodium hydroxide and to complete the reaction.

Decomposition of Copper Base Alloys. To the weighed sample in the plastic Petri dish, 15 ml. of 2:1 perchloric acid is added, followed by 2.0 ml. of concentrated nitric acid. The dish is swirled occasionally to hasten decomposition of the sample. After complete decomposition, the sample is cooled to room temperature. Exactly 5.0 ml. of diluted hydrofluoric acid is added and the Petri lid, which has previously been coated with sodium hydroxide and dried, is placed over the sample immediately. The Petri dish is carefully transferred to a preheated drying oven at 70° to 72° C. for about 18 hours. The temperature is critical because the polyethylene Petri dishes used throughout this procedure start to soften slightly above 72° C., but the temperature should be as high as possible to speed the reaction to completion.

Decomposition of Aluminum-Base Alloys. To the weighed sample in the plastic Petri dish, 1.0 ml. of 5% mercuric nitrate is added, followed by 15 ml. of 2:1 perchloric acid. After the reaction subsides and complete decomposition of the alloy is accomplished, cool the sample to room temperature. More mercuric nitrate may be added dropwise if decomposition of the sample is incomplete. Four milliliters of concentrated nitric acid is added. If decomposition of the sample is incomplete or quite slow, place the Petri dish containing the sample under the heating lamp and warm carefully. This will usually make decomposition of the aluminum complete. The mixture is cooled to room temperature, and exactly 10.0 ml. of diluted hydrofluoric acid is added. The dried, coated lid of the Petri dish is immediately placed over the sample and transferred to a preheated drying oven at 70° to 72° C. for about 18 hours.

Decomposition of Iron-Base Alloys The weighed sample is placed in the bottom of a plastic Petri dish and 1.0 ml. of 5% mercuric nitrate is added. Amalgamation of the iron is increased by placing the sample under the heating lamp for about 1 minute with occasional swirling. The dish containing the sample is removed from under the lamp and 15 ml. of 2:1 perchloric acid is added immediately, followed by 5.0 ml. of 1:1 nitric acid. The sample is swirled occasionally, and if it does not go completely into solution, it is returned under the heat lamp and swirled occasionally until complete decomposition is accomplished. High carbon steels, of course, will have a slight residue of carbon, even after prolonged heating; this does not appear to be a problem for the complete recovery of silicon. Mo-W steels will also have a residue; however, after the addition of HF and heating in the oven, complete decomposition of the sample is accomplished.

After complete decomposition of the sample and cooling to room temperature, 5.0 ml. of dilute hydrofluoric acid are added and immediately the dried coated lid of the Petri dish is placed over the sample. The complete Petri dish is transferred immediately to a preheated drying oven at 70° to 72° C. for about 18 hours.

Preparation of Miscellaneous Samples for Diffusion. Cryolite, titanium oxide, phosphoric acid, dolomite ores. The weighed sample is placed in the bottom of the plastic Petri dish and 15 ml. of 2:1 perchloric acid is added. Exactly 5.0 ml. of diluted hydrofluoric acid is added and the dried, coated lid of the Petri dish is placed over the sample immediately. The complete dish is transferred immediately to the preheated drying oven at 70° to 72° C. for about 18 hours.

Analysis of Silicon after the Diffusion. After the samples have been in the drying oven for approximately 18 hours, the tops from the Petri dishes are carefully removed. The portion in the bottom of the dishes can now be discarded. The sodium hydroxide portion, which contains the silicon, is washed thoroughly with distilled water into plastic beakers (250-ml. capacity), and 75 to 80 ml. of saturated boric acid solution are added. If a dilution must be made because of high silicon content, the dilution and the aliquots must be made at this point. This dilution, and subsequent pipetting can now be done in glassware. Five milliliters of molybdic acid solution are added, and after 5 minutes the pH of the samples is adjusted to 1.2 to 1.3 using either 1:1 sulfuric acid or 20% aqueous sodium hydroxide. After 8 minutes, but no longer than 12 minutes, 5 ml. of tartaric acid solution is added, the solution mixed, and immediately 4 ml. of reducing solution is added. The solution is diluted to 250 ml. in a volumetric flask, and after 1 hour, is read on a photometer following the same procedure as on the calibration curve. After deducting a blank, the silicon content is calculated from the standard calibration curve. Blanks must be carried through the entire procedure using exactly the same amounts of reagents as are in the samples. If a dilution and aliquot must be made on

the samples, dilute and aliquot the blanks in the same proportion. Since hydrofluoric acid does contain some silicon, in the form of hydrofluosilicic acid, the addition of this reagent must be made in carefully measured portions and diluted and aliquoted in the same manner as the samples.

RESULTS AND DISCUSSION

To establish the accuracy and reproducibility of this method, silicon was determined in various types of available standards; no more than three determinations were performed on any one type of material in any one particular day, and in most instances, the determination was performed singularly on a daily basis. These results are shown in Table I. The ranges obtained by participating laboratories for the National Bureau of Standards, when available in this laboratory, are included to compare only the precision of the diffusion method against the more recognized gravimetric, and in a few cases, colorimetric methods employed by these laboratories.

Table II is included to demonstrate the reproducibility of the diffusion method. Since the materials used were not analyzed by any other method, it is impossible to ascertain at this time the accuracy of these determinations. The sample sizes for the diffusion analysis were varied greatly (from 0.50 to 2.0 grams) in most cases, which would lead one to believe the accuracy would be in the acceptable ranges, unless the silicon is present in more than one form.

Table III illustrates the results obtained by the diffusion method when analyzing spectrographic aluminum standards. The assigned spectrographic analyses are included.

Certain discrepancies will be noted between the results of spectrographic certifications and those of the diffusion procedure. No study was made at this time to ascertain causes of these discrepancies. It is believed, however, that the presence of magnesium silicide in some of these aluminum standards could have caused the results by the diffusion method to be low. A more vigorous decomposition procedure could eliminate this problem.

Chloride ions, in large concentrations, in the presence of strong acid, have an adverse effect upon the diffusion method during the diffusion period. Originally mercuric chloride and/or hydrochloric acid was used for the decomposition of certain alloys. The gas formed from these reagents during the diffusion period in the drying oven combined with the sodium hydroxide layer in the Petri lid and prevented the recovery of silicon. To avoid this problem, reagents containing chloride ions were eliminated.

It was originally thought that the nitrous oxide, which is formed during the diffusion period, might have an adverse effect upon the analysis by attacking the sodium hydroxide coating. Urea was added to the warm solution after the decomposition of the sample to eliminate the formation of the nitrous oxide. It was found later, however, that the formation of the nitrous oxide by following these procedures was not detrimental to the recovery of silicon. Consequently, the urea was omitted in subsequent analyses.

Preliminary investigations were made for the analysis of silicon in stainless steel-type alloys. The decomposition of these alloys by the above suggested procedures proved inadequate. However, acceptable results were obtained by following a more vigorous decomposition. The alloy was attacked with HCl in a platinum dish, then fumed with perchloric acid, followed by the addition of HNO_3 and refuming. HF was added to the solution and the platinum dish was covered with a dried, coated sodium hydroxide Petri lid. The normal diffusion procedure was then followed.

Because of the presence of fluosilicic acid (as H_2SiF_6) in A.R. grade hydrofluoric acid, careful control must be maintained in the additions of this reagent. Blanks must contain the exact amounts of hydrofluoric acid as is added to unknown samples.

Table I. Comparison of Other Methods vs. Diffusion Method

	Range, % Si	Assigned value, %	Range, %	Average, %	No. of determinations
NBS No. 164 (Brass)	0.03 –0.049	0.038	0.032–0.037	0.034	15
NBS No. 158 (Brass)	2.70 –2.74	2.74	2.64 –2.69	2.67	11
NBS No. 62C (Brass)	0.061–0.073	0.068	0.064–0.069	0.066	9
NBS No. 16D (Brass)	0.180–0.196	0.188	0.176–0.189	0.182	7
NBS No. 88 (Dolomite ore)		0.14	0.13 –0.14	0.14	14
NBS No. 5K (Steel)	2.02 –2.12	2.08	2.02 –2.07	2.05	5
NBS No. 170 (B.O.H. steel)	0.055–0.063	0.060	0.055–0.062	0.058	15
NBS No. 15f (B.O.H. steel)	0.037–0.045	0.042	0.041–0.045	0.043	15
NBS No. 152 (Steel)	0.239–0.250	0.244	0.231–0.238	0.235	6
NBS No. 85b (Al)	0.17 –0.19	0.18	0.17 –0.18	0.18	8
NBS No. 80c (Al)	0.67 –0.69	0.68	0.65 –0.70	0.67	8
NBS No. 100a (Steel)		0.243	0.227–0.253	0.243	3
NBS No. 132a (Steel)		0.190	0.183–0.192	0.188	3
NBS No. 14d (Steel)		0.126	0.120–0.124	0.121	3
Std. cryolite ore		1.3	1.24 –1.35	1.30	6

Table II. Reproducibility of Diffusion Method

Cryolite bath "A"	Si, p.p.m. 32.3, 32.3, 31.0, 28.0, 32.3, 30.8, 29.7, 27.2, 32.4, 27.1, 27.8, 26.3
Natural cryolite "B"	Si, p.p.m. 186, 198, 178
Titanium oxide	Si, % 0.25, 0.26, 0.27, 0.27 0.29
H_3PO_4 "A"	Si, % 0.39, 0.42, 0.37, 0.35, 0.40, 0.36
H_3PO_4 "B"	Si, % 0.029, 0.031

Table III. Comparison of Diffusion Method vs. Other Methods: Spectrographic Standards

Spectrographic assigned analysis, % Si	Diffusion, %
0.043	0.036
0.070	0.054, 0.060, 0.059
0.27	0.21, 0.22
0.42	0.43, 0.41, 0.41
0.33	0.30, 0.32
0.16	0.14, 0.14
0.004	0.003
1.26	1.21, 1.25
0.040	0.036

The minimum time required for complete diffusion of silicon was not evaluated. It was convenient in this laboratory to have the diffusion period cover between 16 and 20 hours, which was overnight, and the results of Tables I, II, and III represent these time periods.

It is not believed that the addition of tartaric acid in the color development of silicon in this procedure is necessary because little or no phosphate is believed to diffuse into the sodium hydroxide portion. However, tartaric acid was added throughout these determinations as a safety feature.

No study was made, at this time, to ascertain the maximum amounts of SiF_4 that can be diffused and collected by the amounts of NaOH that are used throughout this procedure. Likewise, no study was undertaken at this time to determine silicon in organic materials; however, since fluoride is determined using diffusion procedures (*11*) in organics, it would seem likely that silicon in organosilicons known as silicones, silanes, or siloxanes could be determined by this procedure.

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Determination of Residual Monomers and Other Volatile Components in Styrene Based Polymers by Gas Chromatography

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▶ **A gas chromatographic method was developed for the direct determination of residual monomers, nonpolymerizable volatiles, and volatile additives in styrene based polymers. The method is simple, highly sensitive, and is applicable to many polymeric systems. The method is based on the direct injection of solutions or dispersions of polymers in *N,N'*-dimethylformamide (DMF) using toluene as an internal standard. Additives, pigments, and stabilizers do not interfere in the monomer determination.**

KNOWLEDGE of residual monomer levels in polymeric systems is of great interest in the plastics industry. Fabricating, strength, and permanence properties, as well as taste and odor of certain foods in contact with the polymer, may be affected. In recent years residual monomer levels in polymers decreased because of improved polymerization technology. Previously used methods, such as titration of double bonds (*4, 5*), or ultraviolet spectrophotometric methods (*1*), are not easily applicable to the determination of monomers at low concentrations. The determination of such monomers in pigmented, stabilized, or partially soluble polymers is very lengthy and tedious. The determination of monomers in copolymers and terpolymers presents an even more difficult problem. Polarography has been used for the determination of acrylonitrile (*3*). The gas chromatographic determination of residual monomers in latex systems has been reported (*2, 6–8*).

In this work, a gas chromatographic method was developed for the determination of residual monomers and other volatile components in styrene-based polymers. *N,N'*-dimethylformamide (DMF) was chosen as solvent because it interferes least with the direct determination of monomers of interest. Monomers—such as acrylonitrile, butadiene, styrene, alpha-methylstyrene, and cresylic additives—were determined to parts per million.

EXPERIMENTAL

Apparatus. A Wilkens Model 600 HY-Fi gas chromatograph equipped with straight bore injection block and hydrogen flame detector is used. The gas chromatograms are recorded on 0–1 mv. Brown strip chart recorder. Two columns in series are used: 3-foot, 1/8-inch o.d. 20% Tween 81, followed by 10-foot, 1/8-inch o.d. 10% Resoflex 446 on Chromsorb W, 30 to 60 mesh. Nitrogen is used as the carrier gas with a flow rate of 30 cc./minute measured with flowmeter at room temperature. The columns are held at 120° C. and the injection block is held at 210° C. A hydrogen flow rate of 23 cc./minute is used for the detector. The detector is operated at an impedance of 10^9 ohms, an output sensitivity of 1× and attenuated between 1× and 128×, depending on monomer concentration. The sample as a solution or dispersion (rubber-containing polymers form dispersions rather than solutions) is injected with a 50-μl. syringe (Hamilton N-705).

Reagents. Acrylonitrile, 99.8%, commercial grade; styrene, 99.8%; alpha-methylstyrene, commercial grade; ethylbenzene, reagent grade; toluene, reagent grade; and *N,N'*-dimethylformamide (DMF), technical grade.

Commercial DMF contains low boiling point impurities that must be removed. This can easily be done by distillation. An 85 to 90% center cut through a 15-inch Vigreux column is usually found to be chromatographically clean.

Table I. Relative Retention Data

Compound	Relative retention times (toluene = 1)
Butadiene	0.40
Acrylonitrile	0.76
Toluene	1.00
Ethylbenzene	1.40
Styrene	2.25
DMF	3.75

Table II. Weight Per Cent Volatiles

Polymer	Acrylonitrile Added	Acrylonitrile Found	Ethyl Benzene Added	Ethyl Benzene Found	Styrene Added	Styrene Found
Polystyrene	...	...	0.087	0.084 ± 0.003	0.183	0.178 ± 0.007
	...	...	0.043	0.043 ± 0.002	0.091	0.090 ± 0.003
	...	...	0.043	0.046 ± 0.003	0.045	0.047 ± 0.003
Styrene–acrylonitrile copolymer	0.008	0.0074 ± 0.0003	0.069	0.069 ± 0.002	0.091	0.093 ± 0.008
Styrene–acrylonitrile–butadiene terpolymer	0.024	0.022 ± 0.003	0.043	0.045 ± 0.002	0.137	0.140 ± 0.004
	0.008	0.008 ± 0.0008	0.07	0.073 ± 0.003	0.064	0.068 ± 0.007

Preparation of Monomer Containing Polymer Standards. PURIFICATION OF POLYMERS. Polymers are dissolved in chloroform and precipitated with methanol while mixing in a high-speed blender. The precipitated polymers are dried at 60° C. for 24 hours in a vacuum oven. The purity of polymers used for standardization is checked by the gas chromatographic method described below.

PREPARATION OF STANDARD SOLUTIONS. Purified polymer, 0.500 gram, is dissolved in 5 ml. of distilled DMF to which 1 ml. of a 0.5% solution of toluene in distilled DMF is added. Known levels of monomer are then established by adding appropriate aliquots of standard monomer solutions. The amount of monomer added in this manner is varied between 0.00005 to 0.005 gram. This corresponds to 0.01 to 1.0% of monomer in the polymer.

Calibration graphs are prepared by plotting the ratio of peak height of monomer to toluene peak height *vs.* per cent monomer. Straightline relationships are obtained for the range of concentration of interest.

Procedure. The sample, 0.500 gram, is weighed into a 10-ml. glass-stoppered Erlenmeyer flask and dissolved in 5 ml. of purified DMF and 1 ml. of 0.5% toluene in DMF. Five microliters of solution are injected into the gas chromatograph, set up as outlined above. The polymer remains in the injection block, and is removed periodically by reaming. The frequency of cleaning depends on the work load; cleaning every fifty injections is preferred.

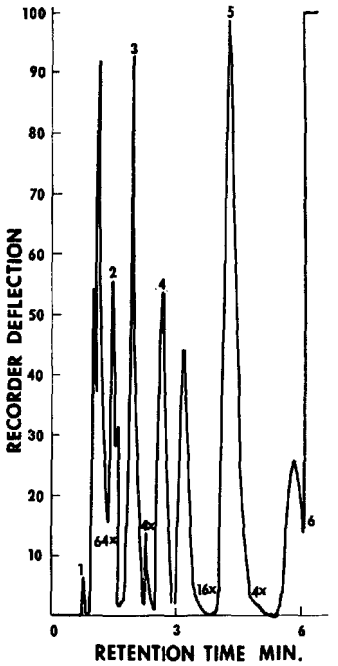

Figure 1. Gas chromatogram of styrene–acrylonitrile–butadiene terpolymer

Identified components are: 1. Butadiene; 2. Acrylonitrile; 3. Toluene; 4. Ethylbenzene; 5. Styrene; 6. Solvent

RESULTS AND DISCUSSION

Good resolution is obtained for the monomers of interest in several polymeric systems. The relative retention times for the components of interest are shown in Table I. The polymers analyzed were: Polystyrene, styrene-acrylonitrile copolymer, high-impact polystyrene (containing styrene-butadiene rubber), and styrene–acrylonitrile–butadiene terpolymer.

Gas chromatograms, showing the components of interest, are seen in Figure 1 for the styrene–acrylonitrile–butadiene terpolymer. The sensitivity of the instrument is capable of detecting less than 10 p.p.m. of monomer. The resolution of minor components is improved, if necessary, by using temperature programming. DMF was chosen as a solvent because it offers several advantages, as compared to other solvents. It is not only a good solvent for many styrene-based polymers, but its boiling point (154° C.) is higher than the monomers of interest, thus the monomers move through the instrument ahead of the solvent. Another advantage is that the DMF is easy to purify. The purification is a simple distillation, as outlined above, and the solvent is stable after purification. A series of polymers was analyzed using this method. The precision of the method is indicated in Table II.

This method is also equally applicable to other polymers soluble in DMF. An example of such polymer is polyvinyl chloride–vinylacetate copolymer. Figure 2 is the gas chromatogram of volatiles in a sample of this copolymer.

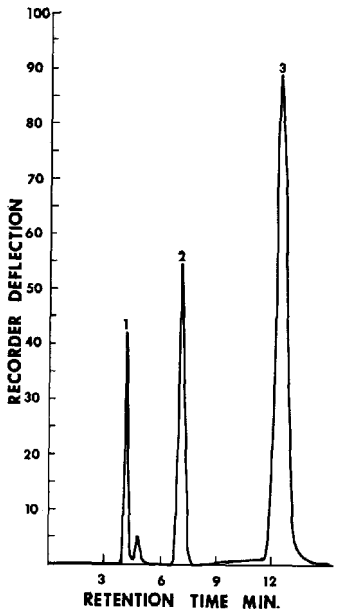

Figure 2. Gas chromatogram of polyvinylchloride–vinylacetate copolymer in DMF solution

Toluene as an interval standard
Components: 1-vinylchloride, 2-vinylacetate, 3-toluene
Column: 10-foot, 1/4-inch o.d., 10% Resoflex 446 on Chromosorb W, 30 to 60 mesh
Carrier gas: N_2
Flow rate: 25 cc./minute
Detector: H_2 flame
Sample size: 5 μl.

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Determination of Polyphenyls in Working Environments of Organic Reactors by Spectrophotometric Methods

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▶ This paper describes the analysis of air for polyphenyl vapors present as the components of the nuclear moderator-coolants Dowtherm A (diphenyl-diphenyl oxide mixture) and Santowax R (ternary terphenylic mixture). Samples were collected on cellulose powder beds for long sampling period and on silica gel tubes for immediate controls. The quantitative determination of the total polyphenyl concentration, together with the percentage determination of components, were carried out by ultraviolet spectrophotometry. Qualitative and semiquantitative tests were also devised, based on the use of detector tubes containing silica gel impregnated with concentrated sulfuric acid containing formaldehyde and iron (III). The concentration of polyphenyls in working environments is given according to sampling positions and operation conditions.

POLYPHENYLS, which are widely used as a moderator-coolant in some types of nuclear reactors (*1*, *2*, *6*), have irritating properties to exposed respiratory passages and the mucous membrane tissue (*5*, *7*).

For this reason the Medical Service of Casaccia Nuclear Center (Rome, Italy) has felt the need to develop analytical methods to control polyphenyl concentration in working environments.

The technical products, used at present in the experimental organic reactor R.O.S.P.O. (Reattore Organico Sperimentale Potenza O) near Rome and which will be employed also in the organic reactor P.R.O. (Progetto Reattore Organico), abuilding near Bologna, consist essentially of a ternary terphenyl mixture (Santowax R) containing 12% *ortho*-, 28% *para*-, and 60% *meta*- terphenyl, and of a binary mixture (Dowtherm A) containing 76.5% diphenyl oxide and 23.5% diphenyl.

Two analytical procedures were devised for the determination of polyphenyls: a colorimetric method, which was particularly useful for qualitative and semi-quantitative analysis of organic vapors, and an ultraviolet method which gave very good results for quantitative analysis and for the determination of the components percentage in every vapor mixture. Three types of air sampling procedures were also devised to assure an efficient control of polyphenyls in the different working conditions.

EXPERIMENTAL

Reagents. Diphenyl and diphenyl oxide (Carlo Erba, Milano) and *o*-, *m*-, and *p*-terphenyls (Light's, England), were of analytical grade. The commercial products Dowtherm A and Santowax R were supplied by Dow Chemical International (Canada) and by Monsanto Chemical Co. (USA), respectively.

Best quality standard grade cellulose powder (Whatman) and silica gel 0.2–0.5-mm. diameter (Merck) were used as the vapor adsorbers. Both the products were washed twice with dichloromethane, dried at 105° C., and stored in a desiccator. All the other chemical reagents were of analytical grade.

POLYPHENYL STANDARD SOLUTIONS. Solution I: 0.1 gram of the various products were dissolved in 100 ml. of dichloromethane (1 mg./ml.).

Solution II: 10 ml. of Solution I were diluted to 100 ml. with glacial acetic acid (100 μg./ml.).

Solution III: 1 ml. of Solution I was diluted to 100 ml. with dichloromethane (10 μg./ml.).

FORMALDEHYDE SOLUTIONS. Solution I: 1 ml. of 35% formaldehyde was diluted to 100 ml. with glacial acetic acid.

Solution II: 1 ml. of Solution I was diluted to 25 ml. with glacial acetic acid; both solutions had to be prepared daily.

SULFURIC ACID CONTAINING Fe(III) SOLUTIONS. Solution I: 8.5 grams of $FeCl_3 \cdot 6\,H_2O$ were dissolved in 37 ml. of conc. sulfuric acid and diluted to 250 ml. with water.

Solution II: 5 ml. of Solution I were diluted to 100 ml. with conc. sulfuric acid; this last solution had to be prepared daily.

Equipment. The spectrophotometer was a Beckman DU, model G-2400, equipped with 10-mm. quartz cells.

A 100-ml. Dräger pump (W. Germany) and 5- × 100-mm. tubes were used for immediate qualitative and semiquantitative determinations. A vacuum oil pump (Soc. La Mirus, Milano) connected to a dry gas meter (Soc. Brunt, Milano) supporting a fritted glass funnel filled with cellulose powder was utilized for long period air samplings.

Procedures. COLORIMETRIC REACTION WITH FORMALDEHYDE. SULFURIC ACID AND IRON (III). Benzene (*3*) and diphenyl (*8*) are often determined by means of the chromogenic reaction with formaldehyde and sulfuric acid containing some iron (III). This colorimetric reaction was adapted to the polyphenyls of interest.

One milliliter of polyphenyl standard Solution II (0.5 ml. for diphenyl) was added with 0.2 ml. of formaldehyde (Solution II) and 8 ml. of sulfuric acid (Solution II).

Different colors were so obtained: pink for diphenyl oxide, emerald green for *p*-terphenyl, and blue for diphenyl, *o*- and *m*-terphenyl. Although the sensitivity is good, the absorption maxima and the color intensity are greatly affected by the ratio of CH_2O to polyphenyls, by the elapsed time, and by the temperature. For these reasons the standard curves, obtained in the range 0 to 10 μg./ml. of polyphenyls, were not linear and showed an error of ±20%. Therefore we have used these colorimetric reactions only for qualitative and semiquantitative purposes, by preparing suitable detector tubes filled with silica gel supporting the reagents.

ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION. A more accurate method for the quantitative determination of polyphenyls, which can also be successfully applied to determine the component percentages of any vapor mixture, has been thus developed, based on the peculiar ultraviolet absorption of the different compounds dissolved in dichloromethane.

Besides having a higher sensitivity, this method is simple and accurate, and Beer's law is followed in the range 0 to 10 μg./ml. with an accuracy of ±5% both for the five single compounds and the two technical mixtures.

QUANTITATIVE DETERMINATION OF DIPHENYL-DIPHENYL OXIDE AND *o*-, *m*-, *p*-TERPHENYL MIXTURES, AND COMPONENTS PERCENTAGE CALCULATION. Dowtherm A and Santowax R standard curves can be utilized only as long as the vapor composition does

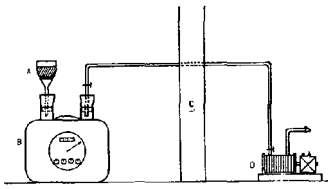


Figure 1. Experimental device for polyphenyl sampling in the R.O.S.P.O. reactor room; *A*: cellulose powder bed; *B*: air flow-meter; *C*: reactor room wall; *D*: oil pump.

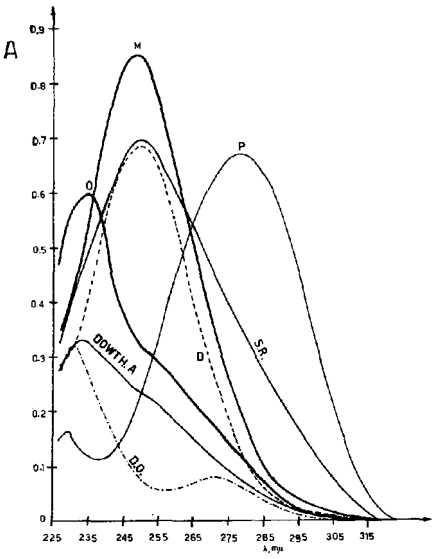


Figure 2. Ultraviolet absorption spectra of diphenyl (D), diphenyl oxide (D.O.), ortho-terphenyl (O), meta-terphenyl (M), para-terphenyl (P), Dowtherm A and Santowax R (S.R.) in dichloromethane; concentration: 5 μg./ml.

not change from that of the two starting products. On the other hand, the different chemical-physical properties (melting point, boiling point, and vapor pressure) of the various components can give rise to vapors having a composition differing from that of the starting products. Therefore a general method for the quantitative determination of any mixture of diphenyl-diphenyl oxide and *o*-, *m*-, *p*-terphenyl has been developed.

Binary Mixture Diphenyl-Diphenyl Oxide. As the spectra of Dowtherm A components present two peaks, at 230 and 250 mμ for diphenyl oxide and diphenyl, respectively, it is possible to determine their concentrations in any mixture by setting up a two-equation system (*4*); the solution of such a system gives:

$$\text{Conc. D. } (\mu\text{g./ml.}) = 7.99 \times \text{Abs. Mixt. } (250\ m\mu) - 1.53 \times \text{Abs. Mixt. } (230\ m\mu) \quad (1)$$

$$\text{Conc. D.O. } (\mu\text{g./ml.}) = 17.29 \times \text{Abs. Mixt. } (230\ m\mu) - 7.94 \times \text{Abs. Mixt. } (250\ m\mu) \quad (2)$$

By adding the Equations 1 and 2, we obtain the total concentration in the mixture:

$$\text{Mixt. total conc. } (\mu\text{g./ml.}) = \text{Conc. D.} + \text{Conc. D.O.} = 15.76 \times \text{Abs. Mixt. } (230\ m\mu) + 0.05 \times \text{Abs. Mixt. } (250\ m\mu) \quad (3)$$

The components percentages in the mixture will be naturally obtained by dividing Equation 1 and 2 by Equation 3 and multiplying by 100.

These percentages can also be obtained by plotting the ratio [Abs. Mixt. (250 mμ)]/[Abs. Mixt. (230 mμ)] as a function of the components percentages: this ratio increases linearly from 0.19 for pure diphenyl oxide to 2.19 for pure diphenyl.

Ternary Mixture *o*-, *m*-, and *p*-Terphenyls. Since the three isomers, *o*-, *m*-, and *p*-terphenyls, show three peaks at 235, 250, and 280, mμ, respectively, it is possible to obtain their concentrations in any mixture, by setting up a three-equation system the solution of which gives:

$$\text{Conc. } o\ (\mu\text{g./ml.}) = 12.750 \times \text{Abs. Mixt. } (235\ m\mu) - 8.375 \times \text{Abs. Mixt. } (250\ m\mu) + 0.610 \times \text{Abs. Mixt. } (280\ m\mu) \quad (4)$$

$$\text{Conc. } m\ (\mu\text{g./ml.}) = 9.205 \times \text{Abs. Mixt. } (250\ m\mu) - 4.515 \times \text{Abs. Mixt. } (235\ m\mu) - 2.295 \times \text{Abs. Mixt. } (280\ m\mu) \quad (5)$$

$$\text{Conc. } p\ (\mu\text{g./ml.}) = 7.860 \times \text{Abs. Mixt. } (280\ m\mu) - 0.975 \times \text{Abs. Mixt. } (235\ m\mu) - 0.880 \times \text{Abs. Mixt. } (250\ m\mu) \quad (6)$$

By adding Equations 4, 5, and 6, the total concentration of the three isomers in any mixture can be obtained:

$$\text{Mixt. total conc. } (\mu\text{g./ml.}) = 7.260 \times \text{Abs. Mixt. } (235\ m\mu) + 6.180 \times \text{Abs. Mixt. } (280\ m\mu) - 0.050 \times \text{Abs. Mixt. } (250\ m\mu) \quad (7)$$

If the third term of the Equation 7 is omitted, the errors are very low (<+1%). Finally, since the first and second terms are fairly similar, it is possible to calculate their average and to obtain a very simple equation which is approximate at ±5%:

$$\text{Mixt. total conc. } (\mu\text{g./ml.}) = 6.72\ [\text{Abs. Mixt. } (235\ m\mu) + \text{Abs. Mixt. } (280\ m\mu)] \quad (8)$$

This relation has been controlled by plotting: [Abs. Mixt. (235 mμ) + Abs. Mixt. (280 mμ)] as a function of known concentrations of several terphenylic mixtures. A straight line starting from zero and having a slope 1/6.72 was effectively obtained. Therefore the total terphenyl concentration in any mixture can be rapidly obtained by two absorption measurements at 235 and 280 mμ, respectively.

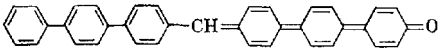
The percentages of *o*-, *m*-, and *p*-terphenyls in the mixture are naturally obtained by dividing Equations 4, 5, and 6 by Equation 7 and multiplying by 100.

Table I. Absorption Maxima and Molecular Extinction Coefficients of Polyphenyls with CH_2O, H_2SO_4, and Fe(III)

Polyphenyls	λ Max. mμ	ε
Diphenyl	590	11,500
Diphenyl oxide	515	3,200
o-Terphenyl	620	7,700
m-Terphenyl	635	6,200
p-Terphenyl	700	9,600
Santowax R	640	6,700
Dowtherm A	530	3,300

Air Sampling and Determination of Polyphenyls in Working Environments. Three different air-sampling methods, having a very good efficiency, were devised according to the technical requirements.

a) Polyphenyls were determined rapidly by means of detector tubes filled with silica gel supporting sulfuric acid, formaldehyde, and iron(III). The chromatic reactions described above are probably caused by the condensation of two molecules of polyphenyls with one molecule of formaldehyde under oxidation of iron (III):



Therefore 30 parts of formaldehyde should react with 460 parts of terphenyl; effectively 1 μg. of formaldehyde reacts with 10 to 15 μg. of terphenyl.

The maximum allowable concentration (M.A.C.) for terphenyls (Ind. Hyg. Dept., U.S.A.) being 50 mg./cubic meter (50 μg./liter), 5 μg. of formaldehyde should be a suitable quantityfor 1 to 2 liter suction (10 to 20 Dräger pump strokes).

Therefore 1.5 grams of silica gel were mixed with 1 ml. of sulfuric acid con-

Table II. Ultraviolet Absorption Maxima and Molecular Extinction Coefficients of Polyphenyls in Dichloromethane

Polyphenyls	λ Max. mμ	ε
Diphenyl	250	19,000
Diphenyl oxide	230	11,000
o-Terphenyl	235	30,000
m-Terphenyl	250	38,000
p-Terphenyl	280	30,000
Santowax R	250	33,000
Dowtherm A	231	11,000

taining 0.5 mg. of Fe(III) and 5 μg. of formaldehyde. The mixture was then introduced into the tube and gently compressed with a thin glass rod. After closing the ends with two plugs of glass wool, the detector tube was ready for use.

By changing the formaldehyde quantity, it was possible to determine different ranges of polyphenyls in the air. This type of detector tube allows one to distinguish the vapors (Dowtherm A gives a pink-violet color and Santowax R a blue-green color), and to obtain the approximate polyphenyl concentration in the air by the height of the colored band after 10 to 20 pump strokes.

b) Quantitatively polyphenyls were determined by means of silica gel tubes and ultraviolet spectrophotometry. Silica gel proved to be a good adsorber for the polyphenyl vapors when a moderate volume of air was passed through the tube. Moreover, the elution of polyphenyls by dichloromethane was rapid and quantitative.

For this reason silica gel tubes were used for a rapid and accurate polyphenyl determination, by sucking 2 to 3 liters of air through them using 20 to 30 Dräger pump strokes.

The adsorber was then transferred into a graduated cylinder containing 10 ml. of dichloromethane. An hour later the solution was examined by the ultraviolet spectrophotometric method.

c) A different procedure was devised for prolonged air sampling in the R.O.S.P.O. reactor room which is a working environment with a very limited accessibility.

An oil pump, placed out of the reactor room, was connected to the gas meter by means of a long polyethylene tube (Figure 1). By maintaining the flow rate at about 2 liters/minute, a total air volume of 0.5 to 1.0 cubic meters could be examined during the 4- to 8-hour controls. A 30-mm. bed of cellulose powder, contained in a 40-mm. fritted glass funnel, was a suitable filtering device for polyphenyls. After collection of the sample, the adsorber was left overnight in the presence of 100 ml. of dichloromethane. The cellulose powder was then filtered through a fritted glass funnel under a low vacuum, and washed twice with some dichloromethane to a final volume of 150 ml. The solution so obtained was finally examined by the ultraviolet spectrophotometric method. In this manner it was possible to determine up to 0.1 mg./cubic meter of a polyphenylic mixture and also the percentage composition.

Table III. Percentage Determination of the Three Isomers in Terphenylic Mixtures

Total concn., μg./cc.	Theoretical percentage			Found percentage		
	o%	*m*%	*p*%	*o*%	*m*%	*p*%
5	20	20	60	20.6	20.0	59.4
10	20	20	60	16.3	21.6	62.1
5	33.3	33.3	33.3	32.0	32.0	36.0
10	33.3	33.3	33.3	31.3	32.3	36.4
10	55	15	30	52	20.2	27.8
5[a]	~26	~70	~ 4	21.2	77.7	1.1
5[b]	~12	~60	~28	10.5	63.0	26.5
10[b]	~12	~60	~28	10.0	63.5	26.5

[a] Technical product OM-2.
[b] Technical product Santowax R.

Table IV. Efficiency of the Cellulose Powder Bed for Santowax R

Airflow, liter per min.	% Santowax R retained			Air total volume, cubic meters	Santowax R concn., mg. per cubic meter
	I layer	II layer	III layer		
1	99.0	1.0	0.0	0.40	5.3
1	98.8	1.2	0.0	0.40	15.5
2	97.0	2.0	1.0	0.80	13.2
2	95.5	3.5	1.0	0.80	20.5

Table V. Terphenyl Concentrations in the R.O.S.P.O. Reactor Room

Sampling place[a]	Experimental conditions[b]	Adsorber[c]	Concn., mg./cubic meter	M.A.C. concn.
C	3	C.P.	10	0.20
C	2	C.P.	0.9	0.018
C	2	C.P.	1.9	0.038
C	2	C.P.	1.4	0.028
C	2	C.P.	0.90	0.018
C	1	C.P.	0.80	0.016
C	1	C.P.	0.20	0.004
C	1	C.P.	0.10	0.002
A	2	C.P.	0.20	0.004
A	2	C.P.	0.15	0.003
A	1	C.P.	0.10	0.002
B	4	SiO_2	10	0.20
C	4	SiO_2	280	5.60
D	4	SiO_2	35	0.70
C	4	C.P.	40	0.80
D	4	C.P.	10,	0.20
A	4	C.P.	10	0.20
B	2	SiO_2	<5	<0.10
C	2	SiO_2	<5	<0.10
D	2	SiO_2	<5	<0.10

[a] A = Ground floor
B = Inspection floor (height 4 meters)
C = Charging floor (height 10.5 meters)
D = Engines floor (height 14.5 meters)
[b] 1 = With reactor out
2 = Normal operating conditions (temp. 220° to 230° C.)
3 = Like 2, but during a fuel rod changing
4 = High temperature tests (330° to 340° C.)
[c] C.P. = Cellulose powder bed
SiO_2 = Silica gel tubes

RESULTS

The absorption maxima (λ Max.) and the molecular extinction coefficients (ε) of the five pure products and of the two commercial mixtures, Dowtherm A and Santowax R, are reported in Table I for the colorimetric method, and in Table II for the ultraviolet method. The absorption spectra of the seven substances are shown in Figure 2.

Some synthetic mixtures and two commercial products were measured to check the component percentage calculation. Table III shows the results obtained by applying Equations 4, 5, 6, and 7. These results seem satisfactory for obtaining sufficient information on the composition of terphenylic mixtures.

The air sampling efficiency for method a) is assumed to be 100%, because of the well defined colored bands obtained. A 100% efficiency was experimentally

found for method b). Effectively, after a 10-liter absorption, silica gel was divided into three equal portions, but no Santowax R was found in the last two. A very good efficiency was found also for method c): the bed of cellulose powder being divided in three 2-cm. layers by means of two filter paper disks. The results obtained with different airflow and concentration conditions are shown in Table IV.

The sampling and analysis methods described above were used to control the terphenyl concentrations in R.O.S.-P.O. reactor room. Table V shows the values found with different working conditions: at 220° to 230° C. (normal operating conditions) this concentration ranged from 0.1 to 10 mg./cubic meter according to the sampling place, while at 330° to 340° C. (high temperature test) it ranged from 10 to 280 mg./cubic meter depending on the sampling place.

When the terphenyl concentration was greater than 10 mg./cubic meter, workers had to wear dust proof masks and goggles. The highest concentrations were found at the charging floor during high temperature tests and/or fuel rod changings. In these cases the vapor composition did not deviate much from the starting product Santowax R. On the contrary, with the reactor working in the normal temperature conditions, the terphenyl concentration was lower, but a measurable *ortho*-terphenyl enrichment in the vapors appeared. This tendency increased gradually as the distance of the sampling place from the charging floor increased reaching values up to 70%.

These results can be explained by considering that, at high temperatures and near the vapor escape, the three terphenylic isomers evaporate almost in the same manner, while, at lower temperatures, *ortho*-terphenyl, because of its greater vapor pressure, is the first to evaporate and the last to condense.

ACKNOWLEDGMENT

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Polarographic Determination of Submicrogram Quantities of Molybdenum

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▶ The catalytic reduction wave of molybdate in the presence of nitrate ion has been studied with the view of developing a sensitive, selective method for the determination of traces of molybdenum. In contrast to most catalytic waves, it was possible to develop a procedure in which the wave height is little affected by large amounts of electrolyte. The method has a sensitivity of 0.005 μg. of molybdenum per ml. of solution and has been applied to the determination of this metal in a variety of pure materials. Methods for the separation of traces of molybdenum are presented.

In a study concerned with the biological activity of submicrogram quantities of molybdenum, the need arose for an analytical method for determining this metal in highly purified salts. The sensitivity required exceeded that obtainable by the use of emission spectrographic procedures or the spectrophotometric method using the stannous chloride–thiocyanate method (*5*). Although polarographic methods can rarely be applied to the determination of such small quantities of materials, a highly sensitive method employing catalytic reduction wave for molybdate had been reported (*1–3, 6*).

A comparison of polarographic procedures was undertaken to determine which method would have the widest applicability to the problems at hand. Two supporting electrolytes, nitric acid and perchloric acid, are known to have a catalytic effect in the polarographic reduction of molybdate. Johnson (*3*) used a supporting electrolyte containing $0.05M$ NO_3^- and $0.1M$ H_2SO_4. Under these conditions, three reduction waves were obtained for the molybdate ion; the second (~ -0.3 volt *vs.* the S.C.E.) was catalytically enhanced. Calibration plots were linear over the concentration range 10^{-5} to $10^{-7}M$, but deviated from linearity to a large extent at higher concentrations. Haight (*2*) had previously proposed the use of a $1.0M$ $HClO_4$–$0.75M$ H_2SO_4 supporting electrolyte, but other anions exerted a depressing effect on the molybdate wave and nonlinear calibration curves were obtained. Sinyakova (*6*), in similar fashion, used as a supporting electrolyte $1.0M$ $NaClO_4$ plus $0.75M$ H_2SO_4 and avoided the effect of extraneous ions by extraction of molybdate. Codell (*1*) used a $2.4M$ $HClO_4$ supporting electrolyte for the polarographic determination of molybdenum. The effect of the presence of other anions was not investigated, but essentially linear calibration curves were obtained below $10^{-4}M$.

In the light of this previous work, the conditions giving rise to increased sensitivity and the effect of interfering species were studied. A method was finally developed which had a sensitivity of 0.005 μg. of molybdenum per ml. and a high tolerance to interference from extraneous ions. This method proved so versatile for the required analyses that the study was extended to include the determination of traces of molybdenum in a wide variety of pure materials.

EXPERIMENTAL

Since both perchloric and nitric acid supporting electrolytes had been suggested, it was decided to evaluate the relative merits of these two media. Polarograms of $10^{-5}M$ molybdate solutions were obtained in both nitric and perchloric acids at two concentration levels, $1.0M$ and $0.1M$. The nitric acid supporting electrolytes gave waves

three times as high as the perchloric acid media in both cases. A further advantage is that nitric acid contains less copper and lead impurities than perchloric acid.

The concentration of the nitric acid supporting electrolyte had an important influence on the height of the catalytic wave and a linear relationship was found between nitrate concentration and the magnitude of the catalytic current. Therefore, the highest concentration of nitric acid in which it was experimentally feasible to carry out the reduction was ascertained. With 4.0M HNO_3, mercury was oxidized at a significantly high rate, and the dropping mercury electrode behaved erratically. A supporting electrolyte consisting of 2.4M HNO_3 was chosen as a compromise between high sensitivity and reproducibility of the dropping electrode. Even at this concentration, an H-type cell using an isolated S.C.E. was necessary because of the slow attack of the nitric acid on a mercury pool anode. Higher concentrations of nitrate ion could be obtained without increasing the oxidation of mercury, by adding NH_4NO_3 to the 2.4M HNO_3. At a total nitrate ion concentration of 5.0M, the wave height was almost doubled, but the great increase in the slope of the residual current nullified the advantage of the higher sensitivity.

Since the magnitude of the wave obtained depends upon the concentration of the nitric acid, it was necessary to control the amount of supporting electrolyte more rigorously than is usual in polarographic work. A 12.0M stock solution of HNO_3 was therefore standardized, and 5.00 ml. of this solution was pipetted into the 25-ml. volumetric flasks containing the sample before the final dilution.

Because of the catalytic nature of the molybdate wave, temperature control of the polarographic cell was mandatory. (A temperature coefficient of 7.5% per ° C. was observed at 25° C.)

Using the procedure and experimental conditions described, a perceptible polarogram could be obtained for a solution containing molybdate at a concentration of $5 \times 10^{-8}M$ (0.005 μg. of molybdenum per ml.). The wave height was found to be a linear function of concentration up to $5 \times 10^{-5}M$, at which point the microamperes–Mo concentration ratio gradually decreased. No maximum suppressor was necessary. The value of the capillary constant for the dropping electrode was $2.58m^{2/3}t^{1/6}$.

Sample Treatment. In any method involving small quantities of metals, the analyst must always be concerned with possible losses of the desired constituent through volatilization. To ascertain the possibility of such loss, microgram quantities of molybdenum were dissolved in various acids, which were then evaporated to dryness. The residue was dissolved in nitric acid and analyzed for molybdenum. Evaporation of molybdate solutions in concentrated HCl, H_2SO_4–HF, and H_2SO_4 resulted in no perceptible loss of molybdenum. Fusion in Na_2SO_3 (5 grams) and subsequent solution in acid allowed 100% recovery of the added molybdenum.

Separation and Concentration of Molybdate. Ion exchange, extraction, and chemical methods for the determination of microgram quantities of molybdenum in large amounts of the other metals were developed.

The ion exchange methods were particularly versatile, since conditions could be chosen under which Mo(VI) could be made to exist as either an anion or a cation. For example, in 0.5M H_2SO_4, 6M HCl, 0.1M NaOH, and pure water media, Mo(VI) was strongly retained on an anion exchange resin (Dowex 1). The molybdate could be then readily eluted from the column by treatment with 1.0M HCl. Cation exchange resins were also used to separate Cu^{+2}, Bi^{+3}, UO_2^{+2}, VO^{+2}, and Fe^{+3} from MoO_4^{-2}. All of these ions can be absorbed on Dowex 50 from 0.5M solutions of sulfuric acid, while the MoO_4^{-2} ion was not retained.

Ion exchange methods offered particular difficulties in the separation of titanium. By extracting Mo(VI) from 6 to 7M HCl into 4-methyl-2-pentanone (*4, 7*), it was found possible to determine the quantity of molybdenum present in spectrographically pure titanium.

The extraction procedure was also capable of concentrating molybdate solutions which were otherwise too dilute for analysis. The molybdate was extracted into 4-methyl-2-pentanone and back-extracted into 0.1M H_2SO_4. The sulfuric acid solution was then evaporated and the molybdate residue was dissolved in a small volume of 2.4M HNO_3 for analysis.

The interference caused by MnO_4^-, VO_3^-, and $Cr_2O_7^{-2}$ was eliminated by reduction with hydroxylamine sulfate to Mn^{+2}, VO^{+2}, and Cr^{+3}.

Effect of Presence of Other Reducible Species. The catalytic reduction of molybdate in nitric acid medium resulted in an analytical procedure remarkably free from interferences. No other ion was found which would give a catalytic wave with nitric acid in the same potential region. Since the catalytic effect increased the height of the conventional wave by a factor of 100, no other ion present in the same concentration as the molybdenum would cause difficulty. However, in the determination of traces of molybdenum, interfering species might be present at concentration levels many thousands of times greater than that of the molybdenum. A large portion of this study was concerned with the question of what elements might be troublesome and the development of methods of eliminating interferences from large amounts of materials reducible near the $E_{1/2}$ of molybdate.

The reducible metals that might cause difficulty in the measurement of the molybdate wave could be classified into three types: those that give rise to polarographic waves in the same potential region as the molybdate, those that are reducible at more positive potentials, and those reduced at slightly more negative potentials.

Ions having half-wave potentials in the vicinity of the molybdate wave caused the greatest difficulty. This problem could be alleviated to some extent by changing the pH of the nitrate supporting electrolyte so as to shift the $E_{1/2}$ value for the molybdate reduction. Cu^{+2}, Bi^{+3}, and UO_2^{+2} could not be tolerated in quantities significantly greater than the molybdate, and procedures were devised for their separation.

The Fe^{+3}, VO_3^-, $Cr_2O_7^{-2}$, and MnO_4^- ions are examples of species which are reducible at positive potentials and would be expected to cause difficulty by giving large currents before the molybdate wave. The fact that the molybdate reduction occurs at the relatively positive value of −0.17 volt *vs.* the S.C.E. is advantageous, in that few metals give polarograms at more positive potentials than molybdate.

Ions with half-wave potentials more negative than −0.4 volt *vs.* the S.C.E. should not generally be expected to cause difficulty even when present in high concentrations. Generally, this was the case, but with VO^{+2} and Ti^{+4} ions with half-wave potentials at −0.85 and −0.82 volt, respectively, the waves were so drawn out that they encroached upon the plateau of the molybdate wave. The maximum concentration of vanadyl ion which could be tolerated was 2000 times that of the molybdenum. Ti^{+4} ion could be present in amounts no greater than 200 times the molybdenum without separation.

Procedures for Applications. The proposed method was applied to the determination of molybdenum in a wide variety of materials. The following sections summarize the results obtained where difficulties were caused by large quantities of interfering elements. The proposed methods were checked on synthetic samples or by standard addition of molybdenum and an accuracy of 5% was considered to be acceptable.

COPPER(II) AND BISMUTH(III). Copper would not normally be present as a major component in samples requiring determination of molybdenum. However, a study was made of the

magnitude of its interference because it is one of the more common metals which has a half-wave potential in the same region as the catalytic molybdenum wave. The relative effect of copper is small, since concentrations of Cu^{+2} three times as great as the molybdenum concentration caused a positive error of only +5%. This interference can be minimized by using a supporting electrolyte of higher pH to prevent overlapping of the two waves. Milligram quantities of copper were separated by absorbing Cu^{+2} on a cation exchange resin from 0.5*M* H_2SO_4 solutions, and determining the molybdenum in the eluate. The ion exchange column was 16 cm. long and 1 cm. in diameter. It was equilibrated with 0.5*M* H_2SO_4 before use, and the rate of flow used was about 1 cm. per minute.

Bi^{+3} also has a polarographic wave close to the molybdenum reduction in the nitric acid medium and offered the same type of interference. Removal of the bismuth ion by the cation exchange resin was highly efficient and 25-mg. quantities of the metal were easily separated from a few micrograms of molybdenum.

IRON(III). Since the reduction of ferric ion occurs at positive potentials *vs.* the S.C.E., the only effect is to increase the polarographic currents at zero applied e.m.f. Quantities of ferric ion 100 times greater than the molybdate caused no interference in the analyses. Larger quantities of ferric ion were removed by the cation exchange procedure previously described for Cu(II) and Bi(III). To test the procedure on a sample containing appreciable iron, a 0.5-gram sample of National Bureau of Standards steel was dissolved in sulfuric acid, diluted to 0.5*M* H_2SO_4, and passed through the cation exchange column. A polarogram of the eluate yielded a molybdenum wave corresponding to a molybdenum content of 39.8 p.p.m., which checks well with the approximate value of 0.004% Mo on the analysis certificate.

URANIUM(VI). Uranyl ion is particularly troublesome in the determination of molybdenum, since the half-wave potentials of the two species are identical in HNO_3 medium. Changing the acidity to shift the molybdate wave was ineffective, since the uranium half-wave potential shifted in the same manner. Quantities of uranium(VI) of the same order as the molybdate caused no difficulty because of the catalytic nature of the molybdate reduction. Large quantities of uranium were separated by absorption on the cation exchange column from 0.5*M* H_2SO_4. The capacity of the previously described column was found to be 1.3 grams of uranium. A 2-gram sample of reagent grade uranyl sulfate gave a molybdenum wave corresponding to 0.66 p.p.m. of molybdate. The method was checked by the standard addition of a known quantity of molybdenum to the original uranium sample.

VANADIUM(IV). Vanadyl ion in a nitrate medium has a half-wave potential at −0.85 volt. The irreversibility of this reduction resulted in a drawn-out wave which at high concentrations overlapped the plateau of the molybdenum wave. This encroachment caused difficulty when the molar concentration of vanadyl ion was greater than 2000 times that of the molybdenum present. At higher concentration ratios, it was necessary to separate the vanadyl ion from the molybdate by absorption on a cation exchange resin. In a 0.5*M* H_2SO_4 medium, and using the column and conditions previously described, the capacity of the column was found to be about 200 mg. of vanadium. Using this procedure, 19.2 p.p.m. of molybdenum was found in vanadyl sulfate. The procedure was checked by the standard addition of molybdenum to the original vanadyl salt.

CHROMIUM(VI), MANGANESE(VII), AND VANADIUM(V). These three species, being relatively strong oxidizing agents, do not exhibit polarographic waves, but give rise to reduction currents at 0 volt *vs.* the S.C.E. The above species could be tolerated in amounts up to 100 times the quantity of molybdenum without separation. However, since it was necessary to determine the molybdenum content of reagent grade salts of the above species, the following procedures were devised to remove the interferences.

One- to 2-gram samples of the dichromate and permanganate salt or 0.1 to 0.2 gram of the vanadate salt were added to 5 ml. of 9*M* H_2SO_4, containing 2 grams of hydroxylamine sulfate. Then sufficient HNO_3 and water to yield 50 ml. of 2.4*M* HNO_3 were added. After reduction occurred (instantaneous for Cr and Mn, 1 hour for V), a polarogram of the solution was run and the catalytic wave of the molybdenum was measured.

The procedure was checked by adding known quantities of molybdate to the original samples and the waves were depressed by 15%. The reduction in wave height was caused by the presence of the hydroxylamine sulfate. This decrease in wave height was not caused by chemical reduction of the molybdate by the hydroxylamine, since no further lowering occurred after 5 hours.

Using the standard addition procedure as an internal calibration method, the amount of molybdenum found in reagent grade $K_2Cr_2O_7$, $KMnO_4$, and NH_4VO_3 was 0.65, 1.0, and 59 p.p.m., respectively. The standard deviation of these results was 4%.

TITANIUM METAL. Ti^{+4} in nitric acid solutions has a half-wave potential at −0.81 volt *vs.* the S.C.E. However, because of its irreversible nature, this wave encroached upon the plateau of the molybdate catalytic wave, causing difficulty in its measurement. Ion exchange procedures were tried, but no reasonable method for separating the two metals was found. The extraction of molybdate into 4-methyl-2-pentanone (*4*) was found to be a suitable procedure.

A 1-gram sample of titanium metal was treated with 15 ml. of concentrated HCl. The solution was boiled to dissolve the titanium and to reduce the HCl concentration to the desirable range of 6 to 7*M*. After solution, 10*M* nitric acid was added dropwise while the solution was still hot until the purple color of the Ti^{+3} ion disappeared and then 2 drops more were added. This step was necessary to oxidize all the molybdenum species of molybdate, which is the extractable form. Two extractions were performed, the organic layers were combined, and the molybdate was back-extracted into 20 ml. of 0.1*M* H_2SO_4. The sulfuric acid solution was then evaporated to remove the appreciable quantities of chloride which followed through the extraction procedure. At this stage of the separation, the solution still contained enough Ti^{+4} to cause difficulty in the measurement of concentrations of molybdenum below $10^{-6}M$. To avoid this interference, the sulfuric acid solution was adjusted to 0.5*M* and passed through a 3-cm. column of cation exchange resin which removed the residual titanium. Applying the method to spectrographically pure titanium, a well defined wave 0.53 μa. in height was obtained which corresponded to 0.78 p.p.m. of Mo in the titanium metal.

ALUMINUM (III). Two-gram samples of aluminum sulfate were dissolved in 100 ml. of 2.4*M* HNO_3 and the molybdate polarogram was recorded. The wave heights obtained for two determinations corresponded to a molybdenum content of 0.23 and 0.25 p.p.m. The aluminum salt, however, exerted a slight depressing effect on the catalytic wave, since synthetic samples spiked to contain a total of 1.20 p.p.m. of molybdenum gave results of 1.10 p.p.m.

CHROMIUM (III). A 2-gram sample of chromium(III) ammonium sulfate was dissolved in water containing 1 ml. of 18*N* H_2SO_4 and dilution was made to a volume of 100 ml. containing 2.4*M* HNO_3. No molybdenum was detected polarographically. Synthetic samples containing 20.0 p.p.m. of Mo were analyzed and values of 19.7 and 19.0 were obtained. At a level of 2.0 p.p.m. the results of three runs were 2.0, 2.0, and 2.1 p.p.m.

MANGANESE(III). A 5-gram sample of manganous sulfate was dissolved in

water containing a few milliliters of 9M H_2SO_4. After dilution to 100 ml. containing 2.4M HNO_3, a polarogram was obtained which indicated a Mo content of 0.33 p.p.m. (0.36, 0.33, 0.32). The manganous salt exerted no depressing effect, since the standard addition method for a synthetic sample containing 80 p.p.m. gave 79 p.p.m., while another with a content of 8.0 p.p.m. yielded the theoretical value of 8.0 p.p.m.

TUNGSTEN(VI). No method was devised for determining small quantities of molybdenum in tungsten. Although the tungstate did not directly interfere with the catalytic molybdate wave, the precipitation of tungstic oxide from the nitric acid medium nullified the method. The use of the usual complexing agents such as tartrate, oxalate, and phosphate to keep the tungsten in solution destroyed the catalytic nature of the wave, as previously discussed. However, quantities of tungstate which were small enough so that precipitation did not occur ($10^{-3}M$) caused no difficulty. Samples containing 200 times as much tungsten as molybdenum were run and the expected value was obtained for molybdenum. However, it was not possible to devise either an ion exchange or extraction procedure which was capable of determining small quantities of molybdenum in samples containing tungsten as the major constituent.

Table I. Wave Height of 4 × $10^{-5}M$ Mo Solution

Added species	Wave height, μa.
None (2.4M HNO_3 only)	2.41
0.5M H_2SO_4	2.39
1.0M HOAc	2.35
0.1M HCl	2.36
0.1M H_3BO_3	2.38
0.1M Na_2SO_4	2.45
0.1M NH_4OAc	2.38
0.1M NaOH	2.45
0.01M H_3PO_4	2.25
0.01M Oxalic acid	2.38
0.01M Tartaric acid	2.39

Table II. Determination of Molybdenum in Various Pure Materials

Material	Source	Mo, p.p.m.
Steel	Bureau of Standards sample	39.8
UO_2SO_4	Reagent grade	0.66
$VOSO_4$	Reagent grade	19.2
Ti metal	Spectrographically pure	0.78
$KMNO_4$	Reagent grade	1.0
$(NH_4)_2VO_3$	Reagent grade	59
$K_2Cr_2O_7$	Primary standard	0.65
$MnSO_4$	Reagent grade	0.33
$Al_2(SO_4)_3$	Reagent grade	0.24

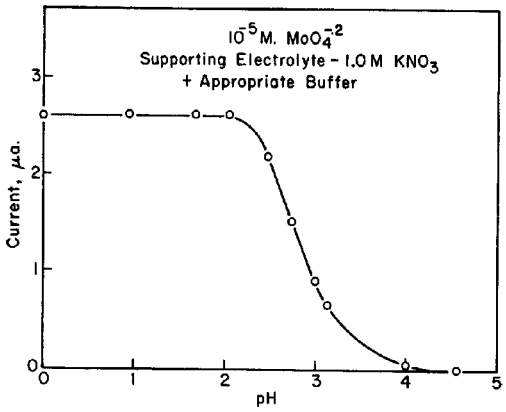

Figure 1. Variation of wave height with pH

RESULTS AND DISCUSSION

Effect of Foreign Electrolytes. One severe drawback in the general application of polarographic methods utilizing catalytic reductions is the influence of foreign electrolytes on the height of the polarographic waves. In the previously reported procedures involving catalytic molybdate reductions, the presence of extraneous salts was avoided by isolation of the molybdenum (*1, 3, 6*). An unexpected advantage of using concentrations of nitric acid as high as 2.4M was that the effect of various species on the polarographic currents was minimized. To evaluate this effect, polarograms of molybdate solutions were obtained in the presence of some common nonreducible salts (Table I).

Table I shows the maximum concentrations that can be tolerated. Higher concentrations resulted in gradual decrease in current values—for example, a 1.8M concentration of H_2SO_4 yielded a wave of 2.23 μa. Anions that form complex ions with molybdate, such as phosphate and tartrate, had a depressing effect at relatively low concentrations. Higher concentrations of such complexing species destroyed the catalytic nature of the reduction.

Effect of pH. In previously reported work there appeared to be a small though significant discrepancy in the value of the half-wave potential of the catalytic molybdate reduction. The explanation of this discrepancy was discovered when polarograms were run at various pH levels while the nitrate ion concentration was kept constant. There was a gradual shift in half-wave potential toward more negative values as the pH increased. The $E_{1/2}$ value changed by −0.155 volt per pH unit over the range from 3M HNO_3 to pH 3.0. These data were obtained using a supporting electrolyte of 1.0M $NaNO_3$ and sufficient H_2SO_4 or acetate buffer to adjust the pH to the desired value. A similar shift in $E_{1/2}$ with pH has been noted for the perchlorate system (*2*).

The height of the molybdate wave was independent of the acid concentration up to a pH of about 2. The wave heights then decreased rapidly and at pH 4 the catalytic nature of the reduction disappeared, as shown in Figure 1.

The variation of $E_{1/2}$ values with pH allowed some latitude in avoiding interference from substances yielding polarograms in the same potential region as the molybdenum. The half-wave potential could be varied from −0.1 to −0.5 volt *vs.* S.C.E., depending upon the nature of other reducible species present. The results of the application of the procedures to pure materials are summarized in Table II.

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Use of Self-Sealing Elastomer Septums for Quantitative Operations with Volatile Solvents

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▶ **The merits and limitations of self-sealing elastomer septums for use in quantitative laboratory operations are evaluated. Data are presented on sorption, permeation, diffusion, and resealing ability for a representative group of elastomers and volatile solvents. The phenomena to be expected in multicomponent permeation are discussed. Various means of decreasing sorption-permeation losses are described, with emphasis placed on the potential of multilayered septums to minimize existing drawbacks to the wide scale use of the septum technique. Quantitative applications of the technique to gas liquid chromatography, infrared absorption, and distillation are described.**

MANY physico-chemical operations, particularly those involving the preparation and sampling of multicomponent solutions on a semimicro scale, require the quantitative manipulation of small amounts of volatile solvents. The conventional techniques that have been evolved for accurately performing such operations usually involve gas phase transfers, require considerable equipment and skill in their execution, and are often time consuming. The difficulties are caused chiefly by the need to avoid evaporation losses when the container closure is opened. Such operations can, in many cases, be considerably simplified by the use of penetrable, self-sealing septums as the closure.

Although the septum-seal technique is well known in industrial applications (*2*), it has not been extensively used in quantitative analytical procedures. This is due in part to the lack of comprehensive data on the properties of septum–solvent systems under actual use conditions. It is the purpose of this study to provide such data, to evaluate critically the capabilities of the septum-seal technique, and to demonstrate its value in many quantitative analytical applications.

EXPERIMENTAL

Apparatus and Techniques. TYPES OF SEPTUMS. Flat septums made of several conventional and several newer types of elastomers were used (Table I). In addition, flange shaped septums (V-11 type, The West Co.) were used for some of the experiments on resealing ability. Except in those cases where a water wash was necessary for physical cleanliness, septums were used as obtained after equilibration at ambient temperature and humidity for at least a month.

CONTAINER. Flat-bottomed borosilicate glass pharmaceutical vials, expressly designed for commercially available septums, were used (3-ml. NO-SOL-VIT flint glass serum vials, Wheaton Glass Co., 165 Broadway, New York, N. Y.). These vials have an effective neck diameter of 8 mm. A tight seal is obtained for flat septums by crimping a thin aluminum cap uniformly around the perimeter of the lip of the vial with a Fermpress Hand Capper No. H-137 (The West Co., Phoenixville, Pa.).

NEEDLES. A 26- or 27-gauge needle was used for routine solvent transfers; larger bore needles were used for special applications as described. The length of the needle point opening must not exceed the thickness of the septum, to ensure that there is never an open path between the inside and outside of the container.

PREPARATION OF MULTICOMPONENT SOLUTIONS. A volume of air, roughly equal to the volume of the sample to be added subsequently, is withdrawn via syringe from a dried, septum-sealed container. After weighing the container, the components are added one at a time via syringe, weighing after each addition. During storage, the containers are kept cold; before weighing, they are brought to room temperature in a desiccator. Before sampling, the container and the syringe are first chilled to an appropriately low temperature but are kept above the glass transition point of the elastomer. For withdrawal of large samples, the empty syringe, on the downstroke, may be used to inject an equal volume of air.

SORPTION. The rate of solvent sorption by the septums was determined by placing three septums on a wide-mesh wire screen suspended ½ inch over a 1-inch layer of solvent, with the entire system kept in a sealed wide-mouth bottle. The bottle containing the solvent was allowed to equilibrate at room temperature prior to inserting the septums, and was then swirled gently several times during the sorption process. After one hour, the septums were rapidly transferred to small, tared weighing bottles and weighed. In those cases where surface condensation was apparent, the septums were first blotted lightly and rapidly with adsorbent paper.

PERMEATION. The rate of solvent permeation through the septum under actual use conditions was determined by following the weight loss of a septum-sealed 3-ml. vial containing 1 ml. of solvent. The vials were stored in a hood with a gentle draft located in a room maintained at 25° C. Each system remained at constant weight for at

Table I. Types of Septums

Name[a]	Elastomer	Density[b]	Color	Hardness[c]	Nominal thickness, mm.
Neoprene	Chloroprene	1.513	Green	58	2
Natural rubber	Isoprene	1.708	Brown	58	2
Butyl	Isobutylene/isoprene	1.492	Grey	55	2
Silicone	Silicone rubber	0.903	White	55	2.7
Genthane[d]	Polyurethane	1.380	White	53	1.8
Viton[e]	Vinylidene fluoride/ hexafluoropropylene	1.870	Black	62	2
Hypalon[e]	Chlorosulfonated polyethylene	1.428	Red	73	1.6

[a] Except for the silicone (9-mm. diameter), all septums were supplied by The West Co., Phoenixville, Pa., and were 13 mm. in diameter. The neoprene and natural rubber were stock items, with typical formulations described elsewhere (*5*); the others were specially fabricated for this study. The silicone septums are those supplied by the Perkin-Elmer Co., Norwalk, Conn., for use with their GLC equipment.
[b] Average values for the actual septums.
[c] Measured to ±5 units with a Durometer Hardness Meter A2, The Shore Instrument & Manufacturing Co., New York, N. Y.
[d] Trademark, General Tire and Rubber Co.
[e] Trademark, E. I. du Pont de Nemours & Co.

Table II. Comparative Sorption during First Hour

Solvent	B.p.	Sorption in mg. of solvent/sq. cm. septum: Neoprene	Natural	Butyl	Silicone	Genthane	Viton	Hypalon
Ether	34.6	26	36	19	37	6.0	12	17
Carbon disulfide	46.5	48	53	42	27	11	0.6	48
Diethyl amine	55.5	23	26	14	30	15	7.9	15
Acetone	56.5	8.3	5.1	0.2	9.1	24	42	9.1
Chloroform	61.5	69	54	34	45	108	12	86
Methanol	64.7	0.3	0.2	0.0	1.4	4.3	1.5	0.3
n-Hexane	69	8.0	20	15	28	0.2	0.0	4.7
Carbon tetrachloride	76.7	37	53	20	40	10	0.8	21
Ethyl acetate	77	20	14	2	18	22	32	12
Ethanol	78.5	0.4	0.5	0.1	2.0	3.5	0.7	0.2
Benzene	80.1	24	28	14	21	19	3.6	21
Acetonitrile	81.6	1.1	0.6	0.05	0.8	17	14	0.9
Water	100	0.2	0.05	0.0	0.0	0.7	0.05	0.3
Acetic acid	118	5.4	2.7	0.7	4.0	13	7.6	5.8

Table III. Maximum[a] Sorption by Septums

Septum	Sorption, gm. of solvent/gm. septum: CH_3CN	CH_3CH_2OH	CH_3COCH_3	$CHCl_3$	C_6H_6	CCl_4
Neoprene	0.016	0.021	0.21	2.58	2.24	2.50
Natural	0.009	0.015	0.077	2.57	2.14	2.97
Butyl	0.008	(0.001)	(0.10)	2.06	1.72	3.60
Silicone	0.012	(0.038)	0.18	2.39	1.14	2.81
Genthane	1.00	(0.15)	1.34	6.47	2.15	0.57
Viton	0.94	(0.064)	1.96	0.58	1.30	(0.073)
Hypalon	0.053	(0.056)	0.22	5.14	3.15	3.73

[a] Septums exposed to solvent vapor for 14 days at 25° C. Those systems not at sorption equilibrium are enclosed in brackets.

least several hours, thus establishing the absence of leaks. Care was taken to avoid contacting the septum with liquid during the handling processes. Systems were followed for the time required (days to years) for permeation equilibrium to be established, as indicated, by a linear region in the permeation curve.

RESULTS

The utility of self-sealing septum closures for containers of volatile substances depends essentially on two factors: the extent to which the septum acts as a two-way barrier, both before and after puncturing, and the compatibility of the septum with the container contents.

Sorption. The comparative order of magnitude of sorption during the first hour of exposure for various septum-solvent combinations is listed in Table II. Spot checks of the reproducibility of the measurement technique indicate that the average deviation is about ±8% for sorption values greater than 1 mg./hour/sq. cm. For systems with lower sorption values, surface condensation effects become prevalent and lead to larger, positive errors.

Many of the septum-solvent combinations studied show sorption rates that permit their realistic quantitative use over short periods of time, even before resorting to any of the subsequently described measures to reduce sorption losses. Thus, assuming that a maximum error of 1% can be tolerated for 1 gram of solvent, and the use of a container with the standard 0.5 sq. cm. opening for 1 hour at 25° C., a suitable septum can be found for every solvent in Table II with the exception of chloroform.

The extent of sorption over a longer time interval is shown in Table III for a limited number of septum-solvent combinations. In most cases, the values approach maximum sorption, as estimated from the time required to reach a permeation steady state. It is of interest to note that even with this small sampling of systems, the sorption values range over three orders of magnitude, and that one septum sorbed 6.5 times its weight of solvent without disintegrating. Visual inspection indicated that some septums had swelled to three or four times their initial volume. In applications where physical restrictions are placed on the volumes to which the elastomer may swell, the extent of sorption would undoubtedly be diminished. In many cases where swelling was extensive, the septums did not return to their initial dimensions on desorption. Caution is consequently necessary in selecting solvents with which to wash the septums free of leachable components.

Permeation. The Barrer time lag method (*3*) was used to compare the behavior of various septum-solvent combinations under use conditions. A number of relatively volatile solvents used frequently in the laboratory were examined. They were selected principally to cover a wide range of functional groups while fitting within a narrow range of boiling points. In most cases, the steady state region of the permeation curves showed excellent linearity.

Data are listed in Table IV for D, the diffusion constant, P, the permeation constant, and the permeation index, designated as Π. Π is the observed rate of permeation in units of mg.-mm./hour/sq. cm. for saturated vapor systems at 25° C. Spot checks of the precision

Table IV. Permeation Behavior of

Solvent	$p_{mm.}$, 25° C.	Neoprene: Π[a]	$P \cdot 10^8$	$D \cdot 10^7$	Natural: Π	$P \cdot 10^8$	$D \cdot 10^7$	Butyl: Π	$P \cdot 10^8$	$D \cdot 10^7$
Ether	537	14.5	26	1.65	30	53	3.6	11.4	20.1	0.85
Carbon disulfide	361.6									
Acetone	229.2	3.4	10.7	0.62	1.87	6.0	0.98	0.014	0.0045	
Chloroform	197.4	48	360	1.13	48	360	1.62	23.5	178	0.70
Hexane	151.3	2.4	17.3	1.08	11.1	79	3.8	11.9	85	0.79
Carbon tetrachloride	115.2	18.5	310	0.34	24.5	410	1.02	13.3	223	0.31
Ethyl acetate	95.8	6.5	74	0.56	6.9	79	1.37	0.19	2.14	0.10
Benzene	95.2	13.5	138	0.73	16.0	168	1.48	7.0	70	0.26
Acetonitrile	84.3	0.20	1.19	0.38	0.18	1.09	0.69	0.0046	0.028	
Ethanol	59.0	0.027	0.26	0.14	0.057	0.56	0.65	[b]		
Acetic acid	15.8							0.038	1.78	0.009

[a] Units: Π in mg.-mm./hour/sq. cm., P in ml. (S.T.P.)-mm./second/sq. cm./cm. of Hg, D in sq. cm./second. [b] System lost <2.5

of the measurement technique indicated an overall average deviation of ±2% for the values of D, P, and Π for unpunctured septums.

In general, the permeation constants show considerably greater variability among molecules similar in size and shape than do the diffusion constants, thus emphasizing the importance of specific solubility effects in vapor permeation. Comparisons of the solubilities calculated via $P = SD$ (3) to the data for equilibrium systems listed in Table III indicate agreement to within about half of an order of magnitude for most systems.

RESEALING AFTER PUNCTURE. Failure of the septums to reseal properly after puncture by a needle would be expected to lead to increased solvent losses, both by an increase in the surface area available for sorption, and by permitting transport of solvent by capillary or orifice flow as well as by diffusion. The data in Table V indicate, however, that no effect significantly above experimental error occurs for almost all of the septums tried, even for a number of punctures considerably exceeding normal use requirements. (A test on a flange-type silicone rubber septum was suspended after 125 punctures with the sealing ability of the septum unimpaired. Weight loss of ethylene oxide at room temperature, a pressurized system, was followed to ensure a sensitive test.) The swelling of the septums undoubtedly eventually aids the inherent elasticity of the elastomer in sealing the puncture holes.

The largest diameter needle used with safety on a 2-mm. septum has been 16-gauge. Wider needles, when withdrawn, have occasionally left a nonsealing hole, particularly at low temperatures. Silicone (and to a lesser extent butyl) septums are of value in such cases, in view of their low glass transition temperature.

MULTICOMPONENT SORPTION AND PERMEATION. The sorption and permeation behavior of a multicomponent vapor mixture in equilibrium with a liquid mixture does not follow an additive relation based on the behavior of the pure vapors due to various interaction effects. These effects include the nonideality of vapor-liquid systems and the reciprocal plasticizing effect—i.e., each permeant will influence the solubility and diffusion coefficients of the other permeants to some extent. When interaction occurs, P and D become dependent not only on the concentration (or pressure) of the individual component, but on the composition of the system as a whole. In principle, the difference between the actual permeation behavior of mixtures and the behavior calculated from the pure components may be used as a quantitative measure of interaction effects.

For a steady state of permeation to occur for a multicomponent system, the relative composition of the permeating vapors, and consequently of the

Table V. Resealing Ability of Septums

Septum	Shape	No. of punctures[a]	Weight loss, gm.,[b] in 28 hr.	±a.d., %[c]	Weight loss, gm. in 72 hr.	±a.d., %
Silicone	Flange	0	0.37	3		
		10	0.34	3		
		25	0.34			
		50	0.31			
Neoprene	Flange	0	0.022	14	0.105	6
		10	0.026	4	0.117	3
		25	0.021		0.104	
		50	0.030		0.127	
Butyl	Flange	0	0.010	11	0.057	8
		10	0.012	7	0.064	2
		25	0.010		0.058	
		50	0.009		0.056	
Neoprene	Flat	0	0.078	12	0.26	9
		10	0.082	2	0.26	2
		25	0.092		0.30	
		50	0.106		0.34	

[a] Random punctures made with a 26-gauge needle.
[b] Solvent was ether, at 25° C.
[c] Average deviation of duplicate runs.

Table VI. Typical Results Obtained by Use of Septum-Sealed Containers in Internal Standard Gas Liquid Chromatography[a]

Mixture[b]	Ethylene oxide, gm.	Propylene oxide, gm.	Age when run,[c] days	K[d]	±a.d.[e]
1	0.0376	0.0378	0	1.371	0.005
2	0.0498	0.0416	0	1.375	0.003
2			1	1.362	
2			3	1.354	

[a] Conditions: 20-μl. sample, 0.25-inch diameter column consisting of 2 meters of polyethylene glycol 1500 in series with 1 meter of 1,2,4-butanetriol, both on firebrick, 42° C. column, 45 ml./min. He flow, thermal conductivity detector.
[b] In about 8 grams of acetone.
[c] Stored at room temperature.
[d] Calibration constant, K = peak height ratio, ethylene oxide/propylene oxide, times weight ratio, propylene oxide/ethylene oxide.
[e] Duplicate runs.

Representative Solvent-Septum Systems

Solvent	Genthane			Viton			Hypalon		
	Π	$P \cdot 10^8$	$D \cdot 10^7$	Π	$P \cdot 10^8$	$D \cdot 10^7$	Π	$P \cdot 10^8$	$D \cdot 10^7$
Ether	1.59	2.8	0.34	8.7	15.4	0.51	12.1	21.3	0.78
Carbon disulfide				0.017	0.045	0.044			
Acetone	34	107	0.52	34	109	2.5	3.7	11.9	0.45
Chloroform	82	620	1.78	1.92	14.5	0.093	33	250	1.74
Hexane	0.016	0.117		[b]			1.29	9.2	0.15
Carbon tetrachloride	1.59	27	0.11	0.013	0.22	0.0035	11.1	185	0.20
Ethyl acetate	8.7	100	0.73	21	250	0.94	4.5	52	0.33
Benzene	8.8	90	0.44	0.33	3.4	0.066	11.5	117	0.42
Acetonitrile	9.0	55	0.70	9.0	55	0.74	0.093	0.57	0.12
Ethanol	0.58	5.7	0.051	0.014	0.133	0.017	0.0037	0.036	

mg./15,000 hour.

liquid phase that supplies the vapors, must remain constant. Equation 1 must therefore apply under the assumptions of negligible sorption losses and the absence of interaction effects. Here,

$$\frac{P_i p_i}{\sum P_i p_i} = \frac{P_i p_i^0 X_i}{\sum P_i p_i^0 X_i} = X_i \qquad (1)$$

for the ith component, p is the actual vapor pressure, p^0 is the vapor pressure of the pure substance, and X is the mole fraction in the vapor. It is apparent that a steady state is achieved only when the product $P_i p_i^0$ is equal for each component of the system. When this condition exists, the relative composition of the liquid phase will remain invariant, and at any arbitrary initial value, irrespective of the amount of the liquid lost from the system.

For real systems, where interaction effects occur and where $p_i = k_i p_i^0 X_i$, both P_i and k_i depend on the relative concentration of the components. It is thus possible, during permeation from some systems, for a specific composition to be reached at which the product $P_i k_i p_i^0$ becomes equal for all components. Steady state permeation will occur from then on, and the composition of the liquid phase will become invariant. The particular composition at which this occurs may be termed a "permeation azeotrope," in analogy to distillation phenomena.

The use of the above concepts in the a priori selection of a two-component system leading to a permeation steady state is illustrated below. For a neoprene septum, the product Pp^0 for benzene is 1.31×10^{-4}; for ether, 1.39×10^{-4}: the close agreement suggests that a steady state may occur. This is borne out experimentally. The starting composition of the benzene-ether mixture was 55.4 wt. % benzene: after 280 hours, during which 65% of the original 1.598-gram (2 ml.) charge was lost, the remaining liquid phase contained 58.8% benzene. (The composition is based on GLC assays of several microliters withdrawn via syringe.) For from 70 to 350 hours, the permeation curve gave an excellent straight line. The observed value of Π was 16.8, somewhat larger than the value of either component alone, and indicative of interaction effects.

The reciprocal plasticizing effect is illustrated by the system shown in Figure 1. Here, ethyl acetate ($\Pi = 21$), n-hexane ($\Pi = 6.5 \times 10^{-4}$), and a distillation azeotrope of the two solvents (b.p. 65.1° C., 39% ethyl acetate) are allowed to permeate through Viton septums. The calculated value of Π for an infinite volume of azeotrope is 8.3: the observed value is 9.9. (For the same solvent with a Genthane septum, Π calculated, 3.4; observed, 2.6.) As the concentration of ethyl acetate remaining in the vial is depleted by the selective permeation, Π drops, and approaches the value for pure hexane. However, after 5000 hours, 61% of the original 1.562-gram (2 ml.) azeotrope charge had permeated out of the system, whereas the residual liquid phase still contained 3.5% ethyl acetate. Thus, it is clear that at least 38% of the hexane initially present in the charge had passed through the septum, although virtually no hexane permeation would occur in this time period in the absence of ethyl acetate.

SEPTUM-SOLUTION INTERACTIONS. Leaching, or the migration of a constituent from the septum to the solution, is a common occurrence (*2*) with the prolonged use of a septum as a closure. Although the bulk solution may never come in direct contact with the septum, sufficient vapor condenses on the inner septum surface to form a liquid phase. Some of this liquid eventually returns to the bulk solution, carrying with it material extracted from the septums.

Adsorption of nonvolatile solutes from the solution must also be considered if the solution comes in contact with the septum during the mixing step.

In the present study, in which septums were selected without regard for suitability of composition and were used without prior treatment, leaching occurred with nearly every slowly permeating septum solvent combination used. This was shown either by a yellow color appearing in the solvent, or by the presence of a trace of residue in the container after the solvent had permeated completely. For short periods of time, however—i.e., one day, leaching was insignificant even for systems eventually yielding solutions of intense color. In one specific trial, Viton septums were soaked overnight in a minimum volume of carbon disulfide. No additional infrared bands were noted in the 2- to 16-micron spectrum of the carbon disulfide, obtained *vs.* fresh solvent at a 1-mm. pathlength. Exhaustive prewashing in a Soxhlet apparatus with the solvent to be used has been found to be an effective means of minimizing leaching.

TECHNIQUES FOR MINIMIZING THE LIMITATIONS OF SEPTUMS. The choice of the elastomer used in the septum, as well as the composition of the fabricated septum, are perhaps the most important factors in determining sorption-permeation losses. Of the septums studied, Viton and butyl have the broadest suitability spectrum. Of the other currently known elastomers, the polysulfides are reportedly (*4*) unexcelled in gas impermeability, although sulfide leaching effects occur.

The requirement of self-sealing properties limits the choice of plastics in conventional septums to elastomers. Conceptually, however, an effective septum could be composed of three laminated layers: a bottom layer that minimizes leaching and the adsorption of nonvolatile components, a middle layer that acts as the main sorption and permeation barrier, and a top layer of a self-sealing elastomer. The development of one septum with nearly universal applicability would be of considerable value. A start in this direction has already been made. A recent report (*5*), for example, has shown that an epoxy film lining on selected septums, although ineffective as a sorption barrier, nevertheless considerably reduced leaching. A crude approximation to a two-layer septum, made by placing a 2-mil polypropylene insert under a neoprene septum, was found in this study to decrease the one-hour sorption losses of acetone and iso-octane nearly fivefold.

It is usually possible to significantly decrease losses by lowering the temperature. The overall temperature dependence of the rate of permeation, Q, for saturated vapor systems may be approximated by Equation 2,

$$\ln \frac{Q_2}{Q_1} = \left(\frac{E_p + 23\ T_B}{R}\right)\left(\frac{T_2 - T_1}{T_1 T_2}\right) \qquad (2)$$

obtained by use of the Arrhenius equation for permeability, the Clausius-Clapeyron equation for vapor pressure, and Trouton's rule for the heat of vaporization. For example, the permeation of a solvent with a boiling point of 100° C. and an activation energy of 10 kcal. undergoing a temperature change from 25° to 0° C. would decrease by 94%.

Sorption and permeation losses may be decreased by decreasing the exposed surface area. Further, since these losses are systematic, some correction for their effect by calibration is possible. For multicomponent systems, changes in the relative concentrations of the components due to permeation may be minimized by use of the steady-state principle.

Alternatively, when long storage with intermittent use is required, the use of a self-sealing septum in conjunction with an impermeable stopcock is of value. A container of this type for small volumes is shown in Figure 2*A*. It has a Teflon stopcock of 4-mm. bore, and a volume of only 0.25 ml. between septum and stopcock.

APPLICATIONS

GAS LIQUID CHROMATOGRAPHY. The septum technique is particularly valuable for the quantitative application of the internal standard method in gas liquid chromatography on a semimicro scale. Accuracy and precision approaching that of conventional volumetric macroscale procedures may be obtained even for very volatile sol-

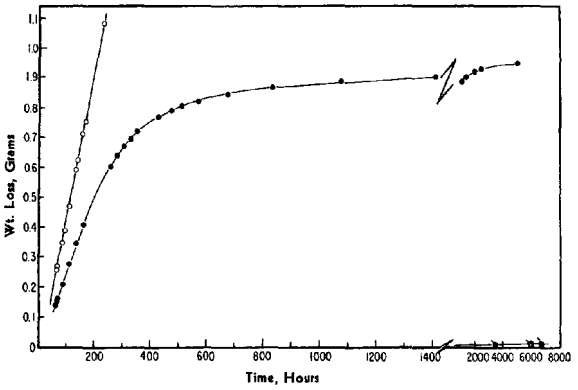

Figure 1. Multicomponent permeation

Permeation through a Viton septum at 25° C. for
- ◘ n-Hexane
- O Ethyl acetate
- ❍ 2 ml. of 39 wt. per cent ethyl acetate in n-hexane

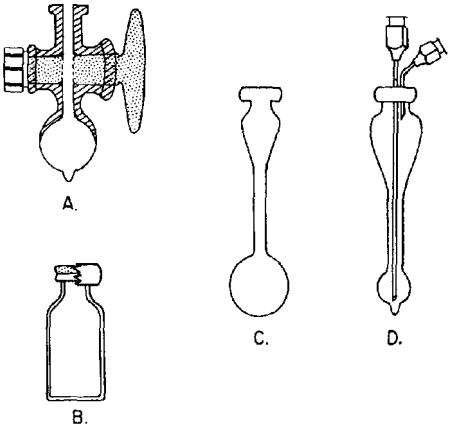

Figure 2. Typical septum-sealed containers for various purposes

vents, as is demonstrated by the following results for ethylene oxide (b.p. 10.7° C.). Milligram quantities of ethylene oxide were first stripped from the samples and collected in acetone at dry ice temperatures via distillation. A silicone rubber septum (V-11, X-9711, The West Co.) was used for its elasticity at these temperatures. Propylene oxide (b.p. 35°C.) was added as internal standard. Typical results for several calibration solutions used in this assay are listed in Table VI. Less than a 2% decrease in the calibration constant occurred after 3 days, even though the system was deliberately stored at room temperature.

INFRARED. Barring rapid adsorption of the solute, carbon disulfide solutions may be handled with greater accuracy in Viton-stoppered containers than in conventional standard taper glass stoppered volumetric flasks. This is readily apparent from comparison of the evaporation losses listed in Table VII to the previously listed sorption losses.

CONDENSATION TRAPS. Condensation traps of various designs using septum seals are shown in Figure 2. They may be used as receivers for distillation or GLC fractions, or as a trap for any slow-moving gas stream. For the microdistillation application (*1*), two hypodermic needles penetrate the septum: a large bore (16-gauge) distillation needle and a small bore (27-gauge) vent needle (Figure 2*D*). The glass column outlet is carborundum-ground to give a tight fit in the head of the distillation needle. Near the end of the distillation, a closed syringe is attached to the vent needle, and the distillation needle is raised above the level of the distillate. The residual distillate in the latter needle is then drawn into the receiver by means of the vent needle. To ensure complete recovery, a distillation of a final 50-μl. fraction can be used to wash the inside of the needle. Both needles are then withdrawn, yielding a closed system.

MISCELLANEOUS APPLICATIONS. Septum-sealed containers in the shape of *C*, Figure 2, are useful in ampuling small quantities of volatile solutions for long term storage. Micro solutions for paper and thin layer chromatography may be prepared and sampled accurately. Some nuisance and health problems, such as sampling lachrymators and other obnoxious substances, may be conveniently minimized or eliminated.

Table VII. Carbon Disulfide Evaporation Losses from Glass Stoppered Volumetric Flasks at 25° C.

Conditions	Unit of loss	Flask capacity 1 ml.	10 ml.	10 ml.
Dry neck, closed, steady state	mg./min.	0.02	0.05	0.06
Dry neck, opened for 1 minute	mg.	2.6, 2.3	5.0, 5.8	4.0, 4.3
Wet neck,[a] opened for 5 seconds	mg.	8.3	12	13
Wet neck,[a] closed	mg./10 min.	21	17	35

[a] Flask inverted to simulate mixing operation.

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Time Constant of a Thomas Autometer and Significance of Indicated Response

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▶ The time constant of a Thomas sulfur dioxide analyzer was determined by measurements at various concentration levels. The arithmetic mean time constant was found to be 46.0 seconds with a standard deviation of 5.5 seconds. A study was made of the peak values observed when known concentrations of sulfur dioxide were injected into the sample air stream for periods of a few seconds to 200 seconds. The area under the curve of gas injection time in seconds *vs.* peak height in parts per million was employed to calculate the actual concentrations producing a given peak on the instrument. Peak height was dependent upon injection time and concentration. The integrated value of a series of peaks corresponded to the actual average concentration. This method may be applied to determine the time constant of many types of sensing instruments.

AN UNDERSTANDING of the significance of mean and peak concentration levels is necessary in the evaluation of continuous air pollution measurements. In ordinary pollution records the instantaneous pollution levels are smoothed out and an average value over a long period is tabulated. For this kind of tabulation a slow responding sensor and recorder is desirable since such an instrument can act as an integrating device and hence facilitate the reading of the trace.

Where short periods of special interest are being studied the instantaneous fluctuations in the concentration of the pollutant become more important. A fast responding instrument would follow closely behind the actual instantaneous pollutant levels and would produce a trace characteristic of the actual fluctuations that do occur in a dynamic atmosphere.

In either situation "a clear understanding of the principle of operation of the basic sensor and a knowledge of its dynamic response" (*1*) are essential if valid data are to be obtained.

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Even with slow response instruments some useful information on instantaneous concentrations can be obtained by a proper interpretation of peak heights and other parameters of the concentration–time trace.

In this paper, time constant theory based on a first-order response of the sensor, as developed for thermometers and other meteorological instruments (*3*), has been applied to the continuous measurement of air pollutants. A method for the determination of the characteristic time or time constant of a Thomas SO_2 autometer is outlined. This technique is applicable to many continuous measuring instruments for air pollution studies.

THEORY

Suppose the atmosphere that is being sampled by a continuous sensing meter at a steady gas concentration, θ_0, is subjected to a fumigation at time $t = 0$ by an additional increment of this gas at a steady concentration, θ_F; then the rate of change in concentration with time is

$$\frac{d\theta}{dt} = \frac{\theta_F - \theta}{J} \qquad (1)$$

where J is defined as the time constant when units of time are expressed as seconds. θ_F is a concentration which may be higher or lower than θ_0. The indicated concentration, θ, will lie at a point between θ_0 and θ_F. If θ_F is lower than θ_0, $\frac{d\theta}{dt}$ will be negative. This constant depends upon the chemical reaction rate, the air sampling rate, the liquid flow rate, the physical dimensions of the contacting system and sensing element, and the assumption that the air pollutant concentration remains constant for a sufficient interval to achieve equilibrium.

Equation 1 may be rewritten and integrated to give

$$\ln (\theta - \theta_F) = -\frac{1}{J}t + c \qquad (2)$$

At zero time, the instantaneous concentration θ will be the same as the concentration θ_0 and $\ln (\theta - \theta_F) = c$. Equation 2 then becomes

$$\ln (\theta - \theta_F) = \ln (\theta_0 - \theta_F) - \frac{1}{J}t \qquad (3)$$

or

$$\theta = \theta_F + (\theta_0 - \theta_F)e^{-\frac{1}{J}t} \qquad (4)$$

From Equation 3 it can be seen that if $\theta - \theta_F$ or $\theta_F - \theta$ is plotted on semilog paper against time, t, a straight line should be obtained. The slope of this line is $-\frac{1}{J}$ (unless the log to base 10 is used, in which case the slope must be multiplied by 2.303).

From Equation 4, for time $t = J$

$$(\theta - \theta_F) = (\theta_0 - \theta_F)e^{-1} \qquad (5)$$

In other words this equation states that the initial pollutant concentration difference, $\theta_0 - \theta_F$, will have been reduced to $\frac{1}{e}$ or 36.8% of its original value in time $t = J$. Thus the time required to reach 63.2% of the final value, θ_F, is equal to J.

The time constant, J, also known as the characteristic time, is independent of the concentration range, the initial and final times—i.e., any small segment of the concentration trace may be analyzed to give the same time constant—and the initial concentration, whether it is greater or smaller than the final concentration.

From Equation 5 the time required for the measuring instrument to come within a given percentage of the final value may be calculated in terms of J. The instrument will have reached 63.2% of its final value in time, J, 90% in $2.3J$, and 99% in $4.6J$.

EXPERIMENTAL

Apparatus. The sulfur dioxide measurements were made with a Thomas autometer of the integrating type (*4*). The absorbing solution in the countercurrent absorber was 5×10^{-5} normal sulfuric acid containing 2×10^{-3} molar hydrogen peroxide and 2×10^{-3} grams per liter of Dowicide B. Rate of solution flow was 3.3 ml. per minute and the air flow was adjusted to 20 cu. feet per hour. A con-

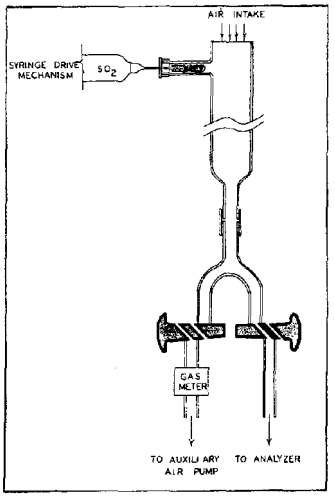

Figure 1. Sulfur dioxide injection apparatus

ductivity cell with a constant of 0.068 reciprocal centimeters was employed as the sensing element. The dimensions of the contacting column with spiral insert were 68 cm. in length and 1 cm. in diameter.

The gas contacting and sensing system was enclosed in a thermostatically controlled cabinet maintained at 120° F. The recorder was equipped with a fast chart drive gear train, giving a chart speed of 3 inches per minute.

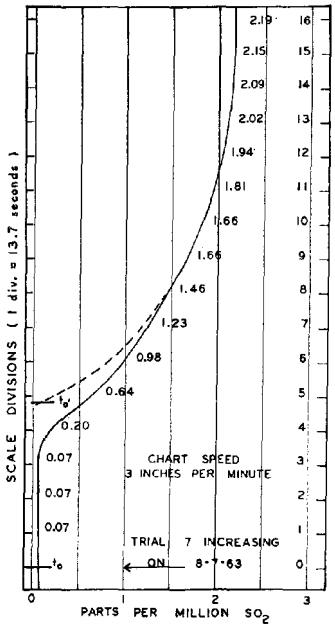

Figure 2. A typical trace of a Thomas autometer showing the response to an abrupt change from a steady state of low to high concentration

A motor driven compensator was employed in conjunction with a Hamilton gastight syringe. The mixing chamber used in this dynamic system was built as described by Kuczynski (*2*).

The injection apparatus and stopcock assembly are shown in the diagram, Figure 1, which is self-explanatory.

Procedure. The analyzer was operated for several hours in order to bring it to proper operating temperature. After the air sample flow was adjusted to 20 cu. feet per hour and the liquid flow to 3.3 ml. per minute, the instrument was then calibrated as described by Thomas, Ivie, and Fitt (*4*).

An auxiliary air pump, as indicated in Figure 1, was adjusted to supply 20 cu. feet of air per hour. The syringe was filled with sulfur dioxide gas as described by Kuczynski (*2*) and at-

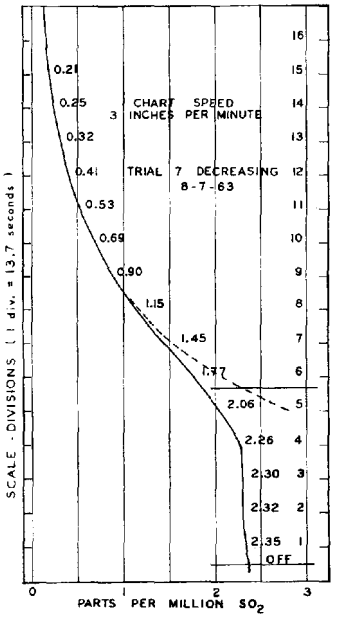

Figure 3. A typical trace showing the response to an abrupt change from a steady state of high to low concentration

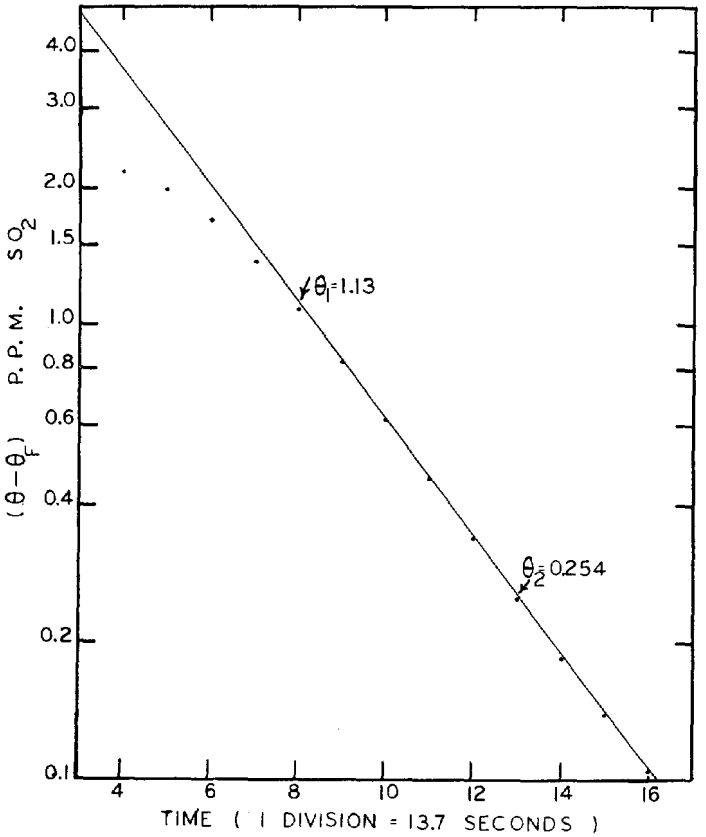

Figure 4. Log of difference between instantaneous and final concentrations vs. time for increasing curve shown in Figure 2

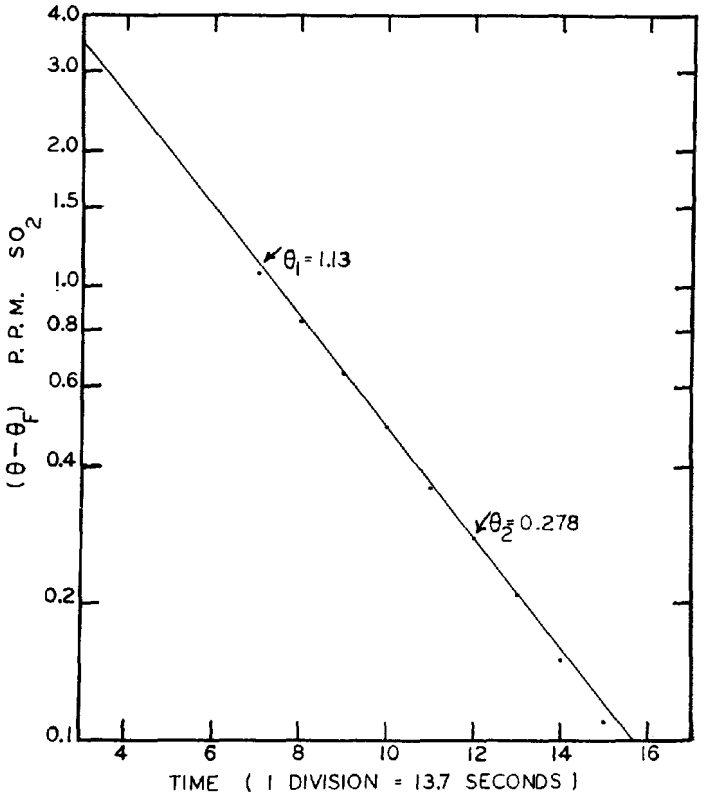

Figure 5. Log of difference between instantaneous and final concentrations *vs.* time for decreasing curve shown in Figure 3

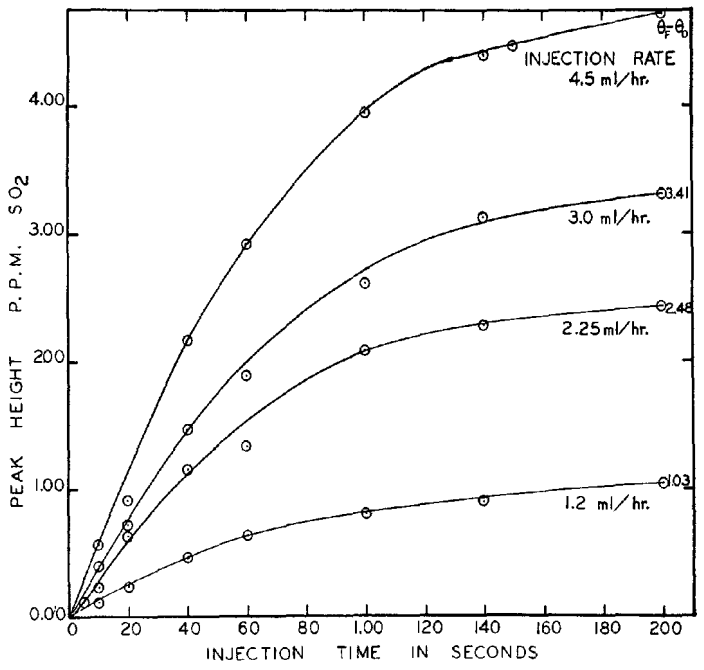

Figure 6. Magnitude of peak SO_2 concentration levels attained at various gas injection times

tached to the syringe drive mechanism. The exhaust of the auxiliary air pump was discharged to the outside atmosphere to avoid contamination of the intake air supply. The air intake and gas mixing system was carefully shielded to prevent local draft effects on the SO_2 dilution chamber. Room air was used, without further purification, for the analyzer and the SO_2 dilution.

The auxiliary air pump established steady state conditions, since a lapse of 5 to 10 minutes occurred in filling the dead volume of the injection system after each injection of gas.

The system was brought to equilibrium with the analyzer sampling room air and the SO_2 gas mixture flowing through the mixing chamber and the auxiliary pump. Then both stopcocks, Figure 1, were turned simultaneously and time, $t = 0$, was noted on the chart. When the recorder reached a steady state, the injection was cut by turning the stopcocks again simultaneously to their original position and this point, $t = 0$, for the decreasing curve was noted on the recording chart. The analyzer was allowed to return to ambient air conditions. This procedure was repeated several times for different concentration levels.

Peak traces, characteristic of short injection periods varying from 10 to 200 seconds, were obtained by modifying the time constant procedure so as to maintain the gas injections over measured periods of time. After each injection the analyzer was allowed to return to its original steady state.

Simple harmonic traces were obtained by admitting to the analyzer a series of short gas injections with timed "on" and "off" periods, until, as indicated by the chart trace, equilibrium was reached. The mean equilibrium value and the mean height of the peaks from this average value were measured.

A lapse of about one minute was found between the time the gas mixture was turned "on" or "off" stream to the analyzer and the time the recorder showed any indication that a change in the gas sample had taken place. The trace then rose or fell slowly and passed through an inflection point, after which it followed the calculated exponential curve; (Figures 2 and 3). The instantaneous concentration at equal intervals of time on the chart were tabulated. From each of the instantaneous values, θ, the final value, θ_F, was subtracted. The remainder was then plotted on semilog paper against the time interval and a straight line, as predicted by theory, was obtained as shown in Figures 4 and 5.

The time constant was calculated from the slopes of the straight lines obtained.

The exponential lines in Figures 4 and 5 were used to calculate the true trace that would have occurred had the instrument responded in the manner predicted by theory. Broken lines in Figures 2 and 3 illustrate the calculated traces. Where this trace crosses θ_0, the time, t_0', is measured in seconds to yield the lapsed time. It should not

be confused with the time constant, as the latter does not take into account any lag of time before the instrument indicates any change in concentration.

Areas under the trace curves, produced by a short-period gas injection, were calculated as the product of the peak height and the width measured at 60% of the height. Thus, area units are given in parts per million–seconds. By comparison with planimeter measurements of the actual areas bounded by the trace, the above calculated values were found to be lower than the true values by about 15%. This error is caused by the tapering of the trace curve at the beginning and end of each injection. However, for the purposes of this study, it does not affect substantially the derived data pertaining to the actual concentrations producing related peaks.

RESULTS AND DISCUSSION

The time constant, J, found for the SO_2 analyzer used in this study was 46.0 seconds with a standard deviation of 5.5 seconds. The values for 17 trials for the increasing curves and 21 trials for the decreasing curves at various concentrations are given in Table I. Means and ranges of J in seconds at various concentration levels are listed in Table II.

The time constant values obtained for the increasing curves are, on the average, four seconds higher than the values for the decreasing curves. From theory, these values should be the same regardless of whether the change in concentration is to a higher or lower level. This anomaly may be caused by the fact that the decreasing curve was easier to analyze. It was more difficult to obtain the final concentration, θ_F, for the increasing curve because of an unsteady final reading, caused by small fluctuations in the supply of SO_2 by the injection system. An improvement was effected by use of a more elaborate syringe drive mechanism but this did not eliminate the variations completely.

At the lowest concentration the curves were difficult to analyze. This may explain the wider range of values obtained at this level as compared to those at higher concentration levels (Table II). The higher value for the time constant at the lower concentration level may indicate some systematic error in the method.

The mean lapsed time for the increasing curve is lower than that for the decreasing curve. This is the reverse of what was found for the time constant. A mean lapsed time of about 70 seconds was found to occur from the time that gas injection commenced until the recorder trace showed a rise at a rate predicted by the exponential curve or at the characteristic response time of the instrument.

Peak heights attained for various

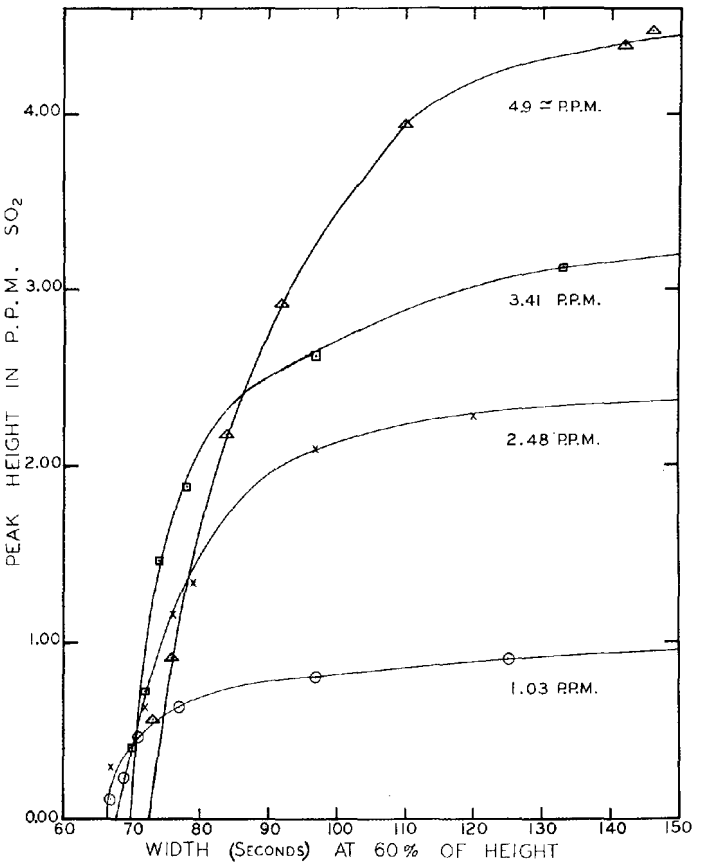

Figure 7. Magnitude of peaks at various concentration levels vs. the time–width of the corresponding traces

Table I. Time Constant and Lapsed Time Values Obtained for a Thomas SO_2 Autometer at Various Gas Injection Rates

Gas injection rate, ml./hr.	Increasing curve			Decreasing curve		
	θ_F, p.p.m. SO_2	J, sec.	Lapsed time, sec.	θ_F, p.p.m. SO_2	J, sec.	Lapsed time, sec.
2.25	2.55	45.5	66.3	0.07	43.2	70.0
2.25	2.55	44.5	73.1	0.07	41.3	72.5
2.25	2.30	36.3	66.0	0.08	44.5	67.5
2.25	2.30	48.8	65.0	0.07	44.8	71.0
2.25	...	...	...	0.07	41.3	72.0
2.25	2.40	37.4	72.0	0.07	44.2	69.4
1.2	1.30	48.2	57.5	0.04	49.3	67.5
1.2	1.30	47.9	...	0.07	51.1	59.4
1.2	1.10	57.1	57.0	0.07	56.9	58.0
1.2	1.10	59.0	62.5	0.07	46.5	64.0
1.2	1.12	56.8	56.0	0.07	45.3	67.5
1.2	1.10	49.2	63.0	0.07	46.9	63.0
4.5	4.9	50.5	67.5	0.07	40.9	81.0
4.5	4.9	42.5	68.0	0.07	41.5	87.0
4.5	4.9	42.8	72.5	0.07	45.3	82.0
4.5	...	...	...	0.07	38.7	99.0
3.0	3.40	51.2	64.0	0.09	46.0	77.0
3.0	3.50	51.3	68.0	0.09	44.4	80.0
3.0	3.50	48.0	64.0	0.09	41.9	80.0
3.0	...	...	...	0.09	39.7	77.0
3.0	...	...	...	0.09	38.7	79.0
Mean		48.1	65.2		44.4	73.5
Standard deviation (s)		6.1	5.1		4.2	9.5

Average J (38 results), 46.0 seconds; s, 5.5.
Average lapse (37 results), 69.9 seconds; s, 8.9.

injection times and concentrations are shown in Figure 6. The peak height is proportional to injection time at all concentrations, but the slope of each curve changes considerably beyond an injection time of 40 seconds.

From a plot of the 60% width against peak height, Figure 7, for various concentrations it is evident that narrow peaks, 60 to 80 seconds, are due either to a lower concentration of SO_2 acting for a period up to about one minute, or to a higher concentration acting for a shorter period of time. In all cases however the actual concentration of SO_2 is greater than the peak value attained by the recorder trace. Wide peaks (over 90 seconds) have a distinctive width and height at each concentration; hence if the height and width of a peak are known, the approximate concentration of SO_2 causing this peak may be determined by locating height and width on the graph and interpolating between the concentrations plotted.

The percentage of the final value attained by a peak for a given fumigation time is shown in Figure 8. The average percentage of the final value attained at various concentration levels and injection times is indicated on the graph by a circle. If the duration of the fumigation was 46 seconds the analyzer would indicate a maximum concentration equal to 50% of the actual concentration present in the fumigating cloud. A continuous fumigation lasting over 210 seconds would be required for the analyzer to indicate a concentration equal to the actual concentration of SO_2 in the parcel of air causing that reading. The indicated concentration of SO_2, expressed as a fraction of the actual concentration, will be a constant for a given injection time. This fraction, then, is independent of the concentration being injected into the system and depends only on the injection time.

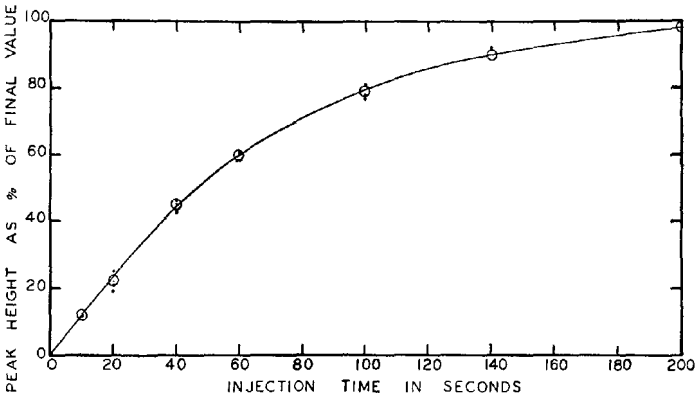

Figure 8. Percentage of actual concentration levels attained at varying duration of fumigations under steady state conditions

Time constant theory predicts that the instrument will respond to 99% of the final concentration in $4.6J$ seconds. In the case of this autometer it would be about 212 seconds. For fumigations of shorter duration than 212 seconds the concentrations recorded as observed peaks would be less than the true concentration and less than the value predicted by the time constant because the latter requires a steady state change. The influence of purging and dilution in the sampling and liquid absorption system of the analyzer tends to prevent the trace from reaching the concentration levels that occur in a changing atmosphere.

The results of an attempt to simulate conditions that might be found in the outside atmosphere are presented in Table III. It is not suggested that SO_2 concentrations occurring in the atmosphere follow any simple harmonic wave pattern. It is probable that local sources produce fluctuations which occur at sudden and irregular intervals. As sources become farther removed from the sampling point, greater mixing can take place and a more homogeneous atmosphere with less abrupt changes may be expected.

Values given in the first two columns of the table indicate the time cycle used for the SO_2 concentrations recorded in column three. The "on" and "off" operation was continued until a continuous steady response was obtained. The mean equilibrium value, θ_M, and the height of the peaks, A, from this mean value are recorded in columns four and five. As expected, the sine wave form of the trace becomes more evident as the "on" and "off" times

Table II. Mean and Range of Values for the Time Constant at Various Gas Injection Rates

Gas injection rate, ml./hr.	Number of determinations	Time constant, sec. Mean	Range
	Increasing curve		
1.2	6	53.0	47.9–59.0
2.25	5	42.5	36.3–48.8
3.0	3	50.2	48.0–51.3
4.5	3	45.3	42.5–50.5
	Decreasing curve		
1.2	6	49.3	45.3–56.9
2.25	6	43.2	41.3–44.8
3.0	5	42.1	38.7–46.0
4.5	4	41.6	38.6–45.3

Table III. Concentration Data from Experiments Showing Simple Harmonic Wave Pattern Fumigations

Injection time, seconds On	Off	θ_F, SO_2 p.p.m.	θ_M, SO_2 p.p.m.	A, SO_2 p.p.m	$\frac{\theta_M}{\theta_F}$ (theor.), %	$\frac{\theta_M}{\theta_F}$ (actual), %
10	10	2.09	1.08	0.00	50	51.7
30	30	2.06	0.99	0.11	50	48.1
60	60	2.01	0.98	0.45	50	48.8
15	15	1.95	0.92	0.01	50	47.2
45	45	1.93	0.97	0.30	50	50.3
20	20	1.88	0.92	0.06	50	48.9
Mean					50	49.2
10	20	4.24	1.49	...	33.3	35.1
20	30	4.24	1.72	...	40.0	40.6
20	20	4.22	2.09	...	50.0	49.5
60	60	4.22	2.01	0.80	50.0	47.6
Mean					43.3	43.2

are increased. This is evident in the higher values obtained in column A when the "on"-"off" cycle was of longer duration. The theoretical value of θ_M/θ_F in per cent is listed in column six. It is obtained by dividing the time that the injection is on by the total time. The actual concentration ratio in per cent is given in column seven. It is calculated by dividing the mean equilibrium value, θ_M, by the final value, θ_F, and expressing the result in per cent. The final value, θ_F, is obtained by allowing the instrument to come to a steady state with constant injection of a given gas mixture.

Agreement is evident between the actual concentrations read from the chart and the calculated theoretical values. Hence the integrated value of a series of peaks obtained on the autometer corresponds to the actual mean concentration of SO_2.

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Analysis of Pentaerythritol Tetranitrate and Its Hydrolysis Products by Thin Layer Chromatography and Radio Scanning

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▶ **A study was made of the hydrolysis of C^{14}-tagged pentaerythritol tetranitrate (PETN) by 1*N* HCl in 75% aqueous dioxane. Thin layer chromatography was employed to resolve hydrolysis mixtures into the four nitrate esters and pentaerythritol (PE). Radio scanning was used to locate the compounds. PE, PETN, and PE-trinitrate were identified by comparative chromatography in several solvents and the unavailable mono- and dinitrates of PE were located by their nitrate/carbon ratio. The scanning technique also provided quantitative data which indicated that the four esters of PE have similar rates of hydrolysis.**

PENTAERYTHRITOL tetranitrate (PETN) is usually assayed as nitrate in biological (*4–6, 20*) as well as in chemical (*1, 10–12, 15, 20–22*) systems. PETN is also determined in explosives by differential potentiometric titration (*17*) and is identified in pharmaceutical preparations by infrared spectrometry (*3*). PETN, known to yield a series of hydrolysis products under acidic (*2*), neutral (*2*), and alkaline (*2, 18*) conditions, is also converted to pentaerythritol (PE) in vivo (*8*). To study the metabolism of PETN and its mechanism of action as an anginal prophylactic, it is necessary to have specific assay methods for PE and its mono-, di-, tri-, and tetranitrates. Because the cited procedures lack the required scope and specificity, thin layer chromatography, radio scanning, and nitrate assay techniques were applied to develop qualitative and quantitative procedures for the five compounds under consideration.

EXPERIMENTAL

Apparatus. Thin layer chromatograms were scanned for radioactivity with a Nuclear Chicago Actigraph II (Model 4502) equipped with a TLC adapter (Model 1039). The area under each peak was determined with a Keuffel and Esser compensating polar planimeter (No. 4236M).

The ultraviolet irradiation source was a Hanovia analytical lamp 79A10.

Reagents. C^{14}-PE labeled at C-1 and C-2 was synthesized from acetaldehyde with specific activity of 1.6 mc. per mmole and was employed to prepare C^{14}-PETN (m.p., 140–141.5°). To minimize the danger of working with explosive material, the labeled PETN was mixed with 7 parts by weight of C.P. lactose. The activity of the lactose–PETN mixture was 0.59 mc. per gram.

PETN from Hercules Powder Co. was a mixture containing the same proportion of lactose as the radioactive material.

Pentaerythritol trinitrate was supplied by Hercules as a 1% solution in acetone.

PE was purchased from Eastman Kodak Co.

Procedure. A portion of the labeled PETN mixture was diluted with 9 parts by weight of the cold mixture. Lactose was extracted with water and the PETN was dissolved in acetone to prepare a 2 mg. per ml. solution. An aliquot (5.0 ml.) of the solution was transferred to a 10-ml. pear-shaped microflask and the solvent was evaporated. Redistilled dioxane (3.75 ml.) and 1.25 ml. of 4*N* HCl were added to the residue. The flask was fitted with a condenser and maintained at reflux temperature. Samples were withdrawn after 4, 5, and 6 hours.

Aliquots (50 μl.) of the hydrolyzate were spotted on 2- × 8-inch glass plates coated with 300 microns of silica gel G (Brinkmann Instruments, Inc.) bound with $CaSO_4$. The unidimensional ascending technique was used for development in the following solvents:

A. Toluene + ethyl acetate (1:1)
B. Ethyl acetate saturated with water
C. Ethanol + water (9:1)
D. 1-Butanol + concentrated NH_4OH + water (4:1:3, upper phase)
E. Ethanol + chloroform (1:1)

The chromatograms were scanned to find the R_f value and C^{14} content of each spot. The instrumental conditions for scanning were collimator, 1/16; time constant, 50 seconds; rate of scan, 0.255 cm. per minute; and counting range, 3K.

For the location of nitrate compounds, thin layer separations were performed

Table I. R_f Values for PETN and Its Hydrolysis Products

Ref. compound	R_f, solvent A		R_f, solvent B		R_f, solvent C		R_f, solvent D		R_f, solvent E	
	Ref. comp.	Hydrolyzate	Ref. comp.	Hydrolyzate	Ref. comp.	Hydrolyzate	Ref. comp.	Hydrolyzate	Ref. comp.	Hydrolyzate
PE	0.00	0.00	0.00	0.00	0.63	0.63	0.26	0.26	0.18	0.18
...	...	0.05	...	0.37	...	0.77	...	0.61	...	0.61
...	...	0.20	...	0.69	...	0.77	...	0.76	...	0.74
PE-trinitrate	0.50	0.50	0.80	0.80	0.77	0.77	0.79	0.79	0.79	0.79
PETN	0.70	0.70	0.84	0.84	0.77	0.77	0.80	0.80	0.79	0.79

on larger (4- × 8-inch) glass plates which were ruled into $^1/_2$-inch segments for chromatography. The method of Coldwell (*7*) was modified to determine R_f values. After the chromatograms were air-dried to remove solvent, they were sprayed with a 1% solution of diphenylamine in absolute ethanol, air-dried, and irradiated with ultraviolet light for 15 seconds. The nitrate compounds became blue.

PE was detected with a spray reagent freshly prepared from 4 volumes of a 2.0% aqueous solution of sodium metaperiodate and 1 volume of an aqueous solution containing 1.0% $KMnO_4$ and 2.0% Na_2CO_3 (*13*). Areas containing PE became yellow; the background was violet.

Nitrate assays were conducted with phenoldisulfonic acid (*16*). Each area for assay was scraped from the thin layer chromatogram and mixed with 0.1 ml. of glacial acetic acid and 0.2 ml. of phenoldisulfonic acid solution (Harleco). After the mixture was cooled in ice water, 0.8 ml. of concentrated NH_4OH was added and the contents were mixed. The reaction mixture was allowed to reach room temperature, then centrifuged. The supernatant liquor was transferred to a small (0.9-ml. capacity) cell and its absorbance at 408 mμ was determined against a reagent blank in a Beckman DV spectrophotometer.

RESULTS

Thin layer chromatograms of partially hydrolyzed PETN revealed the presence of 5 components. Figure 1 illustrates the use of diphenylamine to determine R_f values, as well as the qualitative and quantitative applications of radio scanning. Table I records the R_f data obtained in 5 solvent systems with these methods and with regenerating permanganate.

By comparative chromatography in solvent A, the two fastest moving components were identified as PETN (R_f 0.70) and PE-trinitrate (R_f 0.50). These identifications were confirmed by the nitrate carbon ratio (Table II). The carbon content of a spot was calculated from the area under the scanning curve and the areas given by known quantities of C^{14} applied to chromatograms as PETN (*8*). The nitrate content of a spot was determined after elution as described above.

Chromatograms developed in solvent A produced a spot for which no reference compound was available. This spot was located at R_f 0.20 by scanning (Figure 1) and by spraying with diphenylamine (Table I). The nitrate carbon ratio showed the compound to be PE-dinitrate (Table II). The same ratio was obtained from eluates of the R_f 0.69 spot on chromatograms developed in solvent B.

Scanning chromatograms developed in solvent A showed a spot at R_f 0.02 (Figure 1) whereas differential staining showed the presence of a nitrate at R_f 0.05 and of a reducing agent at R_f 0.00 (Table I). Eluates of the material at R_f 0.05 gave a nitrate/carbon ratio corresponding closely to the proportion calculated for PE-mononitrate. The composition of this substance was confirmed by a combination of thin layer chromatography in solvents B, D, and E and subsequent nitrate and C^{14} assays of the second slowest spot removed from each of these chromatograms.

Table II. Identification of PETN and Hydrolysis Products by Nitrate and Carbon Contents after Chromatography with Solvents A and B

Compound	Nitrate/carbon ratio	
	Calcd.	Found[a]
PE	0.0	...
PE-mononitrate	1.03	1.06
PE-dinitrate	2.07	2.08
PE-trinitrate	3.10	2.90
PETN	4.13	3.58

[a] Determined from the nitrate assay of the eluate of a spot and from the C^{14} content determined by scanning the same spot.

PE was identified by its R_f in all 5 solvent systems, as determined with the permanganate spray reagent and by its R_f in solvents B, C, D, and E as determined with scanning. Eluates of

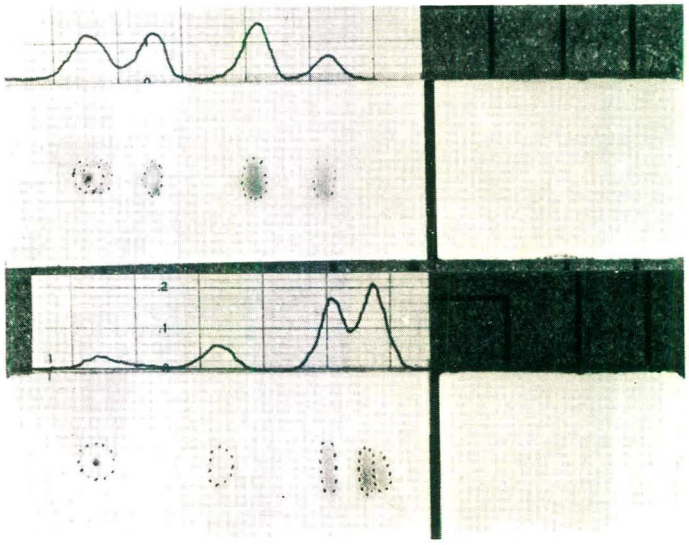

Figure 1. Thin layer chromatograms and radio scanning curves after hydrolysis of PETN for 5 hours with 1N HCl in 80% dioxane

Top, solvent A gave a mixture of PE and PE-mononitrate at R_f 0.02, PE-dinitrate at R_f 0.20, PE-trinitrate at R_f 0.50, and PETN at R_f 0.70

Bottom, solvent B gave PE at R_f 0.00, PE-mononitrate at R_f 0.37, PE-dinitrate at R_f 0.69, and a mixture of PE-trinitrate and PETN at R_f 0.82

the PE were contaminated with inorganic nitrate which tended to migrate very slowly from the point of application.

Table III shows the data obtained by hydrolyzing C^{14}-PETN for 4, 5, and 6 hours with 1*N* HCl in 75% aqueous dioxane under reflux. The standard deviation was calculated from the percentage error determined by repeated scanning of radioactive areas.

Table III. Recovery of C^{14} in Hydrolysis Mixtures of PETN after Chromatography with Solvents A and B[a]

Compound	% of C^{14} Identified after 4 Hours	5 Hours	6 Hours
PE	0	7.7 ± 1.1	31.9 ± 0.7
PE-mononitrate	0	13.4 ± 1.7	25.6 ± 1.9
PE-dinitrate	23.0 ± 1.7	34.7 ± 0.8	27.7 ± 2.1
PE-trinitrate	38.9 ± 0.9	27.8 ± 2.1	11.1 ± 1.4
PETN	38.9 ± 0.9	14.8 ± 1.9	5.6 ± 0.8
Total recovery	100.8	98.4	101.9

[a] Data are expressed ± standard deviation calculated from per cent error determined by repeated scanning of radioactive areas.

DISCUSSION

Although nitrate assay with phenoldisulfonic acid is nonspecific, this colorimetric technique may be coupled with thin layer chromatography to determine the quantity of each PE-nitrate ester present in mixtures of the four possible esters. Two solvent systems (A and B) are employed to develop quantitative data. Solvent A resolves the three polynitrate esters, but does not separate PE-mononitrate from PE. Solvent B has the shortcoming of failure to separate PE-trinitrate from PETN. In our experience, the use of both solvents provides confirmatory data in close agreement not only with respect to the fully isolated components, but also between combined PE and PE-mononitrate in solvent A and the sum of the individual values for these compounds from resolution in solvent B, and between combined PE-trinitrate and PETN in solvent B with the sum of the values obtained separately from solvent A. It is expected that the methodology will permit closer investigation of the conversion of PETN to PE observed in vivo (*8*).

The data in Table III indicate that the chemical hydrolysis of the four ester linkages in PETN proceeds sequentially and rather slowly. Because relatively large quantities of the intermediate esters accumulated in the hydrolysis mixture, it is evident that the partially esterified compounds are not hydrolyzed at a greatly faster rate than PETN. These findings have interesting implications relative to the rates of absorption and hydrolysis of PETN in the gastrointestinal tract.

A brief study showed that *N, N'*-diphenylbenzidine, employed in lieu of diphenylamine, yielded blue color with PE-nitrates. This finding supports the oxidative mechanism (*9*) of color development. However, *N,N'*-diphenylbenzidine was not markedly more sensitive than diphenylamine (*14, 19*) at least in conjunction with thin layer chromatography.

Each of the solvent systems employed in this study effects migration in the same sequence—namely, with R_f increasing with esterification. This situation facilitates qualitative biological investigation without complicating the identification of the principal metabolite (PE, which has R_f values of 0.00, 0.18, 0.26, and 0.63 in these solvents).

ACKNOWLEDGMENT

The authors appreciate the contributions of Edward Merrill, who was responsible for the synthesis of the radioactive compounds; Alexander Nutzul, who provided special technical assistance; and Neil Stasilli, who statistically analyzed the quantitative data.

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Separation of Scandium from Yttrium, Rare Earths, Thorium, Zirconium, Uranium, and Other Elements by Anion Exchange Chromatography in Ammonium Sulfate Media

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▶ Sc(III) is adsorbed on a strongly basic anion exchange resin, Dowex 1, X-8 (sulfate form), from 0.1*M* $(NH_4)_2SO_4$–0.025*M* H_2SO_4 solution. Under these conditions Y(III), rare earths(III), Al(III), Be(II), Cd(II), Co(II), Cu(II), Ga (III), Ge(IV), Mg(II), Mn(II), Ni(II), V(IV), and Zn(II) are not adsorbed to any great extent, while Mo(VI), Ta(V), Th(IV), Zr(IV), and U(VI) are strongly retained by the exchanger. Sc(III) can be quantitatively separated from macroamounts of any of the cations above. An anion exchange chromatographic procedure for the separation of the rare earths(III), Sc(III), Th(IV), Zr(IV), and U(VI) has also been developed, where all five of the metallic ions can be chromatographically separated by a consecutive elution with $(NH_4)_2SO_4$, HCl, and $HClO_4$.

ALMOST ALL colorimetric, gravimetric, and chelatometric reagents for Sc (III) react with many other metal ions and therefore are not specific. Y(III), rare earths(III), Zr(IV), Th(IV), and U (VI) are the most troublesome elements, and usually cause serious interference in both the separation and the determination of Sc(III). This study centered on the establishment of an effective anion exchange separation procedure for Sc(III) from the elements above, which would lead to the determination of Sc(III). The different methods currently used to separate and determine Sc(III) have been reviewed in two monographs (*6*, *7*). Since the recent progress in ion exchange separation of Sc(III) has been reviewed by Hamaguchi *et al.* (*2*, *3*), it will not be discussed here.

A systematic study of the adsorption of cations on Dowex 1, X-8 in $(NH_4)_2SO_4$ media showed that the differences in equilibrium distribution coefficients between Sc(III) and a considerable number of metal ions is great enough for a good separation. This fact made it possible to separate Sc(III) from Y(III), rare earths(III), Zr(IV), Th(IV), and U(VI) as well as many other metal ions. Furthermore the procedure described here provides a simple method for separating five metals—rare earths (III) or Y(III)–Sc(III)–Zr(IV)–Th(IV)–U(VI)—consecutively using $(NH_4)_2SO_4$ and very common mineral acids.

EXPERIMENTAL

Reagents and Apparatus. Analytical reagent quality chemicals were used whenever possible. Stock solutions of Sc(III), Y(III), and rare earths(III) were prepared by dissolving an appropriate amount of the respective oxides (99.9% purity) in a minimum amount of 3*M* H_2SO_4, evaporating to dryness, and diluting to a definite volume with water to bring the concentration of each to 2.5 mg. per ml. of H_2O. Standard solutions of the other ions were prepared by dissolving the sulfates in water or H_2SO_4 of known concentration to give 10 to 20 mg. of the ion per milliliter of the solvents. A triplicate determination was made using an appropriate analytical method to standardize each stock solution.

Ion Exchange Resin. Strong base type anion exchanger, Dowex 1, X-8, 100 to 200 mesh, sulfate form was used. An appropriate amount of resin (Cl form) was purified by placing it in a large column and backwashing with water to remove fine particles. Then it was washed with 3*M* H_2SO_4 to convert it to the sulfate form until the effluent gave a negative test with $AgNO_3$. Finally the resin was washed thoroughly with water until the effluent gave a negative test with $BaCl_2$. The resin was stored in a large desiccator containing saturated KBr solution.

Ion Exchange Columns. Conventional ion exchange columns, 9-mm. i.d. and 30 cm. long, with glass wool and buret tap at the bottom were used. The columns were fitted with 200-ml. dropping funnels connected by one-hole rubber stoppers. The columns were loaded with 10.0 grams of resin slurried with water. The resulting resin bed was 21 cm. long.

Procedure. DISTRIBUTION COEFFICIENT MEASUREMENT. One milliliter of the stock solution of each metal was transferred to a 50-ml. glass-stoppered Erlenmeyer flask and evaporated to dryness. Thirty milliliters of $(NH_4)_2SO_4$ solution of varying concentration with or without free sulfuric acid, and 1 gram of the dried resin were then added to the flask. The flask was stoppered and shaken for 20 hours mechanically at room temperature. The resin was removed by filtration and an aliquot of the filtrate was analyzed for cation by an appropriate method as described later. The distribution coefficient, K_d, was calculated by the following relationship:

$$K_d = \frac{\text{amount of metal ion/gram of dry resin}}{\text{amount of metal ion/ml. of solution}}$$

COLUMN SEPARATION. Before starting the elution the column should be pre-equilibrated with the eluent, 0.1*M* to 0.07*M* $(NH_4)_2SO_4$–0.025*M* H_2SO_4 solution, by passing several column volumes of eluent through the column. Add to the column 10 to 20 ml. of a mixture of Sc(III) and the other metal ions. The sample solution should be approximately 0.1*M* in $(NH_4)_2SO_4$ and 0.025*M* in H_2SO_4. The effect of the concentration of free acid is critical; thus, excess sulfuric acid should be avoided. Wash the column with 60 ml. of 0.1*M* $(NH_4)_2SO_4$–0.025*M* H_2SO_4 and collect the effluent. This fraction contains Y(III) and rare earths(III) as well as many other ions including Al(III), Be(II), Cd(II), Co(II), Cu(II), Ga(III), Ge(IV), Mg(II), Mn(II), Ni (II), V(IV), and Zn(II). Then elute Sc(III) with 50 ml. of 1*M* HCl or 60 ml. of 0.5*M* H_2SO_4; collect the effluent and titrate with EDTA as outlined in Table I.

When Mo(VI) is accompanied by Sc(III), elute Sc(III) first with about 200 ml. of 0.1*M* $(NH_4)_2SO_4$–0.025*M* H_2SO_4, then Mo(VI) with 90 ml. of 0.5*M* NaOH–0.5*M* NaCl. If Th(IV) and U(VI) are present, wash the column

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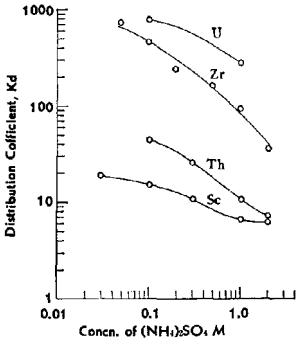

Figure 1. Distribution coefficients of Sc(III), Th(IV), Zr(IV), and U(VI) as function of $(NH_4)_2SO_4$ concentration

Free acid concentration is kept constant at 0.025*M* H_2SO_4. Resin, Dowex 1 X-8

first with 0.1*M* $(NH_4)_2SO_4$–0.025*M* H_2SO_4 solution to remove rare earths (III) and the other nonadsorbable ions above. Sc(III) is recovered in the 100- to 200-ml. fraction of the same eluent, while Th(IV) and U(VI) remain strongly adsorbed on the column. Elute Th(IV) with 40 ml. of 4*M* HCl, then U(VI) with 30 ml. of 1*M* $HClO_4$. Determine Th(IV) and U(VI) in the effluents, respectively, as outlined in Table I. If the sample solution contains rare earths(III) or Y(III), Sc(III), Th(IV), Zr(IV), and U(VI), elute first rare earths(III) or Y(III) and Sc(III) chromatographically with 200 ml. of 0.1*M* $(NH_4)_2SO_4$–0.025*M* H_2SO_4; then Th(IV) with 60 ml. of 1*M* $(NH_4)_2SO_4$–0.025*M* H_2SO_4; Zr(IV) with 50 ml. of 4*M* HCl; and finally, U(VI) with 30 ml. of 1*M* $HClO_4$.

RESULTS AND DISCUSSION

In Figure 1 the values for the distribution coefficients of Sc(III), Th(IV), Zr(IV), and U(VI) in sulfate media are given as a function of $(NH_4)_2SO_4$ concentration. The concentration of free acid is kept constant at 0.025*M* H_2SO_4. The figure indicates the possibility of separating Sc(III) from U(VI), Zr(IV), and Th(IV) as well as consecutive chromatographic separation of the four metals. Most metal ions show no or only slight adsorption on the strongly basic anion exchanger from the sulfate or sulfuric acid media (*1*, *4*, *5*). Therefore the anion exchange-sulfate system seems to provide a basis for a specific separation of Sc(III) from many other ions.

It must be noted here that the distribution coefficients of the metal ions depend markedly on the free sulfuric acid concentration. The distribution coefficients of Sc(III), Th(IV), and U(VI) in ammonium sulfate system in the absence of the free acid are shown in Table II.

In 0.1*M* H_2SO_4 media the distribution coefficients of Sc(III) are approximately 4 over the concentration range of 0.03 to 2*M* $(NH_4)_2SO_4$. When the free acid concentration increases to 0.5*M* H_2SO_4, the distribution coefficient of Sc(III) becomes practically zero regardless of the concentration of ammonium sulfate.

Results of separations of Sc(III) in which a high ratio of other metal ions

Table I. Analytical Methods Used

Cation	Method
Al(III), Ga(III), V(IV)	Titration with EDTA using a mixture of 1-(2-pyridylazo)-2-naphthol and its Cu salt as indicator
Be(II)	Colorimetrically with *p*-nitrobenzene-azo-orcinol as reagent
Cd(II), Mg(II), Zn(II)	Titration with EDTA using Eriochrome Black T
Co(II), Cu(II), Ni(II)	Titration with EDTA using Murexide as indicator
Fe(III)	Titration with EDTA using Variamine Blue B, hydrochloride as indicator
Ge(IV)	Colorimetrically with phenylfluorone as reagent
La(III), Lu(III), Sc(III), Sm(III), Th(IV), Y(III)	Titration with EDTA using Xylenol Orange as indicator
Mn(II)	Titration with EDTA using Pyrocatechol Violet as indicator
Mo(VI)	Back-titration with $CuSO_4$ in excess of EDTA using 1-(2-pyridylazo)-2-naphthol as indicator
U(VI)	Colorimetrically with hydrogen peroxide as reagent
Zr(IV)	Back-titration with $Bi(NO_3)_3$ in excess of EDTA using Xylenol Orange as indicator

Table II. Distribution Coefficients

[$(NH_4)_2SO_4$ medium in absence of free H_2SO_4]

	$(NH_4)_2SO_4$, *M*						
	0.01	0.03	0.1	0.3	1.0	2.0	3.0
Sc(III)	90	76	56	28	10	6	...
Th(IV)	225	276	161	68	34	21	...
U(VI)	...	...	1000	820	548	246	201

Table III. Separation of Sc(III) from Foreign Metals in $(NH_4)_2SO_4$ Medium

Sc, mg.		Foreign ions, mg.		
Added	Found		Added	Found
2.56	2.80	Al(III)	44.8	44.7
	2.60	Be(II)	20.0	20.4
	2.65	Cd(II)	47.6	49.1
	2.59	Co(II)	42.3	42.8
	2.48	Cu(II)	49.4	49.0
	2.50	Ga(III)	40.2	39.8
	2.60	Ga(III)	10.0	10.2
	2.59	Ge(IV)	20.0	20.3
0.930	0.931	La(III)	10.6	10.6
	0.934	La(III)	96.5	97.3
1.86	1.83	La(III)	106	105
		Th(IV)	9.28	9.39
		La(III)	57.9	55.7
	1.83	Th(IV)	28.7	27.8
		U(VI)	50.0	49.1
0.930	0.896	Y(III)	50.8	51.3
		Th(IV)	19.1	19.0
		Zr(IV)	8.98	9.07
		U(VI)	50.0	50.0
	0.927	Lu(III)	2.10	2.13
2.56	2.55	Mg(II)	59.6	59.6
	2.35	Mn(II)	44.4	44.0
	2.58	Mo(VI)	10.0	10.0
	2.51	Ni(II)	50.0	50.7
0.930	0.925	Sm(III)	9.95	10.1
	0.928	Sm(III)	20.0	20.2
	0.929	Th(IV)	9.28	9.62
	0.929	Th(IV)	18.6	18.9
2.56	2.53	V(IV)	40.0	39.5
	2.59	Zr(IV)	38.9	38.9
	2.62	Zn(II)	50.1	52.0

to Sc(III) is used are presented in Table III. The separation of Sc(III) from large amounts of foreign metals is quantitative. La(III), Sm(III), and Lu(III) are selected as typical rare earth metals. Because Y(III), rare earths(III), Zr(IV), and Th(IV) do not show noticeable adsorption on the anion exchanger from HCl media, the procedure described seems to be useful for their separation. In addition, rare earths(III), Th(IV), and U(VI) fractions are recovered sharply from the column without any troublesome tailing. However, when large amounts of Th(IV), Zr(IV), or U(VI) (or all of them) are present, the Sc(III) breakthrough tends to appear in a slightly earlier fraction of effluent, but the separation is still good.

The flow rate of eluent does not affect the chromatographic separation of Sc (III); a range of the flow rate from 0.5 to 1.5 ml. per minute can be used without disturbing the elution patterns of Sc(III) or the other metals. Among the metals tested qualitatively, Ta(V) and W(VI) showed strong adsorption on the resin from the sulfate media, 0.1*M* $(NH_4)_2SO_4$–0.025*M* H_2SO_4, while Fe(III) and In(III) were weakly adsorbed. At the lower acid concentration employed here [0.025*M* H_2SO_4–0.1*M*-$(NH_4)_2SO_4$], Ti(IV) is seriously hydrolyzed, partly passing through the column and partly being adsorbed strongly on the resin. Ti(IV) does not show any adsorption from the 0.5*M* H_2SO_4–0.1*M* $(NH_4)_2SO_4$ medium.

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Cation Exchange Separation of Titanium and Zirconium Using Perchloric Acid

Application to the Analysis of PZT Ceramics

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▶ **A description is given of a cation exchange procedure for a quantitative separation of zirconium and titanium from lead and bismuth, and from each other, using $HClO_4$–NH_4F mixtures and $HClO_4$ as eluents. This procedure has been applied to the analysis of high-fired lead oxide–zirconium oxide–titanium oxide ceramic material (PZT).**

THE USEFUL PIEZOELECTRIC properties of ceramic $BaTiO_3$ has stimulated a search for other ferroelectrics suitable for fabricating piezoelectric ceramics. Shirane, Suzuki, and Takeda (*14*) and others (*13*) described the properties of solid solutions of $PbTiO_3$ and $PbZrO_3$ and Jaffe, Roth, and Marzullo (*6, 7*) studied piezoelectric properties of lead zirconate–lead titanate (PZT) solid-solution ceramics.

Small compositional changes can produce marked changes in final piezoelectric properties. These variations can be minimized by close control of the constituents at all stages of processing. To date, the composition of PZT ceramics usually are determined empirically by measuring their physical and electrical properties. Knowledge of the composition during processing, and particularly in the finished ceramic, could be more easily obtained if the dissolution procedure and the method for separating Ti and Zr from the resulting solution, and from each other, were simplified.

Brown and Rieman (*3*) used ion exchange techniques employing an HCl–citric acid eluent and Belyavskaya, Alimarin, and Kolosova (*1*) used 1*N* HCl in an ion exchange procedure for the separation of Ti from Zr. However, because either relatively large effluent volumes are required or pH control is critical, use of these methods has been limited. Other investigators (*11, 12*) have utilized anion exchange techniques and H_2SO_4–Na_2SO_4 and HCl media, respectively, to separate Zr from a number of elements, including Ti. Use of the chloride ion is undesirable in cases where cations form either insoluble chlorides or unknown complexes. Thus, many current ion exchange procedures suffer from one of three disadvantages: use of relatively large effluent volumes, critical control of eluent pH, or the presence of an undesirable anion.

In an investigation of the behavior of titanium(IV) in $HClO_4$, Beukenkamp and Herrington (*2*) reported the possibility of titanium(IV)-perchlorate complexes forming at $HClO_4$ concentrations above 2*M*. From their work in separating vanadium from titanium and other cations, Fritz and Abbink (*5*) proposed that Ti(IV) could be separated from other tri- or quadrivalent metal ions using $HClO_4$–H_2O_2 eluent systems.

This paper describes a cation exchange procedure for a quantitative separation of zirconium and titanium from each other, using an $HClO_4$ eluent system. The method as applied to the analysis of PZT ceramics is briefly described. Solutions containing titanium and zirconium in amounts between 10 to 100 mg. of each element have been separated from each other.

EXPERIMENTAL

Column Preparation. The borosilicate glass ion exchange columns were 30 × 1.0 cm. (i.d.) and 10 × 1.0 cm. (i.d.). The resin used was Dowex AG–50WX8, 100- to 200-mesh, hydrogen form. Twenty-seven grams of resin, dry weight, were used in the larger columns, and 9 grams, dry weight, were used in the smaller columns. The resin was washed several times with distilled water, and the finest particles were decanted after each washing. The resin then was washed with 1*N* HCl, followed by distilled water until a negative chloride test was obtained.

Reagents. TITANIUM ELUENT. A solution of 25% $HClO_4$ was prepared by diluting 178 ml. of 70% $HClO_4$ to 500 ml. with distilled water.

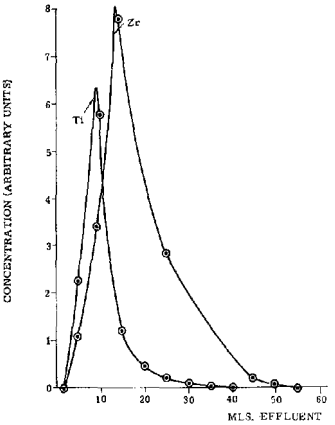

Figure 1. Elution curves of titanium and zirconium

1% $HClO_4$–0.1 *M* NH_4F, flow rate 1 ml. per minute

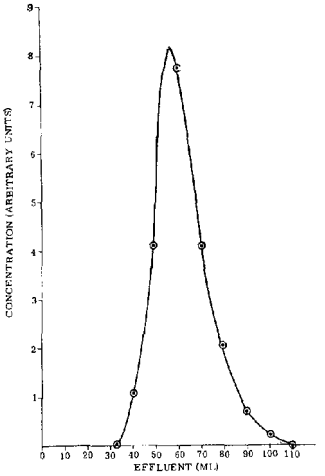

Figure 2. Elution curve for titanium

25% $HClO_4$, flow rate 1 ml. per minute

TITANIUM AND ZIRCONIUM ELUENT. 14 ml. of 70% $HClO_4$ and 3.7 grams of A.R. ammonium fluoride were diluted to 1000 ml. with distilled water.

CUPFERRON SOLUTION. Six grams of cupferron were dissolved in 100 ml. of distilled water. The solution was filtered through Whatman No. 42 filter paper before use.

STANDARD TITANIUM AND ZIRCONIUM SOLUTIONS. Spectropure titanium metal was dissolved in concentrated hydrochloric acid under reflux conditions. Zirconium oxychloride was dissolved in 5% $HClO_4$ solution, and the solution was standardized gravimetrically using cupferron (*9*, *10*).

STANDARD PZT MATERIAL. PZT material prepared from A.R. grade lead oxide, bismuth oxide, titanium dioxide, and zirconium dioxide. The mixture was ball-milled, dried, and calcined at 900° C. This material was passed through a No. 325 Bureau of Standards sieve before being used. Table I contains the per cent compositions of the PZT material used. The titanium and zirconium contents of the standards were determined by neutron activation analysis in order to check their validity as standards.

Procedure. TREATMENT OF STANDARDS. *Ti-Zr*. Known mixtures of titanium and zirconium prepared from the standard solutions were evaporated to near dryness in the presence of hydrogen peroxide. Ten milliliters of concentrated sulfuric acid were added, and the resulting mixture was evaporated to a volume of 1 to 2 ml. After dilution to 1 to 2% H_2SO_4 concentration, several drops of 30% hydrogen peroxide were added, and the solution was boiled to remove excess hydrogen peroxide to prevent possible resin damage and formation of anomalous complexes. The titanium and zirconium were separated by an ion exchange procedure described in the section on "Recovery of Titanium and Zirconium."

PZT. Samples of standard PZT material were dissolved by fuming with 72% $HClO_4$ and taken to a volume of 3 to 4 ml. The solution was diluted to 100 ml. with distilled water, several drops of 30% H_2O_2 were added, and the resulting solution was placed on the 10 × 1.0-cm. (i.d.) columns, allowing a flow rate of 2 ml. per minute. The zirconium and titanium was eluted using the $HClO_4$–NH_4F eluent at a flow rate of 2 ml. per minute. The effluent solution of zirconium and titanium was fumed with H_2SO_4 to remove the fluoride ion, and then treated in the same manner as described for titanium and zirconium in the preceding paragraph.

TREATMENT OF SAMPLES. The preparation of PZT samples was identical to the method described for preparation of the standard PZT material in the previous section.

RECOVERY OF TITANIUM AND ZIRCONIUM. Sulfuric acid solutions of zirconium and titanium were put on the 30 × 1.0-cm. (i.d.) columns at a flow rate of 1 ml. per minute. The titanium was eluted using 25% $HClO_4$ as the eluent, and the zirconium was subsequently eluted, using the $HClO_4$–NH_4F eluent. At a flow rate of 1 ml. per minute, 125 ml. of 25% $HClO_4$ was required to elute the titanium and 60 ml. of $HClO_4$–NH_4F eluent were used to elute the zirconium. The titanium and zirconium were analyzed gravimetrically using cupferron as precipitant (*9*, *10*).

ELUTION CURVES. Elution curves of titanium and zirconium were determined with separate columns for the perchloric acid–ammonium fluoride eluent system, using standard techniques. The columns used were 30 × 1.0 cm. (i.d.), and the flow rate was 1 ml. per minute. Each titanium fraction and each zirconium fraction was analyzed by a gravimetric procedure using cupferron as the precipitant (*9*, *10*). The elution curve of titanium, using 25% $HClO_4$ as the eluent, was obtained by the same procedure as described above.

RESULTS AND DISCUSSION

The elution curves for titanium and zirconium, using the 1% $HClO_4$–0.1 *M* NH_4F eluent, are shown in Figure 1. Figure 2 illustrates the elution curve of titanium using 25% $HClO_4$ as the eluent. Since the titanium-fluoride complex is not retained by the resin, fluoride must be removed from the effluent collected in the separation of lead and bismuth from titanium and zirconium. Removal of the fluoride results if the effluent is fumed with H_2SO_4 until the H_2SO_4 wets the entire inside of the flask (*8*). The presence of the peroxide complex of titanium is not essential to the separation of zirconium and titanium. However, because of the color of the complex, it was possible to observe the elution of titanium from the column. In several cases, a yellow band was observed at the top of the column after the titanium had been eluted from the top of the column. This band formed when the sulfuric acid concentration was lower than 1% while putting the zirconium-titanium solution on the column. Failure to elute the yellow band caused a low recovery of titanium. A quantitative recovery of titanium was achieved by eluting alternately with 5 ml. of 25% perchloric acid and 5 ml. of distilled water until the band was no longer visible.

The analytical results from a series of determinations made on mixtures of zirconium and titanium are tabulated in Tables II and III. Table II contains data obtained from mixtures prepared from standard zirconium and titanium solutions, while Table III contains data

Table I. Weight Per Cent Composition of PZT Standards

PZT Standard	PbO	Bi_2O_3	ZrO_2	TiO_2	K_2CO_3[a]
1	67.56	1.43	19.56	11.24	0.21
2	66.65	1.41	23.67	8.27	...
3	67.70	1.43	19.60	11.27	...
4	68.79	1.45	15.03	14.62	0.11

[a] The potassium present in PZT Standards 1 and 4 accompanies the Ti and Zr, and does not interfere with subsequent analysis. The analysis of potassium was done by emission spectrography.

Table II. Analysis of Ti-Zr Mixtures

TiO_2, mg.			ZrO_2, mg.		
Taken	Found	% Recovery	Taken	Found	% Recovery
45.9	45.7	99.6	...	...	...
69.0	69.2	100.3	40.1	40.0	99.8
96.6	95.5	98.9	40.1	40.1	100
82.8	82.9	100.1	40.1	40	99.8
69.0	69.1	100.1	60	60.1	100.2
96.6	97.1	100.5	60	59.9	99.8
...	...	...	40.1	40.1	100

Average % Recovery of TiO_2 = 99.9%
Average % Recovery of ZrO_2 = 99.9%

Table III. Analyses of Standard PZT Material

PZT standard	TiO_2 content	Mean error	ZrO_2 content	Mean error	By activation analysis TiO_2 content	By activation analysis ZrO_2 content
1	11.12%	−0.12	19.57%	−0.01	...	...
2	8.20%	−0.07	23.66%	−0.01	8.18%	24.05%
3	11.26%	−0.01	19.60%	...	11.27%	20.38%
4	14.53%	−0.09	15.05%	+0.02	15.39%	14.46%

resulting from the analysis of several PZT materials. Table III also includes data on the PZT material obtained by neutron activation analysis. The other elements present in PZT, except potassium, are left on the cation column after the first ion exchange separation. These can be separated or stripped from the column with HNO_3 (*4*) and determined using standard methods.

The method described has been successfully applied to the analysis of a series of PZT materials which were calcined at 900° C. and hot-pressed at temperatures ranging from 1050° to 1300° C. The application of this method to our specific problem warranted no concern with impurities However, additional work is being carried out at the present time to determine the ion exchange behavior of a large number of cations using $HClO_4$ solutions as eluents. Procedures are being developed for the preparation of spectropure compounds of several elements, including Be and Zr, using ion exchange techniques with $HClO_4$ eluents to separate the major constituent from its impurities.

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Anion Exchange Separation of Gallium, Indium, and Aluminum

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▶ Two methods are described for the chromatographic separation of aluminum, gallium, and indium on the strongly basic anion exchange resin Dowex 1, X8. Media consisting of 90 and 70% 2-methoxyethanol-1–10% 6*N* and 30% 2*N* hydrochloric acid, respectively, followed by 1*N* hydrochloric acid are used in one case to effect the sequential elution of aluminum, gallium, and indium in this order. By means of the other method, gallium is first eluted with 80% acetone–20% 3*N* hydrochloric acid whereafter 90% acetone–10% 6*N* hydrochloric acid is used to remove indium from the resin. Subsequently aluminum is desorbed by washing the resin with 70% acetone–30% 2*N* hydrochloric acid. By means of these methods the quantitative separation of milligram quantities of these elements can be effected even when aluminum is present in great excess. Based on these facts successful analyses of samples of aluminum metal for gallium and indium have been performed.

NO INVESTIGATIONS concerning the anion exchange separation of aluminum, gallium, and indium in mixed aqueous and nonaqueous solvents containing hydrochloric acid have been carried out in the past. In pure aqueous hydrochloric acid solutions, however, a separation method has been used by Kraus, Nelson, and Smith (*6*) for the sequential elution of aluminum, indium, and gallium in this order using hydrochloric acid of varying concentration. This method has been modified by Gregory and Jeffery (*2*) for the separation of gallium in the presence of a large excess of aluminum and was applied to the analysis of Bayer liquors. A rapid method was described by Nadezhina (*8*) which is suitable for isolating small amounts of gallium from con-

siderable quantities of aluminum, iron, etc. This method is based on the successive use of anion exchange in 4*N* hydrochloric acid and cation exchange reactions. For the separation of gallium from aluminum on Russian anionites, 7*N* and 3.7*N* hydrochloric acid solutions were employed by Denisova and Tsvetkova (*1*) and Laskorin *et al.* (*7*).

None of these methods, except that developed by Kraus *et al* (*6*), includes any procedures for the separation of gallium from indium.

Investigations of mixed aqueous hydrochloric acid systems containing 2-methoxyethanol-1 or acetone show that by using chromatographic techniques an effective separation of aluminum, gallium, and indium can be carried out.

EXPERIMENTAL

Reagents. The resin used for the separation experiments and measurements of distribution coefficients was Dowex 1, X8 (100–200 mesh, chloride form). Before being transferred to the ion exchange columns the resin was soaked either in 90% 2-methoxyethanol-1–10% 6*N* hydrochloric acid or 80% acetone–20% 3*N* hydrochloric acid, depending on which method is subsequently employed for separation. For the determination of the distribution coefficients the air-dried form of the resin was used.

Standard solutions of aluminum, gallium, and indium were prepared by dissolving reagent grade chlorides in 6*N* hydrochloric acid. Also used was chemically pure methyl glycol and acetone.

Apparatus. In all cases the resin bed in the columns used had a length of 75 cm. and a diameter of 1.0 cm.

Procedures. A. Separation of Aluminum, Gallium, and Indium in 2-Methoxyethanol-1–Hydrochloric Acid Medium.

Pretreatment of Resin Bed. The resin was transferred to the column and treated with 100 ml. of a mixture consisting of 90 volume % 2-methoxyethanol-1 and 10 volume % 6*N* hydrochloric acid.

Sorption Step. Two milliliters of 6*N* hydrochloric acid containing aluminum, gallium, and indium were diluted to 20 ml. with 2-methoxyethanol-1 and the solution was passed through the resin bed at a flow rate of 0.2 to 0.3 ml. per minute.

Washing and Elution. After sorption the resin was washed with 200 ml. of the same mixture as used for pretreatment. This volume was in all cases more than sufficient to elute quantitatively all of the aluminum. Following the removal of aluminum the adsorption bands of gallium and indium were further developed by washing with 100 ml. of a solution consisting of 70 volume % 2-methoxyethanol-1 and 30 volume % 2*N* hydrochloric acid. Afterward, gallium and indium were eluted by means of 240 ml. of 1*N* hydrochloric acid. The first 110 ml. of eluate contained only gallium, whereas the next 70 ml. contained neither gallium nor indium. In the last fraction, from 180 to 240 ml., all the indium was found (Figure 1).

B. Separation of Gallium, Indium, and Aluminum in Acetone–Hydrochloric Acid Medium.

In this case the resin was pretreated with 100 ml. of a mixture consisting of 80 volume % acetone and 20 volume % 3*N* hydrochloric acid.

Sorption Step. Four milliliters of 3*N* hydrochloric acid containing gallium, indium, and aluminum were diluted with 16 ml. of acetone and the mixture was passed through the column at a flow rate of 0.2 to 0.3 ml. per minute.

Washing and Elution. To elute gallium, 200 ml. of the same mixture as used for pretreatment was passed through the resin bed. Afterward, a solution consisting of 90 volume % acetone and 10 volume % 6*N* hydrochloric acid was used to remove indium from the column. For complete elution of indium usually 140 ml. of this mixture were sufficient. Then aluminum was eluted by passing a mixture consisting of 70 volume % acetone and 30 volume % 2*N* hydrochloric acid through the resin bed. Quantitative elution of aluminum can usually be achieved with 100 ml. of this solution (Figure 2).

C. Analysis of Aluminum Metal. One gram of the sample was dissolved in hydrochloric acid containing a few drops of nitric acid. The solution was evaporated to dryness on a water bath and the residue taken up in 6*N* hydrochloric acid and again evaporated to dryness. Finally the residue was dissolved in 20 ml. of 6*N* hydrochloric acid. A 2-ml. aliquot of this solution was then diluted to 20 ml. with 2-methoxyethanol-1 and the separation was carried out as described above under A. In the experiments involving the addition of known amounts of gallium and indium, the 2-ml. aqueous component of this sorption solution consisted of a 1-ml. aliquot of the aluminum metal solution and of 0.5 ml. each of the gallium and indium solution of the same acid concentration.

If the gallium or indium content of the sample is low, either the whole sample solution 6*N* in hydrochloric acid is diluted correspondingly with 2-methoxyethanol-1 and passed through the column as described above, or the residue is taken up in 2 ml. (instead of 20 ml.) of 6*N* hydrochloric acid. In the latter case, aluminum chloride is precipitated when adding the 2-methoxyethanol-1. After filtration and washing with a few milliliters of a mixture of the same composition, the analysis can be continued as described under A. The residue contained no traces of gallium or indium.

Table I. Distribution Coefficients of Al, Ga, and In at Varying Concn. of Solvent at Constant Overall HCl Concn. of 0.6*N*

Medium	Distribution Coefficients 5-mg. load: Aluminum	Gallium	Indium
90% 2-Methoxyethanol-1	<1	20	70
80% 2-Methoxyethanol-1	<1	10	30
70% 2-Methoxyethanol-1	<1	8	28
90% Acetone	38	<1	2
80% Acetone	25	<1	10
70% Acetone	8	20	36

The distribution coefficients of aluminum, gallium, and indium in the various mixtures were determined employing the batch equilibrium method (*4*).

The determinations of Al, Ga, and In in the corresponding eluate fractions were carried out titrimetrically with 0.01*M* or 0.001*M* solutions of EDTA (disodium salt) in the presence of suitable indicators.

RESULTS AND DISCUSSION

A. Methyl Glycol System. Determinations of the distribution coefficients of aluminum, gallium, and indium at varying 2-methoxyethanol-1 concentrations at a constant overall hydrochloric acid concentration of 0.6*N* (10% 6*N* hydrochloric acid in the mixtures) have shown (see Table I) that in the region from 70 to 90% 2-methoxyethanol-1 the separation factor of indium in respect to gallium is approximately 3. Since aluminum is practically nonadsorbable under these conditions the separation factor between this element and gallium or indium is

Table II. Separation of Al, Ga, and In in 2-Methoxyethanol-1–HCl Medium on Dowex 1

Taken, mg. Al	Ga	In	Found, mg. Al	Ga	In
5	5	5	4.97	5.01	5.02
10	5	5	10.02	5.02	4.98
50	5	5	49.86	4.99	5.03
100	5	5	99.62	5.03	5.01
100	10	10	100.2	9.97	9.98
100	25	25	100.3	25.05	24.98
100	50	50	100.5	50.1	50.08
100	75	75	100.8	74.9	75.2
100	100	100	99.8	100.2	100.1

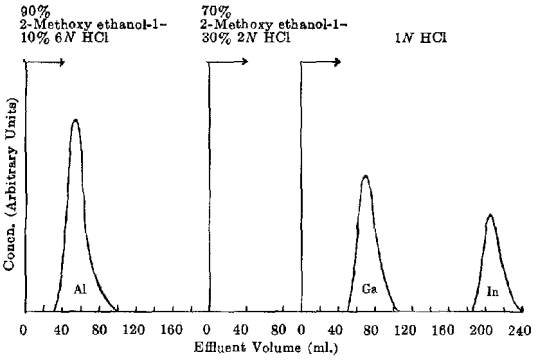

Figure 1. Separation of Al, Ga, and In in 2-methoxy ethanol-1–HCl media

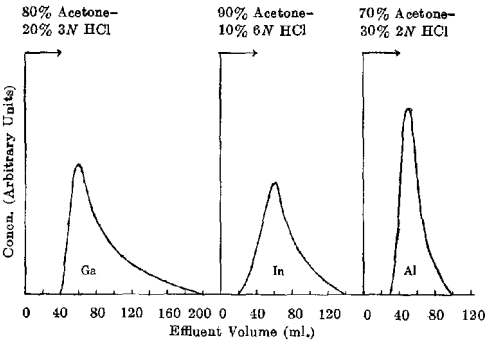

Figure 2. Separation of Ga, In, and Al in acetone–HCl media

even much higher, so that easy separation is feasible.

Based on these results a series of separation experiments have been carried out by using 90% 2-methoxyethanol-1–hydrochloric acid mixture and 1*N* aqueous hydrochloric acid (see Experimental, procedure A). The results of these investigations, as well as a typical chromatogram, are shown in Table II and in Figure 1. In all cases, quantitative separation of these three elements can be achieved.

Elution of gallium and indium with 1*N* hydrochloric acid (see Figure 1) is necessary because the time required for elution would be lengthened considerably when desorption is attempted with the 90 or 70% 2-methoxyethanol-1–hydrochloric acid mixtures. Washing the resin before elution of gallium and indium with 70% 2-methoxyethanol-1–30% 2*N* hydrochloric acid is necessary to develop the adsorption zones of gallium and indium—that is to get them farther apart than is the case when only washing with 90% 2-methoxyethanol-1–10% 6*N* hydrochloric acid alone. An alternative would be to separate the adsorbed gallium and indium by means of solvent-gradient elution using aqueous 0.6*N* hydrochloric acid to dilute a certain volume of 90% 2-methoxyethanol-1–10% 6*N* hydrochloric acid mixture employed as eluent. This technique has previously been shown by Korkisch and Feik (*5*) to be suitable for the separation of cadmium from zinc.

B. Acetone System. From the values of the distribution coefficients shown in Table I it is seen that the adsorption of aluminum in 80 and 90% acetone–hydrochloric acid mixtures is rather high when compared with that of gallium and indium. This is remarkable, since in pure aqueous hydrochloric acid solutions of any normality no adsorption of aluminum on strongly basic resins has hitherto been observed (*6*). In 70% acetone (see Table I), however, the degree of adsorption of aluminum is already much less, whereas gallium and indium are much more strongly retained in this than in the media of higher acetone content. Based on these findings the sequential separation of gallium, indium, and aluminum in this order by using in succession 80, 90, and 70% acetone solutions of the same overall hydrochloric acid concentration of 0.6*N* becomes possible (see Experimental, procedure B).

In Table III the results of several of such separations using variable amounts of aluminum, gallium, and indium are recorded. From these results, as well as from Figure 2, it is seen that in all cases—even when 100-mg. amounts of aluminum are taken—quantitative separation and recovery of all three elements was achieved.

C. Application. Table IV shows results of analyses of two aluminum samples, the gallium contents of which were previously determined by neutron activation analysis (*3*). The percentages of gallium found by the method described in Experimental, procedure C, are the mean values of 6 parallel analyses and the values are slightly higher than those determined by gamma spectrometric measurements. In order to test the separation procedure when variable quantities of gallium and indium are present, known amounts of gallium and indium (the latter element not being contained in the aluminum

Table III. Separation of Ga, In, and Al in Acetone–HCl Medium on Dowex 1

Taken, mg.			Found, mg.		
Ga	In	Al	Ga	In	Al
5	5	5	5.02	5.03	5.0
5	5	10	5.04	4.97	9.97
5	5	50	4.96	5.01	49.78
5	5	100	5.01	5.03	100.2
10	10	100	9.96	10.0	100.8
25	25	100	25.1	25.0	100.5
50	50	100	50.08	50.2	100.2
75	75	100	74.87	74.92	99.5
100	100	100	100.7	100.3	100.4

Table IV. Determination of Ga and In in Al Samples

Sample No.	Gallium found, %			
	Present method		Activation analysis (*3*)	
8206	0.0250		0.0233–0.0246	
7994	0.118		0.110–0.113	
	Added, mg.		Found, mg.	
	Ga	In	Ga	In
8206	5	5	5.0	5.01
	10	10	10.02	9.97
	15	15	14.93	14.96
	20	20	20.02	20.04
7994	5	5	4.98	5.02
	10	10	9.97	9.96
	15	15	15.01	14.89
	20	20	19.97	20.05

samples) were added prior to the column separations (see Experimental, procedure C). From the results shown in Table IV it is seen that in all cases quantitative recovery of gallium and indium was achieved. The values given in Table IV of the gallium yields have been corrected by subtracting the gallium originally present in the samples from the gallium added.

Iron(III) ions present in the sorption solution show a behavior very similar to that of gallium, so that a separation of the two elements under these experimental conditions is impossible.

Precision. The following values for precision were obtained: standard deviations in the 2-methoxyethanol-1–hydrochloric acid system; ±1.64 (Al), ±1.72 (Ga), and ±1.68 (In): standard deviations in the acetone–hydrochloric acid system; ±1.75 (Ga), ±1.82 (In), and ±1.55 (Al). The 5-mg. quantities of gallium and indium and the 100-mg. amounts of aluminum added and subsequently found (Tables II, III, and IV) were taken as the basis for the calculation of the standard deviations.

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Anion Exchange Behavior of Alkali and Alkaline Earth Elements in Dioxane–Mineral Acid Media

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▷ **A distribution study was made of the behavior of Group I and II elements between the solution phases dioxane–HCl–H_2O and dioxane–HNO_3–H_2O and Dowex 1-X8 resin, and the most favorable separation conditions were ascertained. Group II elements (Mg, Ca, Sr, and Ba) were separated from each other by a dioxane–HNO_3–H_2O eluent using a gradient elution technique. Only a partial separation of Group I elements was effected by the same technique. A separation of Group I from Group II employing dioxane–HCl–H_2O as eluent was demonstrated. The effect of dioxane content, acid concentration, loading, and analytical advantages are discussed.**

ION EXCHANGE coupled with mixed solvent elution techniques has proved to be successful as a general separation method. Both anion and cation exchange resins combined with various alcohol or acetone solutions of mineral acids as solvents have been employed for the separation of transition elements (*1, 6, 20*), U and Th (*11–13*), the rare earths (*3, 4, 16*), and Group I and II elements (*5, 7, 8, 19*).

Dioxane offers considerable promise in mixed solvent ion exchange systems because of its extremely low dielectric constant [2.2], high miscibility with aqueous acid media, and fair solubility for some inorganic salts in mixed aqueous solutions. The HNO_3 and HCl components of the eluent solution lend themselves to simplicity of removal after separation, whereas many good selective ion exchange systems for Groups I and II in aqueous media containing complexing agents (*15, 17, 18*) may require destruction for removal. It might also be noted that dilute HCl or HNO_3 alone will not cause Groups I or II to be absorbed on an anion exchange, column (*2, 14*); it is mandatory that an organic solvent be present in order to enhance complex formation or ion association, thus causing the species to have a tendency to exist in the resin phase (*11*). Although studies involving lithium in mixed solvents have been reported (*9, 10*), no systematic fundamental study with a low dielectric, mixed solvent anion exchange system has been applied to Group I. Further, it was anticipated that a low dielectric system might enable one to perform Group II separations at lower over-all percentages of organic solvent than those reported with alcohol–HNO_3–H_2O systems (*7, 8*). Thus both the dioxane–HNO_3–H_2O and dioxane–HCl–H_2O systems were examined with a strongly basic anion exchange resin for most elements in Groups I and II over a series of different dioxane and acid concentrations. Batch experiments were first employed to survey the whole realm of concentrations involved and then column techniques were used to evaluate the more favorable analytical possibilities.

EXPERIMENTAL

Reagents and Solutions. Hydrochloric acid, nitric acid, and salts of Group I and II elements were of reagent grade and used directly with no further purification. The 1,4-dioxane used specifically was Fisher "Certified" reagent grade. For most experiments Dowex 1-X8, 100 to 200 mesh (J. T. Baker Co.) was used. The resin was purified in the chloride form by passing, in a column operation, a large excess of 6*M* HCl, washing throughly with excess distilled, deionized water until a negative acid test, passing absolute ethyl alcohol, air drying for a day, heating at 70° C. for 2 hours, and then storing in a desiccator dried by $CaCl_2$ until used. The nitrate form of the resin was prepared exactly as the chloride using 5*M* HNO_3.

Stock solutions of alkali and alkaline earth chlorides and nitrates were prepared by dissolving the respective salts in either 0.1*M* HCl or 0.1*M* HNO_3 as desired. Radioactive tracers Na^{22}, K^{42}, Rb^{86}, Ba^{133}, and Sr^{85} were added to their respective solutions. These tracers were obtained from Oak Ridge National Laboratory and IsoServe Inc.

Sample solutions of about 51 ml. were prepared by mixing 1.0 ml. of stock metal solution to a solution of known volumes of acid solution and dioxane. Calculations involving concentrations were made neglecting the small (~1%) volume changes of the equilibrated systems. For all sample solutions used the concentration of metal used, unless otherwise stated, was $1.4 \pm 0.1 \times 10^{-3}N$. Thus a 0.98*M* HNO_3 solution, $1.4 \times 10^{-3}N$ in Ba, was prepared by adding 1.0 ml. of 0.073*N* $Ba(NO_3)_2$ (0.1*M* in HNO_3) with 10 ml. of 5.0*M* HNO_3 and 40 ml. of dioxane.

Batch Experimental Procedure. In all cases a nitrate solution was used with a nitrate form resin, a chloride solution with a chloride form resin. To an exactly known weight (approxi-

Table I. K_D Values for the System Dioxane–HCl–H_2O

Over-all concentration of mixed solvent system[a]		Element								
Dioxane, %	HCl, M	Li	Na	K	Rb	Cs	Mg	Ca	Sr	Ba
88	0.10	14	13	13	16	22	36	103	72	77
88	0.002	24	27	27	30	33	131	218	241	258
78	0.49	2.4	2.1	2.8	2.8	2.9	5.1	6.7	6.7	5.7
78	0.10	2.0	2.6	3.6	2.8	3.0	7.4	9.4	10	9.6
78	0.002	0.6	1.7	3.9	3.2	4.1	4.0	6.2	7.2	7.6
59	2.9	≤0.3	1.0	0.8	≤0.1	0.9	≤0.6	≤1.1	0.9	0.8
59	0.49	0.6	0.5	1.0	0.6	<0.5	<0.8	1.8	1.5	1.0
59	0.002	0.3	0.5	0.8	0.3	<0.4	≤0.9	≤0.4	<0.1	≤0.2
39	2.9	0.7	0.3	<0.3	0.6	<0.4	≤0.6	≤1.0	0.6	0.5

[a] A series of runs at 39% and 20% dioxane from 0.002M to 5.9M HCl, not reported here, all yielded K_D values below 1.

mately 1 gram) of resin, in a ground glass 125-ml. Erlenmeyer flask, was added 25 ml. of the typical sample solution described above and the mixed system was agitated slowly with a mechanical shaker for a period of 12 to 20 hours at room temperature. Measurements taken over an extended length of time showed that apparent equilibrium was attained after about three hours. Appropriate samples were then taken and measured either by scintillation counting (Na^{22}, K^{42}, Rb^{86}, Ba^{133}, and Sr^{85}) or by flame photometry (Li at 671 mμ, K at 766 mμ, Cs at 456 mμ, Mg at 285 mμ, and Ca at 423 mμ). Counting was performed so as to minimize statistical errors. Most batch experiments were run in duplicate. The batch distribution coefficient, K_D, is defined as follows:

$$K_D = \frac{\text{concentration of metal/1 gm. dry resin}}{\text{concentration of metal/1 ml. solution.}}$$

Column Operation Procedures. Separations were performed with Dowex 1-X8 (200 to 400 mesh, nitrate or chloride form) with 1.1-cm. diameter columns of various lengths. The resin was preequilibrated with the same medium as the sample. The sample (approximately $1.4 \pm 0.1 \times 10^{-3}$ meq. in 1 to 5 ml.) was introduced and then either a gradient elution or a constant condition elution was used. For example, Group II elements were separated with a 21-cm. column using a gradient system such that the dioxane percentage decreased from 88 to 59 in decreasing increments of about 2–3% per 2 ml. of eluent. A similar technique was used attempting to separate Group I elements using a 48.5-cm. column and an approximate decrease of about 0.5% per 4 ml. from 93% dioxane-0.49M HNO_3 to 78% dioxane-0.49M HNO_3. Separation of Group I from Group II was effected using a constant system consisting of 78% dioxane-0.49M HCl. Elution curves were characterized by appropriate scintillation counting of tracers or by flame photometry.

RESULTS AND DISCUSSION

The over-all results of extensive batch experiments for the systems dioxane–HCl–H_2O and dioxane–HNO_3–H_2O are summarized in Tables I and II, respectively. Both systems show, in general, that as one goes down in either group or across from Group I to II an increase in K_D occurs. Another observation common to both systems is that K_D for a particular element increases significantly when the organic solvent content is raised, holding other conditions constant. Also noted is that, in general, for equal conditions, the chloride system produces higher K_D values. One further observation for both systems is that selectivity for the resin, at low organic solvent content, is not enhanced significantly by increased acid concentration.

The effect of organic solvent content upon K_D is shown in Figure 1 for two representative elements of Groups I and II in a low ionic strength environment. As seen, K_D increases appreciably as higher percentages are encountered. This phenomenon has been well observed for many mixed organic solvent systems (*11*) and is believed to be predominantly a function of the dielectric constant of the system. Group I and Group II data obtained by varying the solvent used, as given in Table III, indicate that the over-all dielectric constant of the solvent is the major factor here. When mineral acids are introduced the dielectric constant effect is lessened, especially in Group II. Methanol (dielectric constant 32.6) yields comparable K_D values for Ba. These phenomena, most probably acid complexing ability, are still under study. However, it is still evident that a high percentage of a low dielectric medium must be employed in order to cause Group I species to be highly absorbed on an anion exchange resin. Comparable percentages of the same organic solvent are also required for Group II absorption.

The effect of kind and concentration

Table II. K_D Values for the System Dioxane–HNO_3–H_2O

Over-all concentration of mixed solvent system		Element								
Dioxane, %	HNO_3, M	Li	Na	K	Rb	Cs	Mg	Ca	Sr	Ba
93	0.49	13	29	38	[a]	[a]	87	135	738	[a]
93	0.10	18	30	40	[a]	[a]	77	92	361	[a]
93	0.002	20	32	47	[a]	[a]	84	91	300	1002
88	0.98	4.1	6.3	6.0	7.4	11	11	32	131	371
88	0.49	3.9	5.9	5.1	7.5	7.3	9	19	54	158
88	0.10	4.8	7.0	8.1	8.9	9.7	6	18	40	105
88	0.002	4.4	7.9	9.7	11	11	11	22	37	105
78	0.49	1.6	1.0	1.4	2.2	1.9	0.5	3.4	7.0	16
78	0.002	0.5	1.0	0.5	...	...	≤0.5	1.0	2.5	6.4
69	0.49	...	...	...	...	...	≤0.5	1.0	2.3	5.1
69	0.002	...	...	...	...	...	≤0.5	≤0.5	≤0.5	0.7

[a] Species insoluble at concentration involved.

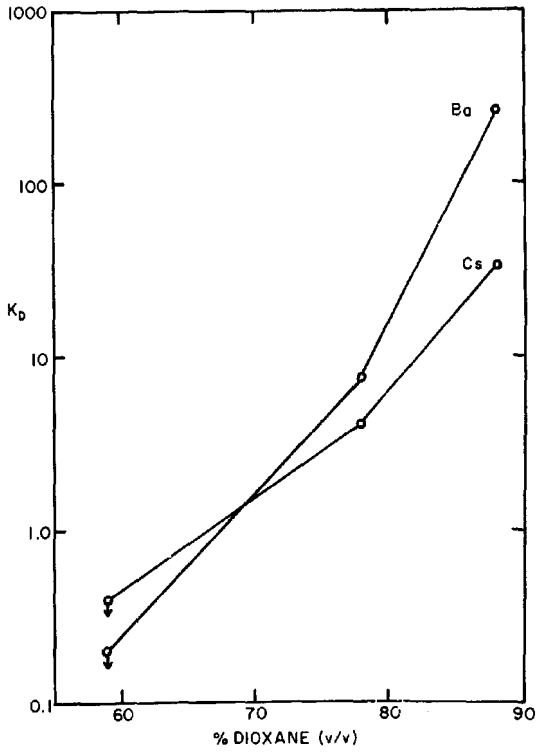

Figure 1. Effect of dioxane concentration upon K_D of representative Group I and II elements on a strongly basic anion exchange resin. 0.002M HNO_3

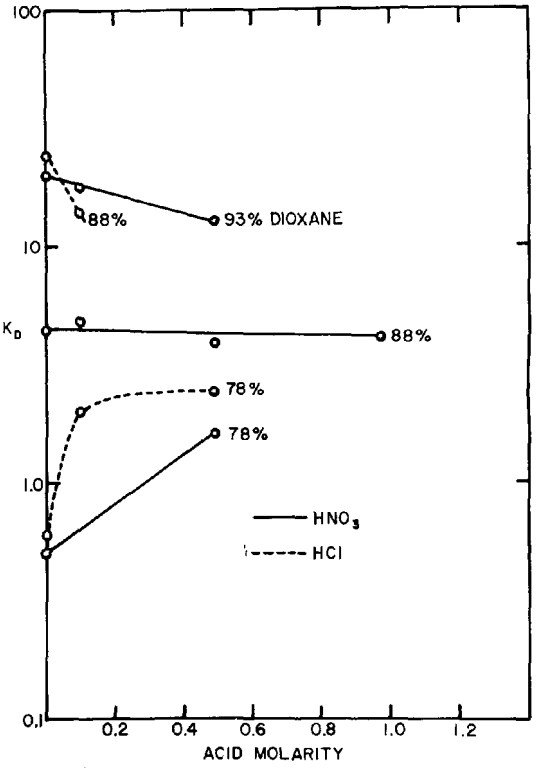

Figure 2. Effect of acid concentration upon K_D for lithium in various dioxane solutions

of acid upon K_D is shown in Figure 2. Qualitatively both acids have the same effect. At the higher organic solvent contents, K_D decreases with acid concentration and at the lower contents the reverse is true. This may be explained on the basis that at higher organic solvent contents, acid competes for the resin because of the association of the acid ions, whereas at lower organic solvent content the acid is not associated sufficiently to prevent it from acting as a complexing agent for the salt. The more or less constant values for the 88% dioxane-HNO_3 system represents an intermediate stage. This view is supported in part by the fact that absorbability of HCl and HNO_3 from mixed dioxane-H_2O solutions increases with increasing dioxane content as seen in Table IV.

The effect of resin loading upon K_D of typical elements Na and Sr was investigated for the range 2.5×10^{-3} to 3.7×10^{-1} meq. on a 1-gram resin. For Dowex 1-X8 (100 to 200 mesh) this represents approximately a 0.1 to 15% loading factor. K_D values for Na at dioxane percentages 78, 88, and 93 and for Sr at dioxane percentages 69, 78, and 88 were evaluated in this range where the HNO_3 concentration was 0.49M. In all cases negligible dependence upon loading was observed. Only at the lowest percentage dioxane solutions was a very slight decrease of K_D observed as higher loading was introduced.

Figures 3 and 4 illustrate some analytical separation relationships from element to element for the HCl and HNO_3 systems. It is evident that the HNO_3 system offers, in general, greater over-all separation factors, especially for Group II. The HNO_3 system (Figure 4) also shows that where the slope for Group II remains somewhat constant as the organic solvent content is increased, the slope for Group I increases slightly offering better separation factors. These more favorable separation factors for Group I at high organic solvent contents are offset by high K_D, thus requiring lengthy, large volume, broad band elutions. The HCl system, however, does offer a Group I–Group II separation at 78% dioxane-0.49M HCl. The column separations are subsequently described.

Figure 5 shows the results of a 88% to 59% dioxane-0.49M HNO_3 gradient elution column separation of four elements of Group II. In each case about 95% pure element was realized.

Table III. Dependence of K_D Upon Organic Solvent

Solvent	Dielectric constant of pure solvent ϵ	K_D Na	K_D Ba
p-Dioxane	2.2	32	6.4
Isopropyl alcohol	18.3	7.5	2.1
Acetone	20.7	2.8	...
Ethyl alcohol	24.3	1.2	...
Methyl alcohol	32.6	0.6	0.3

Conditions employed: Na values obtained at 93% (v./v.) organic content, 0.002M HNO_3. Ba values obtained at 78% (v./v.) organic content, 0.002M HNO_3.

Table IV. K_D Values of HCl and HNO_3 in Various Dioxane Concentrations

Concentration dioxane, %	K_D HCl	K_D HNO_3
0	<0.5	<0.5
80	2.1	1.1
90	...	4.2
95	13	...

Conditions employed: 25 ml. of 0.1M acid agitated with 1 gram of resin in same form as acid anion.

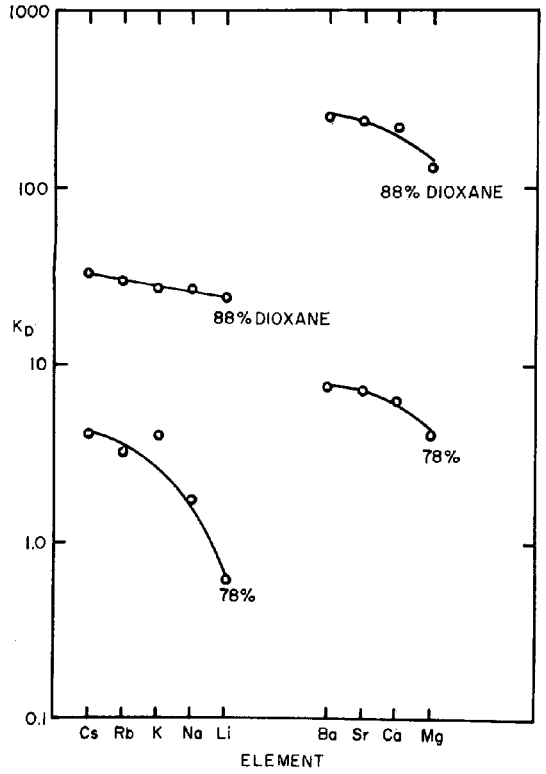

Figure 3. Periodic variation of K_D with Group I and II elements; 0.002M HCl and varying dioxane percentages

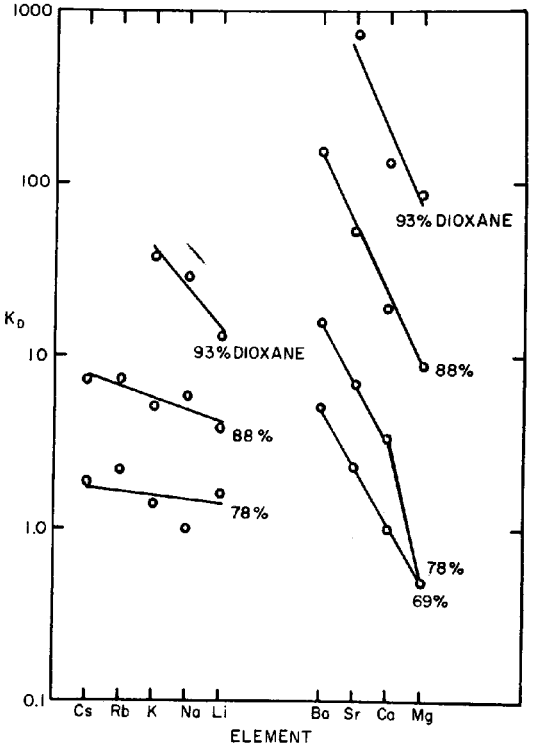

Figure 4. Periodic variation of K_D with Group I and II elements; 0.49M HNO_3 and varying dioxane percentages

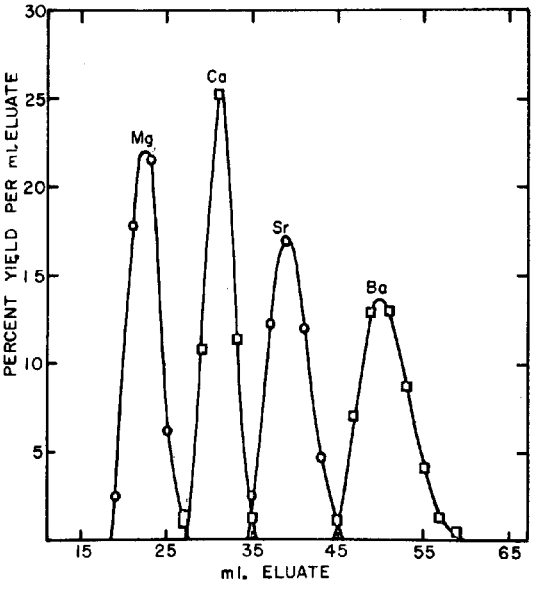

Figure 5. Gradient elution behavior of Group II elements

21-cm. column, 0.30 ml. per minute flow rate, 1.0-ml. sample, 1.4 ± 0.1 × 10^{-3} meq. each element, eluent 0.49M HNO_3 varying from 88% to 59% in dioxane

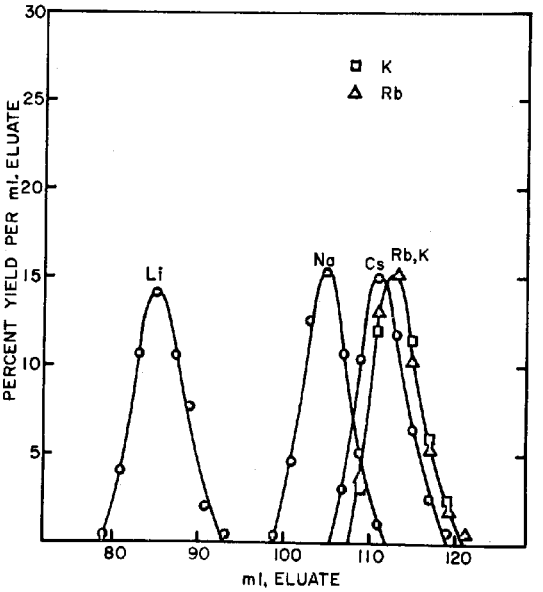

Figure 6. Gradient elution behavior of Group I elements

48.5-cm. column, 0.30 ml. per minute flow rate, 5.0-ml. sample, 1.4 ± 0.1 × 10^{-2} meq. each element, eluent 0.49M HNO_3 varying from 93% to 78% in dioxane

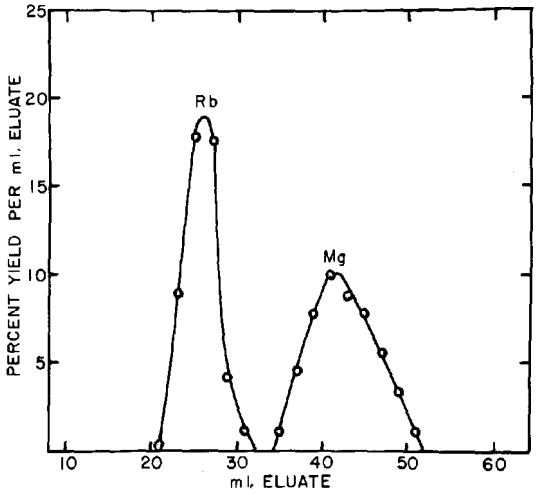

Figure 7. Separation of alkali and alkaline earth elements

20.5-cm. column, 0.33 ml. per minute flow rate, 1.0-ml. sample, 1.4 ± 0.1 × 10^{-3} meq. each element, eluent 78% dioxane-0.49M HCl

An even better separation is possible using a longer column. The gradient technique causes a pronounced sharpening and compressing of the bands. Previous attempts using a constant elution technique resulted in considerably broader, more contaminated separations.

Figure 6 shows the results of an attempt at separating Group I elements from each other using a long column and a gradient elution system employing 93% to 78% dioxane-0.49*M* HNO_3. Lithium may be separated from all the others; however, complete Na-K, Na-Rb, and Na-Cs separations are not deemed possible. Another system employing 78% dioxane-0.002*M* HCl eluent did not demonstrate any clear-cut separation of Li or any other element from the rest, only partial separations of each. The lack of complete separations could be anticipated from the low separation factors offered by the systems.

The experimental column behavior of Rb and Mg, shown in Figure 7, using 78% dioxane-0.49*M* HCl as an eluent demonstrates the feasibility of separation of Group I from Group II. These two elements represent the least favorable separation factor between the two groups. Batch experimental data (Table I) show Rb typical of Group I whereas Mg has the lowest K_D for Group II elements. The group separation was further confirmed by a similar separation of Rb from Ba.

The approach to separations involving dioxane-acid coupled with gradient elution has offered several analytical advantages. Group II elements can be separated in a time comparable to most ion exchange methods used presently and more important the volumes involved are very small eliminating any additional concentration. Further, the gradient elution technique is capable of automatic treatment. Also the fact that the eluate is merely a simple aqueous HCl or HNO_3 solution containing a volatile organic substance might be an advantage in those cases where additional chemical steps are involved. The separation of Group I from Group II can now be accomplished by an anion exchange approach. This technique should also lend itself to use where a Group II trace element is to be separated from a nonadjacent Group II matrix element. With regard to use of these separations in an analysis of a complex material, most interferences should be easily removed by prior passage of the sample through an anion exchange column using an aqueous HCl medium. According to Kraus and Nelson (*14*) only Groups I and II, some elements of Group III, Ni, Cr, and Th are eluted. This aqueous system, however, does not fractionate the Group I and II elements, whereas some separations have been achieved here with nonaqueous media.

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Thermal Expansion Apparatus for Use with Differential Thermal Analysis Equipment

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▶ **Auxiliary apparatus is described for use in conjunction with differential thermal analysis (DTA) instruments to measure thermal expansion of solids. By use of the temperature programmer, amplifiers, and recorder in DTA equipment, the necessary additional apparatus is minor. Sample expansion is mechanically and electrically amplified and recorded automatically with excellent accuracy. This instrument can determine coefficients of thermal expansion of solid samples over a wide temperature range. For polymers, it provides a measurement of both the glass transition temperature (T_g) and, through use of expansion coefficients above and below T_g, measurements of crystallinity in some cases. Considerably less effort is required to obtain results that are equivalent to dilatometric data than with previously reported methods.**

SEVERAL EXPERIMENTAL METHODS have been used to determine glass transition temperature, T_g, of polymers. These include measurement of changes in specific volumes (*5*, *7*), various dynamic mechanical properties (*1*, *20*), specific heat (*6*), viscosity (*26*), static dielectric constant (*19*), penetration (*11*, *23*), use of strain gages (*13*), differential pressure (*15*), beta-ray absorption (*27*), x-ray diffraction (*21*), thermal expansion (*2*, *9*, *16*), broad line NMR (*18*), and differential thermal analysis (*8*, *17*, *24*, *25*). Many of these methods are time consuming. Considering the importance of T_g in the physical behavior of polymers, it is desirable to have a rapid and automatic method with which measurements can be carried out routinely.

Automatic dilatometers were described by Boyer and Spencer (*7*). The determination of height of a mercury column in the dilatometer is not easily read automatically with high precision, nor are commonly used liquid baths readily controlled by an automatic temperature programmer.

Use of penetrometer measurements to determine melting and glass transition temperatures of polymers was described by Edgar and Ellery (*11*, *12*). In addition, Rybnikar (*22*, *23*), reported temperatures for the onset of viscous flow of the amorphous phase by the penetrometer method. Extensive work by Grieveson (*14*) showed that under high loads, 400 grams per sq. mm., the T_g's determined by the penetrometer method ranged from 3° to 10° C., with an average difference of 5° C., higher than T_g's from dilatometer measurements.

Thermal expansion measurements are equivalent to dilatometric methods for determining T_g. One method of recording thermal expansion is to measure the change in dimension by an optical lever (*10*). The tripod displacement is an inconvenient function to record. The vertical displacement of the core of a variable reluctance transformer furnishes a more easily recorded variable. The latter has been used to record thermal expansion although few instrumental details were given (*16*).

DTA equipment usually has both automatic temperature programming and recording so that unattended measurements can be made. Determination of T_g by DTA requires a very uniform heating rate, a sample geometry that does not change radically on heating, and a high degree of sensitivity. These requirements are necessary because transition temperatures are evidenced only by a shift in base line. To avoid these difficulties and yet retain the use of the major, expensive components of a DTA apparatus, it is necessary to measure some other sample property and substitute this signal for the ΔT signal in conventional DTA.

The DTA apparatus used in this study (*3*), has four basic components: a temperature programmer to produce a defined, variable temperature program; amplifier and circuitry to measure precisely sample temperature, T; a similar amplifier and circuitry to determine the temperature differential, ΔT, between sample and inert reference; and an x-y recorder which records T on the x axis and ΔT on the y axis.

This work describes an auxiliary instrument to permit recording precise measurement of the change in dimensions of a test sample during a

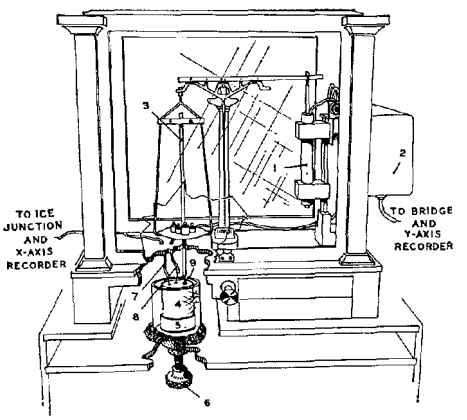

Figure 1. Recording thermal expansion apparatus

1. Movable core transformer in rack and pinion mount
2. 100 turns per inch vernier
3. Quartz extension rod
4. Aluminum furnace block surrounded by liquid nitrogen Dewar flask
5. Quartz base plate
6. Sample position vernier
7. Temperature program thermocouple
8. Sample temperature thermocouple
9. Quartz foot on sample

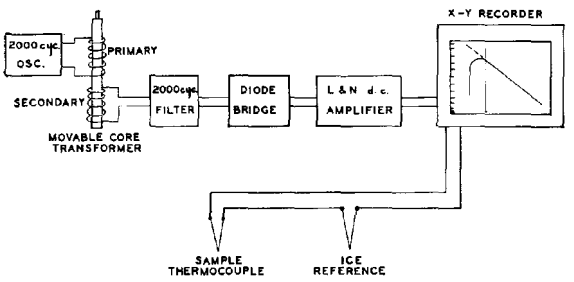

Figure 2. Block diagram: thermal expansion apparatus

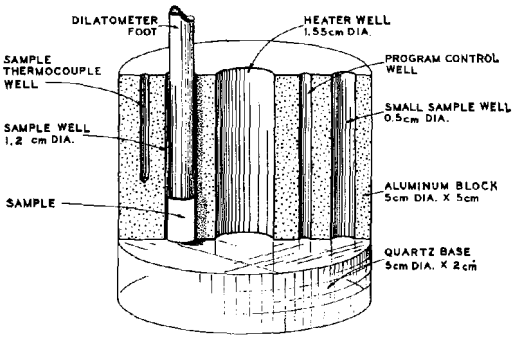

Figure 3. Cutaway drawing of aluminum sample furnace

controlled temperature program. It substitutes a signal proportional to a change in length of the test sample, ΔL, for the ΔT signal in DTA. Thus, the four basic components of the DTA, with their attendant high precision and concomitant high cost, are utilized to make other than DTA measurements.

EXPERIMENTAL

Instrumentation. The thermal expansion apparatus used in this study is shown in Figures 1 and 2. The primary sensing element is a Computran 70–3005 movable core transformer driven by the 50-volt output of a 2000-cycle Type 1214-E General Radio unit oscillator. The 2000-cycle source was chosen to avoid 60-cycle harmonic interference. The output of the transformer secondary winding is passed through a 2000-cycle narrow band-pass filter and is rectified by a diode bridge of standard design. The rectified signal is fed via shielded cable to a Leeds & Northrup Model 9835-A direct current amplifier. The output of this amplifier is applied to the y axis of a Moseley Autograph x-y recorder operated in the null potentiometer mode at a sensitivity of 0.5 mv. per inch.

The sample temperature is measured by a 27-gage copper-constantan thermocouple with an ice reference junction. The output of the thermocouple is applied directly to the x axis of the recorder. The recorder sensitivity of 0.5 mv. per inch provides a 10° C. per inch temperature scale which is adequate for most expansion coefficient measurements. Further amplification of the signal is obtainable if required via a second Leeds & Northrup Model 9835-A amplifier.

An analytical balance, Ainsworth Type TC, was used in this instrument so that the load placed on the sample could be controlled precisely. The quartz knife edges give excellent low friction bearings of well known reliability. The balance beam was lengthened by a factor of two on the transformer core side of the major knife edge so that a direct twofold mechanical amplification was obtained. The beam was extended with beam material taken from a second balance to avoid thermal distortion.

The field winding of the transformer, shown as a cylinder in Figure 1, is carried on a precision vernier rack and pinion support. The vernier covers a distance of 1 inch in 100 turns. A similar vernier screw is placed under the sample carriage so that precise positioning of the sample and initial nulling of the system are possible. This system is necessary because of the high electrical amplification of the apparatus and the narrow range of the direct current amplifier.

The aluminum sample furnace which is used is shown in Figure 3. The sample wells pass completely through the aluminum block so that the base of the sample is resting on a thick quartz plate. In this way, the thermal expansion of the apparatus as detected by the balance foot without a sample is limited to that of quartz. A relatively small drift is noted as shown on the blank run in Figure 4. The block is heated by a 100-watt cartridge heater inserted in the aluminum block (see Figure 3). Liquid nitrogen is used as coolant.

The apparatus, as described here, has a maximum usable sensitivity of 2.5×10^{-5} inch of sample expansion per inch of recorder deflection. The ultimate sensitivity of the apparatus is limited by the vibration of the room and cement floor. The transformer output is linear in the range 1×10^{-5} to 1×10^{-2} inch where zero is taken as the zero induction point of the transformer.

RESULTS AND DISCUSSION

Figure 4 shows three typical records from the recording thermal expansion apparatus. The lowest line represents the expansion of a 1-inch length of quartz. This illustrates instrument sensitivity; in practice this is probably as small an expansion coefficient as will be encountered.

The middle line shows the expansion of a copper bar 1 inch long. The calculated expansion coefficient agrees within 0.2% of the value cited in the International Critical Tables. By contrast, ICT values required a specimen 3 feet long and tedious optical measurements. This contrast illustrates the ease with which measurements can be made by our method.

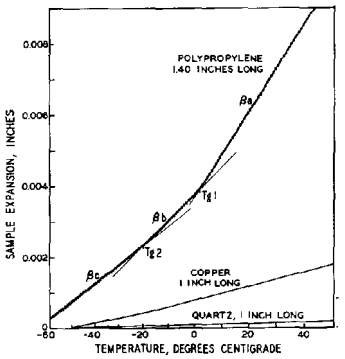

Figure 4. Record of thermal expansion

The upper line in Figure 4 shows the expansion record for a sample of polypropylene. The record indicates the ease of determining the T_g of polymers and shows clearly the two widely reported T_g's for polypropylene. Through use of the three expansion coefficients β_a measured above the higher T_g, β_b, the coefficient between the two glass transitions, and β_c determined below the lower T_g, it is possible to calculate tacticity values as described by Beck, Hiltz, and Knox (4).

For example, in the sample measured in Figure 4, $\beta_a = 1.32 \times 10^{-4}$, $\beta_b = 0.798 \times 10^{-4}$, and $\beta_c = 0.480 \times 10^{-4}$; linear expansion coefficients are converted to cubical form by multiplying by three to give

$$\beta_a - \beta_b = 1.566 \times 10^{-4}$$
$$\beta_b - \beta_c = 0.480 \times 10^{-4}$$

Utilizing the correlation cited (4) leads to:

amorphous isotactic content =

$$\frac{1.566}{7.2} = 21.8\%$$

and amorphous atactic content =

$$\frac{0.624}{7.2} = 8.7\%$$

A check is available by comparing the crystallinity from this method, 100 −

21.8 − 8.7 = 69.5% *vs.* the value of 66% from density-crystallinity correlations.

The recording thermal expansion apparatus described in this paper has been demonstrated to have high sensitivity. While it is discussed as an attachment or addition to a specific DTA apparatus (*3*), its fundamental design can be incorporated into a suitable attachment for any well designed DTA machine. The speed and ease of operation which we have demonstrated recommend it for general use.

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Automatic Data Processing, Interpreting, and Reporting of Results of Emission Spectrographic Analyses

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▷ **A generalized Fortran computer program has been developed which calculates and reports the results for the common-matrix method of emission spectrographic analysis. If the input contains data for more than one line for an element, the program computes the proper value to report corrected for interference from other elements. The elements to be determined, the lines used for their determination, and the element to be used as the internal standard are left entirely to the option of the user. The computer calculation costs for an IBM 7090 at $500 per hour is only 27 cents per sample of 15 elements.**

ONE OF THE IMPORTANT applications of emission spectrometry is in making a rapid survey of the elements present and estimating their concentration in miscellaneous inorganic materials. When the wide variety of materials to be analyzed precludes the use of calibration data for specific mixtures of elements, most laboratories have adopted a general purpose procedure which, though less accurate, will give semiquantitative results without special calibration. The so-called common-matrix emission method (*1*) has been used successfully for this purpose in the Emeryville laboratories for many years. This method is considered to give an accuracy within a factor of two for each detectable element.

The common-matrix emission method may be briefly described as follows. The sample is diluted with a known, but variable, amount of lithium carbonate and burned in an electric arc; the emission spectrum is recorded photographically. Several portions may be burned and a separate spectrum obtained for each portion to reduce the effects of random fluctuations. Each spectrum is inspected for one or more lines of each element of interest, and the transmittances of these lines are measured with a densitometer.

The lines chosen are always lines for which calibration data have been obtained previously. In general, calibrations are prepared for several lines of different sensitivities for each element to permit reliable measurements over a wide range of concentrations. The transmittance for each line is converted to a corresponding intensity value using an emulsion calibration curve (gamma curve). Then the intensity for each of the selected lines on a given spectrum is divided by the intensity of the lithium line on the same spectrum.

If several spectra are obtained for a sample, the resulting intensity ratios are averaged and the corresponding concentration of the element is read from a calibration curve. If the intensity ratio is above the upper end of the calibration curve or below the lower end, the concentration is considered as being greater than, or less than, the value corresponding to the upper or lower end of the calibration curve. A greater-than value is also taken when the transmittance of the spectral line is less than some limiting value. These values, when corrected for the dilution in lithium carbonate, give the concentrations of the elements in the sample.

Several different concentrations may be computed for a given element through the measurement of several spectral lines or occasionally through the use of more than one (rarely more than two) different dilutions of the sample in lithium carbonate. These various results are seldom identical, usually concordant, and occasionally quite different. In arriving at a decision as to the result to report for a given element, it is convenient to divide the various results into four classes.

Class 1. Calculated as described above when both the transmittance and the intensity ratio fall within predetermined limits.
Class 2. Greater-than values.
Class 3. Less-than values.
Class 4. Not detected. This condition is encountered when an analysis for a given element is requested but no spectral line is observed. The concentration is taken as less than the con-

centration for the lower end of the calibration curve.

If there is a single class 1 value and the particular spectral line has little interference from other elements, the class 1 value is reported. Where there are two or more class 1 values, some intermediate value is reported, taking into account such factors as the amount of spectral interference, the reliability of the transmittance measurements, and the lithium carbonate dilution factor. Higher dilutions are usually considered to be more reliable because these reduce interelement effects. If there is no class 1 value but there are class 2 or class 3 values, the result is reported as (greater than the largest class 2 value assuming little interference from other elements) or less than the smallest class 3 value. If there are both a class 2 and a class 3 value, the result is reported as being between these two values. Class 4 values are reported only when there is no other result available for that particular element.

The operations described above for the analysis of a sample can be divided into four steps:

1. Preparation of the sample and obtaining the spectrum
2. Selecting the proper lines and measuring the transmittances
3. Computing the concentrations for each element
4. Evaluation of the results

An inexperienced analyst can be trained to carry out steps 1 and 2 in a very short time; he might, however, have difficulty in choosing the best line for a given element because the most obvious line may be caused by interference from another element. Step 3 is likewise easily learned, but this operation is very tedious, time-consuming, and subject to errors because of the large amount of data to be handled. Step 4 requires a great deal of experience and judgment.

The most obvious application of a computer to emission analyses is in step 3. However, the use of a computer in step 4 is perhaps of even greater value, both because of the time saved and because of the elimination of much of the training required for the analyst. The computer, if properly programmed, has the additional advantage of making consistent and more objective decisions which are free from arithmetical errors. The goal of this project has been to develop a program which will accept the transmittances of the selected lines as input and then prepare a finished analytical report. Ideally, this report should be equivalent to the report which would be written by the most highly trained analyst after a detailed analysis of all of the data.

Although the program described below nearly reaches this ideal goal, there are always unusual cases which are very difficult to anticipate or which occur so seldom that their inclusion in the program is not justified. When such situations occur, they are best handled by suitable modification of the report. This program incorporates one feature not usually included in the manual calculations. All lines used in the analysis are checked for possible interference from other elements and a correction is applied where necessary.

Table I. Work Sheet for Common Matrix Emission Analysis

Report No. 149824. Sample No. 2.
Sample weight, 0. Ash weight, 0. Dilution, 10.0. State, ash

Element		Transmission			Intensity ratio				Concn.[a]
Silicon	2514.3	8.0	4.5	3.0	2.00	2.37	3.38	2.58	>10.000[b]
Magnesium	2795.5	9.0	5.4	9.8	1.83	2.07	1.40	1.77	0.142
Magnesium	2779.8	85.0	70.0	83.0	0.14	0.18	0.12	0.15	0.045
Lead	2833.1	23.5	19.0	35.0	0.83	0.77	0.46	0.69	0.232
Iron	3008.1	1.0	1.0	1.0	9.94	7.69	8.14	8.59	>10.000
Tin	3175.0	100.0	100.0	100.0	0.	0.	0.	0.	ND[c] 0.030
Aluminum	2660.4	22.0	16.5	20.5	0.88	0.87	0.77	0.84	2.258
Molybdenum	3132.6	56.0	21.5	40.0	0.34	0.69	0.40	0.48	0.015
Copper	3274.0	1.0	1.0	1.0	9.94	7.69	8.14	8.59	> 0.100
Copper	2961.2	100.0	100.0	100.0	0.	0.	0.	0.	ND 1.000
Sodium	3302.3	59.0	19.0	26.5	0.32	0.77	0.61	0.57	0.123
Titanium	3372.8	4.2	3.3	5.5	3.22	2.98	2.16	2.79	1.710
Titanium	3217.1	44.5	30.0	43.5	0.44	0.51	0.37	0.44	1.173
Silver	3382.9	76.0	47.0	60.0	0.19	0.32	0.25	0.26	< 0.010[d]
Nickel	3414.8	5.8	1.0	2.0	2.54	7.69	4.60	4.94	0.731
Nickel	3391.0	51.0	14.0	28.5	0.36	1.00	0.57	0.64	0.435
Manganese	2576.1	38.0	24.5	38.5	0.52	0.62	0.42	0.52	0.386
Strontium	4077.7	70.0	59.0	70.0	0.23	0.24	0.19	0.22	< 0.010
Chromium	4351.8	5.7	1.0	3.0	2.57	7.69	3.38	4.55	2.000
Chromium	4359.6	55.0	18.0	41.0	0.34	0.81	0.39	0.52	1.458
Calcium	4302.5	9.3	3.5	9.0	1.78	2.85	1.50	2.04	0.252
Calcium	4318.7	30.0	15.5	30.5	0.66	0.92	0.53	0.70	0.301
Barium	4554.0	64.0	43.0	60.0	0.28	0.35	0.25	0.30	< 0.010
Tungsten	4008.8	20.0	11.3	19.5	0.96	1.19	0.80	0.98	1.650

[a] Based on sample before dilution with lithium carbonate.
[b] > = Greater than amount specified.
[c] ND = Not detected. If present, concentration is less than amount specified.
[d] < = less than amount specified.

PROCEDURE

General Description of the Program. This program is designed for the handling of groups of 1 to 5 samples which are submitted together on a single request. Sample data and the transmittances for each of the lines of interest, with numbers identifying the lines, are punched into IBM cards. These data, together with the calibration data and the program cards, are the input to the computer. The first part of the program closely parallels the manual operations described above. It computes for each spectrum the relative intensity and intensity ratio for each line. Thus, if there is more than one spectrum for the same sample dilution in lithium carbonate, the intensity ratios are averaged and the corresponding concentration computed. The film calibration curve and the curve of element concentration *vs.* intensity ratio are all defined in terms of power series with the constants given on separate calibration data cards.

After completing these preliminary calculations, the computer prints a work sheet on which are tabulated the input data, the computed intensity ratios, the averaged ratio, and concentration for each line. In the absence of any better symbol, left-hand and right-hand parentheses are used to indicate less than and greater than. A separate page is used for reporting the data for each sample. Table I shows a typical work sheet. The work sheet is very useful for checking both the accuracy of the input data and the reasonableness of the final report.

The final phase of the program consists of correcting the results for possible interference from other elements, choosing the proper value to report for each element, and then preparing the final report. Because no correction is made for possible interference on class 3 or class 4 values, these values are all picked out first and stored for possible later reference. If there are several class 3 or class 4 values for an element, only the smallest value is retained. The correction for interference from other elements and the choice of the best values to report are accomplished by computing the least-squares solution for a set of simultaneous equations using suitable weighting factors for each equation. Each of the individual equations has the following form:

$$C_i + \sum_{k=1}^{n} K_{kj} C_k = C_{ij}^{\circ} \qquad (1)$$

where

C_{ij}° = uncorrected concentration for element i as observed at line j

C_i = true concentration of element i

C_k = true concentration of interfering element k

K_{kj} = correction factor for interfering element k at line j

n = the number of interfering elements for element i at line j

Class 1 results are considered to be more reliable than class 2 results, provided there are not excessive interferences at the lines used for obtaining the class 1 results. Because the extent of possible interference has not been determined at this stage of the calculations, class 1 and class 2 results are calculated independently of each other. The terms, C_k, in Equation 1 for correction for interference always use class 1 results as first choice, and class 2 results if no class 1 results are available.

The weighting factors used in the solution of the equations for class 1 lines are products of four separate weighting factors: a function of the transmittance of the particular line; a function of the lithium carbonate dilution factor; a function of the concentration; and a function of the amount of interference at a given line from other elements.

The simultaneous equations are actually solved three different times. In the first solution, only weighting factors for transmittance, dilution, and concentration are used. Then the ratio of the correction due to the interference to the observed concentration is computed for each line and the corresponding weighting factor is multiplied by the other three factors which are left unchanged. The equations are solved again, a new set of interference weighting factors is computed, and the equations are solved for the third time.

After completing the above calculations, the percentage of interference at each line is again computed and then decisions are made as to the result to report for each element by considering the following choices in order.

1. If there is any class 1 line for which the interference is less than 20% of the uncorrected value, report the computed class 1 result.
2. If there is any class 2 line with a correction for interference less than 20% and also a class 3 or class 4 result, report the true concentration as between the computed class 2 result and the class 3 or class 4 result.
3. If there is any class 2 line with a correction for interference less than 20%, report the computed class 2 result.
4. If there is a class 3 result, report it.
5. If there is any class 1 line for which the interference is between 20 and 40% of the uncorrected value, report the computed class 1 result with an appropriate note on the final report stating that the result is suspect.
6. If there is a class 4 result, report it.
7. If there is no result except a class 1 value with interference in excess of 40%, or a class 2 value with interference in excess of 20%, omit all reference to this element on the report.

Quite often the sample being analyzed by emission spectrometry is an ash of some organic material. Depending upon the particular circumstances, it may be preferable to report the results based either on the ash or on the original sample. If the sample is described by the input data as an ash and both the sample and ash weights are given, the results are converted to the basis of the original sample. However, if any result is less than 0.001% based on the original sample, then all the results are reported on the basis of the ash. In any case the basis on which the results are calculated is indicated in the report.

After the decisions have been completed as to the results to be reported, the program starts preparation of the final report which is printed in duplicate. This report summarizes all the results for the 1 to 5 samples which may be submitted as a single request. The only elements listed on the final report are those for which some satisfactory results are available. If an element is determined and reported for one sample on a request but not for other samples on the same request, the appropriate spaces in the table of results are left blank. All reported concentrations are rounded to 1 or 2 significant figures depending upon the class of the result and the size of the first significant digit. All class 2, 3, and 4 results are reported to only one significant figure. Class 1 results are reported to two significant figures if the first significant digit is less than three and to one significant figure otherwise. No result is reported to more than three decimals in any case. Table II shows a typical report.

Computer Costs. An estimate of the computer costs was obtained using data for three groups of samples. These data were punched into cards and the cards reproduced to give a total of eight sets which were used as one large batch of data for input to the computer. The number of individual samples, the number of lines, and the number of elements determined for each set and for the entire batch of eight sets are given in Table III. Because each of the original samples was arced three times so as to obtain three transmittances for each line, the input for the eight sets contained 4680 transmittance values. The time required on an IBM 7090 operated under Monitor for loading, processing, and reporting the results for this large batch of samples was only 3.09 minutes. Independent tests have shown that about 0.5 minute is required to load the program and the calibration data.

Table II. Analytical Department Final Report No. 149824, Common Matrix Emission Analysis

Sample No.	1	2	3	4	5
Silicon	0.3	>10.[a]	>10.	>10.	10.
Magnesium	5.	0.10	0.16	0.09	0.24
Lead	<0.01[b]	0.23	0.29	0.4	0.024
Tin		ND[c] 0.03	0.05		0.06
Iron	>10.	>10.	>10.	>10.	>10.
Aluminum	0.15	2.2	2.2	1.8	1.7
Molybdenum	<0.01	0.013	0.029	0.020	0.013
Vanadium	<0.01		0.01[d]	<0.01	0.010
Copper	0.1–1	0.1–1	0.1–1	0.1–1	0.1–1
Sodium	0.11	0.12	0.10	0.19	0.3
Titanium		1.7	4.	1.3	0.5
Silver		<0.01			
Nickel	0.10	0.4	1.6	0.6	0.3
Cobalt				<0.01	
Manganese	0.18	0.4	1.6	0.4	0.7
Potassium	0.2[d]				0.4
Strontium	<0.01	<0.01	<0.01	<0.01	<0.01
Chromium		1.5	5.	2.0	5.
Calcium	1.3	0.25	1.6	0.3–1	0.7
Barium	<0.01	<0.01	<0.01	<0.01	0.013
Zirconium			0.3		
Tungsten					1.0
Report based on	Ash	Ash	Ash	Ash	Ash

[a] > = Greater than the amount specified.
[b] < = Less than the amount specified.
[c] ND = Not detected. If present, concentration is less than amount specified.
[d] = Result may be in error because of serious interference.

Table III. Data Used for Estimating Computer Costs

	Data in each set			Total for 8 sets
	Group 1	Group 2	Group 3	
Samples	5	4	2	88
Lines	114	51	30	1560
Elements	86	32	28	1168

On this basis a sample containing 15 elements (20 lines) would require 0.033 minute for processing the data and reporting the results. Assuming a computer cost of $500 per hour, the program and calibration loading cost is $4.16 per batch of samples and the computing cost is $0.27 per sample of 15 elements.

The loading cost can be significantly reduced by combining several independent programs to form a set of subroutines. This is because of time required to prepare the computer for loading each independent program and to the unnecessary reloading of library subroutines, most of which are required by all programs. The programs are all loaded consecutively and then each program reads the corresponding input data, carries out the calibrations, writes the report, and then passes control to the next subroutine.

DISCUSSION

Several months of routine use have shown this program to be quite successful. The program does a satisfactory job of choosing the proper value to report, the results are free from calculation errors—assuming no errors in input—and the report of the results is neat and clear. This program is also of economic value in actual calculation and reporting costs, in addition to the saving of the time required to train the analyst.

One difficulty noted in the development of this program concerned the problem of the proper value to report when different lines for an element give widely divergent results because of different amounts of interference. Experience has shown that the weighting factor for interference must decrease quite rapidly with increasing amounts of interference. Otherwise, inconsistencies between the various corrected values for an element can cause errors in the concentrations of the interfering elements because a least-squares solution calculates results for which the sum of the squares of all the errors is a minimum.

Another difficulty concerns obtaining an adequate correction for interference when the only concentration available for the interfering element is a greater-than value. The best solution to this problem would be always to include adequate data in the input for all the interfering elements; however, since this solution is not always practical, the procedure followed in the program makes the best use of the data available.

Although the common-matrix method used in this laboratory is based on the use of the 2475.3 A. lithium line as the internal standard, there is nothing in the program to prevent the use of any other element desired. Each line included in the calibration data is assigned a serial number which is punched into the sample data cards along with the observed transmittances. The data for line No. 1 (which must be the first line punched in the data card) are automatically taken as the internal standard.

Furthermore, because all the calibration data are prepared on data cards and not written into the program, all of the calibration data used by the program are easily changed at any time by changing the appropriate data cards. Sufficient storage space has been provided in the program to handle up to 45 different elements with a total of 99 different lines. Data for 60 different lines can be entered for any one sample. The number of elements and lines, within the above limits, can be changed as desired. The above provisions make it possible for other laboratories, with an equivalent computer, to use this program without modification. Moreover, since the program is written in Fortran II (also in Fortran IV), minor modifications, such as changes in the input or output format, can be accomplished without difficulty.

The authors can supply on request a more extensive report which describes the operation of the program with complete listings of all the source decks.

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Spectrophotometric Determination of Tin(IV) by Extraction of Stannic Iodide into Ethyl Iodide

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▷ Tin(IV) in 1.2*M* HCl solution reacts with 4*M* KI to produce a yellow species which can be extracted into C_2H_5I. By measuring the absorbance of the C_2H_5I phase at 410 to 440 mμ, Sn(IV) concentrations in the range of 0.0001*M* to 0.001*M* can be determined. The Sn concentration can be determined within 1% of the total Sn present. The method has been applied to the determination of Sn in alloys whose other principal constituents were Cu, Pb, Zn, and Sb. Pb(II) and Cu(II) must be removed by treatment with a small amount of KI. The I_2 produced by reaction with Cu(II), as well as that which results from air oxidation during the extraction process, is removed with excess $Na_2S_2O_3$. At 440 mμ 0.01*M* solutions of Sb(III) do not interfere. At 410 mμ Sb(III) interferes when present in concentrations greater than 0.001*M*, but can be corrected for if the Sb(III) concentration is known.

DETERMINATION of Sn in alloys containing Pb and Cu usually involves time-consuming procedures for separating Sn from the other constituents. The HNO_3 separation and gravimetric determination as SnO_2 is recommended in most textbooks (*16*). Recently, Stan (*25*, *26*) has separated Sn from Pb, Cu, Bi, and Cd by dissolving the alloy in an aqueous acetone solution of KI and I_2. The $Sn(OH)_4$ is precipitated quantitatively and the other elements remain in solution as iodo complexes. A widely used separation procedure (*8*) involves solution of the alloy in H_2SO_4 and H_2O_2 which precipitates Pb(II) as $PbSO_4$, followed by reduction of Sn(IV) to Sn(II) and Cu(II) to Cu(I) with H_3PO_2 and subsequent precipitation of Cu(I) with NH_4SCN. The Sn(II) can then be titrated in an inert atmosphere with a suitable oxidizing agent such as I_2, or determined polarographically (*20*). A number of ion exchange separations have been reported (*3*, *5*, *9*), but these are advantageous only if a complete analysis of the alloy is required. The separation of Sn from most elements by benzene extraction of SnI_4 has been reported by several workers (*10*, *17*,

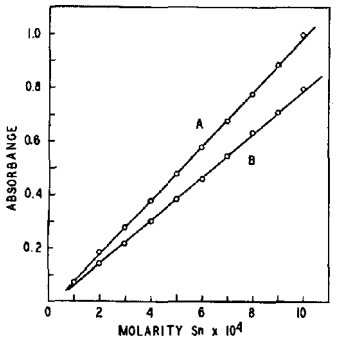

Figure 1. Calibration curve at 410 mμ

A. Solution originally 0.0005*M* in $SnCl_4$ after extraction into C_2H_5I

B. Solution originally 0.0005*M* in $SnCl_4$, 0.05*M* in $CuCl_2$, and 0.004*M* in $PbCl_2$ after removal of Cu(II) and Pb(II) and extraction into C_2H_5I

27). After separation, the Sn(IV) is transferred to an acidic aqueous phase and determined spectrophotometrically with various colorimetric reagents.

Dithiol (*23*), pyrocatechol violet (*22*), and phenylfluorone (*14, 18, 19, 28*) have been recommended as colorimetric reagents for Sn(IV). Of these reagents, only phenylfluorone appears to be specific for Sn(IV) and with its use no prior separations are necessary if Sb is kept in the +5 state. EDTA titrations without prior separations have also been reported (*6, 15*).

The present work is an extension of the qualitative procedure for Sn(IV) in the presence of Sb(III) reported by Paul and Gibson (*21*). It is based upon measurement of the yellow SnI_4 extracted by C_2H_5I from an aqueous HCl solution containing Sn(IV) and a large excess of KI. The Cu(II) and Pb(II) are removed with a small amount of the same reagent used to develop the color. The method is rapid and after preparation of the calibration curves, a tin analysis including solution of the sample can be completed in less than an hour. Also, very small samples are required.

EXPERIMENTAL

Apparatus. The absorbance measurements were made with a Beckman Model DU Spectrophotometer, using 1-cm. Corex cells.

Reagents. Potassium iodide solution, 4*M*. Sodium thiosulfate solution, 0.1*M*. Ethyl iodide, Baker Analyzed Reagent. Starch indicator, 1% solution preserved with HgI_2.

Procedure for Samples Containing No, Cu, or Pb. Dissolve the alloy in 5 to 10 ml. of concentrated HCl in a volumetric flask. After solution is complete, add 30% H_2O_2 dropwise with mixing but without heating until approximately 3 ml. (several times the theoretical quantity) have been added. If the mixture is heated during the oxidation process, some Sn(II) will remain unoxidized as indicated by an $HgCl_2$ test on a portion of the sample after dilution. The excess H_2O_2 can be removed by boiling after the oxidation process is complete or by allowing to stand overnight at room temperature.

Dilute the solution with 1.2*M* HCl to a volume such that the Sn concentration is 0.0001*M* to 0.001*M* and pipet a 1-ml. aliquot into a 25-ml. glass-stoppered Erlenmeyer flask. Treat with 5 ml. of 4*M* KI and 4 drops of starch solution. Unless the KI has been freshly prepared, a slight starch–I_2 color will be evident. Add $Na_2S_2O_3$ dropwise until the starch–I_2 color disappears, then 5 drops excess. Add enough water so that the final volume is constant. In this work, the final volume was 7 ml., but a 10-ml. final volume may be more convenient. Excessive dilution of the water phase should be avoided since, as will be shown later, the absorbance decreases as the KI concentration is reduced.

Add 5 ml. of C_2H_5I with a pipet and shake for 1 minute. Allow to stand for 10 minutes, then shake for 1 more minute. Remove the organic phase with a medicine dropper and transfer to a centrifuge tube. The walls of the tube appear to have a great affinity for water droplets, and practically all of these can be removed by pouring the organic phase into a second test tube and centrifuging for about 1 minute before transferring the sample to the cell. Measure the absorbance at 410 to 440 mμ against a blank prepared from 1 ml. of 1.2*M* HCl treated as above with KI, starch, $Na_2S_2O_3$, and C_2H_5I.

As will be shown later, about 95% of the Sn(IV) is extracted into the organic phase. The absorbance of the C_2H_5I phase is far less sensitive to small variations in the volume of the water phase than to variations of equal magnitude in the volume of the C_2H_5I phase. In this work the addition of small amounts of reagents to the water phase and the adjustment of its final volume were made using droppers which delivered 20 drops per ml. A micrometer-type buret could be used if one desired to know these volumes more precisely.

The calibration curve was constructed from similar measurements on $SnCl_4$ solutions of concentration 0.0001*M* to 0.001*M*. These solutions were prepared by dilution of a 0.0100*M* stock solution of $SnCl_4$ prepared in turn from NBS Spectrographic Tin Standard No. 435 (99.95% Sn) dissolved in HCl and H_2O_2 as described above.

Procedure for Alloys Containing Cu and Pb. Dissolve the sample in HCl and H_2O_2 without heating as described above and dilute to the proper volume with 1.2*M* HCl.

Remove the Cu(II) and Pb(II) from a 2-ml. aliquot with 10 drops of 4*M* KI. If the amounts of Cu(II) and Pb(II) in the sample are small, precipitation may not occur. In this case, the 2-ml. aliquot is treated with 8 drops of 4*M* KI, 1 drop of 1*M* $CuCl_2$, and 1 drop of a saturated solution of $PbCl_2$. If no

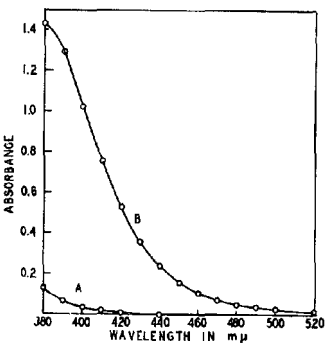

Figure 2. Absorption spectra of C_2H_5I and SnI_4 dissolved in C_2H_5I

A. C_2H_5I (vs. H_2O)

B. 0.0008*M* $SnCl_4$ treated with KI, starch, and $Na_2S_2O_3$ after extraction into C_2H_5I

blue copper color is visible in the 2-ml. sample, the 1 drop of $CuCl_2$ should be added. If the amount of Pb in the alloy is unknown, it is advisable to add the 1 drop of $PbCl_2$. The combined volume of added KI, $CuCl_2$, and $PbCl_2$ should not exceed 10 drops.

Centrifuge and pipet a 1-ml. aliquot into a 25-ml. glass-stoppered Erlenmeyer flask. Continue as above by adding KI, starch, $Na_2S_2O_3$, and C_2H_5I. If no $CuCl_2$ has been added, the dropwise addition of $Na_2S_2O_3$ provides a rough estimation of the Cu content of the alloy.

The process of removing the Cu(II) and Pb(II) dilutes the sample by approximately 20%. If volumes are quantitatively measured, absorbance values may be divided by 0.8 and the original calibration curve may be used. For analysis of Cu-Pb alloys, however, it is better to construct a calibration curve using the procedure described in this section.

RESULTS AND DISCUSSION

Both calibration curves are shown in Figure 1 using a wavelength of 410 mμ. Curve *B* was used in the analysis of all Cu-Pb alloys.

Figure 2 shows the absorption spectrum of C_2H_5I (*vs.* H_2O) and that of a 0.0008*M* solution of Sn(IV) after treatment with KI, starch, and $Na_2S_2O_3$ and extraction into C_2H_5I. The optimum wavelengths for measurement lie between 410 and 440 mμ. Below 410 mμ the absorbance of the solvent becomes appreciable and less reproducible. Plots similar to Figure 1 show that Beer's law is obeyed at 420 mμ, 430 mμ, and 440 mμ as well as at 410 mμ. Most of the measurements reported in this work were made at 410 mμ. Use of the higher wavelengths is desirable for higher Sn(IV) concentrations, and also when Sb(III) is present.

Extractant. Ethyl iodide was the most satisfactory solvent for the extraction. Methyl iodide appears to

extract equally well, but because it is more volatile than C_2H_5I, it was not studied extensively. The high solubility of SnI_4 in CS_2 reported in the literature (*24*) led to an investigation of the possibility of using CS_2 as a solvent. This reagent, although volatile, is more stable and much less expensive than either CH_3I or C_2H_5I and shows no absorption at 420 to 440 mμ. The absorbance of SnI_4 in CS_2 is about 10% less than in C_2H_5I, and Beer's law appears to be obeyed. However, the colored species is much more unstable than in C_2H_5I. In CS_2 the absorbance begins to drop within a few minutes after the cell is placed in the instrument, and results were not reproducible from day to day. It is quite possible that with more careful control of the time of shaking and the time of reading the absorbance, a suitable procedure could be developed for this solvent.

There are some difficulties involved in the use of C_2H_5I as the solvent. The treatment of the sample and blank as described earlier removes the color in the C_2H_5I caused by the presence of I_2. However, the blank usually shows some residual absorbance which varies with the individual C_2H_5I sample, and the length of time the bottle has been open. At 410 mμ the absorbance of the blank (*vs.* H_2O) may vary from 0.003 to 0.038. Also, the blank tends to increase in absorbance after it has been in the instrument for more than an hour. This means that a new blank must be prepared each hour. This necessity may be avoided by running the samples against water and subtracting the solvent blank from each measurement. The solvent blank is valid for a 4- to 8-hour period.

To determine the percentage of Sn(IV) extracted by C_2H_5I, the following experiments were conducted. One milliliter of 1.2*M* HCl treated with KI, starch, and $Na_2S_2O_3$ was equilibrated with 5 ml. of C_2H_5I containing a known weight of Fisher Certified SnI_4. In the second experiment, a 1.2*M* HCl solution of Fisher Certified SnI_4 was prepared and a 1-ml. aliquot treated with KI, starch, and $Na_2S_2O_3$ according to the usual procedure. This solution was then equilibrated with C_2H_5I. The results of both experiments indicated that about 95% of the Sn(IV) was extracted into the C_2H_5I.

Stability. Both the C_2H_5I and the aqueous HCl solution of Fisher Certified SnI_4 gave chemical evidence of decomposition into SnI_2 and I_2 after standing about two weeks at room temperature. However, over a period of an hour the C_2H_5I solutions showed no change in absorbance.

Shaking Procedure. The maximum absorbance was obtained using the recommended extraction procedure. Absorbance measurements made after 1 minute of shaking without the 10-minute standing period tended to be 2 to 3% low. The minimum standing period was 8 minutes.

The absorbance depends greatly on the manner of shaking. Vigorous shaking by hand was employed in all this work, and there was no difficulty in obtaining reproducible results by this method. Magnetic stirring gave results which were both different and variable. No other mechanical devices were tried. It is believed that these variations result from differences in the degree of air oxidation of KI and are related to the amount of excess $Na_2S_2O_3$ present as discussed below.

Thiosulfate Concentration. $Na_2S_2O_3$ is used in the procedure to remove I_2 from the KI reagent and to reduce the I_2 which results from the reaction of Cu(II) with KI. The amount of $Na_2S_2O_3$ to use for these purposes is determined by the presence in the reaction mixture of starch indicator, which has no effect on the absorbance because it is not extracted into the C_2H_5I. The presence of excess $Na_2S_2O_3$ in the reaction mixture is also necessary to remove I_2 from the C_2H_5I and to remove the I_2 which may result from air oxidation of KI during the extraction process.

Other reagents were investigated as substitutes for $Na_2S_2O_3$ but none were found to be satisfactory. Ascorbic acid and metallic copper were too slow and metallic mercury reduced the Sn(IV) as well as the I_2.

The absorbance depends on the amount of excess $Na_2S_2O_3$ present. One to two drops of excess $Na_2S_2O_3$ are required to prevent air oxidation of KI during the extraction process. When Cu(II) is present, the minimum amount is required since Cu(II) reduces the rate of oxidation (*4*). The absorbance decreases with further addition of $Na_2S_2O_3$ but the rate of decrease after the addition of 5 drops is small as can be seen from Table I. The use of different shaking techniques would undoubtedly require some change in the amount of excess $Na_2S_2O_3$ required.

In use the recommended procedure gave no evidence of decomposition of $Na_2S_2O_3$ into S. Some experiments were conducted in which the $Na_2S_2O_3$ and KI were added as one solution, and under these conditions a precipitate of S was visible. Since a solution of S in C_2H_5I absorbs at the wavelengths used and since the compound $SnI_4 \cdot S_8$ has been reported to exist in certain organic solvents (*12*), the pressure of varying amounts of S can cause considerable variation in the absorbance. Reproducible results could not be obtained when a precipitate of S was observed.

Acidity. The absorbance increases with increasing acidity as shown in Table II, although there is no change in the general shape of the absorbance curve. Since the rate of oxidation of I^- increases with increasing acidity (*1*) and since at higher acidity there is a greater tendency for $Na_2S_2O_3$ to decompose into S, it did not seem desirable to work with solutions having an acidity greater than 1.2*M*.

Table I. Effect of Excess $Na_2S_2O_3$ on Absorbance of 0.0005*M* Sn(IV) Solution Extracted into C_2H_5I

Drops of 0.1*M* $Na_2S_2O_3$ present in excess, in 7-ml. volume before extraction	Absorbance at 410 mμ
2	0.535
3	0.515
4	0.496
5	0.480
6	0.478
8	0.474

Table II. Effect of Acidity on Absorbance

Sn(IV) concn. × 10^4, moles/liter	Absorbance at 410 mμ, KI = 4*M*		
	0.8*M* HCl	1.2*M* HCl	1.6*M* HCl
2	0.165	0.184	0.212
8	0.763	0.776	0.895

Table III. Effect of Iodide Concentration on Absorbance

Sn(IV) concn. × 10^4, moles/liter	Absorbance at 410 mμ, HCl = 1.2*M*		
	3.0*M* KI	3.5*M* KI	4.0*M* KI
2	0.108	0.153	0.184
8	0.543	0.705	0.776

Iodide Concentration. The absorbance decreases when the iodide concentration is reduced as shown in Table III. The 4*M* KI is close to being a saturated solution. Increasing the iodide concentration by adding solid KI rather than the 4*M* solution to the reaction mixture causes difficulties in extraction and separation of the phases caused by the precipitation of KCl. Substitution of a 4*M* solution of NaI for KI reduces the absorbance by about 12%, which probably results from the differences in the mean ionic activity coefficients of NaI and KI in concentrated solution (*11*).

Interference of Cu(II) and Pb(II). If the Cu(II) and Pb(II) are not removed as recommended in the procedure, they will remain in solution as complex iodo anions and cause a lowering of the absorbance. The

Table IV. Effect of Cu(II) and Pb(II) on Absorbance of 0.0005*M* Sn(IV) at 410 mμ (HCl = 1.2*M*, KI = 4*M*)

Pb(II) concn., moles/liter	Cu(II) concn., moles/liter	Absorbance
0	0	0.480
0	0.05	0.445
0.004	0	0.470
0.004	0.05	0.430

reason for the lowering is not apparent.

The minimum concentrations of Cu(II) and Pb(II), which cause interference, are $2 \times 10^{-4}M$ and $5 \times 10^{-4}M$, respectively (before addition of KI). The greater the Cu(II) concentration, the greater the lowering of the absorbance. The lowering of the absorbance by Pb(II) appears to be independent of the Pb(II) concentration above a Pb(II) concentration of $5 \times 10^{-4}M$ and is of smaller magnitude than the Cu(II) lowering. If both Cu(II) and Pb(II) are present, the amount of the lowering is not additive. Consequently, both ions must be removed. Data showing the effect of Cu(II) and Pb(II) on the absorbance are presented in Table IV.

The removal of Cu(II) and Pb(II) by treatment with a small amount of KI appears to be essentially complete as indicated by the fact that there is no lowering of the absorbance after correcting for dilution. Eight to 10 drops of 4*M* KI are required to reduce the solubility to the point where interference does not occur. Approximately 1 ml. of 4*M* KI is required to begin to dissolve the precipitates of PbI_2 and CuI as iodo complexes.

Other Diverse Ions. The reaction of Sb(III) with excess KI produces a yellow color in aqueous solution which can be used for the quantitative determination of Sb(III) (*7, 13*). The absorbance produced by extraction into C_2H_5I of Sb(III) concentrations up to 0.01*M* is negligible at 440 mμ. At 410 mμ the extraction of 0.001*M* Sb(III) produces an absorbance of 0.005 and the absorbance appears to be linear over an Sb(III) concentration range of 0.001 to 0.005*M*. If it is necessary to use the wavelength of 410 mμ for the determination of Sn(IV), then a curve must be constructed from which the Sb(III) correction can be determined.

Bi(III) which also forms a yellow iodo complex in aqueous solution (*2*) produces no absorption at any of the wavelengths under investigation when present in $10^{-3}M$ solution.

As(III) interferes at all wavelengths when present in concentrations of $1 \times 10^{-4}M$. Since this element is not commonly present in the class of alloys under investigation, no provision was made for removing it or correcting for its presence.

Fe(III), when present in concentrations greater than 0.01*M*, appears to serve as an oxygen carrier for the oxidation of KI. The procedure could probably be adapted to the determination of Sn(IV) in the presence of large amounts of Fe(III) by use of additional excess $Na_2S_2O_3$.

The method is not suitable for the determination of Sn(IV) in the presence of Sn(II) because the Sn(II) becomes partially oxidized during the extraction procedure. The absorbance of freshly prepared Sn(II) extracted into C_2H_5I is about 50% that of Sn(IV), and thus in a determination of total Sn, all the Sn must be present as Sn(IV). This should be the case if the sample is dissolved according to the recommended procedure.

The following cations produced no interference when present in concentrations of 0.05*M* [100 times the average Sn(IV) concentration]: Co(II), Ni(II), Cr(III), Mn(II), Al(III), Hg(II), Cd(II), and Zn(II).

Results of Analysis of NBS Alloys. The procedure was applied to the determination of Sn(IV) in 5 NBS alloys. In all cases it was possible to determine the Sn(IV) concentration within 1% of the total amount of Sn present. The results are shown in Table V.

Table V. Analysis of National Bureau of Standards Alloys

Sample No.	% Cu	% Pb	% Zn	% Sb	Other, <1%	% Sn Known	% Sn Found
37	70.29	0.964	26.89	...	Fe, Ni	1.013	1.01
37b	70.34	0.90	27.07	...	Fe, Ni	1.00	0.992
52c	89.25	...	2.12	...	Ni, Pb, Fe, S	7.85	7.87
53d	0.268	85	...	9.92	Bi, As, Ni	4.94	4.92
54d	3.62	0.62	...	7.04	As, Bi, Fe, Ag, Ni	84.69	84.1

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Optimum Conditions for Chemical Analysis by X-Ray Absorption-Edge Spectrometry

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▶ Solutions are presented to the related problems of optimizing sample path length (absorber thickness) and x-ray detector timing periods for chemical analysis by x-ray absorption-edge spectrometry. Application of the law of propagation of errors leads to an equation representing necessary conditions to be satisfied to minimize probable errors in chemical analysis. Numerical solutions of the derived equations have been computed and are presented graphically for the general case, using four different timing periods, and for more practical cases utilizing one or two timing periods. The selection of cases is discussed with respect to sample parameters, including elemental atomic number. Experimental procedures are discussed elsewhere.

X-RAY ABSORPTION-EDGE spectrometry (XAES) is characterized by certain unique advantages over other spectrochemical methods that justify its consideration for many chemical analytical applications. The most important advantages are the marked freedom from sample matrix effects and the relatively few interferences encountered. XAES is accurate and convenient to apply. On the other hand, the sensitivity attainable is somewhat less than that of some other spectral methods.

The literature contains, however, no recent extensive analysis of principles and limitations. Such analyses are required to understand the application of XAES to the determination of chemical elements throughout the periodic table, particularly with respect to problems such as optimum sample form and thickness and optimum counting times and timing ratios. The purpose of this paper is to present such an analysis. Experimental procedures and data will be presented in another paper.

XAES as applied to chemical analysis is referred to by Liebhafsky *et al.* (*9*), who describe its history as "differential absorptiometry across an edge." Glocker and Frohnmayer (*6*) are credited with the genesis of XAES in 1925, but its limited application to chemical analysis during the past 38 years has largely been the consequence of inadequate instrumentation.

In 1946, Engström (*5*) described spectrographic applications of the principle, including chemical analyses of light elements such as carbon, nitrogen, and oxygen in living cells. Linsdtröm (*11*) has described more recent applications to quantitative cytochemistry, and Cosslett and Nixon (*3*) have reviewed the general field of absorption microanalysis.

Representative applications of XAES to chemical analysis have been described by Barieau (*1*), who developed procedures for the analysis of molybdenum and zinc; by Dunn (*4*), who has discussed the advantages and disadvantages of XAES analysis and described instrumentation for precise determination of zirconium and other elements midway in the periodic table, utilizing a two-point wavelength measurement technique; and by Hakkila who has described methods using secondary radiation from preselected targets, rather than white radiation monochromatized by a crystal, for the analysis of uranium and yttrium (*7*) and the determination of cobalt in complex mixtures (*8*).

One of the most difficult problems to resolve is that of predetermining the optimum sample path length or absorber thickness. A related problem is the optimization of counting periods. The required relations for solutions of the problems have been derived, numerical solutions to the equations computed, and the results presented graphically as functions of pertinent parameters, both for the general case and for simpler and more useful experimental procedures. A distinction is made between optimum thickness for chemical analysis and that for absorption-edge fine structure studies.

OPTIMIZATION OF PATH LENGTH AND COUNTING TIMES

The related problems of determining optimum absorber thickness and optimum allocation of counting times to minimize statistical error, together with total counting time in measurements involving the absorption or transmission of radiation, have been discussed by Rainwater and Havens (*13*) and Rose and Shapiro (*14*). The former authors considered the special case when the background is negligible and the cross-sectional area of the beam is fixed. Rose and Shapiro extended the analysis of the effects of background and variation of beam cross-section within the absorber. Both of these papers, however, dealt only with absorptiometry, that is, incident and transmitted beam intensity measurements for constant quality radiation—i.e., for a single incident polychromatic or monochromatic beam.

In XAES, it is necessary to consider the effect of the necessity to make measurements at one or more wavelengths on each side of an absorption edge. Inasmuch as x-ray beams used in XAES generally are collimated, however, and because the entire beam cross-section (except a negligible scattered fraction) passes through the sample and into the detector, it is not necessary to consider variations in beam cross-section. Furthermore, under most experimental conditions, the background may be neglected in comparison with transmitted beam intensity.

General Conditions for Optimization. The classical relation applicable to each side of an absorption edge of a given element, describing the fractional decrease in intensity, I, of monochromatic x-radiation in an absorber of thickness dx, is

$$dI/I = -\mu dx$$

and, for a pair of measurements on each side of an edge one obtains for an absorber sample consisting of the pure element

$$\left.\begin{aligned} i_1 &= I_1 \exp -(\mu_1 x) = I_1 \exp -[(\mu_m)_1 \rho x] \\ i_2 &= I_2 \exp -(\mu_2 x) = I_2 \exp -[(\mu_m)_2 \rho x] \end{aligned}\right\} \quad (1)$$

Subscripts 1 and 2 refer to measurements made at the short and long wavelength sides, respectively, of the absorption discontinuity under study.

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For an absorber consisting of more than one chemical element, as a solid or liquid unknown analytical sample

$$\left.\begin{aligned}\mu_1 &= (\mu_m)_1 C + \sum_j [(\mu'_m)_j]_1\, C'_j \\ \mu_2 &= (\mu_m)_2 C + \sum_j [(\mu'_m)_j]_2\, C'_j\end{aligned}\right\} \quad (2)$$

In this paper the concentration term, C, is used in the conventional analytical sense of mass of element per unit sample volume—that is, volumetric concentration. The summations in Equations 2 are carried over all chemical elements in the sample other than the element sought. The subscript j refers to these other elements. These relations may be simplified by defining γ on each side of an absorption edge by the following equations.

$$\left.\begin{aligned}\mu_1 &= (\mu_m)_1 C + \gamma_1 \\ \mu_2 &= (\mu_m)_2 C + \gamma_2\end{aligned}\right\} \quad (3)$$

Equations 3 may be combined with Equations 1 to yield

$$\ln (I_1 i_2 / i_1 I_2) = [(\mu_m)_1 - (\mu_m)_2]\, Cx + (\gamma_1 - \gamma_2)\, x \quad (4)$$

If λ_1 and λ_2 each approach λ_E, the wavelength corresponding to the midpoint of an absorption edge, then

$$\lim_{\lambda \to \lambda_E} (\gamma_1 - \gamma_2) = 0 \quad (4a)$$

and, defining $\Delta\mu_m$

$$\lim_{\lambda \to \lambda_E} [(\mu_m)_1 - (\mu_m)_2] = \Delta\mu_m \quad (4b)$$

Equation 4 may be expressed as

$$C = [1/(x\Delta\mu_m)] \ln (I_1 i_2 / i_1 I_2) \quad (5)$$

These relations are similar to those employed by Glocker and Frohnmayer (*6*) and by Engström (*5*).

Assume that I and i are measured by collecting counts during a specified timing interval; then the intensities at each side of an edge are defined as

$$\left.\begin{aligned}i_1 &= n_1/t_1 \\ I_1 &= N_1/T_1\end{aligned}\right\} \text{ and } \left.\begin{aligned}i_2 &= n_2/t_2 \\ I_2 &= N_2/T_2\end{aligned}\right\} \quad (6)$$

and Equation 5 may be expressed as

$$C = [1/(x\Delta\mu_m)] \ln (N_1 t_1 T_2 n_2 / T_1 n_1 N_2 t_2) \quad (7)$$

If it is assumed that the only errors to be considered are statistical counting errors, the law of propagation of errors as expressed by Birge (*2*) may be applied thus

$$E_Z^2 = \sum_k (\partial Z/\partial z_k)^2 (E_Z)_k^2$$

Because E_Z is a function solely of directly measured quantities z_k, then

$$Z = Z(z_1, z_2, z_3, \ldots . z_k)$$

In XAES one may elect to determine either C or $\Delta\mu_m$, but not both simultaneously. One of these quantities must be known with adequate precision. N, n, T, t, and x are directly measured quantities. The uncertainties in the timing periods T and t are at least an order of magnitude less than those associated with the quantitative detection of x-ray photons. Furthermore, it may be assumed that the uncertainty in the measurement of sample path length is negligible. Under these assumptions the concentration of the element sought may be written as

$$C = C(N_1, n_1, N_2, n_2)$$

and the law of propagation of errors for XAES as

$$S_C^2 = (\partial C/\partial N_1)^2 S_{N_1}^2 + (\partial C/\partial n_1)^2 S_{n_1}^2 + (\partial C/\partial N_2)^2 S_{N_2}^2 + (\partial C/\partial n_2)^2 S_{n_2}^2 \quad (8)$$

because it may be demonstrated [Liebhafsky (*10*)] that x-ray emission is a random process whenever ideal operating conditions are attained. X-ray photons reaching a detector then fluctuate according to a unique Gaussian distribution, and the standard deviations pertaining to their measurement are given by

$$S_{N_1} = N_1^{1/2},\ S_{n_1} = n_1^{1/2},\ S_{N_2} = N_2^{1/2}, \text{ and } S_{n_2} = n_2^{1/2}$$

because standard deviations are root-mean-square errors when a normal distribution is assumed, and

$$\left.\begin{aligned}S_N^2 &= \bar{N} \\ S_n^2 &= \bar{n}\end{aligned}\right\}$$

when the number of counts collected is high enough. For the purposes of this paper, it is assumed that $\bar{n} \simeq n$, and $\bar{N} \simeq N$, as measured. These considerations permit expressing Equation 8 as

$$S_C^2 = [1/(x\Delta\mu_m)^2] (1/N_1 + 1/n_1 + 1/N_2 + 1/n_2) \quad (9)$$

If τ is defined as the total time required to collect all counts, then

$$\tau = T_1 + T_2 + t_1 + t_2 \quad (10)$$

The individual counting times may be normalized for expression as timing ratios, thus

$$\left.\begin{aligned}R_1 &= T_1/\tau \\ r_1 &= t_1/\tau\end{aligned}\right\} \text{ and } \left.\begin{aligned}R_2 &= T_2/\tau \\ r_2 &= t_2/\tau\end{aligned}\right\} \quad (11)$$

From Equations 1, 6, and 11 one obtains the relations

$$\left.\begin{aligned}N_1 &= I_1 R_1 \tau \\ n_1 &= I_1 \exp -(\mu_1 x) r_1 \tau\end{aligned}\right\} \text{ and } \left.\begin{aligned}N_2 &= I_2 R_2 \tau \\ n_2 &= I_2 \exp -(\mu_2 x) r_2 \tau\end{aligned}\right\} \quad (12)$$

The parameters α, β, and K are defined as

$$\left.\begin{aligned}\alpha &\equiv \mu_1 x \\ \beta &\equiv \mu_1/\mu_2 \\ K^2 &\equiv I_1/I_2\end{aligned}\right\} \quad (13)$$

From Equations 9, 12, and 13 one obtains

$$S_C^2 = (\mu_1^2/\Delta\mu_m^2 I_1 \tau a^2) \times \{1/R_1 + K^2/R_2 + \exp(\alpha/r_1) + [K_2 \exp(\alpha/\beta)]/r_2\} \quad (14)$$

The term P^2, proportional to the expected error, may be defined as

$$P^2 \equiv I_1 \tau (\Delta\mu_m/\mu_1)^2 S_C^2 \quad (15)$$

or, by combining equations one obtains

$$P^2 = 1/\alpha^2 [1/R_1 + K^2/R_2 + \exp(\alpha)/r_1 + K^2 \exp(\alpha/\beta) r_2] \quad (16)$$

As discussed by Rose and Shapiro (*14*), and because our P^2 is proportional to their P^2, optimizing P^2 can be considered as either optimizing S_C^2 for a given τ or optimizing τ for a given S_C^2. Optimum conditions must correspond then to a minimum P^2 for a given K and β.

The differential of P^2 may be written as

$$d(P^2) = -(dR_1/\alpha^2 R_1^2) - (K^2 dR_2/\alpha^2 R_2^2) - [\exp(\alpha) dr_1/\alpha^2 r_1^2] - K^2 [\exp(\alpha/\beta) dr_2/\alpha^2 r_2^2] + \{[\exp(\alpha)/r_1][(\alpha/2) - 1] + K^2 [\exp(\alpha/\beta)/r_2][(\alpha/2\beta) - 1] - R_1^{-1} - K^2/R_2\}\, 2\, d\alpha/\alpha^3 \quad (17)$$

Only three of the four R's (R_1, R_2, r_1, and r_2) are independent, because by Equations 10 and 11, one obtains

$$R_1 + R_2 + r_1 + r_2 = 1$$

or

$$dR_1 + dR_2 + dr_1 + dr_2 = 0 \quad (18)$$

Reduction of Optimum Conditions for Experimental Practice. The balance of this section relates to consideration of the general case and three specific cases involving selected restraints on the timing periods, including discussion of the parameters β and K and the selection of optimum conditions in practice. The four cases considered are: case A, three R's independent; case B, $R_1 = R_2 = R$, and $r_1 = r_2 = r$; case C, $R_1 = R_2 = r_2 = R$, and $r_1 = r$; and case D, $R_1 = R_2 = r_1 = r_2 = 1/4$.

Case A: Three R's Independent. From Equations 17 and 18, four relations requisite for optimum conditions may be derived for case A by requiring that $d(P^2) = 0$

$$\exp(\alpha_a/2)[(\alpha_a/2) - 1] + K \exp \times (\alpha_a/2\beta)\ [(\alpha_a/2\beta) - 1] = 1 + K \quad (19)$$

$$(R_2/R_1)_a = (T_2/T_1)_a = K \quad (20)$$

$$(r_1/R_1)_a = (t_1/T_1)_a = \exp(\alpha_a/2) \quad (21)$$

and

$$(r_2/R_1)_a = (t_2/T_1)_a = K \exp(\alpha_a/2\beta) \quad (22)$$

The subscripts a refer to the values of the subscripted quantities that are solutions of Equation 19, 20, 21, and 22. Equation 19 gives α_a as a function of β and K, while Equations 20, 21, and 22

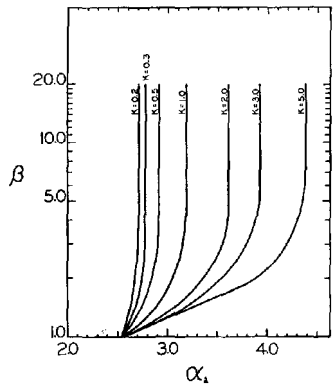

Figure 1. Plot of α_a vs. β and K for case A

yield the timing ratios as functions of β and K. Curves of α_a *vs.* β for selected values of K are shown in Figure 1.

If the values of α_a and the timing ratios are substituted into Equation 16, then P_a^2 is a function of β and K of the form

$$P_a^2 = (1/\alpha_a R_{1a})[1 + K^2(R_1/R_2)_a + (R_1/r_1)_a \exp(\alpha_a) + K^2(R_1/r_2) \times \exp(\alpha_a/\beta)] \quad (23)$$

and Equation 23 represents the minimum possible value of P^2 for a given K and β. The corresponding minimum expected deviation in the calculated value of C can be found by use of Equations 15 and 23.

In most XAES work, it is impractical or inconvenient to use a different timing interval for each separate count. Thus, it would be beneficial to examine the minimum value of P^2 when restrictions are imposed on the R's as in cases B, C and D described above.

Case B: $R_1 = R_2 = R_1$ and $r_1 = r_2 = r$. With Equations 17 and 18 coupled to the restriction

$$dR = dR_1 = dR_2 = -dr_1 = -dr_2 = -dr \quad (24)$$

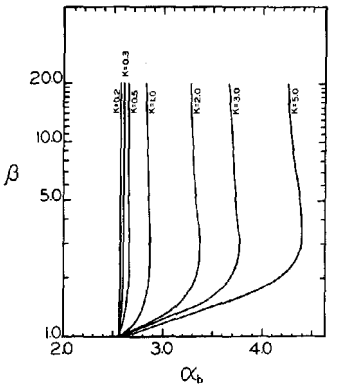

Figure 2. Plot of α_b vs. β and K for case B

and, dropping the subscripts on the R's, then $d(P^2) = 0$ when

$$\exp(\alpha_b)[(\alpha_b/2) - 1] + K^2 \exp(\alpha_b/\beta) \times [(\alpha_b/2\beta) - 1] = [(1 + K^2) \exp(\alpha_b) + K^2 \exp(\alpha_b/\beta)]^{1/2} \quad (25)$$

and

$$(t/T)_b = (r/R)_b = [\exp(\alpha_b/\beta) + K^2 \exp(\alpha_b/\beta)/(1 + K^2)]^{1/2} \quad (26)$$

in which the subscript b identifies values of the quantities for case B. In Figure 2, α_b is plotted *vs.* β and K.

Case C: $R_1 = R_2 = r_2 = R$, and $r_1 = r$. In a similar manner, it may be shown that

$$\exp(\alpha_c/2)[(\alpha_c/2) - 1]\{[1 + K^2 + K^2 \exp(\alpha_c/\beta)/3]\}^{1/2} + K^2 \exp \times (\alpha_c/\beta)\ [(\alpha_c/2\beta) - 1] = 1 + K^2 \quad (27)$$

and

$$(t/T)_c = (r/R)_c = \{3 \exp(\alpha_c)/ \times [1 + K^2 + K^2 \exp(\alpha_c/\beta)]\}^{1/2} \quad (28)$$

In Figure 3, α_c is plotted *vs.* β as a function of K.

Case D: $R_1 = R_2 = r_1 = r_2 = 1/4$. An analogous equation may be written as

$$\exp(\alpha_d)[(\alpha_d/2) - 1] + K^2 \exp(\alpha_d/\beta) \times [(\alpha_d/2\beta) - 1] = 1 + K^2 \quad (29)$$

and α_d is plotted *vs.* β as a function of K in Figure 4.

Determination of Relative Error in Cases B, C, and D. If one substitutes α_b and $(t/T)_b$ into Equation 16, denoting this value of P^2 by P_b^2, one obtains P_b^2 as a function of β and K, such that

$$P_b^2 = (1/\alpha_b^2 R_b)\{1 + K^2 + (R/r)_b [\exp(\alpha_b) + K^2 \exp(\alpha_b/\beta)]\} \quad (30)$$

Let us now define the function

$$\Phi_b^2 \equiv P_b^2/P_a^2 \quad (31)$$

such that Φ_b is identically the ratio of the expected error in the calculated value of C for case B with respect to that for case A. Considering case A as the minimum possible expected error in the calculated value of C, then $100(\Phi_b - 1)$ is the percentage that the expected error for case B has increased over that for case A. The function Φ_b^2 is plotted *vs.* β for various values of K in Figures 5 and 6.

Similarly, for cases C and D the following equations may be derived for P_c^2 and P_d^2, analogous to Equation 30

$$P_c^2 = (\alpha_c^{-2} R_c)\{1 + K^2 + K^2 \exp(\alpha_c/\beta) + K^2 \exp(\alpha_c/2)\ [1 + K^2 + K^2 \exp(\alpha_c/\beta)]^{1/2}\ 3^{-1/2}\} \quad (32)$$

and

$$P_d^2 = (4\alpha_d^{-2})\ [1 + K^2 + \exp(\alpha_d) + K^2 \exp(\alpha_d/\beta)] \quad (33)$$

Again, one may define

$$\Phi_c^2 \equiv P_c^2/P_a^2 \quad (34)$$

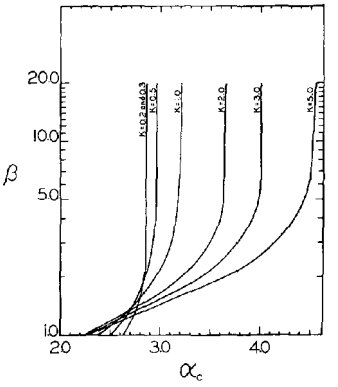

Figure 3. Plot of α_c vs. β and K for case C

and $$\Phi_d^2 \equiv P_d^2/P_a^2 \quad (35)$$

The functions Φ_c^2 and Φ_d^2 are also plotted *vs.* β for selected values of K in Figures 5 and 6.

The Parameters β and K. From Equations 2 and 13 it can be seen that β is dependent only on the sample to be analyzed and will range in value from

$$1.0 \leqslant \beta < (\mu_m)_1/(\mu_m)_2 \quad (36)$$

Also, as C increases, β will increase. The maximum value of β, β_m, has been plotted for various elements and absorption edges in Figure 7. For atomic numbers above 20, β_m is always less than 10.

K, or K^2, defined by Equation 13, is dependent only on the incident x-ray spectrum. If white radiation is used for the incident beam, $K^2 \simeq 1$, since $I_1 \simeq I_2$; but if two adjacent emission peaks, either primary or secondary, are used as sources of incident radiation for λ_1 and λ_2 (one measurement on each side of an edge), then $K^2 \neq 1$ if the intensities of the two peaks are not equal.

Optimization in Practice. As shown by Rose and Shapiro (*14*), the expected error is quite insensitive to

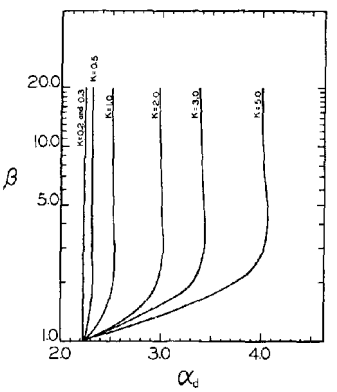

Figure 4. Plot of α_d vs. β and K for case D

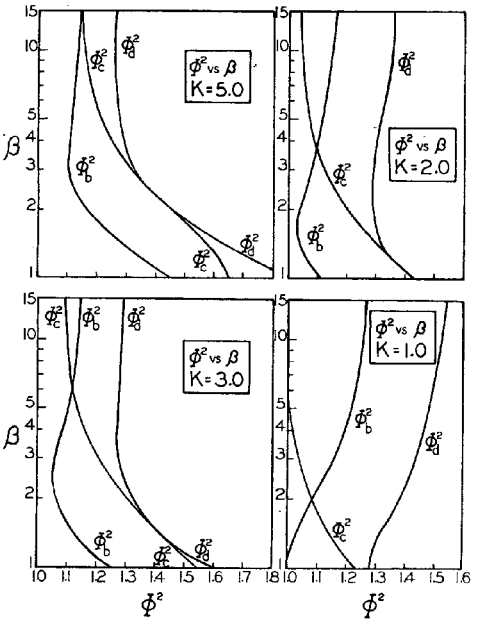

Figure 5. Plots of Φ_b^2, Φ_c^2 and Φ_d^2 vs. β for K = 5.0, 3.0, 2.0, and 1.0

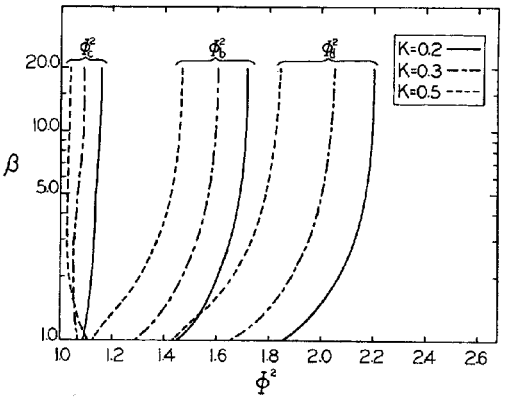

Figure 6. Plots of Φ_b^2, Φ_c^2 and Φ_d^2 vs. β for K = 0.5, 0.3 and 0.2

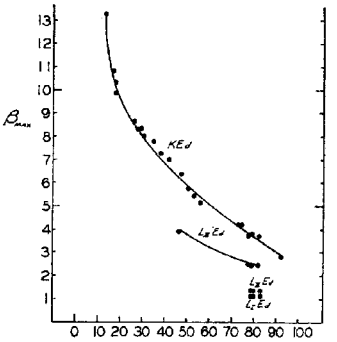

Figure 7. Plot of β_m vs. elemental atomic number for K and L absorption edges

deviations of α and the R's from their optimum values. Calculations show that variations of α or the R's of up to about 30% to 50% from their optimum values will not increase the expected error by more than about 10%.

Thus, for all practical purposes, the final section of a path length and timing ratios within a tolerance of about ±30% will essentially ensure optimum conditions.

Figures 5 and 6 show that for a given β and K it is always possible to find either Φ_b or Φ_c less than about 1.2. Because this corresponds to an increase in the expected error of no more than 20% relative to case A, then, in general, case A can be excluded from consideration because the convenience of using only two timing intervals instead of four is to be preferred over a slight increase in precision.

For case D, Φ_d is always larger than Φ_b or Φ_c, thus the expected error for case D is always larger than for case B or C. Unless the advantage of using only one timing interval outweighs the corresponding decrease in precision, case D should not be recommended.

The remaining two cases, B and C, both require, in general, two different timing intervals, and the criterion for selection between these two will be the value of Φ. The discussion following will be separated into three ranges of K.

$K \simeq 1.0$. If $\beta \geq 2$, case C is to be recommended, and if $\beta \leq 2$, case B is to be recommended, as can be seen from Figure 5. For the complete range of β

$$\alpha \simeq 3.0\ (1.0 \pm 30\%)$$

while the timing ratios are different:

$$\beta \geq 2,\ (t/T)_c \simeq 2.0\ (1.0 \pm 30\%)$$

and

$$\beta \leq 2,\ (t/T)_b \simeq 3.6\ (1.0 \pm 30\%)$$

$K < 1.0$. Figure 6 shows that case C is to be preferred for all values of β, and $\alpha \simeq 2.7\ (1.0 \pm 30\%)$ but $(t/T)_c$ will vary from about 1.0 to 3.3 depending on both β and K.

$K > 1.0$. Unless β is large, Figure 5 shows that case B is to be preferred, but the values of τ and $(t/T)_b$ will depend on the value of β and K.

Optimum Path Length for a Given Sample. Using an arbitrary path length, β, K, and μ_l are to be determined empirically. After determining the optimum case, as discussed above, the value of α corresponding to this case can be used in the first of Equations 13 to compute the optimum path length.

THE THICKNESS EFFECT

The use of the optimum path length will result frequently in the use of a reasonably thick sample. For dilute solutions in water, for example, (case D), the optimum sample path length varies for K absorption edges from about 0.5 mm. for titanium to about 9 cm. for iodine, and from about 1 mm. for cesium to about 2 cm. for uranium if the L(III) absorption edges are used. In general, for chemical analysis by XAES this is advantageous because the fine structure on each side of the edge is smeared out. (For fine structure spectrometry, per se, the thinnest practical samples are used.) On the other hand, the use of relatively thick samples increases the effective width of an absorption edge. A consequence of this is that the observed or apparent value of $\Delta\mu_m$ (distinct from the true value defined by Equation 4b) will decrease with an increase in x or C in the case of analytical procedures utilizing only one measurement on each side of an edge.

The observed value of $\Delta\mu_m$ is a function of spectrometer resolution and will vary with instrumental characteristics and experimental conditions. This so-called thickness effect and the influence of spectral window shape have been discussed by Parratt, Hempstead, and Jossem (*12*). Thus, it becomes increasingly necessary to measure absorption at several wavelengths on each side of an edge and to extrapolate to the edge. These experimental procedures, together with instrumental requirements, will be discussed in a separate paper.

NOMENCLATURE

= incident x-ray beam intensity (counts per second)

$\dot{i}$ = transmitted x-ray beam intensity (counts per second)

μ = linear absorption coefficient ($cm.^{-1}$)

μ_m = mass absorption coefficient (sq. cm. $gram^{-1}$)

$\Delta\mu_m$ = discontinuity or jump in mass absorption coefficient at a critical absorption edge (sq. cm. $gram^{-1}$)

λ = wavelength of x radiation (angstrom units)

N = number of counts collected for incident beam

n = number of counts collected for transmitted beam

T = time required to collect N (seconds)

t = time required to collect n (seconds)

τ = $T_1 + T_2 + t_1 + t_2$ = total time to collect all counts (seconds)

$R \equiv T/\tau$ = fraction of total counting time required to collect N

$r \equiv t/\tau$ = fraction of total counting time required to collect n

x = absorber sample thickness or x-ray path length (cm.)

C = concentration of element in sample (gram $cm.^{-3}$; used in conventional analytical sense of volume concentration, not in terms of mass per unit beam cross-section; C is used in the same sense as ρ or density of a single component absorber)

S_Z = standard deviation of the distribution of the measured value of Z

E_Z = root mean square error in the quantity Z

Z = quantity determined as function of k directly measured quantities, z

z = directly measured quantity

$\ln(a)$ = natural logarithm of the argument a

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Separation of Americium from Curium with Calcium Fluoride

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▶ **Americium(VI) is separated from curium(III) and other trivalent actinides and lanthanides with a column of calcium fluoride. Americium(VI) is soluble in fluoride solutions and passes through the column; curium(III) and other trivalent actinides and lanthanides are not soluble and are retained. The separated americium is determined by alpha pulse height analysis. Americium recovery averaged 102% for process samples in which curium alpha activity was 600 times that of americium. An internal standard, Am^{241}, was used to correct for yield in the analysis of these samples that contained 283 μg. Am^{243} per milliliter. The curium activity of the samples was reduced at least by a factor of 10^5 to 10^6. The relative standard deviation was 1.9% (n = 6).**

A METHOD for the determination of americium in the presence of curium and rare earths was needed for process control and accountability in the transplutonium program (*2*) at the Savannah River Plant.

The radiochemistry of americium and curium and methods for their determination have been reviewed (*7*). Recently, Moore (*6*) reported the results of an intensive study of a coprecipitation technique to separate trivalent lanthanides and actinides from americium(VI). The present method incorporates basically the oxidation procedure described by Moore (*6*); however, Am(VI) is separated by means of a column of calcium fluoride operated like a conventional ion exchange column. Plutonium follows americium through the calcium fluoride column and then is removed by anion exchange.

Calcium fluoride has been used to carry the rare earths and separate them from plutonium (*1*), to separate plutonium from uranium and fission products (*5*), and to separate plutonium from natural waters (*8*). Calcium fluoride has not been used to separate americium from other elements. This new method affords a 50-fold greater separation of americium from curium than is obtained by the precipitation technique.

EXPERIMENTAL

Use reagent grade chemicals and distilled water.

Pretreatment of Calcium Fluoride. Weigh approximately 30 grams of calcium fluoride into a beaker. Add a solution prepared by dissolving 5 grams of ammonium persulfate in 90 ml. of water and then adding 10 ml. of 2*M* nitric acid and 1 ml. of 10% silver nitrate. Stir to break up any lumps. Heat for 15 minutes at 90° C. with slow stirring. Remove from heat and decant the supernate. Filter through Whatman No. 50 paper. Wash the solid with five 150-ml. portions of hot water. Dry the solid at 120° C. for 2 hours. Cool, pulverize, and store in a clean polyethylene bag contained in a bottle. The calcium fluoride is not suitable for use after 5 days of storage.

Pretreatment of Glass Beads. To approximately 30 grams of 60- to 80-

mesh glass beads in a beaker, add 100 ml. of 0.04M potassium permanganate –2M sulfuric acid. Heat to about 60° C. with stirring. Decant and repeat the permanganate–acid treatment. After decanting, wash the beads thoroughly with water until no trace of permanganate color remains. Store the beads under water in a covered container.

Preparation of Calcium Fluoride Column. Place the column (Figure 1) in a 250-ml. filter flask with a test tube arranged to collect the effluent. Add water to the column and then add 60- to 80-mesh pretreated glass beads to form a $^1/_{16}$-inch layer. Drain the water almost to the top of the glass beads and fill the column three-fourths full with 0.1M nitric acid. Level the layer of beads. Add successive portions of pretreated calcium fluoride until a depth of approximately $^3/_8$ inch is attained. Apply vacuum to pack the calcium fluoride to a depth of $^1/_4$ to $^5/_{16}$ inch and drain the liquid to a level just above the surface. Wash the column with 2 ml. of 0.1M nitric acid followed by 2 ml. of water (never allow the liquid level to fall below the surface of the calcium fluoride). Place a clean 15-ml. graduated centrifuge cone under the column and set aside until needed. Leave approximately $^1/_8$ inch of water over the solid. Following treatment of a sample, remove the calcium fluoride and glass beads and thoroughly wash the column with 2M nitric acid and water. Prepare a new calcium fluoride column for each sample.

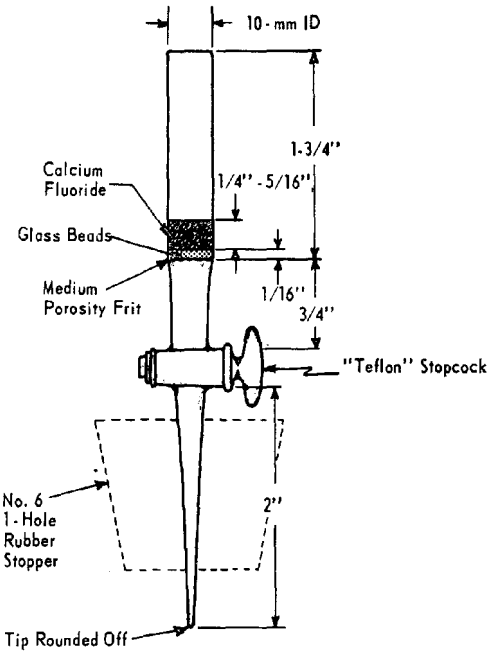

Figure 1. Calcium fluoride column

Sample Preparation. Pretreatment A. Pipet a sample aliquot (1 ml. or less) containing 10^4 to 10^6 d.p.m. (disintegrations per minute) of Am^{243} into 1 ml. of 1M nitric acid in a 15-ml. centrifuge cone. If only an Am^{243} analysis is to be made, add a known and approximately equal activity of Am^{241}. If a total americium analysis is to be made, omit the Am^{241}. Add 4 drops of lanthanum nitrate carrier (5 mg. La per ml.) and mix. If the sample aliquot contains greater than 0.01 millimole of aluminum, proceed through both pretreatments B and C. If the aliquot contains less than 0.01 millimole of aluminum, proceed directly to pretreatment C.

Pretreatment B (Aluminum Removal). To the solution from pretreatment A add 1.5 ml. of 6M sodium hydroxide, mix, and let stand for 5 minutes. Wash the sides of the centrifuge cone with approximately 20 drops of 6M sodium hydroxide. Centrifuge and decant. Wash the precipitate with 2 ml. of water, centrifuge, and decant. Dissolve the precipitate in 4 to 6 drops of concentrated nitric acid, add 1 ml. of water, and proceed to pretreatment C.

Pretreatment C (Acidity Adjustment). To the solution from pretreatment A or pretreatment B, add concentrated ammonium hydroxide dropwise until a precipitate appears; then add 5 more drops and mix. Let the precipitate stand for 5 minutes. Wash the sides of the centrifuge cone with several drops of concentrated ammonium hydroxide, centrifuge, and decant. Wash the precipitate with 3 ml. of 1M ammonium hydroxide, centrifuge, and decant. Repeat the wash with 3 ml. of water. Dissolve the precipitate in 2 drops of 1M nitric acid (heat in a hot water bath if necessary). Dilute to approximately 1 ml. with water. If the sample contains chloride, repeat pretreatment C; otherwise, proceed to the separation procedure.

Separation of Americium from Curium. To the solution from pretreatment C, add 1 drop of 10% silver nitrate. Add 3 drops of freshly prepared 5% ammonium persulfate and mix. Place the sample in a hot (>85° C.) water bath for 12 minutes. Remove the sample from the bath, add an additional 3 drops of fresh 5% ammonium persulfate, mix, and heat for 4 minutes in the hot water bath. Cool the sample to room temperature or below in an ice bath. Adjust the solution volume to 1.5 to 2 ml. with distilled water, and mix. Transfer the solution to the calcium fluoride column and adjust the vacuum to give a flow of approximately 1 drop per 15 seconds (0.2 ml. per minute). Never allow the liquid level to fall below the surface of the calcium fluoride. Wash the sample container and column with three 1-ml. portions of fresh 0.001M ammonium persulfate. Collect washings in the same cone used for collecting feed effluent. After the third wash, allow the column to drain dry. Mix the combined effluent and washes. Read the volume to the nearest 0.05 ml. and record. Proceed with the organic ion exchange procedure if plutonium is present. If plutonium is known to be absent, evaporate or, preferably, electrodeposit (3) a suitable aliquot (100 to 250 μl.) of the solution for alpha counting and pulse height analysis to determine total americium or Am^{243}. Pulse height analysis is recommended for samples with high initial curium-to-americium concentration ratios.

Separation of Americium from Plutonium. To the calcium fluoride column effluent and washes add 5 drops of lanthanum nitrate solution (5 mg. La per ml.) and mix. Add concentrated ammonium hydroxide dropwise until a precipitate appears; then add 5 more drops and mix. Let the precipitate stand for 10 minutes. Wash the sides of the centrifuge cone with several drops of concentrated ammonium hydroxide, centrifuge, and decant. Wash the precipitate with 3 ml. of water, centrifuge, and decant. Dissolve the precipitate in 5 drops of 8M nitric acid. Adjust the volume to about 1 ml. with 8M nitric acid and mix. Add 15 μl. of 2M ferrous sulfamate (freshly prepared), mix, and let stand 1 minute. Add 50 μl. of freshly prepared 2M sodium nitrite and heat in a hot water bath (>85° C.) for 20 minutes. Prepare a column of Dowex 1-X4, 100- to 200-mesh, nitrate-form ion exchange resin (Dow Chemical Co.) to give a flow of 1 drop per 10 to 15 seconds. Wash the column with 5 ml. of 8M nitric acid. Transfer the cooled solution to the column. Successively wash both the cone that contained the sample and the resin column with three 3-ml. portions of 8M nitric acid. Collect the effluent and washes in a 15-ml. borosilicate glass graduated centrifuge cone. Mix the effluent and washes, and read the volume

to the nearest 0.05 ml. Evaporate or, preferably, electrodeposit (*3*) a suitable aliquot (100 to 250 μl.) of the solution for alpha counting and pulse height analysis. Calculate total americium directly. Calculate Am^{243} with a yield correction based on the recovery of Am^{241}. Elute the plutonium from the ion exchange column into a clean 15-ml. graduated centrifuge cone with 10 ml. of freshly prepared 0.25*M* nitric acid–0.02*M* ferrous sulfamate. Read the volume of solution to the nearest 0.05 ml. and mix the solution. Evaporate a suitable aliquot (usually 250 μl.) for alpha counting to determine plutonium.

DISCUSSION

Mechanism of Separation. Americium is separated from curium in this method by an exchange mechanism. Americium(VI) and plutonium(VI) fluorides are soluble whereas the actinide(III) fluorides ($K_{SP} \approx 10^{-16}$) and the lanthanide(III) fluorides ($K_{SP} \approx 10^{-18}$) are insoluble. The hexavalent americium and plutonium pass through the calcium fluoride column; curium and other trivalent lanthanides and actinides exchange with the calcium fluoride ($K_{SP} \approx 10^{-11}$), remain on the column, and release calcium ions to the solution. An experiment was performed in which individual solutions containing from 6.8 to 34 μg.-atoms of lanthanum(III) were passed through separate calcium fluoride columns. The effluent and washes from each column were collected and analyzed for calcium by atomic absorption spectrometry and for lanthanum by microtitration with EDTA. Effluent and wash blanks were also analyzed for calcium to determine the amount of calcium dissolved from the column by the reagents. A plot of microgram-atoms of calcium appearing in the column effluent (corrected for blank) *vs.* microgram-atoms of lanthanum(III) introduced in the column was a straight line with slope 1.04. In another experiment, sixteen 5-ml. aliquots of a solution containing 1.04 mg. of La per ml. were successively passed through a 0.750-gram calcium fluoride column. Each of the 16 effluents was analyzed for calcium and lanthanum. A total of 592 μg.-atoms of calcium was found in the 16 effluents, and a total of 618 μg-atoms of lanthanum was absorbed on the column. These data indicate that the lanthanum ions are removed from solution by a one-to-one exchange with calcium ions in the crystal lattice of calcium fluoride. If the mechanism had been true ion exchange, 1.5 μg-atoms of calcium would have been released per microgram-atom of lanthanum. Although the crystal lattice of calcium fluoride is body-centered cubic and that of lanthanum fluoride is hexagonal, the crystal radii of the cations are very similar: lanthanum (III), 1.04 A; calcium, 0.99 A. In mixed crystals of the type CaF_2–YF_3 and SrF_2–LaF_3, the cationic sites can be occupied by either the divalent or trivalent ion with interstitial fluoride ions providing electrical neutrality (*9*). In our case the following mechanism can be postulated for the removal of lanthanum(III) from solution by calcium fluoride on the basis of the ion-for-ion experimental data.

$$La^{+3} + (X)A^- + CaF_2 \rightarrow LaF_2 \cdot A + Ca^{+2} + (X - 1)A^-$$

where A^- could be any anion, other than fluoride, present in the system.

Calcium Fluoride Column. Early studies with untreated reagent grade calcium fluoride revealed two problems. First, only about 50% americium recovery was obtained, and, second, the flow through the column was slow and difficult to control. Because it was believed that impurities in the calcium fluoride were causing reduction of hexavalent americium passing through the column, calcium fluoride was pretreated with silver(I)-catalyzed persulfate. The pretreated calcium fluoride not only gave americium yields of greater than 90% but also gave much improved flow characteristics. The glass beads (Figure 1), used as a base for the calcium fluoride, also improved the flow characteristics by preventing pluggage of the pores of the sintered glass disk. A flow of 1 drop per 15 ± 3 seconds (~0.2 ml. per minute) was chosen because experiments showed a faster flow would promote curium breakthrough from the column and a slower flow would needlessly increase the time for separation.

Curium breakthrough is also dependent upon the acidity of the solution flowing through the calcium fluoride column. Tests revealed that increasing solution acidities over 0.1*M* acid caused an increase in the amount of curium appearing in the column effluent. For this reason, the amount of acid used to dissolve the carrier precipitate (pretreatment C) prior to oxidation and the amount of persulfate used in the oxidation are closely controlled.

Table I. Analysis of Am^{243} in Process Samples

Process sample No.	Basis of yield factor	Am^{243}, μg./ml. By this method	Am^{243}, μg./ml. By mass spec.	% recovery	Rel. std. dev.
1	MBYC	146	155	94.2	1.3 (n = 4)
2	MBYC	264	283	93.3	2.6 (n = 5)
3	MBYC	266	283	94.0	3.0 (n = 6)
3	Am^{241} internal standard	288	283	101.8	1.9 (n = 6)

For an unknown reason the age of the pretreated calcium fluoride has an effect on the americium recovery. After a period of 5 to 10 days, in most cases, the americium recovery falls below 90%. The curium retention, however, is not affected. To keep americium recoveries high, the calcium fluoride was normally discarded 5 days following pretreatment. However, at least two batches of pretreated calcium fluoride still gave greater than 90% americium recovery one month after pretreatment.

RESULTS

In the determination of total americium in 12 synthetic samples, each containing 2.44×10^4 d.p.m. of americium and 1.34×10^7 d.p.m. of curium, the average recovery was 96.7% with a relative standard deviation of 2.6%. Curium impurity averaged 0.02% by alpha counting. No yield correction was made in calculating results from synthetic samples.

Two yield factors were used in calculating results from analysis of Tramex process (*4*) samples. One was a yield factor based on the Am^{241} internal standard. The other factor was a material balance yield correction (MBYC) that accounted only for losses incurred in the americium–plutonium separation. The MBYC is defined as follows: (d.p.m. of total americium in organic ion exchange effluent + d.p.m. of total plutonium in organic ion exchange elutriant) ÷ (d.p.m. of total americium + plutonium in calcium fluoride column effluent + washes prior to organic ion exchange). The results in Table I were obtained for Tramex process samples in which the initial alpha count ratio of curium to americium was approximately 600 to 1. Curium activity of these samples was reduced by a factor of at least 10^5 to 10^6. Results from mass spectrometric analyses that used Am^{241} as an internal standard are included for comparison. The results obtained by the MBYC method are consistently low compared with results obtained with an internal standard or with the mass spectrometer. Therefore, a 6% correction should be added to each result that is obtained by

the MBYC method. If this empirical correction is made, the relative standard deviation of the resulting data will be increased as a result of the uncertainty of the correction factor.

Similar bias was noted for samples that contained a smaller concentration of americium. Comparison of corrected data from this new method with that from the mass spectrometric method showed an agreement to within ±5% at 17 μg. Am^{243}/ml. The relative standard deviation at this concentration was 5.0% ($n = 5$).

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Infrared Spectra of Transition Metal Alkoxides

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▷ The infrared spectra of a number of transition metal isopropoxides and tetra-*tert*-butoxides have been obtained from 5000 to 285 cm.$^{-1}$ for the first time. Characteristic absorptions for the isopropoxy group have been found at 1160 to 1175 cm.$^{-1}$ and 1120 to 1140 cm.$^{-1}$ They are assigned to isobranching vibrations. The isopropoxides exhibit a doublet at about 1375 and 1365 cm.$^{-1}$ characteristic of the *gem*-dimethyl structure. The major feature of the spectra is a very strong band in the 1000-cm.$^{-1}$ region assigned as the C—O stretch vibration, which is shifted by the influence of the specific metal atom on the C—O vibration. The butoxides have four characteristic absorptions at about 785, 900, 1010, and 1190 cm.$^{-1}$ The band in the 1000-cm.$^{-1}$ region appears to be the C—O stretch vibration; the other bands are attributed to skeletal vibrations of the *tert*-butyl group. The typical C—H deformation of the *tert*-butyl group is observed at about 1360 cm.$^{-1}$ with a weaker band at 1380 cm.$^{-1}$ In the medium infrared region from 715 to 285 cm.$^{-1}$, a small number of very strong absorption bands are found for the *tert*-butoxides. The results suggest that the region would be very satisfactory for characterizing *tert*-butyl compounds.

THE transition metal alkoxides have been investigated for application to the vapor deposition of oxides on refractory substrates such as graphite for protection against oxidation. The alkoxides of Group III B and IV B metals decompose at 300° to 400° C. to the oxide, olefin, and alcohol (*15*). This reaction can be used to prepare fine particulates of high purity oxides. As a part of this investigation the infrared spectra of a number of these compounds were obtained for the first time. The spectra have proved useful in checking the results of synthesis for completeness of reaction and product identification.

The infrared spectra of a number of metal isopropoxides were studied by Bell, Heisler, Tannenbaum, and Goldenson (*3*). Characteristic absorptions were reported for the isopropoxy group at 1175, 1135, and 1110 cm.$^{-1}$, and for the *n*-butoxy group at 1150, 1125, and 1075 cm.$^{-1}$. Ory (*18*) associated the *tert*-butoxy group of various organic compounds with absorptions in the 720- to 770-cm.$^{-1}$, 820- to 920-cm.$^{-1}$, 1000- to 1040-cm.$^{-1}$, and 1155- to 1200-cm.$^{-1}$ regions. Only one alkoxide was included in this study, titanium tetra-*tert*-butoxide. Philpotts and Thain (*19*) reported a strong characteristic absorption for the *tert*-butoxy group in the 800- to 920-cm.$^{-1}$ region from a study of tertiary peroxides. Zeiss and Tsutsui (*24*) found the C—O absorptions for primary, secondary, and tertiary alcohols in the 1050- to 1085-cm.$^{-1}$, 1085- to 1125-cm.$^{-1}$, and 1125- to 1205-cm.$^{-1}$ regions. Other workers have reported characteristic absorptions for the isopropoxy group in the 1175- to 1110-cm.$^{-1}$ region from diisoamyl ether (*20*), diisopropyl methyl phosphonate (*17*), and diisopropyl ether (*2*).

EXPERIMENTAL

The tetraisopropoxides of zirconium, hafnium, and thorium have been synthesized by the method of Bradley (*8*):

$$MCl_4 + 4ROH + 4NH_3 \xrightarrow[5° C.]{C_6H_6} M(OR)_4 + 4NH_4Cl \quad (1)$$

where R is the isopropyl group.

Titanium, zirconium, and hafnium tetra-*tert*-butoxides were formed by ester exchange with *tert*-butyl acetate by the procedure of Mehrotra (*16*). The *tert*-butyl acetate was made by the acetic anhydride method (*10*). The infrared spectrum of dried, redistilled *tert*-butyl acetate was almost identical to that reported by Ory (*18*). Gas chromatographic analysis showed only traces of impurities with an approximate purity of better than 99.9%.

Isopropyl alcohol was dried over sodium hydroxide and redistilled over calcium hydride and calcium sulfate. Benzene was dried over magnesium perchlorate. The tetrachlorides were used as received from Fairmont Chemical Co. Acetic anhydride was dried over sodium carbonate and calcium hydride and redistilled.

The isopropoxides were recrystallized from anhydrous isopropyl alcohol. The crystalline product contains a small amount of bound isopropyl alcohol, which is greatest for the thorium tetraisopropoxide. The thorium compound is much more soluble in isopropyl alcohol, much less soluble in benzene, and insoluble in carbon disulfide and carbon tetrachloride, which are good solvents for the less ionic titanium, zirconium, hafnium, and yttrium isopropoxides.

Yttrium isopropoxide was synthesized for use in stabilizing zirconia in the cubic modification in vapor deposition experiments. Attempts to prepare it by the trichloride-ammonia method were unsuccessful. Yttrium isopropoxide was synthesized by the method of Adkins and Cox (*1*):

$$M + HgCl_2 + 3ROH \xrightarrow[82° C.]{} M(OR)_3 + Hg + 2HCl + {}^1/_2H_2 \quad (2)$$

Adkins and Cox found that for the synthesis of aluminum isopropoxide the reaction was exothermic and was complete after a 4-hour reflux. With yttrium the reaction was slow and a 24-

hour reflux was needed for the reaction to go to completion. A better method for synthesizing thorium was found using sodium isopropoxide (*7*):

$$ThCl_4 + 4NaOR \xrightarrow{ROH} Th(OR)_4 + 4NaCl \quad (3)$$

The infrared spectra in the 5000- to 625-cm.$^{-1}$ region were obtained on a Baird Model B infrared spectrophotometer with 0.135-mm. cell, and with a capillary film. In the medium infrared 715- to 285-cm.$^{-1}$ region, a Perkin Elmer Model 21 double-beam spectrophotometer with a cesium bromide prism was utilized.

A two-solvent system of carbon disulfide and carbon tetrachloride was used for the infrared spectra of zirconium, hafnium, titanium, and yttrium isopropoxides; Nujol was used for the thorium compound. In the medium infrared region Nujol was used for all the isopropoxides except yttrium, which was run in the two-solvent CS_2–CCl_4 system in this region. Approximately 10% concentrations in solvent were used. Titanium, zirconium, and hafnium tetra-*tert*-butoxides are colorless liquids at room temperature. The liquids were run as capillary films. The tetra-*tert*-butoxide of thorium is a semisolid which was mixed with a little Nujol and run as a capillary film. All sample handling and loading into cells were done in a dry box.

Table I. Infrared Absorption Frequencies of Metal Isopropoxides (Cm.$^{-1}$)

$B(OR)_3$ (*3*)	$Al(OR)_3$ (*3*)	$Y(OR)_3$	$Ti(OR)_4$	$Zr(OR)_4$	$Hf(OR)_4$	$Th(OR)_4$
2959	2950	2941	2959	2950	2941	
2915	2915	2857	2924	2899	2882	2899[a]
2857	2841	2825	2857	2849		
	2618	2604	2604	2625	2639	2667
		1550[b]		1550[b]	1563[b]	
1471	1464	1466	1462	1464	1475	1468[b]
			1451	1449	1460	
1422			1425			
1397						
1389	1389		1391			
1377	1374	1387	1381	1370	1379	1377[a]
	1361	1372	1370	1360	1364	1364
	1351	1359				
1333	1333	1339	1328	1333	1348	1337
1325						
1256	1245		1248			
	1206					
	1179				1186	
1174	1170	1176	1159	1166	1170	1164
1136	1134					
1124	1121	1139	1124	1136	1140	1138
	1032	1013	1000	1007	1020	996
953	958	980		958	983	973
		958	950	945	946	943
	859					
839	834	836	852	843	847	840
		828		817	823	826
	769					722[a]
	698					
685	676					
662						

[a] Nujol.
[b] Solvent.

DISCUSSION AND RESULTS

The absorption frequencies of the metal isopropoxides are given in Table I. The bands due to Nujol or a solvent have been designated. For comparison the spectra given by Bell, Heisler, Tannenbaum, and Goldenson (*3*) for $B(OR)_3$ and $Al(OR)_3$ are listed. The spectra obtained in the present work for the isopropoxides of zirconium, thorium, and yttrium are given in Figures 1 through 3. The spectra for zirconium and hafnium isopropoxides are almost identical except for a band at 1186 cm.$^{-1}$ for hafnium, and at 2849 cm.$^{-1}$ for zirconium. Some small frequency shifts also occur, such as the major band at 1007 cm.$^{-1}$ for zirconium isopropoxide and at 1020 cm.$^{-1}$ for the hafnium compound.

The similarity of the spectra of the isopropoxides of titanium, zirconium, hafnium, and thorium is seen in Table I. While the bands for thorium isopropoxide appear at about the same frequency as those for the titanium, zirconium, and hafnium compounds, the relative intensities are markedly different. Some difference might be expected from the more ionic character of the thorium derivative. The splitting of the band at 1449 to 1475 cm.$^{-1}$ is found for zirconium, hafnium, and titanium, but not yttrium isopropoxide, and is masked in thorium isopropoxide because of the strong Nujol band at 1468 cm.$^{-1}$

It is difficult to dry thorium isopropoxide to remove all the adsorbed isopropyl alcohol. A strong broad band due to the hydroxyl group appears at 3200 to 3300 cm.$^{-1}$ but is not found when the thorium isopropoxide is purified by sublimation (at 200° to 210° C. and 0.1 mm. of Hg).

The zirconium, hafnium, and thorium isopropoxides exhibit four strong absorptions in the 990- to 810-cm.$^{-1}$ region. In part these are assigned to skeletal vibrations (*12*, *18*). The 817- and 945-cm.$^{-1}$ bands for zirconium isopropoxide decreased in intensity on distillation of the alkoxide, removing a

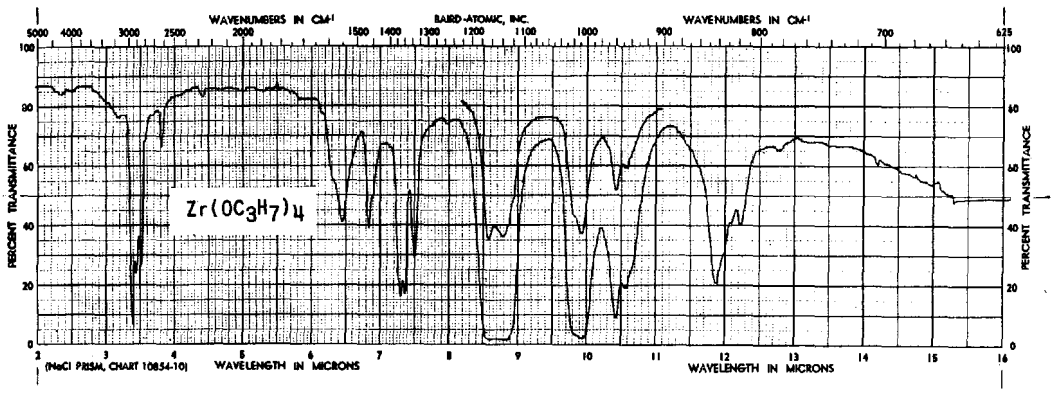

Figure 1. Infrared spectra of zirconium isopropoxide

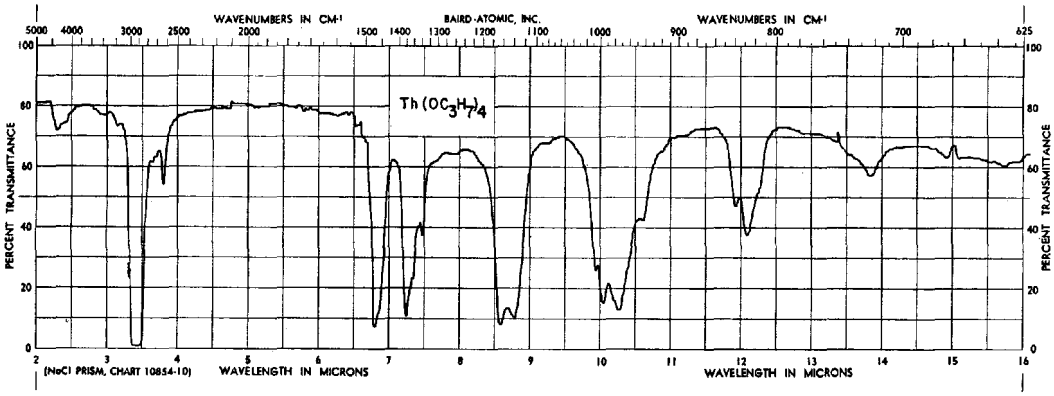

Figure 2. Infrared spectra of thorium isopropoxide

small amount of bound 2-propanol. (The spectrum shown for zirconium isopropoxide is after distillation.) The diminution of the two bands indicates that the bands are partly due to skeletal vibrations from the bound 2-propanol. The hydroxyl absorption band at about 3200 cm.$^{-1}$ almost disappears on distillation. In the 1000- to 800-cm.$^{-1}$ region the titanium compound has two major bands. Apparently these two strong bands observed as skeletal vibrations have shifted to a higher frequency and are located one at 852 cm.$^{-1}$ and the second as a part of the 1000-cm.$^{-1}$ band. The same two bands are observed in the thorium compound, at 840 and 973 cm.$^{-1}$, respectively. All of the isopropoxides exhibit a doublet at about 1375 and 1365 cm.$^{-1}$ characteristic of the *gem*-dimethyl structure (*3*).

Characteristic absorptions appear at 1160 to 1175 cm.$^{-1}$ and 1120 to 1140 cm.$^{-1}$ These are assigned to the isobranching vibrations (*3*).

The yttrium isopropoxide spectrum differed from the spectrum of aluminum isopropoxide reported in the literature. The bands in the 1050- to 800-cm.$^{-1}$ region are shifted to lower frequencies and the aluminum isopropoxide bands at 769, 698, and 676 cm.$^{-1}$ were not observed in the yttrium isopropoxide spectrum. These bands, however, may be due to the partial hydrolysis of the aluminum isopropoxide. We have found absorption bands in the 600- to 800-cm.$^{-1}$ region for partially hydrolyzed yttrium and zirconium isopropoxides. Intermediate oxy-alkoxide compounds such as $ZrO(OR)_2$ are formed in the decomposition to the oxides. In the spectra of the isopropoxides of boron and phosphorus several bands also are reported in this region. At least one band for boron has been attributed to a B—O deformation vibration. This band appears at 700 cm.$^{-1}$ for the B^{10} isopropoxide and at 665 cm.$^{-1}$ for the B^{11} isopropoxide (*12*). These vibrations would be found at lower frequencies for heavier metals such as yttrium.

The characteristic absorptions of the isopropoxide group as given by Bell *et al.* (*3*) are listed in Table II, with the absorption bands observed in the present work. Only two of the three absorption bands they suggested as characteristic have been found for these isopropoxides. Only the phosphorus compound has a distinct "middle" band at 1139 cm.$^{-1}$ The bands Bell *et al.* (*3*) report for boron and aluminum isopropoxides at 1136 and 1134 cm.$^{-1}$ are weak shoulders on the 1124- and 1121-cm.$^{-1}$ bands, respectively. The two bands observed for yttrium, titanium, zirconium, hafnium, and thorium isopropoxides at 1124 to 1140 cm.$^{-1}$ and 1159 to 1176 cm.$^{-1}$ correspond to the 1110- to 1124-cm.$^{-1}$ and 1170- to 1176-cm.$^{-1}$ bands for boron, aluminum, and phosphorus isopropoxides and are listed accordingly in the table. The difference found for phosphorus may be due to differences in symmetry arising from having a pair of unbonded valence electrons.

Table II. Characteristic Absorption of Isopropoxy Groups (Cm.$^{-1}$)

R = $(CH_3)_2CH$—

Compound	Characteristics			Ref.
$B(OR)_3$	1174	1136	1124	(*3*)
$Al(OR)_3$	1170	1134	1121	(*3*)
$P(OR)_3$	1176	1139	1110	(*3*)
$Y(OR)_3$	1176		1139	
$Ti(OR)_4$	1159		1124	
$Zr(OR)_4$	1166		1136	
$Hf(OR)_4$	1170		1140	
$Th(OR)_4$	1164		1138	

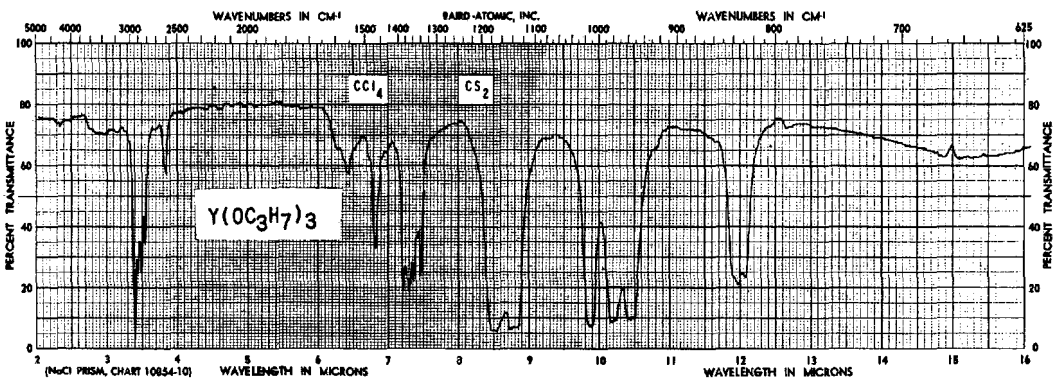

Figure 3. Infrared spectra of yttrium isopropoxide

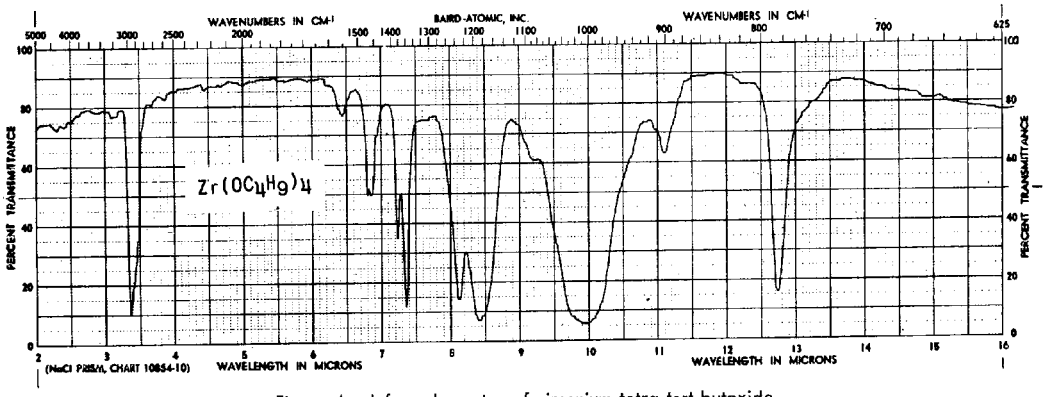

Figure 4. Infrared spectra of zirconium tetra-*tert*-butoxide

An absorption band at 2604 to 2667 cm.$^{-1}$ was repeatedly observed in the alkoxides when the α-carbon, referring to the ether linkage, had a hydrogen attached to it. If the α-carbon had a methyl or alkyl group attached to it, this band was absent. A similar observation has been previously reported (*21*). It is felt that the band is the carbon-hydrogen stretch vibration of the α-hydrogen. The apparent reason for the shift is the decrease in the strength of the bond of the α-hydrogen to the carbon, causing a shift to a lower frequency. As would be predicted, this band was not observed in the spectra of the *tert*-butoxides. A spectrum of aluminum *sec*-butoxide reported in Sadtler Standard Spectra (No. 15298CA) showed a band at 2625 cm.$^{-1}$, which agrees with this assignment.

The spectra of the *tert*-butoxides are expected to be significantly different from the isopropoxides. Because of the size of the *tert*-butyl group, there is a steric blocking to intermolecular association of the butoxides (*5*). The compounds are much more volatile than the isopropoxides. The spectra for zirconium tetra-*tert*-butoxide and thorium tetra-*tert*-butoxide are shown in Figures 4 and 5.

The absorption frequencies of the metal butoxides and *tert*-butyl acetate are given in Table III. The spectra for zirconium and hafnium *tert*-butoxides are almost identical. All the spectra are similar except for the thorium compound.

The characteristic frequencies for selected *tert*-butoxides are given in Table IV in accordance with the tabulation of Ory (*18*). The 785-cm.$^{-1}$ vibration for zirconium *tert*-butoxide has been assigned to a symmetrical skeletal vibration of the *tert*-butyl group (*23*). The 902-cm.$^{-1}$ band has been attributed to a skeletal vibration of the *tert*-butyl group (*19*). Ory attributes the band at 1010 cm.$^{-1}$ to a C—C vibration

Table III. Infrared Absorption Frequencies of Metal Butoxides (Cm.$^{-1}$)

$Ti(OR)_4$	$Zr(OR)_4$	$Hf(OR)_4$	$Th(OR)_4$	*tert*-BuAc
2976	2976	2985	2899	2988
	2924	2914		2924
2914	2865	2890	2817	
				1739
1600				
	1553	1567		
1481	1471	1475		1481
1468	1458	1466	1460	1458
1393	1381	1387	1370	1391
1368	1359	1362	1348	1366
1242	1230	1235		1256
1190	1186	1190	1208	1171
1008	1002	1015	971	1020
				940
909	901	904	883	917
				841
797				
783	785	787	753	761
744				
			671	

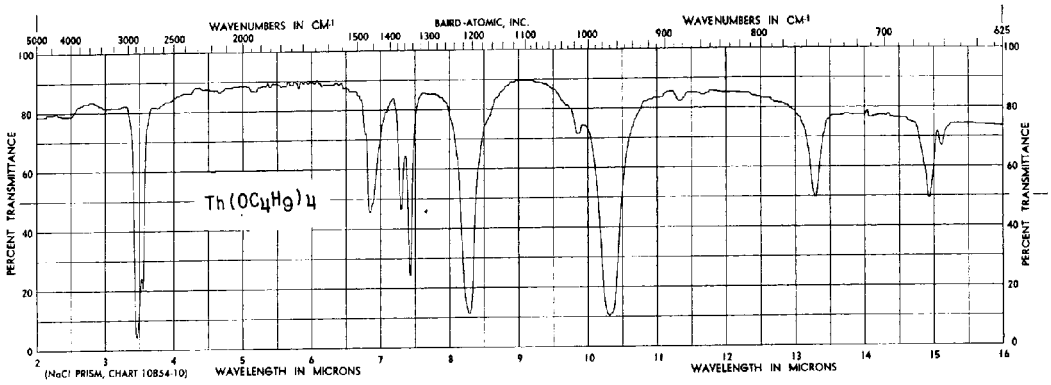

Figure 5. Infrared spectra of thorium tetra-*tert*-butoxide

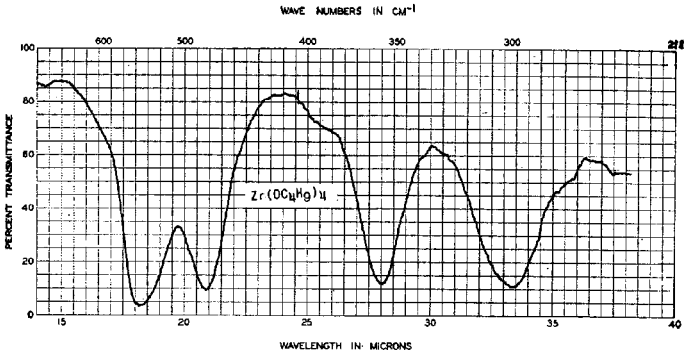

Figure 6. Medium infrared spectra of zirconium tetra-*tert*-butoxide

within the *tert*-butoxy groups and a band at 1190 cm.$^{-1}$ as a C—O stretch vibration [based on earlier work (*24*)]. From a consideration of alkane spectra in general, it is felt that the band in the region of 1170 to 1210 cm.$^{-1}$ is a skeletal stretching of the *tert*-butyl group. The band in the 1000-cm.$^{-1}$ region appears to be the C—O stretch vibration rather than the 1190-cm.$^{-1}$ band as Ory reports. Ory (*18*) felt that the bonding of the *tert*-butyl group to an oxygen attached to a transition metal would cause a lowering of the C—C vibration to the 1000-cm.$^{-1}$ region. But as Bellamy points out (*4*), the *tert*-butyl group is not very sensitive to changes in its immediate environment and frequency shifts are ordinarily very small. The *tert*-butyl group is consistently characterized by strong absorptions at about 1200 and 1250 cm.$^{-1}$, with the 1250-cm.$^{-1}$ band occasionally found shifted into the 1200-cm.$^{-1}$ band. Sheppard (*22*) studied *tert*-butyl halides and found two strong absorptions at about 1150 and 1230 cm.$^{-1}$ and a weak absorption at 1030 cm.$^{-1}$, thus obtaining results similar to Ory's on *tert*-butyl compounds, but without ether linkages present. The intensity of the 1200-cm.$^{-1}$ band found by Ory is similar to that in all the butoxides. The reported spectrum for titanium butoxide is also similar to that of the butoxides reported here, with the same very intense band at about 1000 cm.$^{-1}$ The difference in intensity in this band, which is very weak for a *tert*-butyl group bonded to a carbon atom or to an ether oxygen compared to a carbon atom attached to an oxy-metal link, indicates that the difference arises from the presence of the metal atom. For the *tert*-butoxides that contain no heavy metal atom studied by Ory (*18*), this implies the surprising result that the C—C stretch vibration intensity is much stronger than the C—O stretch vibration intensity. The typical C—H deformation in a *tert*-butyl group is observed at 1359 cm.$^{-1}$, with a weaker band at 1381 cm.$^{-1}$ The isopropoxides can easily be differentiated from the butoxides by this feature and skeletal vibrations in the 1250- to 1110-cm.$^{-1}$ region.

The medium infrared spectra of zirconium tetra-*tert*-butoxide is shown in Figure 6. The spectrum for *tert*-butyl acetate has seven major peaks, which suggests that the region would be very satisfactory for characterizing aliphatic esters (*13*).

The absorption frequencies of the isopropoxides in the medium infrared region are listed in Table V. Those for the *tert*-butoxides are listed in Table VI. The data for *tert*-butyl acetate have been added for comparison. The marked differences in the spectra in this region are particularly useful for identification and analysis. The ester exchange reaction between an isopropoxide and *tert*-butyl acetate can be followed. As the reaction proceeds, the *tert*-butoxide peaks appear and those for *tert*-butyl acetate (and the isopropoxide), of course, disappear. The simplicity of the medium infrared spectra makes this analysis possible. The infrared spectra (5000 to 625 cm.$^{-1}$) of these compounds cannot readily be used in this manner.

If the spectra of aluminum, yttrium, titanium, zirconium, hafnium, and thorium isopropoxides are examined together, a very strong absorption band is found in all the compounds in the region of 1020 to 990 cm.$^{-1}$ In the boron compound no band is observed in this region. In the present work, it has been found that as the zirconium isopropoxide hydrolyzes, the band at

Table IV. Characteristic Absorption of Butoxy Groups (Cm.$^{-1}$)

R = $(CH_3)_3C$—

Compound	Characteristics				Ref.
ROH	1194	1024	918	753	(*18*)
CH_3COOR	1174	1015	843	762	(*18*)
$Si(OR)_4$	1199	1022	841	727	(*18*)
$Al(OR)_3$			901		(*18*)
$Ti(OR)_4$	1190	1008	909	797	
$Zr(OR)_4$	1186	1002	901	785	
$Hf(OR)_4$	1190	1015	904	787	
$Th(OR)_4$	1208	971	883	753	

Table V. Medium Infrared Absorption Frequencies of Metal Isopropoxides (Cm.$^{-1}$)

$Y(OR)_3$	$Ti(OR)_4$	$Zr(OR)_4$	$Hf(OR)_4$	$Th(OR)_4$
			667	
	619			
		582	585	566
532	535	545	538	524
	474			
451		457	451	
420		426		
397	402	402	398	405
		377	380	
			355	

Table VI. Medium Infrared Absorption Frequencies of Metal Butoxides (Cm.$^{-1}$)

tert-BuAc	$Ti(OR)_4$	$Zr(OR)_4$	$Hf(OR)_4$	$Th(OR)_4$[a]
629				
608	597			
			565	580
		548	544	
			490	509
467	476	479	456	465
428	416			
	374			395
353		357	355	
337				
320		300		308

[a] Nujol.

1007 cm.$^{-1}$ disappears from the spectrum. A band at 745 cm.$^{-1}$ for zirconium oxide has been reported (*14*). A band found at 1035 cm.$^{-1}$ for divinylzinc has been attributed to a carbon-oxygen-zinc vibration from the oxidation of divinylzinc (*11*). Recent work on dialkyltin dialkoxides (*9*) is in agreement with the assignment of the C—O stretch vibration to the very strong band in this region. Thus the 1020- to 990-cm.$^{-1}$ band is apparently shifted by the influence of the specific metal on the C—O vibration.

There is no definite correlation of the mass of the metal atom and the degree of shift observed. The lowest frequency band at 996 cm.$^{-1}$ was for the isopropoxide of the heaviest metal, thorium. For aluminum and yttrium the band is at 1032 and 1013 cm.$^{-1}$, which is in agreement with the mass effect. But the results for titanium, zirconium, and hafnium are reversed, with the titanium isopropoxide having the lowest frequency for this vibration. Properties of the metal atom such as covalent radius and electronegativity do not seem to yield a consistent explanation. For many alkoxides a surprising order of volatilities attributed to changes in intermolecular association has been found—Hf > Zr > Ti > Th (*6*). This is consistent with the observed frequency changes of the C—O stretch vibration.

ACKNOWLEDGMENT

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Thermoanalysis of Some Inorganic Fluorides and Silicofluorides

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▶ **Differential thermal and thermogravimetric analyses were conducted on several inorganic fluorides and silicofluorides: potassium fluoride dihydrate, calcium fluoride, lead fluoride, ammonium silicofluoride, sodium silicofluoride, magnesium silicofluoride hexahydrate, calcium silicofluoride dihydrate, and zinc silicofluoride hexahydrate. The experiments were carried out in air at 1-atm. pressure over the temperature range 25° to 800° C. The decomposition reactions are characterized and a previously unreported crystalline transition for Na_2SiF_6 is indicated by the experimental data. The activation energy and order of reaction for decomposition were also determined from the thermogravimetric curve for the sodium silicofluoride.**

DEADMORE, Machin, and Allen (*4, 5*) studied the stability in dry and moist atmospheres of some alkali and alkaline earth metal fluorides, fluosilicates, fluotitanates, and fluozirconates using isothermal weight loss determinations, differential thermal analysis, and x-ray analysis.

Differential thermal analysis and thermogravimetry were used to investigate the thermal behavior of several inorganic fluorides and silicofluorides in air at 1-atm. pressure over the temperature range 25° to 800° C. The compounds examined were potassium fluoride dihydrate, alpha-lead fluoride, ammonium silicofluoride, magnesium silicofluoride hexahydrate, calcium silicofluoride dihydrate, and zinc silicofluoride hexahydrate. Calcium fluoride and sodium silicofluoride were also investigated but over different temperature ranges than previously considered (*4, 5*). The other substances had not been previously studied.

EXPERIMENTAL

Reagents. For purposes of confirmation, all of the following materials, except the reagent grade calcium fluoride and potassium fluoride dihydrate, were identified by x-ray diffraction: calcium fluoride, potassium fluoride dihydrate, reagent (Fisher Scientific Co.); lead fluoride, purified, anhydrous (City Chemical Corp.); ammonium silicofluoride, magnesium silicofluoride hexahydrate, zinc silicofluoride hexahydrate, samples (Davison Chemical Corp.); calcium silicofluoride dihydrate, special, technical, sodium silicofluoride reagent (Fisher Scientific Co.).

Instrumentation and Procedures. The differential thermal analysis (DTA) apparatus has been described (*7, 8*). The temperature difference between the sample and an inert reference material is recorded as a function of the temperature of the reference material. Chromel - Alumel thermocouples protected by borosilicate glass wells are embedded in the sample and reference materials which are contained in borosilicate glass test tubes. The test tubes are inserted into holes drilled in a metal block which is heated in a crucible-type furnace. In this investigation 0.5-gram samples were used

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and an equal volume of alumina served as the reference material.

The thermogravimetric apparatus used was the converted analytical balance described by Campbell and Gordon (*3*) modified for use as a thermobalance. The immersion liquid was found to be unnecessary and is not used. The tube type furnace is lowered over the sample crucible (glazed porcelain Coors No. 0000), which is supported on a quartz rod 12 inches long projecting vertically from the top of the left-hand end of the balance beam. Deflections of the balance beam resulting from changes in weight are recorded on an *x-y* recorder as a function of the temperature in the furnace just above the sample.

In both the DTA and TGA techniques, the furnace is controlled by a Gardsman stepless programming and controlling pyrometer (West Instrument Co.). The heating rates are monitored by recording block or furnace temperature as a function of time on a Brown Electronik potentiometric strip chart recorder or on a Westronics potentiometric strip chart recorder. Temperature discrepancies between DTA and TGA curves can usually be accounted for in terms of the difference between furnace temperature, which is the parameter measured in TGA, and reference temperature, which is the parameter measured in DTA. Of more fundamental importance is the fact that DTA indicates a variety of thermal effects which do not have concomitant mass effects—e.g., fusion.

For further identification, pyrolysis products were heated under the conditions of the DTA experiments to temperatures indicated by DTA and TGA to be significant and analyzed by x-ray diffraction. The slight upward trends in the TGA curves are probably due to thermal effects on the sample and balance and unless otherwise stated are not given any special significance. Replicate runs were made of each experiment in this paper, and the figures are representative curves of the replicate experiments.

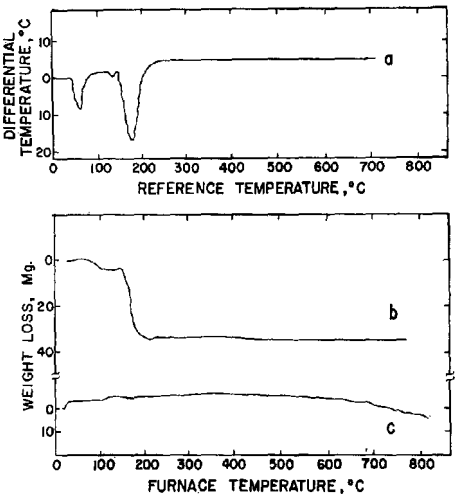

Figure 1. Thermoanalytical curves for binary metal fluorides in ambient air at heating rate of 10°C. per minute

a. DTA curve for 0.500 gram of potassium fluoride dihydrate
b. TGA curve for 0.100 gram of potassium fluoride dihydrate
c. TGA curve for 0.100 gram of lead fluoride

RESULTS AND DISCUSSION

Potassium Fluoride Dihydrate

The DTA curve (Figure 1) shows three endotherms with peaks at 65°, 134°, and 177° C., respectively. During the first endotherm, the sample changes from a solid to a liquid. It solidifies near the completion of this endotherm, and liquefies again during the second endotherm. The third endotherm is due to the final dehydration of the salt. The maximum slope of the first endotherm occurs at 45° C., which corresponds to the reported melting point of $KF \cdot 2H_2O$, 41° C. (*6*).

The TGA curve (Figure 1) shows that during the latter half of the first endotherm, which denotes fusion of the dihydrate, the sample loses water equivalent to approximately one eighth of the total present. If the dihydrate is written as $4KF \cdot 8H_2O$, the reaction may be written as:

$$4KF \cdot 8H_2O_{(s)} \rightarrow H_2O_{(g)} + 4KF \cdot 7H_2O_{(s)} \quad (1)$$

Apparently the resultant hydrate is a relatively stable compound, since on further heating from 107° to 147° C. no further weight is lost. During the second endotherm at 134° C., ascribed by us to the melting of the intermediate hydrate, there are no changes in weight; and consequently it is not caused by the vaporization of liquid water released in the first dehydration (*2*). At 147° C., final dehydration begins. The total weight loss corresponds to the formation of anhydrous potassium fluoride. This was confirmed by x-ray analysis.

Calcium Fluoride. Calcium fluoride does not undergo any thermal reactions below 700° C. This confirms previous work (*4*).

Lead Fluoride. X-ray analysis showed that the sample consisted principally of alpha-lead fluoride.

The thermogravimetric curve in Figure 1 shows a gradual weight loss beginning at about 500° C. By 820° C., 10% of the total weight has been loss, the sample is partially molten, and two phases appear to be present: a yellow liquid and a white solid. The weight loss is probably due to sublimation of the lead fluoride. X-ray diffraction analysis of a sample heated to

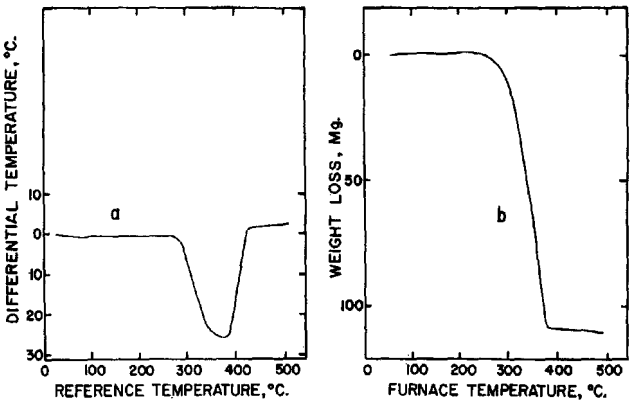

Figure 2. Thermoanalytical curves for ammonium silicofluoride in ambient air at heating rate of 10°C. per minute

a. DTA curve for 0.500-gram sample
b. TGA curve for 0.100-gram sample

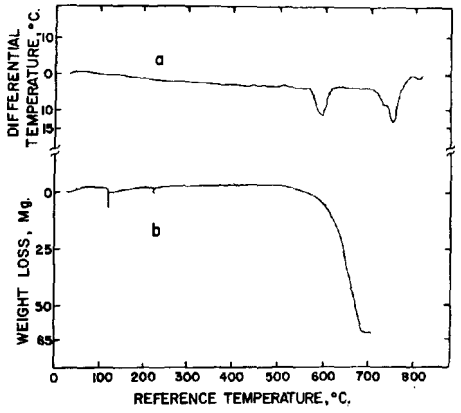

Figure 3. Thermoanalytical curves for sodium silicofluoride in ambient air at heating rate of 10°C. per minute

a. DTA curve for 0.500-gram sample
b. TGA curve for 0.100-gram sample

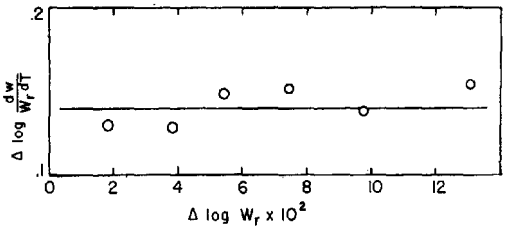

Figure 4. Freeman and Carroll plot for kinetics of thermal decomposition of Na_2SiF_6

750° C. showed only beta-lead fluoride present. The x-ray analysis was conducted at room temperature several days after the sample was heated. The reported transition temperature from alpha- to beta-lead fluoride is 250° C. (*9*). However, the DTA curve does not show any heat change. This may indicate a second-order transition. The DTA curve is not shown, because no thermal changes are observed in the curve.

Ammonium Silicofluoride. The differential thermal analysis and thermogravimetric curves for this compound are shown in Figure 2. The DTA curve shows a single endotherm beginning at 275° C., which is due to sublimation and decomposition. Sublimation was confirmed by x-ray analysis of the solid condensate, which was identified as ammonium silicofluoride. The TGA curve shows a continuous weight loss which corresponds to the endotherm in the DTA curve.

Sodium Silicofluoride. Differential thermal analysis and thermogravimetric curves for the pyrolysis of sodium silicofluoride are shown in Figure 3. X-ray diffraction analysis confirmed that the starting material was Na_2SiF_6. The TGA curve shows loss in weight beginning at 485° and ending at 685° C. The total weight loss corresponds to within 5% of the theoretical weight loss for the decomposition to sodium fluoride and silicon tetrafluoride.

$$Na_2SiF_{6(s)} \rightarrow 2NaF_{(s)} + SiF_{4(g)} \quad (2)$$

The x-ray diffraction patterns of samples heated to 535° and 626° C. are identical and show the presence of Na_2SiF_6 and a small amount of NaF. X-ray analysis of a sample heated to 700° C. shows NaF and unreacted Na_2SiF_6. At 825° C., the residue was sodium fluoride.

The DTA curve shows two endothermal bands. The first of these begins at 565° C. after approximately 5 to 6% decomposition based on the total weight loss after complete reaction. The endotherm is complete after approximately 10% decomposition. The second endotherm is due to decomposition. The first endotherm, which occurs only during the initial stages of decomposition, is attributed to a crystalline transition, since the cooling curve reveals a corresponding exotherm in going from the high to the low temperature form, demonstrating the reversibility of the process. The latent heat of this crystalline transition is estimated to be + 17 kcal. per mole. This estimation was made from the calculated heat of the decomposition reaction at 500° C. and the ratio of the areas of the respective endotherms. The final endotherm represents the decomposition of the silicofluoride.

The Freeman and Carroll (*1*, *6*) method was used to estimate activation energy and order of reaction for the decomposition of sodium silicofluoride from the thermogravimetric curve (Figure 4). This treatment, which involves plotting $\Delta \log dw/W_r dT$ *vs.* $\Delta \log W_r$ at constant $\Delta 1/T$, is based on the relationship:

$$\Delta \log \frac{dw}{W_r dT} = (N-1)\ \Delta \log W_r - \frac{E^*}{2.3R}\,\Delta\frac{1}{T}$$

where

$\frac{dw}{dT}$ = rate of weight loss with respect to temperature
$W_r = \Delta w_c - \Delta w$
Δw_c = total weight loss at completion of reaction
Δw = weight loss at corresponding dw/dT. Data taken at points so that $\Delta 1/T$ = constant, 10^{-5} °K^{-1}.
N = apparent order of reaction

An activation energy of 64 ± 3 kcal. per mole and an order of reaction of unity (1 ± 0.1) were determined for the 90% of the decomposition reaction

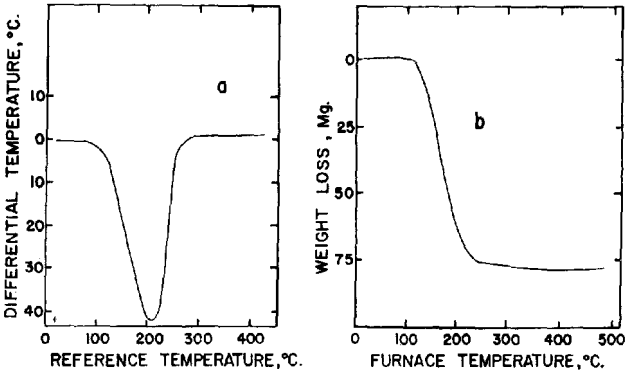

Figure 5. Thermoanalytical curves for magnesium silicofluoride hexahydrate in ambient air at heating rate of 10°C. per minute

a. DTA curve for 0.500-gram sample
b. TGA curve for 0.100-gram sample

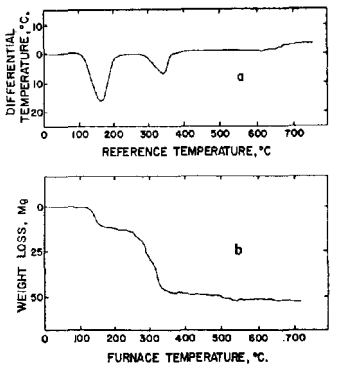

Figure 6. Thermoanalytical curves for calcium silicofluoride dihydrate in ambient air at heating rate of 10°C. per minute

a. DTA curve for 0.500-gram sample
b. TGA curve for 0.100-gram sample

which follows the completion of the crystalline transition.

Magnesium Silicofluoride Hexahydrate. X-ray analysis confirmed that the starting material was $MgSiF_6 \cdot 6H_2O$. The compound dehydrates and decomposes to magnesium fluoride in a single endothermic step beginning at about 100° C. (see Figure 5). The x-ray patterns for two decomposed samples heated to 650° C. show that magnesium fluoride is the decomposition product.

Calcium Silicofluoride Dihydrate. The differential thermal analysis and thermogravimetric curves for this material are shown in Figure 6. Dehydration and decomposition apparently occur in several stages. The first stage of weight loss, beginning at about 110° C., is due to loss of water. The dehydration corresponds to the first endotherm on the DTA curve. The x-ray patterns of samples heated to 250° and 275° C. correspond to the x-ray pattern for anhydrous calcium silicofluoride with expanded lattice parameters. From 236° to 367° C. the final stage of decomposition occurs, which involves the loss of SiF_4. The ratio of the weight loss due to dehydration to the weight loss due to the formation of SiF_4 corresponds to the theoretical value. X-ray diffraction analysis of a sample heated to 650° C. showed that only calcium fluoride is present in the bulk of the final product.

Zinc Silicofluoride Hexahydrate. The TGA curve (Figure 7) shows weight loss beginning at approximately 115° C., and completed at 222° C. The reaction involves both dehydration and decomposition of the zinc silicofluoride hexahydrate. The total weight loss corresponds to the formation of zinc fluoride. The DTA curve shows one large endotherm extending from approximately 115° C. to 324° C., corresponding to the dehydration-decomposition reaction.

If the sample is heated above 500° C., additional weight is lost. At about 600° C. the total weight loss is about 72% of the initial sample weight. This final weight loss is probably due to reaction between zinc fluoride and silica in the sample container. X-ray analysis data substantiate this explanation. Zinc orthosilicate was found in a sample of zinc silicofluoride hexahydrate that had been heated to 780° C. Although this reaction is exothermal, the DTA curve did not show an exotherm, probably because of the relatively small extent of reaction and the relatively slow reaction indicated in the TGA curve.

Table I summarizes the thermoanalysis experiments. The order of thermal stability is generally what may be expected based on free energy considerations. The difference between the thermal stability of ammonium silicofluoride and sodium silicofluoride appears to be primarily due to the entropy effect. A new crystalline transition is reported for sodium silicofluoride at 565°C.

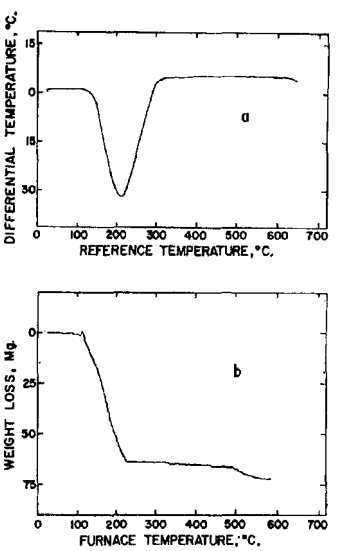

Figure 7. Thermoanalytical curves for zinc silicofluoride hexahydrate in ambient air at heating rate of 10°C. per minute

a. DTA curve for 0.500-gram sample
b. TGA curve for 0.100-gram sample

Table I. Summary of Thermal Stability Data from Thermoanalysis Curves

Compound	Temperature, ° C. Dehydration	Decomposition	M.P.	Crystalline transition
$KF \cdot 2H_2O$	75, 147	Not observed[a]	45, 134	
CaF_2		Not observed[a]		
PbF_2		Not observed[a]		[b]
Na_2SiF_6		485		565
$(NH_4)_2SiF_6$		275[c]		
$MgSiF_6 \cdot 6H_2O$	100	100		
$CaSiF_6 \cdot 2H_2O$	110	236		
$ZnSiF_6 \cdot H_2O$	115	115		

[a] Not observed below 700° C.
[b] Phase transformation is reported to occur from alpha to beta form at 250° C. (9); however, no DTA band was observed in this work, although x-ray showed that transformation did occur. See text.
[c] Sublimation and decomposition.

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Infrared Analysis of Suspended Particulates with Millipore Filters and Attenuated Total Reflection

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▶ Attenuated total reflection has been characterized as being essentially a surface effect. One implication of this is that for a given analysis only a fraction of a milligram of material properly presented to the totally reflecting face is required to produce a good spectrum. Membrane filters, because of their surface retention ability, not only accomplish a separation of particulate material from fluid media but also permit a nearly ideal presentation of the sample to the ATR crystal. In addition, substrate interferences which complicate transmission results, are reduced considerably. This method is especially valuable where the material to be examined is present in very low concentrations normally difficult to isolate from the fluid media or of a microscopic particle size. Several diverse examples are described which illustrate the utility of the technique.

THE APPLICATION of infrared spectrometry to the analysis of particulates suspended in a fluid media must, in general, be preceded by a separation and concentration of the particles. Millipore filters, which are sheets of polymeric material perforated with millions of precisely controlled small pores, have been used for some years for separations of this general kind. The separation may then be followed by a wide variety of analytical procedures depending on the system to be investigated. It is the purpose of this paper to describe the unique combination of Millipore filters and attenuated total reflection to yield a very flexible and sensitive analytical procedure.

Attenuated total reflection is essentially a surface effect. The distance over which interaction between the sample and the radiation occurs, the so-called depth of penetration, is generally less than a few microns. Thus, when ATR is applied to a given sample, the examination reduces to a measurement of the surface properties and not of the bulk properties. This implies that a few micrograms of sample, properly presented to the ATR crystal, are sufficient to yield a good infrared spectrum. The application of Millipore filters to the separation of suspended particulates accomplishes, in a single step, both the separation and proper sample preparation for ATR analysis. The particulates are distributed on the planar surface of the filter in the form of an extremely thin film such that nearly all of the sample can interact with the radiation. Although substrate interferences are reduced or, in some cases, eliminated, compensated techniques may be necessary for some samples. Except for cutting portions of the filter to fit the ATR accessory, no additional sample preparation is required.

A number of spectra have been prepared to illustrate the flexibility and potential uses of such a technique. The applications presented are divided into four general categories: powders dispersed in liquid vehicles; colloidal trace contaminants present in liquids; aerosol mists, fumes, etc.; and biochemical.

EXPERIMENTAL

The infrared spectra were obtained with a Perkin-Elmer Model 521 spectrophotometer equipped with the single and triple-reflection ATR accessories. The prism material was KRS-5 and the angle of incidence was between 41° and 50° in all cases. All sample preparations were performed with standard Millipore filters and filter holders. Experimental parameters specific to a given sample are presented in the discussion associated with that sample.

RESULTS AND DISCUSSION

Powders Dispersed in Liquid Vehicles. Paint analysis can be difficult and time consuming. Nearly all of the components will have absorption bands in the infrared spectrum. In the past it was desirable, but tedious, to separate liquid vehicles from the dispersed pigments. The application of Millipore filters eliminates the tedium and satisfies the separation requirement in one easy step. Vehicle, free of pigment, passes through the filter while the dispersed pigment and toners are collected on the surface

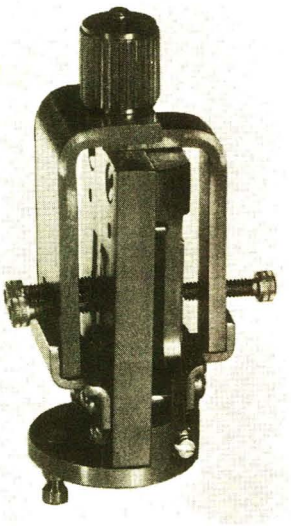

Figure 1. Three-reflection ATR accessory

of the filter. The residual vehicle is removed with an inert volatile thinner and portions of the filter are presented to the three-reflection ATR accessory (Figure 1).

The pigment spectra shown were obtained by a modification of this procedure. An aliquot of paint was diluted with petroleum ether and filtered through a 0.22-micron pore size filter. This was followed by several rinses with petroleum ether. The entire filtering process required about 5 minutes.

Figure 2 shows the spectra of 45 μg. and 5 μg. of pigment from a red paint obtained with the three-reflection ATR at an angle of incidence of 45°. These well defined spectra permitted identification of the pigment as toluidine red. A very weak spectrum of about 1 μg. was obtained by the same technique and this probably represents the lower limit of sensitivity. The sample weights shown were determined from the weight gain and area of the filter and the illuminated area of the three-reflection ATR accessory. The upper curve shows no interferences while the lower

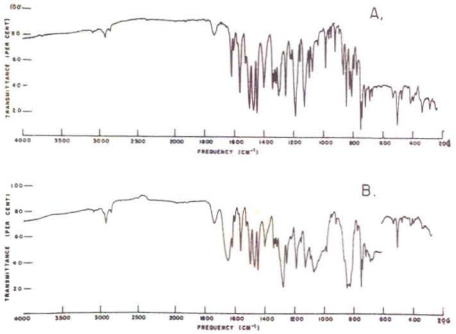

Figure 2. *A.* Three-reflection ATR spectrum of 45 μg. of pigment from a red paint on 0.45-micron pore size filter
B. 5 μg. of same pigment

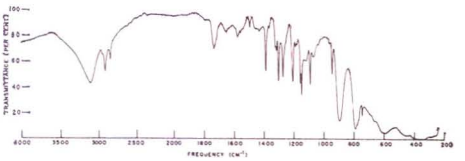

Figure 3. Three-reflection ATR spectrum of pigment from 0.1 ml. of green paint on 0.45-micron pore size filter

curve has several substrate bands clearly visible at 1650 cm.$^{-1}$, 1280 cm.$^{-1}$, and 840 cm.$^{-1}$ These bands may be used as an internal standard to quantize the method. A plot of the ratio of pigment absorbance to substrate absorbance for a series of known quantities of pigment showed good correlation. The technique, therefore, is a relatively rapid method for analyzing both quantitatively and qualitatively the pigments in very small amounts of paints.

Figure 3 illustrates the spectrum for a green paint pigment. The experimental procedure was the same as for the red paint. A phthalocyanine green is indicated by the bands between 1500 and 940 cm.$^{-1}$ Bands at 900 and 795 cm.$^{-1}$ are assigned to a hydrated yellow iron oxide while the series of peaks between 500 and 250 cm.$^{-1}$ indicates the presence of titanium dioxide.

Figure 4 is the spectrum of the two components from a white paint. The curve shown in Figure 4.A was obtained at an angle of incidence of 50°, while curve *B* was obtained at 45°. Titanium dioxide is obviously present as the pigment (Figure 4.A). Effects of the ATR technique on the band shapes may be noted. The sample was prepared by placing a 0.8-micron pore size filter on the support screen of a pressure filter holder. A 0.22-micron pore size filter was placed on top of this filter and the filter holder assembled. Sufficient paint was introduced to cover the filter surface and filtration was conducted for 20 minutes at 50 p.s.i. The vehicle passed through the top filter without pigment and saturated the second filter. While this second filter was examined by the ATR technique to produce spectrum *B*, the transmission technique described by Sloane (*2*), or the normal transmission techniques would possibly be better approaches. The vehicle was identified from the ATR spectrum as a soya modified alkyd.

The spectrum of a writing ink presented in Figure 5 represents an interesting application. The ink is a system of soluble dyes, suspended toners, and colloidal dispersants in water. The sample was prepared simply by saturating the filter with the ink. When dried, the spectrum of all insoluble components can be obtained. The undissolved components, however, remain on the filter surface rather than penetrating into the depth of the pore structure and were identified as a barium sulfate extender and a chrome yellow pigment. The angle of incidence was 45°.

The final spectrum (Figure 6) of this group was obtained at an angle of incidence of 45° for a sample of cream. Cream is a stable dispersion of lipid materials suspended in an aqueous medium. A 0.1-ml. sample of the cream was diluted with 5 ml. of water and filtered through a 0.8-micron pore size filter. The sample was rinsed with 3 ml. of water. Filtration required about 1 hour. Fats, as indicated by the bands at about 1750 and in the 1250-to 1100-cm.$^{-1}$ region, and proteins, indicated by the structure between 1650 and 1400 cm.$^{-1}$, are the primary components shown in the spectrum. Weak, sharp bands near 1400 cm.$^{-1}$ could indicate some calcium lactates.

Colloidal Trace Contaminants Present in Liquids. There are a number of applications that require the analysis of particulate materials suspended in extremely low concentration in a liquid media. The collection of

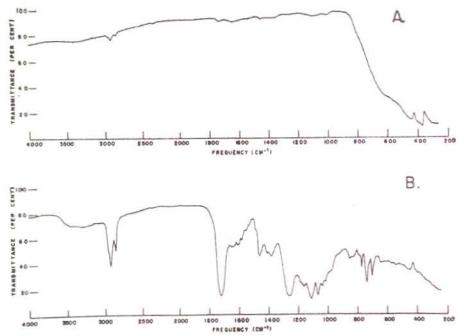

Figure 4. *A.* Three-reflection ATR spectrum of pigment from 0.5 ml. of white paint on 0.45-micron pore size filter
B. Vehicle from white paint

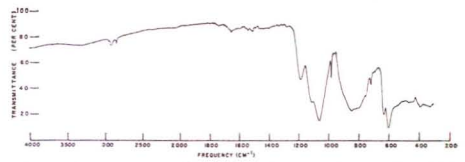

Figure 5. Three-reflection ATR spectrum of solids from green ink on 0.22-micron pore size filter

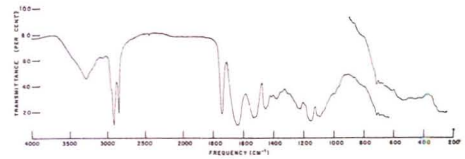

Figure 6. Three-reflection ATR spectrum of solids from 0.1 ml. of cream on 0.8-micron pore size filter

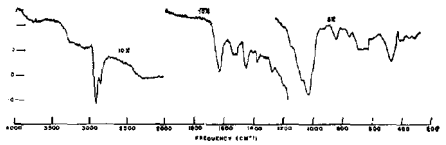

Figure 7. Compensated ATR spectrum of solids from 16 oz. of beer on 0.22-micron poré size filter

these materials in a state where they are free from all components of the suspending liquid is a difficult problem. Membrane filters are ideally suited for this task.

The first sample in this category is beer. Even after pasteurization and proper processing, small quantities of colloids including yeast cells, limit dextrins, proteins, etc., will be present. Sixteen ounces of beer were filtered through a 0.22-micron pore size filter. The filter was rinsed to remove any soluble components. The single-reflection ATR accessory was used at an angle of incidence of 43°. In the first attempt at obtaining a spectrum, substrate bands were evident. Therefore, a compensation technique involving a second ATR unit in the reference beam was employed. The resultant spectrum is shown in Figure 7. The angle of incidence in the reference unit was set slightly higher, thus permitting less penetration in the reference beam than in the sample unit. Ordinate expansion was necessary for this particular sample. The protein or yeast bands between 1650 and 1400 cm.$^{-1}$ are obvious. The absorption band near 1000 cm.$^{-1}$ probably is characteristic of residual celluloses and perhaps the limit dextrins resulting from the action of enzymes on starches.

For the next application, water from a stream was filtered through a 1.5-micron pore size filter. The filter used in this case was the Millipore solvent-resistant OH filter made of polyethylene rather than the cellulose ester filter used in the first example. Substrate bands are observed but do not interfere significantly. In this case the effective area of filtration was 4 sq. cm. and the total quantity filtered was 380 ml. The area of filter presented to the ATR prism was 60 sq. mm. Because of the colloidal material present

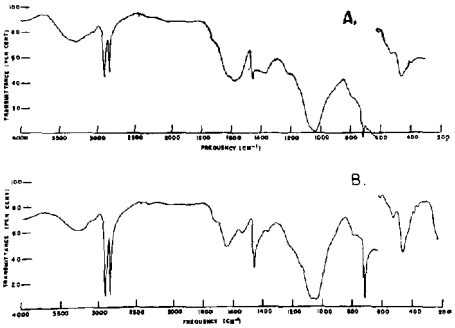

Figure 8. *A.* ATR spectrum of solids from 380 ml. of stream water on type OH 1.5-micron pore filter
B. Treated with dilute HCl

that tended to clog the filter, the sample was filtered at a pressure differential of 60 p.s.i.

Figure 8*A* is the attenuated total reflection spectrum of the solids isolated from the stream water. The angle of incidence was 41° from 4000 cm.$^{-1}$ to 630 cm.$^{-1}$ and 47° from 630 cm.$^{-1}$ to 250 cm.$^{-1}$ The bands near 1580 and 1420 cm.$^{-1}$ are due to heavy metal organic salts. As shown in Figure 8*B*, treatment with dilute hydrochloric acid eliminated these bands. The relatively strong OH stretch and bend indicate some hydrated inorganics may be present and the band near 1100 cm.$^{-1}$ may represent the sum total of contributions from silicates, cellulosics, and polysaccharides. The spectrum was obtained with an ordinate expansion of 2.

A cup of tea was prepared with a tea bag and filtered through a Millipore AA (pore size 0.8 micron) filter. A flush of water followed to remove any soluble materials. The ATR spectrum at angles of incidence of 43° and 47° of the retained solids is shown in Figure 9. It is interesting to note that, whereas the dried filtrate indicated the presence of tannins, the material collected on the Millipore filter is strongly indicative of cellulosics, probably because of the fibrous structure of the tea leaves. The tea bag may have made its small contribution to this spectrum.

Aerosols, Mists, Fumes. Carbon dioxide and water are the products of complete combustion of a hydrocarbon fuel. The automobile engine does not achieve this efficiency and so includes in its exhaust some gaseous species, small carbonized particles, and some aerosol droplets. It is a simple matter to collect the particulate and aerosol materials on a Millipore filter mounted in an aerosol holder. In each case, the sample was collected on a 0.8-micron pore size filter.

The spectra shown in Figure 10 were produced by pressing the Millipore filter against the three-reflection ATR crystal and then stripping the filter away leaving an oily residue on the crystal faces. An ordinate expansion of 10X was required and the angle of incidence was 45° in each case.

Spectrum 10*A* is from the exhaust of a two-cycle engine. Oil is admixed with the gasoline in this car and the spectrum

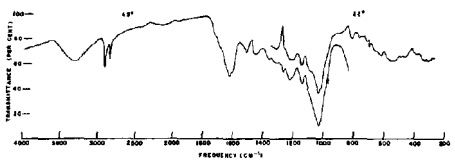

Figure 9. Compensated ATR spectrum of solids from 1 cup of tea on 0.8-micron pore size filter, 2½ × ordinate expansion

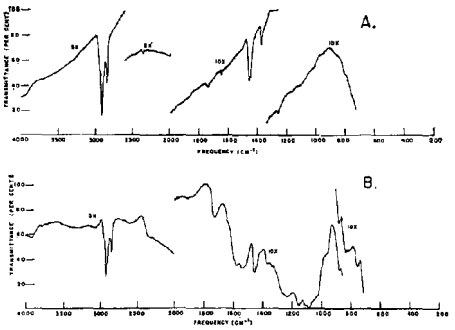

Figure 10. *A.* ATR spectrum of solids from exhaust of a two-cycle engine
B. Exhaust from a four-cycle engine

of the exhaust solids and aerosols is essentially that of a paraffinic hydrocarbon. There is evidence for some oxidation in the presence of a weak carbonyl band at 1750 cm.$^{-1}$ but, for the most part, the spectrum is very clean.

The cleanliness of spectrum 10*A* is even more apparent in comparison with the spectrum 10*B*. The sample was collected from the exhaust of a four-cycle engine. The automobile accelerator was pumped while sampling, producing a considerably enriched spectrum. Hydrocarbons are obviously present. Oxidation has been more severe and there is evidence for the presence of additives in the gasoline, which are possibly sulfonates, as well as some raw gasoline.

Biochemical. The final application was chosen purely as an example of a technique. Biomedical and biochemical investigations have not normally included infrared spectrometry. Perhaps one of the reasons for this is that most of the systems studied contain water and most infrared spectroscopists are reluctant to work with water solutions.

One interesting area of biochemistry is the metabolic mechanisms used by microorganisms. Bacteria are marvelously adaptive. Give them certain nutrients and they thrive. Give them a completely different nutrient and they change their entire metabolic process.

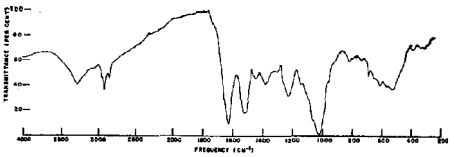

Figure 11. Compensated ATR spectrum of *Serratia marcescens* cultured on Wilson's media on 0.22-micron pore size filter

There has been some work done on infrared analysis of microorganism metabolism. Needless to say, it is a complex subject. There are a number of metabolic pathways and it may be said that the present metabolism is conditioned by the past.

An innoculum of *Serratia marcesens* in physiological saline was filtered through a 0.22-micron filter. The bacteria were retained on the filter surface. Wilson's media was introduced to the back of the filter and the filter was incubated for 24 hours at 32° C. The filter was then dried and a portion was placed in contact with the ATR crystal with the angle set at 45°. A second ATR unit containing a blank piece of filter was used in the reference beam at a slightly higher angle and 5X ordinate expansion was employed (Figure 11). Amide I, II, and III bands at 1630, 1525, and 1230 cm.$^{-1}$ are indicative of the extended form or pleated sheet form of proteins or polypeptides (*1*). The assignment of the band near 1025 cm.$^{-1}$ is a little uncertain but it is probably due to the dextran capsule making up the shell of the bacteria. Another culture grown on a second, but similar media, yielded the same spectrum.

ACKNOWLEDGMENT

We acknowledge the contributions of Seymour Goldwasser of Lever Brothers Research at whose suggestion we explored this technique, and Robert Gore who aided in the interpretation of the spectra.

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Estimation of a Few Nanograms of Fluoride in Presence of Phosphate by Use of Liver Esterase

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▷ The method of Linde, based on the inhibition of liver esterase by fluoride, has been modified to permit the estimation of a few nanograms of fluoride, even in the presence of large amounts of phosphate. Enzyme activity was measured by titration of the butyric acid formed from ethyl butyrate with NaOH. An acetone powder containing the stable esterase was prepared, and the optimal conditions for inhibition of the enzyme by fluoride were determined. The best conditions in terms of both efficiency and results: use of nitric acid–washed glass weighing bottles as incubation vessels; incubation volume, 1.25–2.5 ml.; pH, 3.0–3.3; 25 μl. of acetone powder suspension (2 mg. per ml.); 0.5 ml. of ethyl butyrate solution (1:200 in water); room temperature (inhibition improving somewhat with decreased temperature); incubation time, 1–1.5 hours.

DESIRABILITY of a method for quantitatively determining nanogram (ng., 10^{-9}g.) levels of fluoride in biological tissues has stimulated investigations in this laboratory of the potentials of several of the currently available procedures for adaptation to a submicro scale. Of the methods examined (*2, 3, 5, 6, 8, 9, 12, 14*), that of Linde (*6*) appeared to offer the best possibility of attaining the required degree of sensitivity. This method is based on the extraordinary susceptibility of the enzyme lever esterase to inhibition by fluoride, and it is capable of estimating a minimum of approximately 0.1 μg. of fluoride in a volume of 100 ml.

A disadvantage associated with the other methods is that separation of fluoride from phosphate is required for successful colorimetry, and we found this difficult to accomplish on a submicro scale with an acceptable degree of precision. In contrast, our preliminary findings with the method of Linde suggested that although the sensitivity is lowered by the presence of phosphate, this interference is moderate and can be controlled. Early attempts to reduce the scale of the method resulted in intolerable losses of sensitivity and precision, and the method suffered from the additional disadvantage that the

enzyme lacked satisfactory stability in the liver supernatant employed by Linde.

The following report describes the elaboration of the optimum conditions for the inhibition of liver esterase by fluoride and the attendant modifications of the method of Linde which ultimately permitted the estimation of a few nanograms of fluoride in the presence of large amounts of phosphate.

EXPERIMENTAL

Materials and Apparatus. FLUORIDE-FREE WATER. Bottled distilled water prepared for intravenous injection (Cutter Laboratories, Berkeley, Calif. or Don Baxter, Inc., Glendale, Calif.) was judged to be free of fluoride after comparison of the activity of liver esterase in this water with the activity of the enzyme in distilled water from which the residual fluoride had been removed by adsorption on hydrous zirconium oxide.

STANDARD FLUORIDE SOLUTION. A solution of analytical grade sodium fluoride (22.1 mg. per liter) in fluoride-free water was diluted 1:10 with fluoride-free water so that the concentration of fluoride in the solution was 1 μg. per ml. The solution was stored in a polyethylene bottle.

SUBSTRATE SOLUTION. Ethyl butyrate (Distillation Products, Inc., Rochester, N. Y.) was diluted to a concentration of 1:200 (v:v) with fluoride-free water. The solution was stored at 0° C. and brought to room temperature before use. Because there may be some spontaneous breakdown of the ethyl butyrate, it is best to prepare a fresh solution every week.

CALCIUM PHOSPHATE SOLUTION. This was made up in a manner such that the ratio of calcium to phosphate was the same as for hydroxyapatite (10:6). Reagent grade salts essentially free of impurities which affect liver esterase activity were used. $NaH_2PO_4 \cdot H_2O$ (100 mg., General Chemical Co., New York) and $CaCl_2 \cdot 2H_2O$ (176 mg., Allied Chemical and Dye Corp., New York, N. Y.) were dissolved in about 90 ml. of fluoride-free water. The solution was brought to pH 3.1 with *N* HCl and diluted to 100 ml. One ml. of such a solution contains amounts of calcium and phosphate equivalent to those in 1.2 mg. of hydroxyapatite.

INCUBATION VESSELS. These were Parr weighing bottles (Exax, 20 × 24 mm.) with externally fitted ground glass covers. Before use, all containers were washed once with detergent (Joy; Procter and Gamble, Cincinnati), several times with tap water, once with 30% HNO_3, several times with distilled water, and twice with fluoride-free water. They were kept filled with fluoride-free water and covered until used.

Methods. PREPARATION OF ENZYME POWDER. Homogenize 50 grams of fresh or frozen (−10° C.) and thawed hog liver at room temperature for about 5 minutes in a glass Waring Blendor jar with about 200 ml. of fluoride-free water and add 5 ml. of toluene. Heat the mixture at 37° to 40° C. for 24 hours and filter off the precipitated material. To the filtrate add 5 volumes of ice cold acetone at 0° to 2° C. in a cold room. Let stand for a few minutes to ensure complete precipitation and then filter on a Büchner funnel. Scrape the precipitate onto a Petri dish, spread it into a thin layer, and allow to dry at room temperature in a hood. Pulverize the dried material in a mortar and dry further in an evacuated desiccator over H_2SO_4. Store the resulting powder (about 1 gram) in a convenient fluoride-free container at 0° C. Bring the container to room temperature before opening in order to avoid condensation of moisture on the inside. This powder retains its esterase activity for at least several months when stored at 0° C.

STANDARDIZATION OF ENZYME POWDER. Each time a new batch of enzyme powder is prepared, its activity is measured in order to know the optimum concentration of powder to be used in the fluoride assay. This is done as follows.

Place 10 mg. of powder in a 10-ml. graduated cylinder. Add about 1 ml. of fluoride-free water and crush thoroughly with a stirring rod. Add water to the 5-ml. mark and mix. Allow the larger insoluble particles to sink to the bottom before extracting aliquots of the suspension. To 4 incubation vessels, add 2 ml. of fluoride-free water at pH 3.1 and 25 μl. of powder suspension with thorough mixing by swirling. To two of the vessels add 0.5 ml. of ethyl butyrate solution with thorough mixing and incubate at room temperature (below 30° C.) for 1 hour. Precision is increased by keeping the temperature of the samples as uniform as possible. An aluminum block with depressions to hold the containers is satisfactory for this. Stop the enzyme reaction by adding 0.25 ml. of ethanol, mixing, and immediately placing the vessels in a tray of ice water. Keep the vessels at low temperature until they are titrated and bring each sample to room temperature just before titration. Titrate electrometrically to pH 7.8 with 0.025*N* NaOH added from a 0.2-ml. serological pipet (use the same pipet for all samples) while stirring with a stream of nitrogen delivered through a capillary tube. The nitrogen also serves to eliminate CO_2 which otherwise can introduce titration errors.

The other two samples serve as duplicate blanks not to be incubated and can be titrated during the incubation period. To these, add 0.25 ml. of ethanol followed by 0.5 ml. of ethyl butyrate solution, then titrate as described above. Calculate the enzyme activity by subtracting the average blank titer from the average experimental titer. Duplicate titers should agree within 5% although larger errors can sometimes be tolerated. For optimum inhibition by fluoride, the enzyme activity should approximate 0.1 ml. of NaOH per hour at 25° C. and pH 3.1 (0.075 ml. at 20° and 0.14 ml. at 30° C.).

PREPARATION OF STANDARD CURVE. It may be necessary to run a standard curve either in the presence or absence of phosphate salts depending on the nature of the unknown. If the amount of phosphate to be present in the unknown incubation medium lies above 7×10^{-4} mmoles, the latter is a satisfactory amount since the effect of phosphate on the fluoride inhibition changes only slightly above it. Below 7×10^{-4} mmoles, the level used for the standard curve should approximate that in the unknown. If the unknown contains calcium in the presence of phosphate, the standard curve samples should contain approximately the same amount. In the absence of phosphate, calcium has little effect on enzyme activity or inhibition by fluoride in these concentrations and its level need not be controlled. This is also true for sodium and potassium. We have employed the method of Beveridge and Johnson (4) for the assay of phosphate in the unknown. The procedure for preparing the standard curve is as follows.

To each of 14 incubation vessels add, if necessary, phosphate solution and make up to a volume of 1.9 ml. with fluoride-free water. Both of these solutions should be at pH 3.1. To vessels, in duplicate, add 5, 10, 25, 50, and 100 μl. of standard fluoride solution and adjust the volumes, where necessary, to 2 ml. with neutral fluoride-free water. The four vessels to which fluoride is not added serve as duplicate controls to be incubated and duplicate blanks not to be incubated. Carry out the enzyme assay as described above. The incubation time should be adjusted so that the blank-corrected titer of the controls is 0.1 to 0.15 ml. of NaOH. Express each average blank-corrected titer as a % of the blank-corrected control titer. Plot the obtained values against the logarithms of the fluoride levels on semilogarithmic graph paper. The curve may be nearly linear or exhibit some curvature. Several standard curves obtained under various conditions are shown in Figure 1.

ESTIMATION OF FLUORIDE. A preliminary semiquantitative assay may be necessary in order to obtain a rough idea of the amount of fluoride present in the unknown. Adjust the pH of the unknown to 3.1 and perform the assay by means of the techniques outlined above. Determine the approximate amount of fluoride present in the unknown from the standard curve. On the basis of this estimate, perform an accurate analysis on a convenient amount of the unknown. Run fluoride standards at two levels, above and below the level of fluoride in the unknown, with the amount of fluoride in the higher standard about twice that in the lower one.

Run all samples in duplicate. If the unknown contains phosphate, or calcium plus phosphate, identical amounts must be included in the standards and blanks. In the absence of phosphate, calcium has little effect on the fluoride assay. Ordinarily, the calcium content can be calculated from

the phosphate value. This would be the case, for example, with tooth enamel or bone where the calcium and phosphate are present mainly as hydroxyapatite. Where phosphate is present, carbonate-free NaOH should be used for the titrations in order to attain maximum precision. Plot the per cents of control hydrolysis shown by the standards against the logarithms of their fluoride levels, draw a line between the two plotted points and determine the level of fluoride in the unknown from this line by interpolation.

RESULTS

Investigation of Enzyme Preparations. Although the beef liver supernatant employed by Linde (*6*) is quite satisfactory as a source of esterase for the estimation of fluoride, it slowly loses activity and this necessitates continual restandardization and frequently repeated preparations of the supernatant. The preparation of a stable powder was therefore attempted. Because of its higher esterase content, hog liver instead of beef liver was used as the starting material for the preparation of an acetone powder as described in the experimental section.

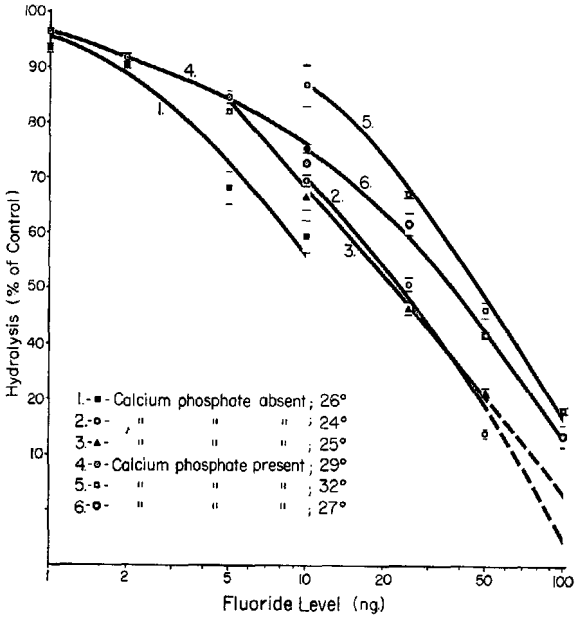

Figure 1. Representative examples of standard curves

Geometrical configurations mark the means of duplicate values which are indicated by the horizontal lines. Incubations were carried out for 1-1.5 hr. at pH 3.1–3.2. Other conditions were as described in Table I and text

Table I. Specific Activity and Relative Purity and Inhibition by Fluoride of Esterase in Hog Liver Fractions

Fraction[a]	Specific activity,[b] ml. NaOH/hr./mg.	Relative purity	Hydrolysis with F^-, % of control
1	0.80	1.00	...
2	0.76	0.95	56
3	2.7	3.4	52

Conditions. The standard fluoride assay procedure was used. Incubation vessels contained 2 ml. of water, 0.5 ml. of ethyl butyrate solution, 25 µl. of the indicated fraction, and, where present, 25 ng. of fluoride in a total volume of 2.55 ml. Incubation time, 0.5 or 1 hr.; pH, 3.0; temperature, 27° to 28° C.

[a] 1—original homogenate; 2—supernatant from heat treatment of homogenate; 3—water soluble portion of acetone powder.

[b] Based on dry weight.

Table I shows the specific activity, relative purity (referred to the original homogenate), and inhibition by fluoride of the enzyme in the major fractions obtained. These are: (1) the original homogenate, (2) the supernatant obtained from heat treatment of the homogenate, and (3) the water soluble portion of the acetone powder. The assays of the fractions were performed under conditions which have been found to be optimal for the estimation of fluoride. The elaboration of these conditions will be considered in subsequent sections. It is apparent that most of the purification was effected when the final powder was taken up in water and the insoluble material was discarded.

There was little improvement in the inhibition by fluoride of the esterase present in fraction 3 as compared with fraction 2. The major advantage of the powder, as compared with the supernatant, resides in the stability of the former which appears to be retained, for practical purposes, over a period of several months of the powder is stored at 0°

In another experiment, the powder was prepared directly from the same liver as was used in the experiment of Table I by grinding the liver with acetone. It was found that the standard curve was much less linear when this powder was used. Therefore, to ensure the best accuracy, the powder should be prepared as described in the experimental section.

Effects of Hydrolysis Products. Amberg and Loevenhart (*1*) have shown that added butyrate accelerates the action of liver esterase and interferes with the inhibition of the enzyme by fluoride. In order to gain a semiquantitative idea of the magnitudes of these effects in our system, the experiment of Table II was performed. It is seen that the findings of Amberg and Loevenhart were confirmed, although the effects of added butyrate were much greater at higher pH. This suggests that butyrate ion rather than butyric acid (pK 4.8) exerts most of the effect.

Table II. Effects of Hydrolysis Products

pH Initial	pH Final With F^-	pH Final Without F^-	Butyrate added[a] µmoles	Substrate hydrolyzed, ml. 0.025N NaOH With F^-	Substrate hydrolyzed, ml. 0.025N NaOH Without F^-	Incubation time, min.	Hydrolysis with F^-, % of control
5.3	3.9	3.8	0	0.093	0.141	50	66
5.6	4.2	4.1	1	0.131	0.167	50	79
5.6	4.7	4.6	5	0.158	0.177	50	89
3.1	3.1	3.1	0	0.067	0.147	90	46
3.1	3.1	3.1	1	0.078	0.162	90	48
3.1	3.1	3.1	5	0.092	0.165	90	56

Conditions. See Table I and text. Incubation temperature, 28° C.

[a] The solution was adjusted to pH 5.9 for the high pH range and pH 3.3 for the low range.

At pH 3.1, 1 μmole of added butyrate had almost no effect, and 5 μmoles did not have a large effect.

In subsequent experiments, results were interpreted in the light of these data, and incubation times were often regulated to lessen variability resulting from differences in formation of hydrolysis products. Table II also shows that lowering pH in itself improves inhibition by fluoride as found by Amberg, Loevenhart, and Peirce (*1*, *7*). More extensive investigations of this are described in the next section.

Effects of pH. The experiments of Table III are illustrative of many experiments which were performed to determine the pH which would confer on the system the greatest possible sensitivity to fluoride while still retaining a practical level of enzyme activity. For the reasons discussed above, incubation time was regulated so that approximately equal amounts of substrate would be hydrolyzed in the absence of fluoride at each pH. Differences in the amounts of butyric acid and butyrate ion present in the control samples were thus a function of pH only.

It should be emphasized that while differences in results within individual experiments are quite reliable, differences between experiments are not, because of variability in reagents and conditions. There was very little change in inhibition by fluoride as the initial pH was lowered from 5.6 to about 4. Between pH 4 and 3 there was a marked increase in inhibition.

A similar phenomenon was noted in the presence of calcium phosphate (Experiment 4). Below pH 3, the enzyme activity fell off very rapidly and there was little, if any, increase in the fluoride inhibition. It is of interest that Stetter (*13*) observed a pH optimum of 3.8 for the inhibition of potato phosphatase by fluoride. It will be noted (Table III) that at pH 3.3 or below, the differences between initial and final pH were very small, which is an added advantage of carrying out the assay at low pH. The overall results suggest that fluoride analyses should be carried out preferably at about pH 3 but not above pH 3.3 unless loss of sensitivity can be tolerated.

Effects of Incubation Time. In view of the antagonism of the fluoride inhibition by butyrate (Table II), it was reasoned that incubation time might have a profound effect on the sensitivity of the analytical system to fluoride. It was found that the fluoride inhibition was maximal if incubation times were kept below those which would afford titers of about 0.15 ml. of 0.025*N* NaOH. This titer represents about 4 μmoles of butyrate. As incubation time and the corresponding titer were increased further, the fluoride inhibition was progressively lowered. Given the other standard conditions of the assay, satisfactory titers were obtained by incubating for 1 to 1.5 hours, depending on temperature.

Table III. The Effects of pH

Expt.	Calcium phate soln., ml.	pH Initial	pH Final With F^-	pH Final Without F^-	Substrate hydrolyzed, ml. 0.025*N* NaOH With F^-	Substrate hydrolyzed, ml. 0.025*N* NaOH Without F^-	Incubation time, min.	Hydrolysis with F^-, % of control
1	...	5.6	4.0	3.8	0.077	0.118	50	65
		4.8	3.9	3.7	0.082	0.125	60	66
		4.4	3.8	3.7	0.083	0.118	60	70
		3.0	3.0	3.0	0.069	0.131	100	53
2[a]	...	5.0	3.8	3.7	0.079	0.147	45	54
		4.1	3.6	3.5	0.081	0.144	60	56
		3.6	3.4	3.3	0.094	0.187	70	50
		3.1	3.1	3.1	0.070	0.194	90	36
		2.6	2.6	2.6	0.020[b]	0.052[b]	120	39
3	...	3.5	3.4	3.3	0.056	0.132	70	42
		3.2	3.0	3.0	0.049	0.129	90	38
4	0.1	3.9	3.6	3.4	0.099	0.137	66	72
		3.6	3.4	3.4	0.105	0.153	69	69
		3.3	3.2	3.2	0.093	0.145	72	64
		3.0	3.0	2.9	0.080	0.137	81	58

Conditions: See Table I and text. The incubation temperature varied between 24° and 30° C. but was constant for all samples in a given experiment.

[a] The incubation volume was 25 ml. instead of the standard 2.5 ml., and the volumes of all constituents added were increased by a factor of 10. The titration values have been corrected to a 2.5-ml. volume for comparison with other experiments.

[b] These values are low because the incubation time of 120 min. was insufficient to compensate for the unexpectedly low enzyme activity at pH 2.6.

Table IV. The Effects of Enzyme Concentration

Expt.	Vol. enzyme solution, μl.	Substrate hydrolyzed, ml. 0.025*N* NaOH With F^-	Substrate hydrolyzed, ml. 0.025*N* NaOH Without F^-	Incubation time, min.	Hydrolysis with F^-, % of control
1	15	0.051	0.081	100	63
	25	0.049	0.098	60	50
	35	0.057	0.099	43	58
2	25	0.053	0.095	60	56
	50	0.062	0.079	30	78

Conditions. See Table I and text. Concentration of added acetone powder suspension, 2.0 mg./ml.; incubation pH, 3.4; temperature, 27° C.

Effects of Enzyme Concentration. The data of Table IV show that 25 μl. of acetone powder suspension (2 mg. per ml.), with activity as prescribed above, was approximately optimal for inhibition by fluoride. Accordingly, we have selected this volume to be used in the standard fluoride assay. In these experiments, the hydrolysis of substrate in the absence of fluoride was kept approximately constant by regulating incubation time.

Effects of Substrate Concentration. It seemed reasonable that by lowering substrate concentration, greater sensitivity to fluoride might be attained because of less competition by the substrate with fluoride for sites on the enzyme. However, just the reverse was observed. For example, in one experiment, lowering the amount of substrate added from 0.5 ml. to 0.1 ml. increased the hydrolysis shown by the sample with 25 ng. of fluoride from 48 to 79% of the control value.

In other cases, small net stimulations of the enzyme by fluoride were observed even at as high a level as 0.3 ml. of substrate. Increasing the level of substrate from 0.5 ml. to 1 ml. did not change the fluoride inhibition markedly. Since very good inhibition has always been obtained with 0.5 ml. of substrate, this level was selected for the standard assay procedure.

Effects of Sodium and Calcium Phosphate. Table V shows the effects of various levels of sodium phosphate solution (Experiment 1) and of a solution prepared by adding calcium chloride to the same sodium phosphate solution (Experiment 2). The maximum amount of phosphate tested was above that which would ordinarily be present in a biological sample to be analyzed for fluoride. Both the sodium phosphate and the mixed salt solution lowered enzyme activity by a small amount in the absence of fluoride. In the presence of fluoride, there was either a smaller lowering or a mild stimulation of enzyme activity.

Table V. Effects of Calcium and Phosphate Salts

Expt.	Salt soln.	Vol., ml.	Substrate hydrolyzed, ml. 0.025N NaOH: With F^-	Substrate hydrolyzed, ml. 0.025N NaOH: Without F^-	Hydrolysis with F^-, % of control
1	Sodium phosphate	0	0.060	0.128	47
		0.10	0.071	0.127	56
		0.25	0.068	0.122	56
		0.50	0.062	0.118	53
2	Sodium phosphate and calcium chloride	0	0.057	0.139	41
		0.10	0.059	0.103	57
		0.25	0.064	0.102	63
		0.50	0.065	0.102	64
3	Calcium chloride	0	0.036	0.070	51
		0.50	0.032	0.068	47

Conditions. See Table I and text. The concentrations of calcium chloride and sodium phosphate added were $1.22 \times 10^{-2}M$ and $7.3 \times 10^{-3}M$, respectively, affording the calcium to phosphate molar ratio of hydroxyapatite (10:6). Temperature, 25° to 26° C.; pH 3.0–3.1; incubation time, 1 hour. The concentration of enzyme was lower in Experiment 3 than in Experiments 1 and 2.

Table VI. The Effects of Incubated Glass

Surface area of glass, sq. cm.[a]	Substrate hydrolyzed, ml. 0.025N NaOH: With F^-	Substrate hydrolyzed, ml. 0.025N NaOH: Without F^-	Hydrolysis with F^-, % of control
10	0.074	0.148	50
15	0.063	0.132	48
22	0.063	0.116	54
35	0.061	0.083	73

Conditions. See Table I and text. Incubation time, 1.5 hours; pH, 3.2; temperature, 29° C.

[a] The sum of the area of the vessel to which the incubation medium was exposed (10 sq. cm.) and the area of the powdered glass estimated as described in the text.

The net effect of the salts in both cases was to cause a marked lowering of the fluoride inhibition between 0 and 0.1 ml. of solution, with relatively little change as the salt level was increased further. The reduction of inhibition was greater in the case of the mixed salt solution. Since a high level of calcium chloride had little effect on either enzyme activity or its inhibition by fluoride (Experiment 3), it would appear that calcium enhances the adverse effect of phosphate on the inhibition of the enzyme by fluoride. Thus, for the purpose of the fluoride assay, the level of calcium should be controlled when phosphate is also present. In the absence of phosphate, such a precaution need not be taken.

In view of the lack of an obvious specific effect of sodium and chloride or of a general salt effect in the range of concentration tested, it is thought that the mixture of calcium chloride and sodium phosphate will suffice to control the effects of calcium phosphate in, for example, tooth enamel and bone. It is important, however, that the salts be essentially free of fluoride and other materials which affect liver esterase activity. This was apparently true in the case of the salts used for the experiments of Table V; however we have found another preparation of calcium chloride to be unsatisfactory (calcium chloride, anhydrous, A. R., Mallinckrodt Chemical Works, control AJA-1).

Effects of Glass. Reducing the incubation volume from the 100 ml. employed by Linde (*6*) to 2.5 ml. resulted in appreciable loss of sensitivity. A possible explanation appeared to be that when the incubation volume is reduced, the surface area of the glass per unit volume of medium is increased. This could affect the enzyme by adsorption, and the fluoride either by adsorption or by the well known reaction of hydrofluoric acid with glass.

The results of an experiment designed to test these possibilities are shown in Table VI. The density of 300-mesh powdered borosilicate glass was determined experimentally, and the approximate surface area per unit weight of glass was established from the particle size and the density under the assumption that the particles were spheres. The surface area of 1 mg. of glass was estimated to be 0.5 sq. cm.; before use, the glass was washed with 30% HNO_3, then several times with distilled water and fluoride free water, and dried at 100° C. The surface area of the portion of the vessel to which the incubation medium was exposed was approximately 10 sq. cm., and this area was added to the area of the powdered glass to give the total areas tabulated in Table VI. The data show that the glass produced a drop in enzyme activity in the absence of fluoride, and a smaller drop where fluoride was present. The net effect was thus a decrease in inhibition by fluoride with increasing quantities of glass.

Another experiment was done to test the ability of glass to adsorb fluoride from acid solution. The fluoride solution, at pH 3, was stirred with the glass for several minutes in polystyrene containers. When referred to the amount of fluoride incubated, the amounts and surface areas of the glass samples were the same as for Table VI. The tubes were then centrifuged and aliquots of the supernatants containing 25 ng. of fluoride were tested for their effects on esterase activity by the standard procedure. It was observed that the fluoride inhibition was about the same at all levels of glass and in the absence of glass. This shows that the glass adsorbed insignificant amounts of fluoride from solution.

We have also observed that fluoride solutions of concentrations in the range of those expected for unknowns to be analyzed by the present method can be stored for at least several days in glass containers at a pH of 3 and a temperature of 0° C. without significant change in their capacity to inhibit liver esterase. The major effect of glass, therefore, is to reduce enzyme activity and to reduce the observed inhibition indirectly by lowering enzyme activity to a greater extent in the absence of fluoride than in its presence.

It was calculated that by reducing the incubation volume from the 100 ml. employed by Linde to the 2.5 ml. used in the present method, the surface area to volume ratio would increase to about 3 times its original value. The observed effect of the powdered glass thus might suffice to explain the loss of sensitivity encountered. It is also apparent, however, that small differences in surface area between containers of approximately the same volume would have little effect on sensitivity or precision.

Effect of Temperature. There was a small drop in the inhibition of liver esterase by fluoride as temperature was increased. As an example of this, in one experiment the hydrolysis with 25 ng. of fluoride was 46% of the control at 25°, whereas at 30° it was 53%. Incubation times were adjusted so as to eliminate the amount of substrate hydrolyzed as a variable. Although it is advantageous to run experiments at as low a temperature as is expedient, it is probable that the added sensitivity to be gained does not justify the difficulties inherent in thermostatic control at a temperature below that of the room. If it becomes important to obtain the ultimate in sensitivity, then this approach might well be exploited.

Effects of Other Conditions. A number of other variables which might influence the results of fluoride analyses in various ways were investigated with the following results.

The use of nitric acid–washed polyethylene tubes instead of glass con-

tainers for the incubation markedly lowered precision both in the presence and absence of fluoride, suggesting that polyethylene affects the enzyme in a variable fashion.

The effect of preincubating the enzyme with fluoride for as long as 30 min. before addition of the substrate was tested. It was found that inhibition by fluoride did not increase and may have dropped somewhat. The enzyme activity itself also suffered a small decrease which probably resulted from inactivation of the enzyme by acid (*7*).

Shaking the samples during the incubation period markedly decreased precision, perhaps because of variability in the area of glass surface exposed to the enzyme.

The influence of the pH of the water used to dissolve the enzyme was tested in one experiment. As the pH was lowered between 7 and 5, enzyme activity, assayed a pH 3.2 by the standard procedure, decreased by about a third. However, the per cent of hydrolysis in the presence of fluoride increased only slightly, from 45% to 49%. The results suggest that it is best to keep the pH of the dissolving water above six, but that this precaution is not critical for the success of the method.

Investigation of Standard Curves. Numerous standard curves have been run under a variety of conditions. Examples of these are shown in Figure 1. There was marked and unpredictable variability in both the intercepts and the slopes of the curves in the same range of fluoride levels. An analysis of variance showed that the interexperimental variability in slope is significantly greater (p, 0.04) than the intraexperimental variability. This suggests that for best results, slope variability should be controlled by running standards at two levels as described above.

Precision, Accuracy, and Sensitivity. Empirical estimates of the precision and accuracy of the method were made as follows. Solutions of pseudo-unknowns containing either 150 or 375 mg. of fluoride per mg. of calcium phosphate (150 and 375 p.p.m., respectively) were prepared. Amounts of these solutions which contained 0.1 mg. of calcium phosphate and either 15 or 37.5 mg. of fluoride were then analyzed by the standard procedure. These levels were chosen because they were the approximate midpoints between convenient levels of standards in low or intermediate ranges which would commonly be employed in the analysis of tooth enamel. The means and standard deviations for 10 determinations at the 15-ng. level, and nine determinations at the 37.5-ng. level were: 16.2 ± 0.65 ng. (±4.0%) and 38.4 ± 1.85 ng. (±4.8%), respectively.

Precision is not markedly affected by the small amounts of carbonate normally expected in the NaOH used as titrant, provided that only small amounts of phosphate are present. However, as the level of phosphate increases, precision drops, so that it is best to employ carbonate-free NaOH where phosphate is present. Precision is thereby made satisfactory up to at least 10^{-2} mmole of phosphate, a higher level than would ordinarily be needed for the estimation of fluoride.

The lower limit of fluoride detectability is about 1 ng. in a volume of 2.5 ml. This limit can be reduced by about one half by decreasing the incubation volume to 1.25 ml. and employing a Beckman combination probe electrode for the titrations. The sensitivity of the method is thus placed at about 0.4 ng. of fluoride per ml. of incubation medium.

DISCUSSION

This method has certain advantages as compared with others. It does not require that fluoride be separated from phosphate before analysis, thus saving time and avoiding the inevitable errors associated with purification. It demands only standard equipment and a minimum of space. The preparation of the liver acetone powder containing the esterase is a simple operation and about a half day of effort affords enough stable enzyme to last for about 4 months even though a new enzyme solution is prepared each working day. It is probable that most biological materials can be analyzed for fluoride by the present method; however, since certain ions can influence the activity of liver esterase (*7*), the lower limit of fluoride, which can be determined, will be governed by the amount of sample which can be taken for analysis without significant interference by these ions. Linde (*6*) has applied his method to blood and urine.

In the case of tooth enamel, calcium phosphate is the only known material which is present in large enough quantities to interfere, and this influence is controlled in the present method. Investigations are in progress relating to the application of the fluoride assay procedure to the analysis of tooth enamel. The results, to be reported later, suggest that the method will be extremely useful for this purpose, especially where less than 1 mg. of enamel is involved.

Although the semilogarithmic type of plot used by Linde (*6*) and in the present work for the standard curves is entirely empirical and, under our conditions, not linear over wide ranges of fluoride level, it can be considered linear for practical purposes over satisfactory ranges. In the idealized case of competitive inhibition, a plot of inhibitor level against $(1 - h)/h$ should be linear, where h is the hydrolysis expressed as a fraction of the control value (*10*). This applies to initial reaction velocities with purified enzymes and is predicated on the assumption that most of the inhibitor remains unbound. Under our conditions, the linearity of this type of plot is not noticeably better than that of a semilogarithmic plot. Because of the greater convenience of the latter, we have continued to employ it for the standard curves.

It is unfortunate that in our system the standard curves did not show greater consistency. The sources of variability of the curves were not investigated; however, it appears quite possible that small changes in certain environmental conditions, such as pH and temperature, could affect inhibition and stimulation of the enzyme by fluoride to different extents. The curves obtained would thus represent a composite effect and would vary accordingly.

Changing certain environmental conditions caused smaller decreases of enzyme activity in the presence of fluoride than in its absence. This phenomenon was noted as substrate concentration was lowered, as phosphate concentration was increased, and as the level of powdered glass was increased. These observations suggest that fluoride acts as a general protective agent against enzyme inactivation. This was particularly obvious in the case of lowering substrate concentration, where inhibition by fluoride sometimes changed to net stimulation. It is thought that in this instance, the normally protective effect of the substrate was lowered, allowing the protective effect of the fluoride to become more obvious.

It is of interest that the increase in fluoride inhibition with decrease in pH is greatest between pH 3 and 4. In this region absolute changes in the amount of butyrate present would be small in comparison to the changes occurring over the higher range studied, which includes the pK of butyric acid (4.8). This suggests that some mechanism in addition to the known antagonism by butyrate ion (*1*) is responsible for the pH action spectrum of fluoride inhibition. Since dissociation of HF is highly pH dependent between pH 3 and 4, the possibility should be considered that HF, or some hybrid thereof such as HF_2^-, is the actual inhibitor, as has been proposed by Reiner *et al.* (*11*) for the case of prostatic acid phosphatase.

ACKNOWLEDGMENT

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SCIENTIFIC COMMUNICATIONS

Submicroanalysis by Radiochromatography

SIR: Published radiometric precipitation techniques have been used to determine as little as 0.01 μg. of calcium as C^{14}-labeled calcium oxalate and F^{18}-labeled calcium fluoride (*1*, *2*). Employing S^{35}-labeled sulfates, P^{32}-labeled phosphates, and improved radiometric techniques, sensitivities as low as 0.0001 μg. for Ca, Sr, Ba, Pb, Be, and Zr have been achieved in this laboratory. When paper chromatographic separations were performed prior to radiometric precipitation, mixtures of the above elements have been analyzed simultaneously.

Two small aliquots of the original sample in HCl are spotted adjacent to each other on a Whatman No. 42 filter strip (2 × 30 cm.); tracer activities of the elements to be analyzed are added to one of the aliquots and the chromatogram is developed. For Ca, Sr, and Ba, a mixture of 2 parts ethanol, 2 parts methanol, and 1 part 2*N* HCl is used. For Pb, a mixture of 5 parts ethanol, 3 parts methanol, and 2 parts 1.6*N* nitric acid is used. For Zr, a mixture of 30 parts acetone, 17 parts isobutanol, and 1 part 12*N* HCl is used and for Be, a mixture of 1 part tetrahydrofuran and 1 part dilute HCl is used.

The location of the unknown element is then determined by scanning the added tracer activities. If several tracers are used the areas are identified by beta absorption techniques.

The labeled sulfates of Ca, Sr, Ba, and Pb are precipitated on the paper by adding S^{35}-labeled sulfuric acid 2 cm. above the area where the unknown was originally spotted and migrating the reagent with a 50% ethanol–H_2O mixture through the elements. The migration is continued at least 10 cm. beyond the unknown area to remove excess acid. For Be and Zr, the labeled phosphates are precipitated by adding P^{32}-labeled phosphoric acid 2 cm. above the first origin and migrating with a mixture of 14 parts isopropanol, 1 part trichloroacetic acid, and 6 parts water.

The paper is then dried and the area cut out for radiometric analysis. The labeled sulfate precipitates are assayed with a liquid scintillation counter and the phosphates with a low background beta scintillation counting system.

Preliminary results have shown that complete chromatographic separations are achieved with the reagents used. In addition, the precipitation on the paper is complete, and the precipitate remains in the areas indicated by the tracers.

For each of the elements a linear relationship was observed between counting rate and weight of the element in the precipitate.

Table I lists detection limits observed for Ca, Sr, Ba, and Pb using 0.3*N* sulfuric acid with 6.3 × 10^6 d.p.m. of S^{35} per meq., and for Be and Zr using 0.1*N* phosphoric acid with 6.3 × 10^7 d.p.m. of P^{32} per meq. These detection limits represent sample counting rates which are twice instrumental background and are inversely proportional to the specific activity of the precipitant.

Table I. Detection Limits

Element	Observed detection limit, μg.
Ca	0.002
Sr	0.005
Ba	0.008
Pb	0.01
Be	0.0001
Zr	0.0002

The radiochromatographic technique described is applicable to many other precipitants such as Cr^{51}-labeled chromate, Ti^{44}-labeled titanate, Zr^{95}-labeled fluorozirconate, C^{14}-labeled carbonate, S^{35}-labeled sulfide, and P^{32}-labeled phosphomolybdate. Therefore, all elements that can be isolated chromatographically can be determined at these low sensitivity levels.

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Coulometric Analysis with Gas Volume Measurement

SIR: A coulometric cell was designed and built which allows the measurement of volumes of gaseous electrolysis products. The cell is air-tight and the gas volume is determined by measuring the amount of water displaced in a graduated pipet by a technique similar to that used in gas coulometers (*2*). Provision was also made for withdrawing gas samples for analysis.

There are several applications of a cell allowing measurement of the amounts of gaseous products in coulometric determinations. If the electroactive species produces a gas on being oxidized or reduced, the amount of gas provides a simple way of obtaining material balance information about the reaction. Analysis of the gas can generally be easily done by mass spectrometry. Information about the kinetics of an electrode reaction can also be obtained. We have found this cell useful in studying the oxidation of hydrazine compounds, where nitrogen is not evolved in the initial electrode reaction, but by an intermediate, following chemical reaction. Some preliminary results are presented here on the oxidation of methyl hydrazines.

The most promising use of this cell is in the study of electrode reactions which occur at potentials sufficiently cathodic or anodic to cause concurrent oxidation or reduction of the solvent. Under these conditions, since the electrolysis does not proceed with 100% current efficiency, coulometric measurements cannot ordinarily be made. However, if the species of interest does not produce a gas upon electrolysis, the difference in coulombs obtained by current-time integration and those calculated from the volume of gas evolved during electrolysis of the solvent should give the total coulombs used in electrolyzing the species of interest. This use of the cell was tested by simultaneously reducing ferric and hydrogen ions at a platinum electrode.

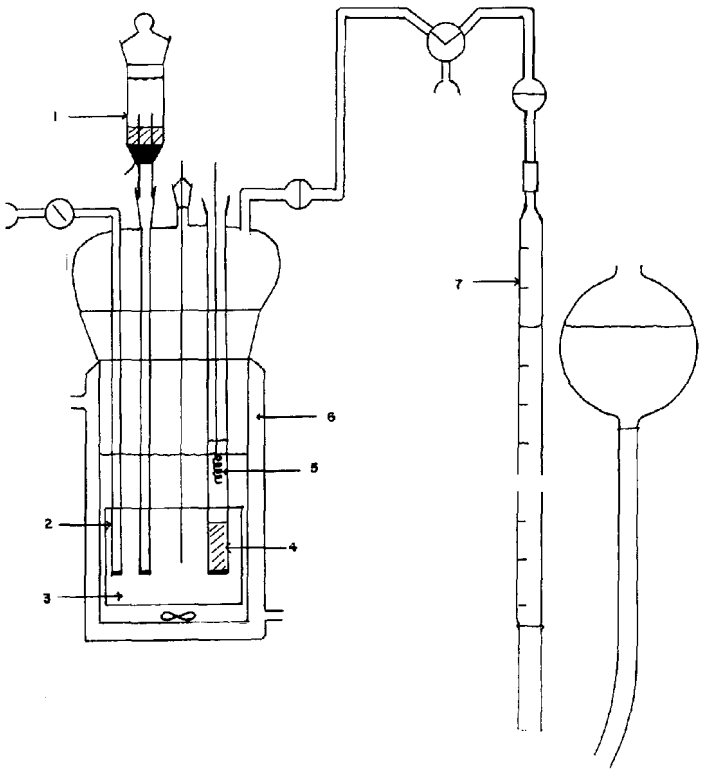

Figure 1. Electrolysis cell

1. Reference electrode. 2. Nitrogen inlet. 3. Platinum gauze electrode. 4. Agar plug. 5. Auxiliary electrode. 6. Cell jacket. 7. Gas pipet

EXPERIMENTAL

Cell and Apparatus. The cell is shown in Figure 1. The working electrode was platinum gauze, the reference electrode was a saturated calomel electrode (SCE) and the auxiliary electrode was a coil of platinum wire. The auxiliary electrode compartment was separated from the main compartment by a fine porosity sintered glass disk and an agar plug. Standard taper and ball joints were used throughout to make the cell gas-tight. The top cell joint was 34/28, the ball joints were 12/12, and the reference and working electrode inlets were 7/25. The seal around the wire leading to the working electrode was achieved with a weatherstrip adhesive (Minnesota Mining and Manufacturing Co., St. Paul, Minn.). The cell was jacketed and a magnetic stirrer was used. The three-way stopcock was used to direct the generated gas either to the measuring apparatus or to some collection apparatus. A 10 ml.. pipet with an attached leveling bulb was used for volume measurement.

We have also used a cell with a rubber stopper top containing standard taper tubes for the reference and auxiliary electrode with equal success. The rubber stopper has the advantage of being simpler to construct and allowing the replacement of the auxiliary electrode chamber when the sintered glass disk becomes clogged. When a magnetic stirrer consisting of a powerful magnet held in the chuck of a stirring motor was employed and was positioned somewhat below the cell, heating of the solution by the stirrer did not occur, and the cell did not have to be

Table I. Coulometric Reduction of Iron(III) in Acidic Solution with and without Hydrogen Evolution

Solution: 25 ml. of 0.1*M* H_2SO_4. Electrolysis time; 10 to 15 minutes

Amount of iron(III) taken, meq.	*E*, volt *vs.* SCE	Vol. of gas, meq.	Coulometer rdg., meq.	Amount of iron(III) found, meq.
0.0	−0.4	0.560	0.568	
		0.554	0.558	
		0.619	0.617	
0.250	0.0	0.0	0.261	0.261
			0.245	0.245
	−0.4	0.237	0.473	0.236
		0.158	0.406	0.248
0.500		0.036	0.525	0.489

Table II. Coulometric Oxidation of Methyl Hydrazines

Solution: 1.0M in H_2SO_4. Oxidations carried out at +1.0 volt *vs.* SCE

	Amount, mmol.	Coulometer rdg., meq.	n	Amount of nitrogen, mmol.
Methyl hydrazine	0.238	0.916	3.86	0.239
1,2-Dimethyl hydrazine	0.510	3.16	6.20	0.532
	0.239	1.42	5.94	0.240
1,1-Dimethyl hydrazine	0.326	1.53	4.7	0.194[a]
		1.92	5.9	0.270[b]

[a] Electrolysis interrupted for about 1 hour after 0.65 meq. oxidation. [b] Electrolysis carried out continuously.

jacketed under stable laboratory temperature conditions.

An electromechanical potentiostat similar to that described by Lamphere and Rogers (*1*) was used. Current-time integration was accomplished with a ball-and-disk integrator attached to a strip-chart recorder.

Procedure. In the reduction studies, the solution in the cell was 0.1M in sulfuric acid and about 25 ml. in volume. Initial saturation with hydrogen was achieved by preelectrolysis at about −0.4 volt *vs.* SCE. Aliquots of standard iron(III) solution were then added and the electrolysis was performed. For the hydrazine oxidation studies the solution was 25 ml. of 1.0M H_2SO_4 and was presaturated with nitrogen.

RESULTS

Results for the electrolysis of ferric and hydrogen ions at various potentials are shown in Table I. When the electrolysis of iron(III) was carried out at 0.0 volt *vs.* SCE, no hydrogen ion reduction occurred and the measured coulombs agreed with those calculated from the equivalent of iron added. Electrolysis at −0.4 volt leads to concomitant reduction of hydrogen ion; subtraction of the volume of hydrogen gas evolved, however, again allows calculation of the amount of iron.

Results for the oxidation of several methyl hydrazines are shown in Table II. Methyl hydrazine undergoes a four-electron oxidation and one mole of nitrogen is formed per mole of hydrazine. 1,2-Dimethyl hydrazine undergoes a six-electron oxidation again with one mole of nitrogen formed per mole of hydrazine. The oxidation of 1,1-dimethyl hydrazine is complicated by slower intermediate chemical reactions. Quantitative nitrogen formation is not observed and the apparant n-value depends upon the rate at which the electrolysis is carried out. Further study of these systems will be reported elsewhere. In all cases the gaseous electrolysis product was identified by mass spectrometry as nitrogen.

The cell should also find use in constant current coulometry (coulometric titrations), especially for the production of strong oxidants and reductants. Adaption of the cell to electrolysis with a mercury electrode should be straightforward. Further work with this cell is in progress.

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CORRESPONDENCE

Gasometric Analysis of Alkyl Azides with Sodium Iodide–Trichloroacetic Acid

SIR: Numerous good methods for the quantitative determination of azide ion are known. However, there are few methods for the determination of the covalently bound azido group. Ugi (*10*) has successfully adapted the reaction of aryl azide with arsenite ion (*1–3*) to the gasometric determination of the aryl azides.

$$ArN_3 + AsO_3^{-3} \xrightarrow{H_2O} ArNH_2 + AsO_4^{-3} + N_2 \quad (1)$$

Messmer and Mlinko (*6, 7*) determined the azido group of 1-azido-1-acetyl sugars by ceric ion oxidation of hydrazoic acid liberated by acid digestion. However, except for certain azides, such as triphenylmethyl, acyl and sulfonyl azides, and the 1-azido-1-acetyl sugars, the azido group is not readily hydrolyzed intact by acid or base. The usual result of such attempts is cleavage of the group to form nitrogen plus a complex mixture of imines, amines, olefins, keto compounds, etc. Hoffman, Hoch, and Kirmreuther (*4*) determined the azido group in guanyl azide and in carbamyl azide by measuring the nitrogen evolved in the reaction

$$RN_3 + 3HI \rightarrow RNH_3^+I^- + N_2 + I_2 \quad (2)$$

Water-insoluble azides were not investigated.

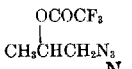
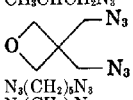
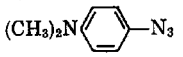
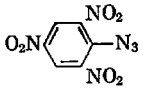
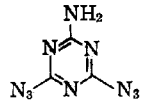
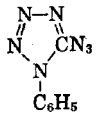
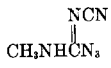
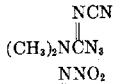
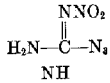
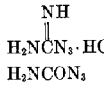
Smith (*8*) reported the reaction of aryl azides with hydroiodic acid to give iodine, nitrogen, and the corresponding arylamine. The determination of the azido group by titration of the liberated iodine was subject to error because of the tendency to form excess iodine by air oxidation of hydroiodic acid (*9*). The preparation and preservation of stock solutions of iodine-free hydroiodic acid constituted a further difficulty in this analytical approach. Leffler has analyzed benzenesulfonyl azides by two methods (*5*). Reaction with triphenylphosphine caused quantitative liberation of nitrogen.

$$(C_6H_5)_3P + C_6H_5SO_2N_3 \rightarrow C_6H_5SO_2N^- - \overset{+}{P}(C_6H_5)_3 + N_2 \quad (3)$$

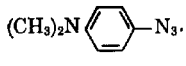
A potassium iodide–aqueous acetic acid combination brought about a quantitative liberation of iodine upon heating.

In this laboratory a method was sought for the analysis of various azides, primarily aliphatic. Ugi's (*10*) procedure was not suitable for simple alkyl azides because of their unreactivity with arsenite ion. Both of Leffler's methods were also unsuitable because of the poor reactivity of alkyl azides toward triphenylphosphine and potassium iodide–acetic acid. A method has been developed which is a modification of the hydroiodic acid reaction. It involves

Table I. Azide Determinations

Compound	Moles N_2/azido group × 100
n-$C_8H_{17}N_3$	99.5 ± 0.6[a]
	100.9
	102.5
$N_3(CH_2)_5N_3$	102.8
$N_3(CH_2)_6N_3$	100.9
$N_3(CH_2)_{10}N_3$	102.1
$NC(CH_2)_3N_3$	100.9
$NC(CH_2)_4N_3$	101.4
$C_6H_5CH_2N_3$	99.2
$(C_6H_5)_2CN_3$	98.6[b,c]
$C_6H_5N_3$	97.8[c,d]
	90.3[d,e]
	104.6[e,g]
	99.0
	100.6
	101.0
	94.0[f]
	91.5[g]
	97.1[e]
	95.8
$H_2NCN_3 \cdot HCl$	
H_2NCON_3	85 2[f,g]
$Cl^- H_3\overset{\oplus}{N}CH_2CH_2NHCON_3$	99.3[g]
NaN_3	101.9[h]
NH_4N_3	101.5

[a] Average of 7 determinations; thiosulfate titration of iodine yielded 99.7%.
[b] Carried out under nitrogen because of oxygen absorption.
[c] Average of 3 determinations.
[d] Arsenite method gave 101.0% for $C_6H_5N_3$, 100.5% for



[e] Slow reaction.
[f] Impure sample.
[g] Very slow reaction.
[h] Sat. aq. solution; also analyzed gasometrically by the neutral iodine method as 102.5%.

the measurement of nitrogen liberated by reaction of the azide with hydroiodic acid generated in situ by the action of 90% trichloroacetic acid (10% water) and sodium iodide. This system will generate hydroiodic acid very rapidly upon demand, but iodine formation by air oxidation proceeds slowly. Trichloroacetic acid also has good solvent properties for many organic substances. With this combination most alkyl and ionic azides react vigorously to give quantitative amounts of nitrogen and iodine.

EXPERIMENTAL

Apparatus. The equipment employed was similar to the standard microhydrogenation apparatus, with mercury leveling bulb, mercury manometer, 100-ml. gas buret, and a 100-ml. 2-necked flask. One neck of the flask contained a glass stopper with a hook for suspending a platinum bucket containing the azide. Rotation of the stopper dropped the bucket directly into the reagent, which was stirred magnetically.

Reagents. Trichloroacetic acid (90%) was prepared by heating a mixture of 9 parts acid to 1 part water until a homogeneous solution results. This solution remains liquid at room temperature. Sodium iodide (B & A granular reagent) was used without grinding. Other forms (crystalline) were not as satisfactory.

Procedure. Three grams of sodium iodide and 15 ml. of trichloroacetic acid were placed in the flask. The azide (0.2 to 0.6 gram, depending on azide content) was weighed in the platinum bucket, which was then positioned on the stopper-hook. A few minutes of stirring was used to allow equilibrium before closing the system and dropping the bucket into the reagent mixture. The reaction time varied considerably from a few seconds to a few days depending on the nature of the azide. Since heat is generated in the reaction, 30 to 60 minutes is required to reattain thermal equilibrium if an air bath is used. The use of a constant temperature bath around the reaction flask greatly speeds up the rate of determination but it was not used for most of the analyses.

RESULTS AND DISCUSSION

Table I shows the results obtained with various azides. Unless otherwise specified the values are for single determinations.

An estimate of the degree of precision obtainable by this procedure was made with octyl azide which had been carefully purified by distillation. Seven determinations gave an average value of 99.5 ± 0.6%.

The reaction with alkyl azides liberates iodine quantitatively as well as nitrogen. However, it is inconvenient to have to neutralize a large quantity of trichloroacetic acid before titration with thiosulfate.

Trifluoroacetic acid has also been tried and found effective but, because of its high vapor pressure and pungent odor, was not evaluated further.

The mechanism of this reaction is under investigation, but is not yet well understood. However, it is obvious that with primary alkyl azides the first step cannot be acid hydrolysis because these azides are quite stable toward trichloroacetic acid in the absence of sodium iodide. Furthermore, displacement of azide ion by iodide ion must be ruled out because in neutral solvents organic azides are quite stable toward iodide ion. This conclusion is based on the fact that alkyl azides can be synthesized in high yield from alkyl iodides and sodium azide in diethylene glycol in which both sodium azide and sodium iodide are very soluble. It is felt that the protonated azido group is highly susceptible to attack by hydroiodic acid, which produces an unstable intermediate which decomposes to the observed products. (By contrast, the quantitative reaction of iodine with azide ion, which requires a sulfur-containing compound as catalyst, occurs only in neutral or basic solution. $I_2 + 2N_3^- \xrightarrow{[S]} 3N_2 + 2I^-$). Whereas secondary and tertiary azides are less stable in acid than the primary azides, this fact should not affect the analytical value of this method. The decomposition of these azides in acids will produce either nitrogen or hydrazoic acid, which would be further converted to nitrogen and ammonium ion. Thus, the quantitative evolution of nitrogen is assured.

ACKNOWLEDGMENT

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Substrates Containing Silver Nitrate for Gas Chromatography

SIR: In stationary phases containing silver nitrate, the activity coefficients of alkenes and dienes become quite small because of the formation of loose adducts between the silver ion and the double bonds. This permits the use of such phases for selective separations involving olefins as well as other compounds. The addition of silver nitrate to substrates for use in gas chromatography was first reported in 1955 by Bradford, Harvey, and Chalkley (*2*). Solutions of silver nitrate in ethylene glycol, glycerol, triethylene glycol (*1*), and benzyl cyanide (*3*) have been used as liquid stationary phases for the separation of olefins. The use of glycols requires moisture-free carrier gas because of their hygroscopic nature. Benzyl cyanide on the other hand limits the operating temperature because of its high vapor pressure.

Several thermally stable organic solvents have been found which can be used with silver nitrate in gas chromatographic studies. These include *p*-xylyl cyanide (Columbia Organic Chemicals Co.), *m*-xylyl cyanide (Columbia Organic Chemicals Co.), 1-naphthylacetonitrile (K & K Laboratories), 3,4-dimethyl phenylacetonitrile (K & K Laboratories), and oleyl nitrile (Armour Industrial Chemical Co.).

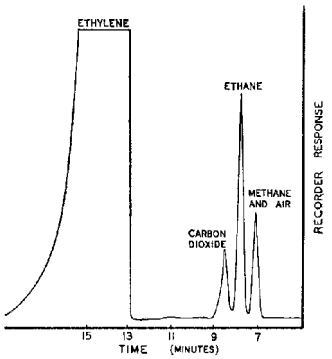

Figure 1. Chromatogram of ethylene and impurities using silver nitrate in *p*-xylyl cyanide as substrate

The choice of solvent is important because it effects the resolution of components other than the olefins. A 1:2 solution of silver nitrate in *p*-xylyl cyanide provides an excellent stationary phase for the gas chromatographic determination of trace impurities in ethylene. The column is made by packing a 30-foot × 1/4-inch column with 36% stationary phase on 60- to 80-mesh Chromosorb. A typical chromatogram is shown in Figure 1, the stable baseline and the resolution of carbon dioxide, methane, and ethane being of some significance.

The column described lasted six months at an operating temperature of 25° C. Where olefin separations require higher than ambient temperatures, 1-naphthylacetonitrile, 3,4-dimethyl phenylacetonitrile, and oleyl nitrile should prove quite satisfactory.

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Correlation of Structure of Phosphate Pesticides with Response in Electron Affinity Detectors

SIR: Electron affinity detectors have proved useful for measuring nano- and picogram amounts of halogenated pesticide residues in mixtures resolved by gas chromatography (*2–5, 7–10, 18–20, 23–25*). Although the discoverers of the technique (*15*) demonstrated that many classes of compounds undergo the electron capture process because of the presence of certain elements or functional groups in the compound, relatively few studies have been carried out on compounds other than those containing halogens. Correlations of electron affinity with biological activity (*13, 16, 17*) and with molecular structure (*11–13, 15*) have been established. Nearly all of these studies have been conducted with electron affinity detectors of one design, the standard parallel-plate detector developed by Lovelock (*12, 15*). In several recent studies (*4, 14*) emphasis has been placed on the use of the pulsed excitation mode to minimize anomalies that are sometimes observed in detectors operated in the direct-current mode.

Compounds containing phosphorus are becoming increasingly important as pesticides. The increasing use of these plant- and animal-systemic phosphate pesticides has emphasized the need for collecting extensive data on the metabolism of new compounds in plants and animals. Gas chromatography is a powerful tool for the determination of these metabolites, and all of the advantages of electron affinity detectors for determining chlorinated pesticide residues should apply to phosphate pesticide residues if the latter undergo the capture process. Relatively few studies have been conducted on the behavior of phosphate pesticides in electron affinity detectors (*1, 3, 5, 6, 20, 22*) and widely different responses were reported for at least one compound, demeton, in two detectors of different geometry (*1*). The present study was undertaken to measure the response of seven phosphate pesticides in electron affinity detectors of three different designs. To permit a correlation of the effect of chemical structure upon response, pesticides of related structures were selected. A study concerned with the behavior of demeton in one of the detectors has been reported previously (*1*). This study was primarily directed toward detectors rather than the development of complete analytical methods.

EXPERIMENTAL

Apparatus. All experiments were conducted with the gas chromatograph, column, and operating conditions previously described (*1*). The column was operated isothermally, benzene solutions of the pesticides were used, and 1.0 μl. of the solution was injected with a 10-μl. Hamilton microliter syringe fitted with a 3-inch needle. Evidence was obtained that the pesticides did not decompose and were not retained on the column once it was properly preconditioned by repeated injections of pesticide.

Electron Affinity Detectors. The three different detectors which were used were the standard Lovelock detector (Micro-Tek Model GC-1600-074-1) (*1, 14*); the adjustable parallel-plate detector (Barber-Colman Model 5120), shown in Figure 1; and the pin-cup detector (supplied by Micro-Tek Instruments, Inc.), shown in Figure 2. All detectors were operated at 170° C. The adjustable parallel-plate detector

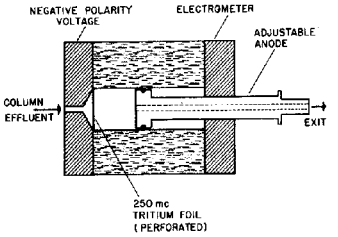

Figure 1. Adjustable parallel-plate electron affinity detector

was operated at five interelectrode distances: 1, 5, 10, 15, and 20 mm. The gap was changed by moving the anode. The maximum interelectrode distance obtainable with this detector was 25 mm. The pin-cup detector was operated at two interelectrode distances: 3 and 10 mm. The gap was changed by disassembling the detector and changing the anode pin.

Pesticides. Demeton (Systox), methyl demeton (Meta-Systox-I), Di-Syston, and DDVP were supplied by Chemagro Corp., Kansas City, Mo.; ethyl parathion, by American Potash Co., Los Angeles, Calif.; methyl parathion, by Thompson-Hayward Chemical Co., Kansas City, Mo.; and para-oxon, by American Cyanamid Co., Princeton, N. J. Chemical names and levels of purity of these pesticides are shown in Table I.

Systox (a 60:40 (w./w.) mixture of thiono-Systox and thiolo-Systox), Meta-Systox-I, and Di-Syston were selected because they are structurally related, differing only in the type of alkyl groups bonded through oxygen to the central phosphorus atom, and in the identity of the electronegative atom bonded to the phosphorus. Ethyl parathion, methyl parathion, and para-oxon are also structurally related, differing only in the type of alkyl groups bonded through oxygen to the phosphorus, or in the identity of the electronegative atom bonded to the phosphorus. DDVP may be considered to be structurally related to para-oxon in that it contains

the P—O group and to be structurally related to methyl parathion and to Meta-Systox-I in that it contains the *O,O*-dimethyl groups. However, it contains the 2,2-dichlorovinyl group instead of the *p*-nitrophenyl or the (ethylthio)-ethyl groups. Hence, it contains a moiety known to possess a high affinity for electrons.

Experimental Program. The experimental program was designed to measure the approximate lower limit of detection (L.L.D.) for each of the eight compounds in all three detectors in most of the modes, to determine the effect of detector parameters on response, and to determine the effect of chemical structure on sensitivity. Standing current–voltage curves for the d.c. mode of excitation were obtained by measuring the standing current at every 5 volts from 5 to 50 volts. Response curves were obtained by recording chromatograms at 5, 10, 20, 30, and 50 volts in the d.c. mode for a pesticide and plotting peak height vs. current. The amounts of the pesticides were chosen to provide well defined peaks significantly above the L.L.D., and within the linear dynamic range of the detector.

The Lovelock detector was studied in both the normal mode and in other modes in which the position of the tritium foil relative to the incoming gas stream was reversed. Standing current–voltage curves and response curves for methyl demeton were similar to those previously reported (*1*), while those for the other pesticides were similar to curves obtained in other detectors in which the arrangement of electrodes, position of the foil, and flow of the carrier gas were similar.

STANDING CURRENT–VOLTAGE CURVES AND RESPONSE CURVES

Standing current–voltage curves for the Lovelock detector, the pin-cup detector, and for the adjustable parallel-plate detector at 1, 5, and 10 mm. have the typical shape reported previously (*4*). The curve for the Lovelock detector rises less steeply than the others, so that the plateau is reached near 30 volts rather than 5 to 10 volts. The curve for the adjustable parallel-plate detector at 20 mm. shows an inflection point and reaches a plateau near 35 volts.

The response curves for all eight compounds in the Lovelock detector resemble the response curve reported by Clark (*4*) for lindane in a similar detector in that maxima in the curves occur at about 20 volts (on the shoulder of the standing current–voltage curve), well below the plateau region.

Figure 3 shows that the response curves for the pin-cup detector are similar for all eight compounds at both gap settings. The response decreases

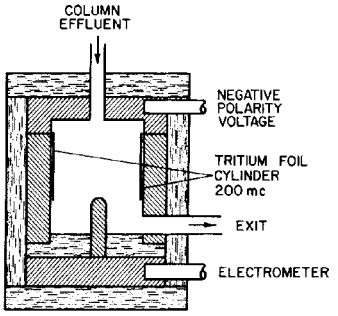

Figure 2. Pin-cup electron affinity detector

continuously to approximately zero with increasing polarizing voltage above 5 volts. With thiono-Systox, thiolo-Systox, and Meta-Systox-I, the curve crosses the zero axis at about 10 volts, so that ionization is produced at higher voltages. The response curves must pass through a maximum below 5 volts, although this behavior was not observed experimentally.

Figure 4 shows that the response curves for the adjustable parallel-plate detector are also similar for all eight compounds. At electrode gaps of 1, 5, and 10 mm., the response decreases continuously with increasing polarizing voltage above 5 volts; these response curves are similar in shape to those obtained with the pin-cup detector. At 15 mm. the response passes through a maximum near 40 volts, and at 20 mm. the response increases continuously with increasing polarizing voltage up to 50 volts. The response curves at gaps of 1, 5, and 10 mm. must pass through a maximum below 5 volts, although this behavior was not observed experimentally.

The change in shape of the response curve as the gap is increased can be

Table I. Purity of Phosphate Pesticides Used in This Study

Common name	Chemical name	Purity
Demeton (Systox)	Mixture of thiono-Systox (*O,O*-diethyl *O*-2-(ethylthio)ethyl phosphorothioate, and thiolo-Systox (*O,O*-diethyl *S*-2-(ethylthio)ethyl phosphorothioate	99%, analytical standard
Di-Syston	*O,O*-diethyl *S*-2-(ethylthio)ethyl phosphorodithioate	99%, analytical standard
Methyl demeton (Meta-Systox-I)	*O,O*-dimethyl *S*-2-(ethylthio)-ethyl phosphorothioate	99%, analytical standard
Ethyl parathion	*O,O*-diethyl *O*-*p*-nitrophenyl phosphorothioate	98.5%, analytical standard
Methyl parathion	*O,O*-dimethyl *O*-*p*-nitrophenyl phosphorothioate	99.8%
Para-oxon	*O,O*-diethyl *O*-*p*-nitrophenyl phosphate	Analytical standard
Dichlorovos (DDVP)	*O*-2,2-dichlorovinyl *O,O*-dimethyl phosphate	97.9%, analytical standard

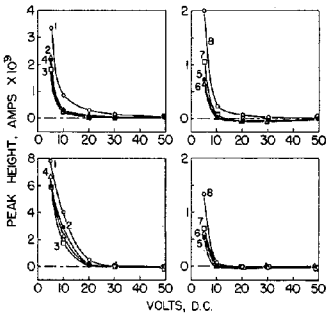

Figure 3. Response curves for pin-cup detector

Number and compound	Upper left and right, 10-mm. gap		Lower left and right, 3-mm. gap	
	ng.	Column T, °C.	ng.	Column T, °C.
1. Ethyl parathion	10	165	100	165
2. Methyl parathion	10	155	100	155
3. Para-oxon	10	165	100	160
4. DDVP	100	100	1000	100
5. Thiono-Systox	600	132	600	132
6. Thiolo-Systox	400	132	400	132
7. Meta-Systox-I	1000	132	1000	132
8. Di-Syston	100	140	100	145

related to the formation of space charges in the detector cavity. Typical response curves for electron affinity detectors show a maximum at a polarizing voltage just below that required for saturation (4); this behavior occurs in the adjustable parallel-plate detector at gaps of 15 mm. or less. However, when the gap is increased to 20 mm., large space charges are created as a positive ion cloud near the cathode and an electron cloud near the anode. The density of the electron cloud increases with increasing polarizing voltage, so that the residence time of the electrons in the cavity increases rather than decreases. Under these conditions the sample molecules encounter proportionately more thermal electrons and the probability of capture increases.

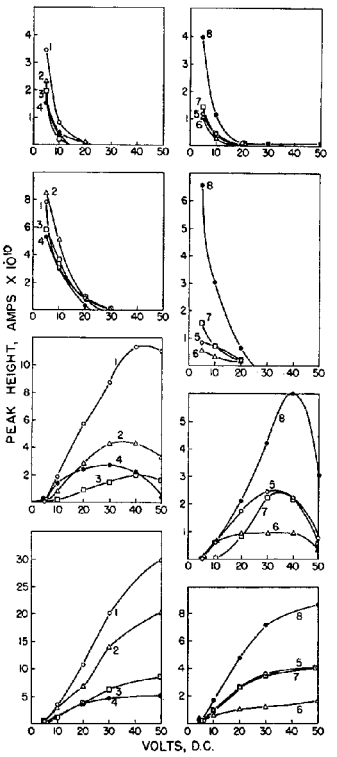

Figure 4. Response curves for adjustable parallel-plate detector

Number and compound	Upper left and right, 1 mm.		Upper center, left and right, 10 mm.		Lower center, left and right, 15 mm.		Lower left and right, 20 mm.	
	ng.	Column T, °C.	ng.	Column T, °C.	ng.	Column T, °C.	ng.	Column T, °C.
1. Ethyl parathion	100	165	10	160	10	160	10	165
2. Methyl parathion	100	162	50	155	10	155	10	155
3. Para-oxon	100	165	25	162	10	160	10	165
4. DDVP	100	107	10	110	10	105	10	110
5. Thiono-Systox	600	140	60	140	60	140	60	140
6. Thiolo-Systox	400	140	40	140	40	140	40	140
7. Meta-Systox-I	1000	140	100	140	10	140	100	140
8. Di-Syston	1000	145	25	142	10	140	10	145

Table II. Sensitivities and Lower Limits of Detection for Eight

Detector	Ethyl parathion				Methyl parathion				Para-oxon				DDVP			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Lovelock	20	3490	1040	1.54	20	1340	352	4.55	20	1890	520	3.06	20	485	107	13.5
Adjustable parallel-plate, 1 mm.	5	31.6	9.2	261	5	140	36.8	65.1	5	19.3	5.3	450	5	20.2	4.46	269
Adjustable parallel-plate, 5 mm.	5	510	148	10.8	5	173	45.5	35.2	5	591	163	9.8	5	156	34.5	46.5
Adjustable parallel-plate, 10 mm.	5	670	195	4.1	5	151	39.7	20.2	5	336	92	8.7	5	1230	272	2.84
Adjustable parallel-plate, 15 mm.	40	1130	329	3.0	40	500	132	7.6	40	145	39.9	25	30	314	69	11.6
Adjustable parallel-plate, 20 mm.	50	3380	980	0.82	50	1830	481	1.66	50	1260	346	2.31	50	630	140	5.7
Pin-cup, 3 mm.	5	970	282	2.84	5	680	179	4.45	5	690	190	4.21	5	172	38	18.9
Pin-cup, 10 mm.	5	1760	510	1.56	5	1620	425	1.88	5	1280	352	2.28	5	420	92	8.7

Column Headings
1 = Voltage at maximum sensitivity
2 = Sensitivity, amp. sec. ng.$^{-1}$ ($\times 10^{12}$)
3 = Sensitivity, amp. sec. mol.$^{-1}$
4 = Lower limit of detection, mol. sec.$^{-1}$ ($\times 10^{14}$)

At a polarizing voltage above 50 volts, the electrons should acquire enough energy to initiate ionization and the response curve should pass through a maximum. Table II shows that the maximum sensitivity is obtained in this detector at a gap of 20 mm. However, limited studies on the eight compounds at only two levels indicate that the linear dynamic range of this detector decreases at a gap of 20 mm. These studies show that electrode spacing is a critical variable in the adjustable parallel-plate detector, and that space charge effects may become highly significant at wide electrode gaps.

CORRELATION OF ELECTRON AFFINITY WITH STRUCTURE

Information about the relationship between the structure of phosphate pesticides and their behavior in electron affinity detectors was obtained by comparing the sensitivities of the various pesticides in the detectors. Sensitivities rather than L.L.D.'s were compared because the latter are greatly affected by errors in estimating the noise level of a detector. The sensitivities and L.L.D.'s for the eight compounds are shown in Table II. Both sensitivity and L.L.D. were calculated from the peak areas as measured with a polar planimeter and at the voltage at which the maximum decrease in current was obtained on the corresponding response curve. The values reported may not represent the greatest sensitivity as no attempt was made to find the exact voltage at which the maximum decrease in current was obtained. In several cases, the maximum decrease in current was obtained at 5 or 50 volts, which were the lowest and highest polarizing voltages studied. Both the sensitivity and the L.L.D. were calculated at these polarizing voltages although the maximum decrease in current may actually occur at polarizing voltages not studied.

The effect of structure on electron affinity was studied with the Lovelock detector and with the adjustable parallel-plate detector at 10 mm. because ionization apparently does not occur in these detectors. Sensitivities for the four compounds in the Systox family clearly show that the electron affinity of the compounds changes in the manner

$$\begin{matrix} S & O & S \\ \| & \| & \| \\ P{-}O & < P{-}S & < P{-}S \end{matrix}$$

as the bonding changes between the phosphorus central atom and the oxygen and sulfur atoms. The electron affinity of the compounds in the parathion family is also influenced by these same P—O and P—S bonds. The electron affinity changes in the manner

$$\begin{matrix} O & S \\ \| & \| \\ P{-}O & < P{-}O \end{matrix}$$

In general, then, the electron affinity of phosphate pesticides changes in the manner

$$\begin{matrix} O & S & O & S \\ \| & \| & \| & \| \\ P{-}O & < P{-}O & < P{-}S & < P{-}S \end{matrix}$$

The central phosphorus atom in thiono-Systox should have a larger positive formal charge ($\delta +$) than the phosphorus atom in Di-Syston because the —OR structure shows a larger electrophilic inductive effect than the —SR structure; and the central phosphorus atoms in para-oxon and thiolo-Systox should have larger positive formal charges ($\delta +$) than the phosphorus atoms in ethyl parathion and Di-Syston, respectively, because the =O structure shows a larger electrophilic inductive effect than the =S structure. However, the electron affinities of the

$$\begin{matrix} S & O & O \\ \| & \| & \| \\ P{-}OR, & P{-}OR, \text{ and } & P{-}SR \end{matrix}$$

structures are smaller than the electron

$$\begin{matrix} S & S \\ \| & \| \\ P{-}SR, & P{-}OR, \text{ and} \end{matrix}$$

affinities of the $\begin{matrix} S \\ \| \\ P{-}SR \end{matrix}$ structures, respectively. Evidently, relative electron affinities of phosphate pesticides are not directly related to electrophilic and nucleophilic inductive effects.

This study also shows that the methoxy group has a lower electron affinity than the ethoxy group when both are bonded to the central phosphorus atom.

It is well known that the mammalian toxicity of phosphate pesticides generally increases as the sulfur atoms bonded to the central phosphorus atom are replaced by oxygen atoms; however, the electron affinity of these pesticides decreases with this change in structure. This relationship between electron affinity and chemical structure is different from the relationship found by Clark (*4*), who reported that the electron affinity for a series of chlorinated pesticides increased as the LD_{50} decreased. Apparently a general relationship exists between toxicity and electron affinity, as suggested by Lovelock *et al.* (*17*), but other factors, especially steric effects and transport of the pesticide to the site of inhibition (*21*), must be more important for cholinesterase inhibitors.

The lower limits of detection for the eight compounds given in Table II were calculated at the polarizing voltage for which the maximum response was

Pesticides in Electron Affinity Detectors

Detector	Thiono-Systox				Thiolo-Systox				Meta-Systox-I				Di-Syston			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Lovelock	20	37	9.6	167	20	49	12.6	127	20	78	17.0	89	20	280	78	20.6
Adjustable parallel-plate, 1 mm.	5	1.7	0.439	2730	5	10.8	2.79	430	5	3.31	0.76	1580	5	21.6	5.9	203
Adjustable parallel-plate, 5 mm.	5	2.97	0.77	2090	5	9.1	2.35	680	5	6.2	1.42	1125	5	42.7	11.7	137
Adjustable parallel-plate, 10 mm.	5	18	4.65	172	5	66	17	47	5	40.5	9.3	86	5	212	58	13.8
Adjustable parallel-plate, 15 mm.	40	25.6	6.6	152	40	78	20.1	50	40	363	84	11.9	40	465	127	7.9
Adjustable parallel-plate, 20 mm.	30	244	63	12.7	30	630	162	4.9	50	115	26.4	30.3	50	740	204	3.93
Pin-cup, 3 mm.	5	34	8.8	109	5	86	22.2	43.2	5	32	7.4	130	5	74	20.4	47
Pin-cup, 10 mm.	5	40.7	10.5	63.4	5	122	28.6	28	5	47	10.9	73	5	14.9	41	19.6

Column Headings
1 = Voltage at maximum sensitivity
2 = Sensitivity, amp. sec. ng.$^{-1}$ ($\times 10^{12}$)
3 = Sensitivity, amp. sec. mol.$^{-1}$
4 = Lower limit of detection, mol. sec.$^{-1}$ ($\times 10^{14}$)

obtained. For some detectors, this voltage might not be used for routine analysis because other voltages might yield a wider linear dynamic range. The lower limit of detection can often be lowered by operating the column at a lower temperature or by changing the temperature of the detector. No attempt was made to determine whether the conditions used in this study were optimum.

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Spectrophotometric Determination of Trace Amounts of Zirconium, Titanium, and Molybdenum in Tungsten

SIR: Ken F. Sugawara in his paper [ANAL. CHEM. **36**, 1373 (1964)] points out correctly that elution of the titanium and zirconium with 8*M* HCl [Wilkins D. H., *Talanta* **2**, 355 (1959)] leads to some tungsten contamination. We have had a very similar experience with this particular eluent which is very effective for eluting titanium, zirconium, and hafnium, but which adversely affects the elution characteristics of all elements that normally follow in the analytical scheme (W, Mo, Nb, Ta).

For instance, we have found some niobium in the 8*M* HCl fraction when the sample contains more than 150 mg. of niobium, and found even more niobium in the 60–10 and 25–20 fractions, even though these eluents normally hold back niobium to a considerable extent [Hague *et al.*, *Nat. Bur. Std.* **53**, 261 (1954)].

The low molybdenum results reported in this paper by Sugawara are obviously not caused by any tailing of the molybdenum (He uses 1000 ml. of 5% HF–25% HCl! This eluent and others such as 25% HCl–20% HF are very effective for eluting molybdenum), but can similarly be blamed on the use of the 8*M* HCl eluent for titanium and zirconium, with part of the molybdenum probably being lost in the tungsten fraction. (Note that all of Sugawara's molybdenum results are somewhat low while the titanium and zirconium results show a normal distribution.)

One does not have to look far for a reason for this "irregular" behavior of the elements following titanium and zirconium (W, Mo, Nb, Ta). Before the use of 8*M* HCl eluent, the column is in the HF form and contains approximately 35 ml. of free 4 to 5% (v./v.) of HF. When the 8*M* HCl is used, the front edge of this eluent therefore consists of 8*M* HCl to 1 to 1.5*M* HF and not just of 8*M* HCl. In this medium tungsten, niobium, and, to a lesser extent, molybdenum move at an accelerated rate through the resin bed and appear prematurely in every subsequent eluate.

Work carried out in our laboratory indicates that a considerable improvement can be achieved by replacing the free HF in the column with either ethanol or methanol prior to using the 8*M* HCl. The best method, however, consists of eluting tungsten, titanium, and zirconium together with the 60–10 eluent and separating the titanium and zirconium from the tungsten (after evaporation of the acids) on a second column by the method of Wilkins (*loc. cit.*) with the additional alcohol replacement step mentioned above.

In this way, the subsequent elution on the first column of molybdenum, niobium, and tantalum can be achieved without the adverse effects cited above.

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Monitoring Countercurrent Distribution with a Recording Refractometer

SIR: Subsequent to this article [ANAL. CHEM. **36**, 903 (1964)], a new Teflon and glass pump has become available and has been used to transport solvents in place of the modified Toepler pump used originally. Because chemical inertness, elimination of mercury, and a simpler control system are made possible, much improvement in reliability has been achieved. A revised wiring diagram and other pertinent details are available to the reader upon request.

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Spectrophotometric Determination of Nickel with 4-*tert*-Butyl-1,2-cyclohexanedionedioxime

SIR: Reagents for the determination of nickel have been adequately reviewed by Dale and Banks (*2*) who noted that the *vic*-dioximes are examples of a nearly ideal reagent for the determination of nickel. Hooker and Banks (*3*) and later McDowell *et al.* (*5*) found 4-isopropyl-1,2-cyclohexanedionedioxime to be ideally suited for the spectrophotometric determination of traces of nickel. Unfortunately, intermediates for the synthesis of this reagent are no longer commercially available. 4-*tert*-Butyl-1,2-cyclohexanedionedioxime is an excellent reagent for the spectrophotometric determination of nickel and this report is concerned with its use as a replacement for 4-isopropyl-1,2-cyclohexanedionedioxime. Solutions of the nickel(II)–4-*tert*-butyl-1,2-cyclohexanedionedioxime complex conform to Beer's law for nickel concentrations from 0.85 to 17 μg. of nickel per ml. of xylene.

Table I. Effect of Diverse Ions on Recovery of Nickel

Ion	Amount, mg.	pH	Recovery of 51 μg. of nickel, %
Aluminum(III)	90.3	4	99
Cyanide[a]	...	10	<1
EDTA[b]	97.2	7	99
EDTA[c]	97.2	7	<1
Ferrocyanide	99.2	7	30
Gold(I)	0.029	7	105
Mercury(II)	99.9	5	101
Peroxydisulfate	103	7	91
Thioacetamide[a]	...	7	105
Yttrium(III)	100	6	99

[a] 1-ml. saturated solution.
[b] (Ethylenedinitrilo)tetraacetic acid added after *vic*-dioxime–nickel complex was formed.
[c] (Ethylenedinitrilo)tetraacetic acid added before *vic*-dioxime–nickel complex was formed.

EXPERIMENTAL

Apparatus. All absorbance measurements were made in 1-cm. silica cells. The absorption spectrum was recorded with a Cary automatic recording spectrophotometer, Model 14, and absorbance measurements were made with a Beckman Model DU spectrophotometer. A Beckman Model H pH meter was used for pH studies. The volumetric glassware was Class A.

Reagents. 4 - *tert* - Butyl - 1,2-cyclohexanedionedioxime, saturated aqueous solution (0.0004*M*). 4-*tert*-Butyl-1,2-cyclohexanedionedioxime was prepared from 4-*tert*-butylcyclohexanol by a method analogous to that of Banks, Hooker, and Richard (*1*). 4-*tert*-Butyl-1,2-cyclohexanedionedioxime is a white, crystalline solid which melts with decomposition at 196° to 199° C. The molecular weight is 198. The results of a semimicrocombustion analysis were 60.82% carbon (calcd. 60.58%) and 9.08% hydrogen (calcd. 9.15%).

NICKEL SOLUTIONS. A stock solution was prepared from Mond nickel dissolved in perchloric acid. This solution was analyzed gravimetrically with heptoxime (*6*) and contained 1.703 grams of nickel per liter. Appropriate dilutions of this stock solution were made to yield standard solutions of lower concentrations of nickel.

Recommended procedure. A volume of solution which contains 8.5 to 170 μg. of nickel is placed in a separatory funnel. For every 17 μg. of nickel present, 3 ml. of a saturated solution of 4-*tert*-butyl-1,2-cyclohexanedionedioxime is added. The pH is adjusted to approximately 7 and enough 10*M* ammonium acetate is added to make the final solution 1*M* with respect to acetate. After the complex has formed, 10-ml. of xylene are added. The contents of the separatory funnel are shaken. After the phases have separated, the aqueous phase is discarded. The absorbance of the organic phase is measured at 386 mμ *vs.* a reference solution. A calibration curve for the spectrophotometric determination of nickel(II) was prepared by taking known amounts of a standard solution of nickel(II), forming the complex, extracting it into xylene, and measuring the absorbance. With modifications this procedure can be used for the determination of nickel in the presence of interfering ions.

The recommended range for this procedure is for 30 to 100 μg. of nickel per 10 ml. of xylene. If the unknown concentration does not fall into this range, the sample may be diluted or the light path may be increased.

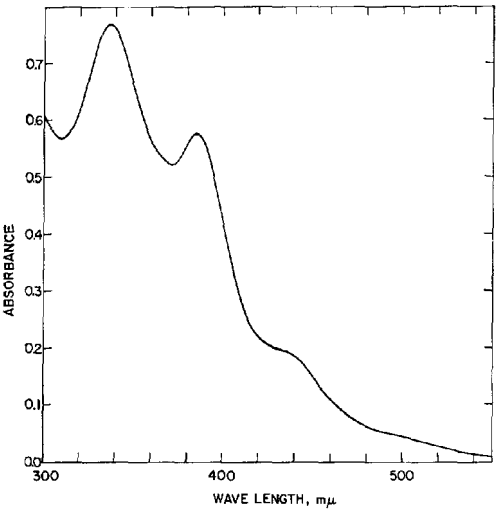

Figure 1. Absorption spectra of nickel(II)–4-*tert*-butyl-1,2-cyclohexanedionedioxime complex in xylene

RESULTS

Nickel(II) reacts quantitatively with 4 - *tert* - butyl - 1,2 - cyclohexanedionedioxime at pH values down to 4.8 to give a pink water-insoluble complex. From a mole ratio plot, two moles of the *vic*-dioxime react with one mole of nickel. Extraction of the complex into xylene is readily and quantitatively accomplished with one equilibration and the xylene solution is stable for 24 hours. Figure 1 shows the absorption spectra of the nickel(II)–4-*tert*-butyl-1,2-cyclohexanedionedioxime complex in xylene. The molar absorptivity for the complex at 386 mμ is 4140 liters per mole-cm.

Interferences. The effect of 100-mg. quantities of several cations and

Table II. Effect of Foreign Cations on Recovery of Nickel

Ion	Amount, mg.	pH	Complexing agent	Recovery of 51 μg. of nickel, %
Cerium(IV)[a]	100	5	NH_4Ac, tiron[b]	100
Chromium(III)	100	5	NH_4Ac, tiron[b]	101
Copper(II)[c]	190	7	NH_4SCN	99
Iron(III)	0.05	7	NaF; $\frac{[Fe]}{[F^-]} = \frac{1}{600}$	101
Manganese(II)	100	6	Tiron[b]	100
Rare earths[d]	...	5	Tartaric acid	99
Thorium(IV)	100	5	Tiron[b]	101
Tin(IV)[a]	100	11	Tiron[b]	100
Titanium(IV)	100	8	Tartaric acid	98
Vanadium(V)	100	8	Tartaric acid	101
Zirconium(IV)	100	11	Tiron[b]	99

[a] Reduced with hydroxylammonium chloride.
[b] 4,5-Dihydroxy-*m*-benzenedisulfonic acid.
[c] Reduced with sulfite.
[d] 19 mg. neodymium, 23 mg. of samarium, 6.5 mg. of praseodymium, 42 mg. of erbium, and 17 mg. of thulium.

anions on the determination of 51 μg. of nickel by extraction of the complex into xylene was investigated. A solution containing a suitable concentration of ion was taken and the pH was buffered at 7 with ammonium acetate. Ten milliliters of a saturated solution of 4-*tert*-butyl-1,2-cyclohexanedionedioxime were added and the solution was equilibrated with xylene. Noninterfering anions in 100-mg. amounts are acetate, bromate, bromide, chloride, chromate, citrate, fluoride, iodate, nitrate, oxalate, perchlorate, sulfate, sulfite, and tartrate. In the presence of citrate, complex formation is slower. Cations which do not interfere in 100-mg. amounts are ammonium, arsenic(III), barium, cadmium, calcium, lead, lithium, magnesium, potassium, silver, sodium, and zinc. The effects of other diverse ions are listed in Table I. Lower recovery of nickel occurred in some instances when other foreign ions such as Ce(IV), Cr(III), Cu(II), Mn(II), Sn(IV), Ti(IV), and V(V) were present. When suitable masking reagents were added, nickel was quantitatively recovered (Table II). Nickel was separated from cobalt(II) by using the hydrochloric acid anionic exchange method of Kraus (*4*).

APPLICATIONS

This method is simple, sensitive, rapid, and accurate and has been used in this laboratory for the determination of traces of nickel in scandium, yttrium, and rare-earth samples.

ACKNOWLEDGMENT

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WORK performed in Ames Laboratory of U. S. Atomic Energy Commission.

Removal of Radioactive Actinides and Lanthanides from Aqueous Solutions with Calcium Fluoride Prior to Flame Photometric Determination of Lithium

SIR: The Tramex (*2*) solvent extraction process is used to separate americium and curium from the lanthanide elements. The aqueous feed to the process contains about 11*M* lithium chloride. The actinides are extracted into the solvent, which is a high molecular weight tertiary amine diluted with diethylbenzene. Because the extraction coefficients of americium and curium are strongly dependent on the lithium chloride concentration, the lithium concentration in the feed solution must be known to within ±2% for adequate process control.

Flame photometry is suitable for the analysis of lithium, but extensive shielding and containment facilities are needed to house the flame photometer and to filter the off-gases unless the lithium is first separated from the radioactive elements. A column of calcium fluoride absorbs trivalent lanthanide and actinide elements (*1*), which are the major source of alpha and beta radiation in the feed solution, while lithium is not retained. Thus, the lithium in the column effluent can be analyzed in a normal manner by flame photometry.

EXPERIMENTAL

Pretreatment of calcium fluoride, pretreatment of glass beads, and preparation of the calcium fluoride column have been described (*1*).

Separation Procedure. Dilute the Tramex feed solution 1000-fold with 0.05*M* nitric acid. The alpha activity of the dilution should be 2×10^6 d.p.m. (disintegrations per minute) per ml. or less and the lithium concentration approximately 0.01*M*. Into a 15-ml. centrifuge cone containing approximately 0.5 ml. of 0.05*M* nitric acid, pipet 500 μl. of the 1000-fold dilution and mix. To the cone add 1 drop of concentrated ammonium hydroxide and mix.

Wash the calcium fluoride column with 2 ml. of 0.1*M* ammonium hydroxide–0.005*M* ammonium nitrate solution and discard the wash. Place a clean 15-ml. graduated centrifuge cone under the column and then carefully transfer the sample solution to the column. Adjust the flow through the column to approximately 1 drop per 15 seconds. Do not allow the liquid level to drop below the top surface of the calcium fluoride.

Wash the centrifuge cone that contained the sample with three 2-ml. portions and a final 1-ml. portion of 0.1*M* ammonium hydroxide–0.005*M* ammonium nitrate solution; transfer the individual washes to the column. Collect the washes with the feed effluent. During the final wash, close the stopcock on the column just before the liquid level reaches the top of the calcium fluoride. Dilute the effluent and washes to 10.0 ml. with 0.1*M* ammonium hydroxide–0.005*M* ammonium nitrate. Stopper the cone and mix well.

Verify the alpha and beta activity

of the solution by mounting an 100-μl. aliquot for gross α- and gross β-counting.

Determine the lithium concentration of the solution by flame photometry. (The working curve should be prepared by analyzing standard solutions of lithium in 0.1*M* ammonium hydroxide–0.005*M* ammonium nitrate.)

The calcium fluoride column may be used for at least three more sample aliquots.

RESULTS AND DISCUSSION

The mechanism for the removal of trivalent lanthanides and actinides from solution by calcium fluoride and the factors affecting the performance of the calcium fluoride column have been described (*1*). The highest decontamination factors are obtained when the sample and washes are basic. The wash solution, 0.1*M* ammonium hydroxide, is made 0.005*M* in ammonium nitrate, which serves as an electrolyte to prevent peptization of calcium fluoride and breakthrough of radioactivity.

Four synthetic samples, each containing 1.2×10^8 d.p.m. of americium-241 alpha activity, were passed consecutively through a single calcium fluoride column. Because the respective decontamination factors, (α d.p.m. in feed)/(α d.p.m. in effluent), were 7.5×10^6, 5.0×10^6, 2.5×10^6, and 7.5×10^6, a column can be used for at least four samples.

The degree of separation of lithium from the trivalent actinides and lanthanides was determined with 16 simulated Tramex feed solutions, each containing 1.2×10^8 α d.p.m. of americium-241. A separate calcium fluoride column was used for each sample. The average decontamination factor was 5×10^6. The effluent and wash solutions from seven of these samples contained less than detectable activity representing complete removal of activity by the calcium fluoride column.

Twelve simulated Tramex feed solutions were passed through four calcium fluoride columns (three samples per column) and were analyzed for lithium by flame photometry. Each of the synthetic samples was 11.0*M* in lithium. The results of the twelve analyses averaged 10.7*M* lithium (97.3% recovery) with a relative standard deviation of 1.7% ($n = 12$). One actual feed solution containing 10^7 α d.p.m. and 1.5×10^7 β d.p.m. per sample aliquot was analyzed for lithium with a relative standard deviation of 1.8% ($n = 5$). This method is being used routinely at the Savannah River Laboratory.

ACKNOWLEDGMENT

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Kinetic Inhibition of Cerium(IV) Reduction by Oxalic Acid

SIR: In a previous paper (*2*) we reported on a detailed kinetic study of the cerium(IV)–oxalic acid reaction in sulfate media to provide basic information useful in choosing optimum reaction conditions for analytical titrations. Our study of this reaction has now been extended to conditions which prevail at the beginning of a titration—the situation where one of the reactants is present in great excess. The primary aim of the experiments reported here is to further confirm the proposed mechanism (*2*) and, if possible, to explain the anomalous induction period described by Rao, Mohan, and Sastri (*3*) for the first addition of cerium(IV) to excess oxalate in sulfuric acid media.

Using the classification scheme of Anbar (*1*), our data for the mechanism fit the sequence

$$MX_n^{+a} \text{ (stable)} + L \rightleftarrows X + MX_{n-1}L^{+a} \text{ (unstable)} \rightarrow MX_{n-1}^{+b} + \text{products}$$

where M, X, and L stand for cerium(IV), sulfate, and oxalate, respectively. According to Taube (*4*, *5*), a likely consequence of this mechanism, if $n > 1$, is that the specific rate of the oxidation-reduction reaction should increase, pass through a maximum, and again decrease as the ratio of L to MX_n^{+a} is increased. We tested this hypothesis, using the techniques described in the first paper (*2*), by following the kinetics of cerium(IV) disappearance in solutions containing a 2- 120-fold excess of oxalate under otherwise identical conditions.

The results are summarized in Table I and show that the specific rate constant for the cerium(IV)–oxalate reaction indeed passes through a maximum and then decreases as the ratio of oxalate to cerium(IV) is further increased.

Table I. Effect of Excess Oxalic Acid on Specific Rate Constant

$4.08 \times 10^{-4}M$ Ce(IV), $0.5M$ H_2SO_4, $5.0 \pm 0.05°$ C.

Oxalic acid, *M*	Specific rate constant, $sec.^{-1}$
0.050	0.022
0.025	0.043
0.020	0.093
0.010	0.093
0.005	0.085
0.002	0.049
0.001	0.021

The most probable mechanistic explanation for the observed trend involves the formation of higher oxalato complexes of cerium(IV) by successive replacement of sulfate ligands by the reducing agent. In selective oxidations of this type such complexes tend to be less reactive than the 1:1 intermediate (*5*). The oxalate to cerium(IV) ratio at maximum specific rate reflects the formation constant of the intermediate and is consistent with independent optical measurements (*2*).

The principal analytical consequence of this kinetic complication will be an apparent induction period at the beginning of titrations where cerium(IV) is titrated into excess oxalate. We believe that the anomalous results described qualitatively by Rao, Mohan, and Sastri (*3*) are caused by this effect.

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Scan Rate Considerations in Combined Gas Chromatography–Mass Spectrometry

SIR: The use of direct introduction of gas chromatographic eluates into a mass spectrometer has increased considerably in recent years (*1, 4–7, 9–11, 13, 15*) and has proved particularly valuable for qualitative analysis of very complex mixtures separated on capillary GLC columns (*2, 3, 8, 12, 14*). Various methods and refinements have been demonstrated in the references cited, and acceptable mass spectra have been shown.

In spite of the considerable number of publications, one question that is invariably asked is "How fast can you scan a mass spectrum?" This enquiry arises when a person is considering purchase of expensive mass spectral equipment and wants to be assured the equipment will meet particular requirements. However, it is not generally appreciated that scan rate is determined not by the fundamental mass spectrometer design but by the frequency limitations of existing amplifier and recording systems and by the resolution of the mass spectrometer. Since the resolution determines how rapidly a mass peak is traversed at a given scan rate, both the resolution and recording system parameters must be specified.

As an illustration we present the mass spectrum of the mercury isotopes (and other mass peaks) obtained at different scan rates on the Atlas-Werke CH4 Mass Spectrometer. Two simultaneous galvanometer traces (Minneapolis-Honeywell Visacorder) are shown for each scan rate (Figure 1). The top trace was from a galvanometer with a natural frequency of 1600 c.p.s. and the bottom trace from a galvanometer with a frequency of 1000 c.p.s. (The different attenuation is of no significance.)

The mass spectrometer was adjusted for a mass resolution of 400—10% valley between the mass peaks 399 and 400 if the peaks are of equal intensity. Both galvanometers retained this resolution in the first scan. The scan rate in this case, HV4, was 0.5 second/octave so that a mass range of 24 to 200 would be scanned in 1.5 seconds. The second scan rate, HV6, covered this range in 0.6 second. Both galvanometers again retained good resolution, but close inspection shows that the slower galvanometer is beginning to lag. Duplicate scans are shown for this rate to illustrate the precision obtainable in fast scanning of mass spectra. As is evident, particularly at masses 193, 200, and 202, significant deviations must be tolerated in fast scan work because of galvanometer inconsistencies, statistical fluctuations, etc.

The next three scan rates illustrated, HV7, HV8, and HV9, indicate that tolerable mass spectra can be obtained when scanning a mass range of 20–200 in a few tenths of a second. However, the original resolution of 400 is reduced, particularly with the 1000-c.p.s. galvanometer, and the "peak clipping" that accompanies the reduction in resolution is evident from the reduction in signal height.

The final illustration, HV10, shows severe distortion of recorded spectra for both galvanometers. It is clear that,

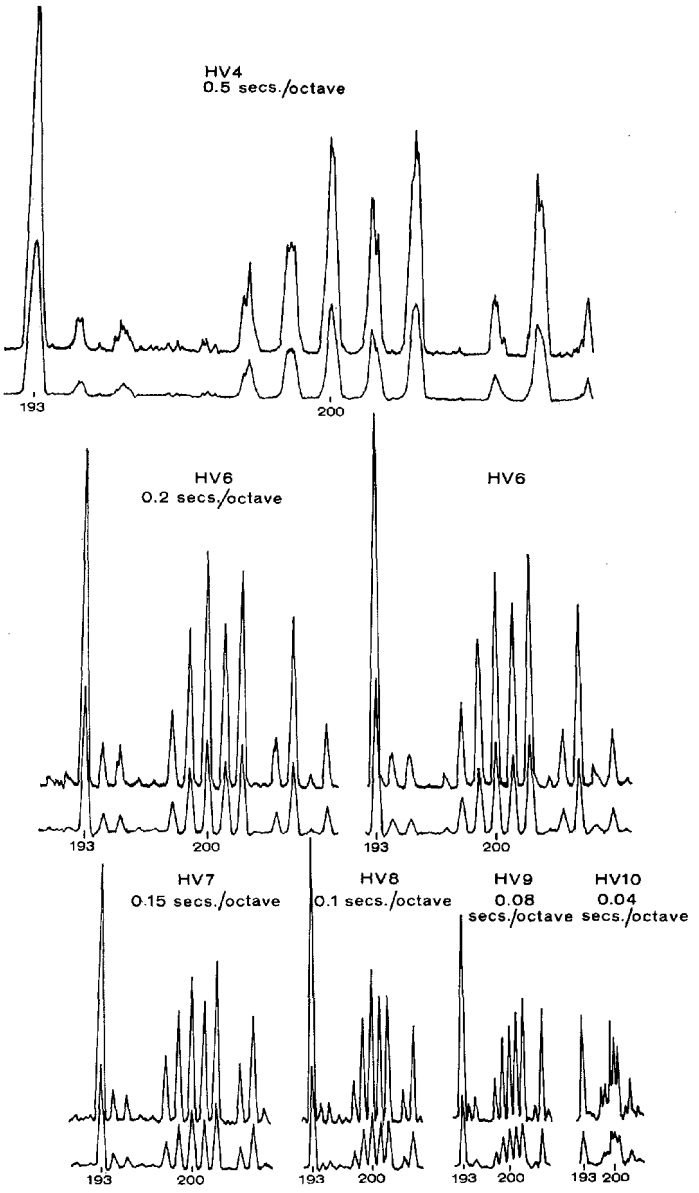

Figure 1. Fast scan mass spectra of mercury isotopes and other ions

at the rate of 24–200 mass units in 0.13 second, resolution is poor and signal clipping is excessive.

The illustrated mass spectra were obtained with an instrument equipped with an electron multiplier so that limitations imposed by time constants were primarily in the recording galvanometers. Frequency response of 1000–2000 c.p.s. is satisfactory for mass spectral scans to 300 mass units at resolution of 300–400. If an electron multiplier is not used, a typical d.c. amplifier operating at high gain will have a time constant of 0.1–0.01 second, and compromise of sensitivity, resolution, or scan rate will be required.

The precision limitations shown by the duplicate scans of HV6 are partly caused by natural statistical error. If an ion peak is traversed in a millisecond, then for a current of 10^{-14} ampere approximately 100 ions will be collected, which may give a 10% counting error. Such a limitation shows that one should not use a higher scan rate than is necessary or use a higher resolution than is required. For most combined GC-mass spectrometry, scan rates of 1–4 seconds and mass resolution of 300 are adequate. Special systems may require extensions of these limits but compromises of quality, sensitivity, and precision will again be necessary.

The possibility of obtaining fast-scan high-resolution mass spectra is also made impractical by this statistical limitation. As resolution is increased, a longer scan time is required if the recording system does not have a faster response and to go from resolution 300 to 10,000 would require scan times of about 30–60 seconds. However, even if a tape recording system with a frequency response of about 5×10^4 c.p.s. is used to store the mass spectral data, the time required to scan across a mass peak when a resolution of 10,000 is used would be about 10^{-4} to 10^{-5} second. The reasonable statistical limit of sensitivity would be about 10^{-12} to 10^{-13} ampere of ion current. At the present time, the integrating properties of photographic detection (*16*) seem preferable and will probably permit two or three orders of magnitude higher sensitivity. Use of a slower scan rate would be practical only in a few cases where the chromatographic peak was eluted very slowly.

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REFERENCE to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

Trimethylphenylammonium Iodide as a Quantitative Precipitant for Gold

SIR: A rapid, selective semimicro gravimetric method for the determination of gold was needed because the classic reduction methods (*4, 7*) are frequently inaccurate or time consuming, and spectrophotometric and titrimetric methods (*2, 8*) usually depend upon prior separations.

Trimethylphenylammonium iodide, first utilized by Pass and Ward (*5*) for a volumetric cadmium method, was later refined by the American Zinc Company (*3*), and further utilized by Burkhalter and Solarek (*1*) for gravimetric analysis of bismuth. The precipitation of gold in the proposed method depends upon the formation of an insoluble salt of the quaternary cation and a tetraiodo anion complex formed when Au(III) reacts with excess iodide ions. The compound is stoichiometric and has the formula $[(CH_3)_3(C_6H_5)N]^+AuI_4^-$. The brown-black flocculent precipitate is easily filtered and contains 23.42% gold by weight.

EXPERIMENTAL

Reagents. Precipitating solution: 40 grams of potassium iodide and 25 grams of trimethylphenylammonium iodide (Eastman Organic Chemicals, reagent 4423) are dissolved in 1 liter of water.

Reagent wash solution: 1 part of the precipitating solution is diluted with 4 parts of water.

Toluene wash solution: 1 liter of toluene is mixed with 25 ml. of ethanol.

Buffer and complexing solution: 150 grams of sodium citrate dihydrate and 200 grams of anhydrous sodium acetate are dissolved in warm water and diluted to 1 liter.

Gold standard solution: 3.9800 grams of 99.999% gold (Western Gold and Platinum Corp., Belmont, Calif.) is weighed, carefully dissolved in 20 ml. of aqua regia, and diluted to 1 liter.

Procedure. A weighed sample containing 5 to 50 mg. of gold or, for evaluation purposes, an aliquot of the standard solution is pipetted into a 250-ml. beaker. Five milliliters of aqua regia are added, and the solution is evaporated to a sirup on the steam bath being careful not to go to dryness. Three milliliters of concentrated hydrochloric acid are added and the sample is again evaporated to a sirup which should finally contain ~1 ml. of concentrated acid necessary to obtain proper pH. The solution is diluted with 25 ml. of distilled water. An ice cube made from distilled water (~40 $cm.^3$) is added so that, with occasional stirring, the temperature of the solution will be maintained below 10° C. throughout the precipitation process. Finally, 15 ml. of the buffer solution is added, followed by 30 ml. of the precipitating solution. Precipitation occurs immediately and is complete within 30 minutes. The total volume should not exceed 120 ml.

The ice cube melts in approximately 30 minutes, and the precipitate is filtered immediately on a weighed gooch crucible and washed sparingly with 5 to 10 ml. of reagent wash solution. The precipitate is now washed more thoroughly with 50 ml. of the toluene wash solution and air-dried to constant

Table I. Effect of Diverse Ions on Gold Recovery

Diverse ions and their weight, mg.[a]																	Gold, mg.		Relative error, %
Al^{+3}	Ba^{+2}	Be^{+2}	Ca^{+2}	Co^{+2}	Cr^{+3}	Cu^{+2}	Fe^{+3}	Ga^{+3}	In^{+3}	Mg^{+2}	Mn^{+2}	Mo^{+6}	Ni^{+2}	Sn^{+4}	Sr^{+2}	Te^{+4}	V^{+5}	Zn^{+2}	Taken	Found	
					50	50	60						30					240	5.0	4.8	−4.0
					32	55	61						25					132	5.9	5.6	−5.1
					16		155						127						8.0	7.9	−1.2
												41.5	58						8.0	7.8	−2.5
											9		270						10.0	10.1	1.0
2		4		128	40	200	28												11.9	11.9	0.0
											19		381						12.8	13.0	1.6
											18		350						14.9	14.8	−0.7
					196		80						90						15.5	15.2	−1.9
						50	80				5	600		5			10		15.9	15.6	−1.9
						38	16												15.9	16.3	2.5
78	200					85	50			118		400			130			182	19.8	19.9	0.5
												330		25					19.9	19.7	−1.0
8	10	3	30	25	3	23	10	60	53	29	15	400	10	6	10			25	19.9	20.2	1.5
																200	100		20.0	19.8	−1.0
				28			50	5	5			27	300				5		20.1	20.2	0.5
												600							21.9	22.4	2.3
											22		495						22.3	21.9	−1.8
3				4		4	5				26		540						22.8	22.8	0.0
5		5		50	20	31	40		6			10	20	15				100	25.9	25.8	−0.4
10				240	95	59	190				90		40					20	31.8	32.4	1.9
												525							32.0	32.5	1.6
						300	10	5	5							5			39.8	39.8	0.0
2	5		120			187	80						120					420	39.8	40.3	1.3
								304	660										42.7	43.4	1.6

[a] All metal impurities were added as chloride salts with the exception of gallium, indium, molybdenum, tellurium, and vanadium, which were added as metals. Mean relative error 1.5%

weight in 10 minutes by the suction used in the filtration.

The precipitate can also be dried at 40° C. without decomposition. However, higher temperatures tend to decompose the compound. The precipitate is nonhygroscopic, and a constant weight is easily obtained. The gravimetric factor for metallic gold is 0.2342. Destruction of the precipitate and recovery of the gold may be accomplished by fuming with a mixture of nitric and sulfuric acids.

RESULTS AND DISCUSSION

Gold in quantities of 5 to 50 mg. was determined in 20 samples without impurities, with a mean relative error of 1.4%. Blanks containing various metal impurities were run with no precipitate formation noted. Table I shows the results obtained with known quantities of gold doped with various metal impurities. Small amounts of nitrates do not affect the precipitation of gold in the strongly buffered solution (pH 4.4 to 4.8.) This pH must be maintained so that elements such as Cu(II), Fe(III), and Sn (IV) remain complexed by the sodium citrate. The solution must be kept cold to minimize solubility and prevent reduction of the gold by the citrate ion. Many elements, including Co(II), Cr(III), Ga(III) In (III), Mn(II), Mo(VI), Ni(II), Zn(II), and the alkaline earths form weak iodo complexes (*6*) and would not interfere with the gold precipitation, even without the sodium citrate, provided hydrolysis of these metals is prevented. The stable complexes of Bi(III), Cd(II), Hg(II), Pb(II), Pd(II), Pt(IV), and Tl(I) cause interference even in the presence of sodium citrate. Silver can be separated as the chloride by filtration, after the initial dissolution of the sample, but care should be taken to maintain a small volume.

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Calculation of Upper Limit of Hydrogens of an Organic Formula for Analysis of Mass Spectra

SIR: In developing computer programs (*3*) for the analysis of mass spectral data, it became desirable to calculate the maximum number of hydrogen atoms (hydrogen value, HV) which a molecule of given integer molecular weight (W) may contain.

A formula has been developed which requires only the use of integer arithmetic. A parameter (x) may be calculated which is related to the integer residue (r) obtained on dividing the molecular weight (W) by 14. The upper limit of hydrogens (HV) for a given molecular weight (W) is then given by the expression:

$$HV = 2(W/14) + x_r \qquad (1)$$

in which the value of x is determined by the residue and obtained from Table I.

Only the integer portion of $(W/14)$ is utilized in Equation 1.

To illustrate the necessary procedure, a few examples have been incorporated in the right hand portion of Table I.

If the molecular weight of a compound is 148, then the appropriate values of r and x are 8 and -4 (See Table I).

Bearing in mind that only the integer portion of $W/14$ is utilized, we have

$$HV = 2(148/14) + (-4)$$
$$= 2(10) - 4$$
$$= 20 - 4 = 16$$

The formula $C_4H_{16}N_6$ is given as a possibility in Table I; however, other combinations of C, N, and O can give alternatives with the same hydrogen value—e.g., $C_{11}H_{16}$ or $C_6H_{16}N_2O_2$.

The above procedure is applicable to intact organic molecules of any level of saturation containing C^{12}, H^1, N^{14}, or O^{16}. Other species -e.g., radicals or isotopic substitutions—should be revised to the corresponding standard forms by adding or subtracting the appropriate weights before the calculation is applied.

The arithmetic basis of these calculations—almost self-evident from the valence rules and the fact of CH_2 weighing 14 - is elaborated elsewhere (*1-4*).

Table I. Values of Parameter (x) and Maximum Hydrogen Values for Sample Molecular Weights

Remainder (r)	x	Examples w	HV	Possible formula
0	0	140	20	$C_{10}H_{20}$
1	−1	141	19	$C_9H_{19}N$
2	2	142	22	$C_{10}H_{22}$
3	1	143	21	$C_9H_{21}N$
4	0	144	20	$C_8H_{20}N_2$
5	−1	145	19	$C_7H_{19}N_3$
6	−2	146	18	$C_6H_{18}N_4$
7	−3	147	17	$C_5H_{17}N_5$
8	−4	148	16	$C_4H_{16}N_6$
9	−5	149	15	$C_{10}H_{15}N$
10	−2	150	18	$C_{11}H_{18}$
11	−3	151	17	$C_{10}H_{17}N$
12	0	152	20	$C_{11}H_{20}$
13	−1	153	19	$C_{10}H_{19}N$
0	0	154	22	$C_{11}H_{22}$

The arithmetic basis of these calculations—almost self-evident from the valence rules and the fact of CH_2 weighing 14 - is elaborated elsewhere (*1-4*).

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Differential Potentiometric Determination of Palladium in the Presence of Platinum in High Grade Palladium-Platinum Materials

Sir: There has been a long-felt need for an accurate method of analysis of high grade palladium materials for palladium. In applying the widely accepted gravimetric, dimethylglyoxime (DMG) method to such materials, one is handicapped by the bulkiness of the palladium DMG precipitate and the resulting need to use relatively small samples. The same could be said of the volumetric methods involving the direct titration of the total amount of palladium present. The same limitations exist—namely, small samples and magnification of minor errors.

In the method presented the difficulty has been overcome by applying the concepts of differential titrimetry discussed in two earlier papers (*3, 5*) to the known reaction of palladium with potassium iodide. As a result, there is no limitation as to the size of the sample that can be used and the error is reduced to less than 0.1% for relatively pure palladium materials. The method is based on the controlled separation of 90 to 98% of the palladium present with a calculated deficiency of potassium iodide followed by the potentiometric titration of the remaining palladium with the same reagent. The nature of the reaction of palladium with potassium iodide and the various ways of detecting the end point are discussed in literature (*1, 2, 4, 6*).

EXPERIMENTAL

Apparatus. A Metrohm recording potentiograph Model E336 (Metrohm, Ltd., Herisaw, Switzerland) with platinum and saturated calomel electrodes was used for titrations.

A Schuco automatic pipet was used for dispensing 50-ml. volumes of the potassium iodide solution with a precision of 0.005 ml.

Reagents. Concentrated potassium iodide solution, 18.72 grams of potassium iodide per liter.

Dilute potassium iodide solution, 9.36 grams of potassium iodide per liter.

Both solutions are standardized against pure palladium.

Procedure. Weigh accurately into a 100-ml. beaker a sample containing from 300 to 350 mg. of palladium. Into a separate 100-ml. beaker weigh an amount of palladium sponge corresponding to the maximum amount of palladium expected in the sample (approx. 350 mg.). Moisten the sample with formic acid and cover the beaker. Add 15 ml. of aqua regia (3 parts HCl + 1 part HNO_3). Digest at moderate heat, then take to dryness. Take up the residue twice more with 5-ml. portions of HCl to dryness. Dissolve the residue, which is still slightly wet, in water by applying some heat. If any insoluble residue is left, filter, ignite the residue, and redissolve in aqua regia as before. Combine the two solutions and adjust the volume to about 120 ml. If gold is expected in the concentrate, add 25 ml. of a SO_2-saturated water solution, and allow to stand 1 hour. If the presence of silver is suspected, add 2 ml. of a 0.1% silver nitrate solution. Heat to coagulate and

filter out gold metal and silver chloride combined. Boil to drive off sulfur dioxide, then add 50 ml. of the concentrated KI solution from the automatic pipet to precipitate the bulk of palladium. Titrate the remainder potentiometrically using the dilute KI solution.

Table I. Accuracy and Precision of Differential Separation of Palladium

(50 ml. of an 18.72-gram-per-liter potassium iodide solution added to each sample solution)

Wt. of Pd sponge, mg.	Palladium, mg. Titrated	Palladium, mg. Precipitated	Deviation Mg.	Deviation %
322.7	21.3	301.4	+0.25	0.08
323.8	22.9	300.9	−0.25	0.08
324.4	23.5	300.9	−0.25	0.08
350.8	49.4	301.4	+0.25	0.08
	Av.	301.15	0.25	0.08

Table II. Effect of Silver and Gold on Palladium Titration

(10 mg. of Pd added as nitrate to all solutions)

	Potassium iodide consumed, ml.		
Ag, mg.	In absence of digestion	After digestion with HCl	Calcd. if all Ag reacted with KI
None	10.05[a]	10.15	
1	10.25	10.10	10.5
2	10.35	10.15	11.0
5	10.85	10.17	12.5
10	13.20	10.12	15.0
Au, mg.		After digestion with SO_2	Calcd. if all Au reacted with KI
1	10.70	10.05	10.8
2	11.30	10.00	11.6
3	12.10	10.05	12.4
5	13.80	10.05	14.1
10	17.60	10.10	18.1

[a] Average of 5 titrations.

DISCUSSION

Effect of Hydrochloric Acid Concentration on Detection of End Point. To establish the effect of increasing HCl concentration on the shape of the titration curve, 10-ml. aliquots of palladium chloride solution containing 1 gram per liter of palladium were adjusted to 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 1, and 5 volume % in HCl and subsequently titrated with a 3.1-gram-per-liter potassium iodide solution. The slope of the titration curves is shown in Figure 1. The best defined titration curves are obtained for the solutions that are the lowest in hydrochloric acid concentration. Since working with solutions too low in acid might be impractical because of the excessive dilution that might be involved, a 0.2 volume % HCl solution was selected for all subsequent tests.

An enhanced potential break is produced in the presence of some sodium acetate of interest whenever the derivative titration is desirable.

Accuracy and Precision. Varying amounts of accurately weighed palladium sponge were treated as per procedure described. The data obtained are shown in Table I.

The amount of palladium titrated shown in the second column was calculated from the stoichiometric amount of freshly prepared potassium iodide consumed in the titration. The amount of palladium precipitated as iodide, shown in column 3, was calculated by difference from the weight of palladium sponge shown in the first column less palladium titrated shown in the second column. In this respect it might be of interest to mention that the amount of palladium shown in the third column was approximately 0.25% in excess of the stoichiometric amount for the reaction $PdCl_2 + 2KI \rightarrow PdI_2 + 2KCl$. This small difference could well be due to noncorrespondence of the potentiometric end points with the equivalence points.

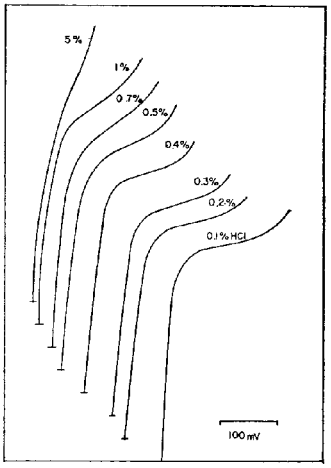

Figure 1. Effect of hydrochloric acid concentration on shape of titration curve

10 mg. of Pd added in each case

Effect of Platinum, Copper, Silver, and Gold on Palladium Titration. In a solution containing palladium and platinum, the latter will not react with iodide for as long as there is palladium present in solution. The potentiometric titration curve for the palladium-iodide reaction showed no signs of interference for the platinum concentrations up to twice that of palladium.

Similarly, copper present in concentrations up to 200 times that of palladium had no effect on the accuracy of the palladium analysis.

Silver and gold, however, do interfere since they form insoluble iodides and their separation preliminary to iodide addition is mandatory. While the separation of gold with some SO_2-saturated water presented no problem, the separation of silver was not found easy. Silver was present in the hydrochloric solution as a soluble polychloride and the only way of removing it was by adding some silver nitrate to the palladium hydrochloric acid solution. Silver chloride acted as a sort of carrier for the soluble silver polychlorides.

The data pertaining to the palladium titration in the presence of silver and gold are shown in Table II. It is obvious from this table that an appreciable amount of silver separates as chloride even in the absence of digestion and does not interfere in the palladium-iodide reaction. On the other hand, the reaction of gold with iodide is almost quantitative and the resulting interference in the absence of digestion with SO_2 is much greater than that of silver.

Table III. Typical Results and Calculations Involved in Differential Analysis of Palladium

(50 ml. of an 18.72 gram-per-liter KI solution added to each sample solution)

Sample	Sample wt. mg.	Poten. titn. KI, ml.	Palladium found, mg. Titd.	Pptd.	Total	%	
Pd sponge	319.4	6.75	19.0	300.4			
	318.3	6.15	17.3	301.0	Av. 300.8		
	320.4	6.88	19.4	301.0			
Pd conc., grav. anal. 65.56%	508.3	11.05	31.2	300.8	332.0	65.32	
	510.9	13.00	36.7	300.8	336.5	65.73	Av. 65.54
	504.1	10.58	29.8	300.8	330.6	65.58	
Pd sponge	347.9	18.00	49.50	298.4			
	339.9	15.55	42.76	297.1	Av. 297.8		
Pd conc., grav. anal. 89.49%	357.0	7.90	21.73	297.8	319.5	89.42	
	357.3	7.80	21.45	297.8	319.3	89.36	Av. 89.39

RESULTS

The nature of calculations involved in figuring out the results is illustrated in Table III. Two grades of palladium concentrate were run each against a proper standard of palladium sponge. Because the analysis of the two grades was not carried out at the same time, the potassium iodide equivalent of palladium is not exactly the same for the two runs. Nonetheless, in both instances, the results obtained by the differential titration method compared favorably with the results obtained by the much longer gravimetric method performed with the greatest accuracy.

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FIFTEENTH Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., March 1964.

Spectrophotometric Determination of Organic Peroxides in Unsaturates

SIR: A sensitive spectrophotometric method based on the oxidation of potassium iodide for the determination of traces of peroxides in organic solvents has been described in a previous publication (*1*). It was applicable to methanol, 2-propanol, pentane, hexane, chloroform, ether, acetone, ethyl acetate, vinyl acetate, benzene, and toluene. Since that time, we have obtained data to show that the procedure is applicable to peroxides in olefins and other unsaturates without interference. This greatly extends the usefulness of the method.

Known amounts of peroxide were added from a stock solution of benzoyl peroxide in 2:1 acetic acid–chloroform to samples of olefins. As shown in Table I good recoveries were obtained after correcting for the original peroxide content of the olefins. There was no iodine absorption by the olefins even when the solutions were allowed to stand for 2 hours before absorbance measurements were made. Five-milliliter samples were used in all cases except for cyclohexene, where 2-ml. samples were taken because of the relatively high initial peroxide content.

A sample of mixed nonenes containing an appreciable amount of peroxide was used to obtain precision data. This sample was analyzed eleven times using 1- to 3-ml. samples. Absorbance measurements were made over time intervals ranging from 15 minutes to 2 hours after KI addition. The 95% confidence limits for the average were 101.1 ± 1.3 p.p.m. active oxygen.

The method was also applicable to the determination of peroxides in compounds containing α, β, and conjugated unsaturation which often interferes with iodometric methods for peroxides. Samples of isoprene (5-ml.), acrolein (2-ml.), and sorbic acid (1 gram) were dissolved in 2:1 acetic acid–chloroform. Known amounts of benzoyl peroxide were added to each and the solutions were analyzed for active oxygen. Good recoveries were obtained as shown in Table I. A correction was made in the case of sorbic acid which gave a yellow solution in the acetic acid–chloroform solvent.

Autoxidation of certain unsaturated organic compounds to form peroxides is well known. The described method was useful for determining small amounts of peroxides in such compounds. Samples of cyclohexene and tetralin which had been retained on the reagent

Table I. Recovery of Peroxides in Presence of Unsaturates

Sample	Type of unsaturation	Active oxygen added μg.	Time of absorbance measurement after KI addition, min.	Active oxygen found, μg.
Octene-1	Olefinic	0	60	0
		336	30	318
		336	60	314
		336	120	320
Mixed octenes	Olefinic	0	60	0
		336	30	324
		336	60	332
		336	120	334
Heptenes	Olefinic	0	60	0
		336	30	332
		336	60	342
		336	120	346
Cyclohexene	Olefinic	0	60	132
		200	60	332
		200	60	344
		200	60	346
Isoprene	Conjugated	0	60	0
		332	30	346
		332	60	340
		332	120	348
Acrolein	α, β	0	60	48
		258	60	318
Sorbic acid	Conjugated α, β	0	60	0
		258	60	250

Table II. Autoxidation of Cyclohexene and Tetralin

Sample	Active oxygen in original sample, p.p.m.	Active oxygen, after distillation p.p.m.	Active oxygen in autoxidized sample, p.p.m. After 1 wk.	After 1 month
Cyclohexene	6250, 6300	<5	1220	4000, 4150
Tetralin	6500	<5	15	510, 560

shelf for a long period of time contained an appreciable amount of active oxygen on analysis. These samples were then distilled under a nitrogen blanket in the presence of excess ferrous sulfate. The active oxygen content of the distillates was reduced to negligible concentrations. The purified samples were placed in clear glass bottles. The cyclohexene was sparged briefly with air and the tetralin with oxygen. The bottles were then sealed and the samples allowed to autoxidize under the diffuse light of the laboratory. Analysis of these solutions showed an increase in the active oxygen content upon standing (Table II).

We have clearly shown that the previously described method is applicable to the determination of peroxides in a variety of commonly used unsaturated compounds. No interference from iodine absorption by the unsaturates was encountered with any of the compounds tested. This is in agreement with the work of Wagner (*2*) who reported that iodine in the presence of excess iodide will not readily add to unsaturates due to formation of the relatively stable triiodide ion. Other unsaturated compounds were not tested because of the limited time available for this study. However, in view of the results reported here, the method should be useful for the determination of active oxygen in many unsaturated compounds.

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Ion Exchangers for Gas Solid Chromatography

SIR: The potential value of ion exchangers in gas solid chromatography was briefly investigated. By modifying the ion exchanger it was possible with this technique to separate compounds of higher boiling point than those hitherto susceptible to gas solid chromatography.

EXPERIMENTAL

Exchangers (52 to 80 mesh) used were 8% cross-linked sulfonated polystyrene (Dowex 50 or Zeo-Karb 225), 2½% crosslinked polymethacrylic acid (Zeo-Karb 226), and zirconium phosphate (Bio-Rad ZP1). In the uncoated state both organic and inorganic exchangers effected separations, but the peaks had sharp leading edges with long trailing edges, typical of nonlinear adsorption isotherms. 1.5% Squalane on Dowex 50–8X in the H^+ form gave symmetrical peaks for the separation of C_6 to C_9 fatty acids (Figure 1). Presumably, the squalane reduced undesirable adsorption by the polystyrene matrix or improved kinetics of the adsorption reactions. Uncoated sulfonated polystyrene could not be used satisfactorily above about 100° C. because of bleeding (hydrogen flame detector), while Zeo-Karb 226 and ZP1 were stable up to 200° C., the maximum temperature used. Consistent with its polar zirconium oxide matrix, ZP1 in the H^+ form gave symmetrical peaks for fatty acids C_4, C_6, and C_8 when the polar diethylene-glycol succinate (DEGS) (at 5% level) was used as modifier, but trailing caused by residual matrix adsorption was not reduced by the nonpolar Apiezon M. Under similar conditions of column length and flow rate ZP1 required a temperature of 176° C. to give retention times comparable to those on Dowex 50 at 90° C., and therefore it gave lower separation factors. This disadvantage of the inorganic exchanger could probably be overcome if the manufacturers produced a more porous material.

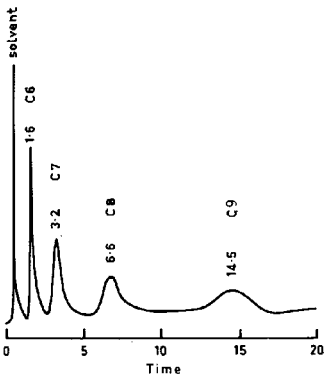

Figure 1. Separation of alkanoic acids on Dowex 50 coated with 1.5% squalane

Column, 200 × 0.4 cm.; temperature, 92°C.; nitrogen inlet pressure, 14 p.s.i.

Other examples of separations achieved are:

1. On Zeo-Karb 225 8X–H^+ form, 52 to 80 mesh, coated with 0.1% squalane, column 200 × 0.4 cm., temperature 76° C., N_2 inlet pressure 12.4 p.s.i.
   (a) Homologous alkan-2-ones C_{7-11} (R_t 0.6, 1.0, 1.8, 3.7, 8.3, respectively).
   (b) Homologous alkanals C_{8-11} (R_t 0.9, 2.0, 4.5, 10.0).
   (c) Separation of decanal (R_t 5.9) from decan-2-one (R_t 7.5).
2. On Dowex 50 8X–H^+ form, 52 to 80 mesh, coated with 1.5% squalane, column 200 × 0.4 cm., temperature 93° C., N_2 inlet pressure 14 p.s.i.
   (a) Octanoic acid (R_t 7.2), oct-2-enoic acid (R_t 11.7), nonanoic acid (R_t 16.9).
   (b) Ethyl caprate (R_t 9.4) from ethyl laurate (R_t 43.5).
3. On ZP1–H^+ form, 52 to 80 mesh, coated with 5% DEGS, column 200 × 0.2 cm., N_2 flow rate 10 ml./minute.
   (a) Hexanoic acid (R_t 5.4) from hex-2-enoic acid (R_t 8.0), temperature 176° C.
   (b) But-1-en-3-ol (R_t 4.8) from but-2-en-1-ol (R_t 10.0), temperature 82° C.

When the load of DEGS on ZP1 was increased from 5 to 10%, retention times were lowered, presumably because of the covering up of sites, rather than increased as would have been expected in gas liquid chromatography. This suggests that the separations achieved were by modified gas solid rather than gas liquid chromatography.

DISCUSSION

As is usual in gas solid chromatography, theoretical plate numbers were much lower in the separations listed (ranging from about 20 for organic acids on ZP1 to 500 for esters on Dowex 50) than in conventional gas liquid chromatography. The technique of using modified gas solid chromatography on ion exchangers would appear, however, to offer the opportunity of making use of various anions and cations otherwise difficult or impossible to incorporate in the stationary phase. These would include for instance Ag^+ for the separation of unsaturated compounds. Exchangers such as zirconium tungstate (Bio-Rad ZT-1), zirconium molybdate (Bio-Rad ZM-1), and ammonium molybdophosphate (Bio-Rad AMP-1) may themselves act as chelating agents.

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Separation and Determination of Trace Quantities of Uranium in Presence of Plutonium

SIR: Existing spectrophotometric methods for the determination of uranium in the presence of large amounts of plutonium are unsatisfactory. An excellent review by Booman and Rein (*1*) describes many of the available methods for the separation and analysis of uranium. Plutonium interferes in the color development of the existing methods and must be separated. Qualitative separation of a small amount of uranium is difficult and none of the procedures described by Booman and others (*3*, *4*) gave qualitative separations in a short length of time. This paper reports a rapid and qualitative separation of the two elements even when there are several thousand times as much plutonium as uranium.

In this procedure uranium is separated from plutonium with tri-*n*-octylphosphine oxide (TOPO) (*4*) from 2*M* HNO_3. Small quantities of sulfamic acid, ferrous ammonium sulfate, and sodium fluoride are added to the nitrate media to prevent the extraction of plutonium, which is reduced to plutonium(III). The separated uranium is then determined spectrophotometrically in the organic phase using 1-(2-pyridylazo)-2-naphthol (PAN) to develop an intense red complex ion at pH 10 in ethanol–cyclohexane.

EXPERIMENTAL

Apparatus and Reagents. Standard uranium solution (0.85 mg. of U per ml.) in 2*M* HNO_3, 0.05*M* TOPO dissolved in cyclohexane, 0.1 wt. % PAN dissolved in ethanol, and 10 vol. % triethanolamine dissolved in ethanol.

The absorbancy curves of the solutions contained in 1-cm. matched silica cells were measured with a Beckman DK-2A spectrophotometer.

Procedure. Quantitatively transfer a sample aliquot containing 10 to 100 μg. of uranium to a 60-ml. separatory funnel. Adjust the acidity of the solution to 2*M* with HNO_3. Add 50 mg. each of NaF, NH_2SO_3H, and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in that order to the solution. The ferrous ion is unstable in 2*M* HNO_3 unless NH_2SO_3H is present. Transfer 5 ml. of the standard TOPO solution into the funnel and equilibrate the two phases for 1 to 2 minutes. The ratio of the aqueous to organic phase is not critical, and may be as high as 5 to 1. The amount of TOPO used in the extraction is sufficient to remove several milligrams of uranium. Remove the aqueous phase and wash the organic phase with 10 ml. of 2*M* HNO_3 containing NaF, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, and NH_2SO_3H.

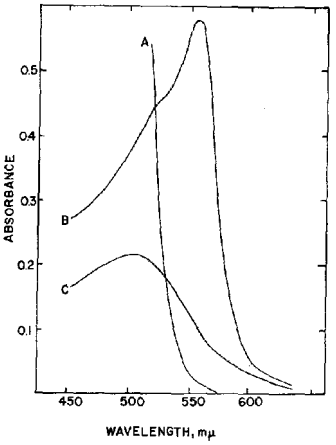

Figure 1. Absorption curves

A. Reagent blank vs. ethanol
B. 6.4 p.p.m. uranium vs. reagent blank
C. 1 p.p.m. plutonium vs. reagent blank

Quantitatively transfer an aliquot of the organic phase to a 10-ml. volumetric flask containing 1 ml. of PAN solution and 2 ml. of triethanolamine solution. Dilute the solution to the mark with ethanol. Allow 30 minutes for the color to reach maximum intensity, and measure the absorbancy of the solution at 555 mμ against a reagent blank. Determine the uranium content from a standard curve, prepared with known amounts of uranium.

RESULTS AND DISCUSSION

Extraction. Tri-*n*-octylphosphine oxide exhibits its greatest selectivity in the extraction of cations from aqueous nitrate media. Both HCl and HNO_3 have high distribution coefficients for the extraction of U(VI) (*4*), but HCl extracts Fe(III), Au(III), Zn(II), Cd(II), Hg(II), and several other cations. Nitric acid inhibits the extraction of many of these cations, which produce interfering red complex ions with PAN. Phosphoric, H_2SO_4, and $HClO_4$ were not used because these acids inhibit the quantitative extraction of U(VI).

Hydrochloric acid, H_2SO_4, and H_3PO_4 can be tolerated in varying concentrations in solutions of 2*M* HNO_3. Table I shows that up to 0.2*M* concentrations of sulfate or phosphate ion can be present without inhibiting the extraction of U(VI). Chloride ion concentrations up to 0.5*M* do not give high results, as would be expected if Fe(III) were being extracted.

Plutonium(IV) or Pu(VI) is quantitatively extracted from HNO_3, but a wide variety of distribution coefficients have been reported for the extraction of Pu(III). Experiments by the author have shown that less than 0.1% plutonium is extracted when a reducing agent, such as Fe(II), is present to prevent oxidation of Pu(III) to Pu(IV). Sulfamic acid must be added in order to stabilize the Fe(II). The uranium remains in the hexavalent state and is extracted. The separation can be made quantitative by the addition of a small amount of fluoride which prevents the extraction of Pu(III).

Fluoride ion also prevents the extraction of Th(IV), Np(IV), Ce(IV), and Zr(IV). These cations normally are extracted from 2*M* HNO_3. Table II presents the effect of several cations on the determination of 67 μg. of uranium in synthetic unknowns. The cations chosen for study as possible interferences were those found in samples received for

Table I. Spectrophotometric Determination of Uranium in Presence of Various Interfering Anions

U taken, μg.	Interference added	U found, μg.
67	0.1*M* HCl	67
67	0.5*M* HCl	67
67	0.05*M* H_2SO_4	67
67	0.2*M* H_2SO_4	65
67	0.05*M* H_3PO_4	67
67	0.2*M* H_3PO_4	65

Table II. Spectrophotometric Determination of Uranium in Presence of Various Interfering Cations

U taken, μg.	Interference added	U found, μg.
67	25 mg. Pu	67
67	2 mg. Fe[a]	66.5
67	15 mg. Np	66
67	22 mg. Th[b]	65
67	5 mg. Ce	67
67	2 mg. Cu	68
67	10 mg. Hg	67
67	4 mg. Al	68
67	2 mg. Sn	68
67	5 mg. Cr	67
67	5 mg. Co	67
67	10 mg. Pb	68
67	4 mg. Zr[b]	66

[a] Ferric nitrate was added in addition to the normal amounts of ferrous ammonium sulfate.

[b] White precipitate formed may have carried down part of the uranium.

Table III. Spectrophotometric Determination of Uranium in Presence of Various Organic Bases

Organic case, (0.2M)	pK	Absorbance, 67 μg. U
Triethanolamine	3.75	0.655
Aniline	9.42	0.560
Ethylenediamine	4.07	0.490
Pyridine	8.77	0.530
n-Tributylamine	3.58	0.660
Quinoline	9.20	0.330
KOH	...	2.0

analysis at this laboratory. None of the cations tested interfered.

Absorbance Curves of the Complex. Uranium forms a red complex ion with 1-(2-pyridylazo)-2-naphthol in basic ethanol solution. The absorbancy curves of a solution containing 6.44 p.p.m. of uranium against a reagent blank, and of a reagent blank against ethanol, are shown in Figure 1. The maximum absorbance of the complex is 555 mμ where the reagents do not have an appreciable absorbance. The absorbancy curve for a solution containing 1 p.p.m. of plutonium and PAN is also shown in Figure 1. The maximum absorbance of the plutonium complex ion occurs at 520 mμ. This maximum can be used to indicate if the uranium was separated quantitatively from the plutonium.

Effect of pH. Cheng (*2*) made a study of the effect of pH on the U-PAN complex in aqueous solution and found that a maximum absorbancy occurs at pH 10. Table III shows the absorbancy of the PAN complex with 6.4 p.p.m. of uranium when various bases are used to develop the color. Tributylamine and triethanolamine both give approximate pH values of 10 in ethanol and a maximum color intensity. Some organic bases, although giving the proper pH values, inhibit a maximum color development. This may be due to competition with the PAN for the formation of uranium complexes.

Effect of Concentrations of Reagents. The absorbance of the uranium complex ion is independent of the volume ratio of ethanol to cyclohexane above 1:1. A triethanolamine concentration greater than 0.5M inhibits color development. Although this effect is small, the triethanolamine concentration should be constant in the solutions. A value of 0.15M was used in these experiments.

Order of Mixing. The triethanolamine must not be added to a uranium–cyclohexane–TOPO mixture unless PAN is present. The color does not develop to its maximum intensity unless the PAN is added prior to the triethanolamine.

Effect of Time. The color will develop at room temperature in 15 minutes, if the triethanolamine is freshly prepared. The color is stable from 15 to 60 minutes after mixing. If the triethanolamine solution is several days old, the color does not develop with as high an intensity as that of fresh material. Therefore, it is best to prepare the triethanolamine solution on the day it is used.

Adherence to Beer's Law. A series of solutions containing varying amounts of uranium, 2 ml. of triethanolamine buffer, 1 ml. of PAN, and sufficient ethanol to give a total volume of 10 ml. were prepared. The absorbances of these solutions were measured at 555 mμ against reagent blanks and plotted against uranium concentrations. The results show that Beer's law is followed between 1 and 20 p.p.m. of uranium. The relative standard deviation in duplicate measurements was 2%. The molar absorbancy index measured from the standard calibration curve was 22,000. Cheng found the value in aqueous solution to be 23,000 (*2*).

The method was specifically designed for the separation and determination of uranium in plutonium. However, in view of the fact that no interfering cations were found, the method can be applied to a wide variety of mixtures containing traces of uranium.

ACKNOWLEDGMENT

The author thanks P. L. Redding for his technical assistance in development of this procedure.

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[1] Mound Laboratory is operated by Monsanto Research Corp. for the U. S. Atomic Energy Commission under Contract No. AT-33-1-GEN-53.

Addendum. Compositional Analysis of n Component Systems by the X-Ray Absorption Method

SIR: It has come to my attention in a private conversation with K. Heinrich, Du Pont Experimental Station, Wilmington, Del., that in the first paragraph of my paper, "The Compositional Analysis of n Component Systems by X-Ray Absorption Method," ANALYTICAL CHEMISTRY, **36**, p. 1877, August 1964, there is a sentence which needs clarification. In the first paragraph, I state, "The wavelengths can be chosen completely at random; with knowledge of the elements present, however, more accurate results can be obtained by a judicious choice of the n wavelengths." Although true theoretically, this was not meant to imply that in a practical case n wavelengths should be chosen indiscriminately because in the measurement of absorption coefficients sufficient precision is not attainable. One should try to pick the wavelengths such that as many absorption edges are straddled as possible. Such a judicious choice will lead to the best practical results.

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Electrochemical Fractionation: Potentiostatic Chromatography and Elution Voltammetry

SIR: The rapid expansion of separation methods based upon countercurrent fractionation does not appear to have yet included a successful application of continuous partitioning between a flowing solution and a stationary electrode, although the principle was suggested by Rogers over 12 years ago (*6*). Electrochemical separations are clearly a part of the general technique based upon heterogeneous equilibria and chromatographic-type operation of an electrochemical cell should be possible. This communication reviews some recent developments of column electrolysis both from the literature and from this laboratory. Two additional techniques are suggested on the basis of analogies between column chromatography and electroanalytical methods.

Batch electrochemical separations—i.e., controlled potential coulometry—rely upon very large partition ratios, $K_p = C_r/C_o$, where C_r is the concentration in the electrode phase and C_o is the concentration in the solution phase. When the deposition is an unalloyed solid metal, $C_r = 1$. The partition ratio is simply $K_p = \exp \phi\ (E - E'^0)$, where ϕ is nF/RT, E is the applied potential, and E'^0 is the formal potential which includes activity and complexation effects. As is well established, K_p can be changed over many orders of magnitude by changing E and E'^0. When two species are present, the separation factor,

$$\beta = \frac{K_{p1}}{K_{p2}}$$

can usually be made very favorable so that quantitative coulometric operation is possible.

Improved electrochemical separations through multiple extractions or countercurrent fractionation does not appear to be necessary from the above considerations, except in occasional cases. However, by analogy with column chromatographic techniques and considering the ease with which the partition ratios can be changed, a new dimension of versatility of operation can be visualized in many electroanalytical methods through the use of column electrodes and flowing solutions.

The major difficulty in the design and preparation of the electrolytic column is the electrode which functions as the stationary phase. High surface to volume ratios and dimensionally thin phases must be obtained, in addition to the usual requirements of electrode inertness, electrical contact, and reasonable voltage range. Mercury would be an ideal material for many systems, but its high surface tension necessitates surface amalgamation of finely divided metals in order to maintain it as a thin layer. A cell which meets many of the requirements is shown in Figure 1. The stationary phase is amalgamated nickel particles of ca. 0.1 mm. average size. Because of the very low solubility of nickel in mercury, this electrode behaves (*5*) very much like amalgamated platinum (*4*). Its potentialities as an indicator electrode for general voltammetric use are being examined.

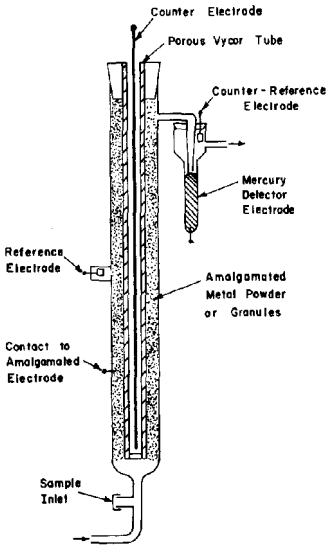

Figure 1. Column electrode and detector cell

The internal resistance of the cell is about 2 ohms with $1M$ NaCl as the flowing phase. The very high dependence of the partition ratio upon electrode potential requires that iR drops be kept to an absolute minimum. Only one counter electrode is shown in the figure, but a second can be positioned around the outside of the amalgamated electrode, separated by an additional porous Vycor tube. Many column cell designs are possible, depending upon application, such as capillary columns with a concentric, amalgamated wire for very small samples. The detector is a simple voltammetric cell with a small mercury pool electrode, over which the eluent flows. It is used to measure limiting currents; it can easily detect 10^{-10} equivalents/sec. ($10^{-6}M$ solution at flow rate of 10^{-4} l./sec.).

A number of alternate electrode materials is available, including lead and noble metal granules as well as other amalgamated metals. Columns filled with crushed graphite have been successfully operated (*1*, *8*) in the fashion of a variable potential Jones reductor. Complications arise when metals are codeposited on graphite (*1*). However amalgamated metals also can give rise to "irreversible" deposition and dissolution, possibly due to intermetallic compound formation. Crystalline mercury selenide, which has been found to be usable as an indicator electrode (*7*), is a further possibility. At this time it appears that the major obstacle is the electrode material; the need for studies of the mechanisms of deposition and dissolution is apparent.

Methods of operation of column electrodes are indicated in general by chromatographic methods. Similar to ion exchange, metal ions can be deposited and then selectively removed by anodic stripping (elution). Stedman (*8*) described the deposition and subsequent removal of copper from crushed graphite. Blaedel and Strohl (*1*) have further described this technique and were able to extend it to separations involving several metals which were deposited on crushed graphite from a sample (0.1 ml, $0.01M$ in each metal ion) injected into the flowing solution.

An extension of the above technique, and perhaps analytically more useful, would be the concentration of trace quantities of reducible metal ions from relatively large volumes of solutions. After deposition the elution can be performed with a linear voltage sweep, provided the anodic process is free of the complications noted above. This procedure which can be termed elution voltammetry, effectively increases the signal to noise ratio (faradaic to residual current) compared to coulometry and amperometry. Since flowing electrolyte solutions of high purity are required for elution, they can be pre-electrolyzed in a separate column. This method of preelectrolysis could be of general use in the purification of electrolyte solutions; the very high electrode area to solution volume ratio in columns would expedite the process by several orders of magnitude compared to conventional methods.

When the separation factor is small so that adequate separation is not obtained in elution voltammetry, fractionation can be used. The sample is carried through a column electrode held at an intermediate potential. It may prove to be possible to overcome irreversibility due to codeposition by superimposing a

sine wave signal on the d.c. potential. The retention volume will be proportional to the partition ratio, as in other chromatographic methods. This method can be given the descriptive name of potentiostatic chromatography.

A further possibility is fractionation through adsorption on electrode surfaces, since this is potential-dependent. In addition to selective adsorption of organic solutes, which is probably trivial except as a purification technique, separation of anions appears to be an attractive possibility. The specific adsorption of many anions on mercury has been measured (*2*, *3*), and it is a highly reversible process.

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X-Ray Fluorescence Spectrometric Analysis of Rubidium(I) and Cesium(I) Salts of 5-Nitrobarbituric Acid

SIR: Previously the analysis of a mixture of several metal-organic compounds employing x-ray fluorescence analysis has been reported (*2*, *3*). It was of interest to investigate whether this method could be extended to the determination of a mixture of rubidium and cesium ions which are normally difficult to separate and determine.

In a previous paper (*4*) it has been reported that 5-nitrobarbituric acid (dilituric acid) quantitatively precipitates rubidium(I) and cesium(I) as $RbC_4H_2O_5N_3$ and $CsC_4N_2O_5N_3$ and that the salts are thermally stable. Since the precipitation is quantitative, it was thought that the two elements could be determined simultaneously by using the ratio plot technique developed previously (*2*).

EXPERIMENTAL

Reagents. DILITURIC ACID. Saturated dilituric acid solution (0.05*M*) in 50% ethanol was prepared from recrystallized White Label dilituric acid (Eastman Kodak Co.) (*1*). Dilituric acid, 0.01*M*, was prepared by diluting the 0.05*M* solution with 50% ethanol.

METAL ION SOLUTIONS. A primary standard solution of 0.00500*M* rubidium was prepared from C.P. rubidium chloride, Fairmount Chemical Co., which had been dried at 105° C. A primary standard solution of 0.00502*M* cesium was prepared from C.P. cesium nitrate, Fairmount Chemical Co., which had been dried at 105° C.

Preparation of Rubidium and Cesium Salts. These standard solutions were used to prepare solution mixtures of the proper mole percentages (Table I). The rubidium and cesium mixtures were precipitated with dilituric acid, heated and weighed on the thermobalance (*4*).

Analysis. The x-ray apparatus has been described before (*2*, *3*). The x-ray spectrometer was operated at 50 kv. and 50 ma. with a LiF analyzing crystal and a scintillation counter operated at 1130 volts. The analyses were conducted as described previously (*2*, *3*). The $K\alpha_1K\alpha_2$ line of rubidium was selected for analysis at 26.64° 2θ and the $L\alpha_1$ line of cesium at 91.77° 2θ.

RESULTS AND DISCUSSION

The $K\alpha_1K\alpha_2$ peak of rubidium was selected for this analysis because it had the strongest peak and had no interferences. The $L\alpha_1$ peak of cesium was selected because there were no interferences and also because the high atomic number of cesium makes the use of the *K* lines impractical.

The same procedure as used previously (*2*) was followed in obtaining experimental data and calculating results. The proper settings of the electronic circuit panel were made to keep the peaks on the chart paper when scanned at 0.25° per minute. The areas under the rubidium and cesium peaks were evaluated by cutting out the peaks and weighing the paper. The paper weights of the peaks and the rubidium/cesium and cesium/rubidium peak ratios are recorded in Table I. The ratios were plotted on semilog paper *vs.* the mole % rubidium and the mole % cesium. Curved lines were obtained. From these data the mole fractions of rubidium and cesium in a sample were

Table I. Analysis by X-Ray Fluorescence Method

Quantity of metal taken				Thermogravimetric analysis, total weight of diliturate		X-ray fluorescence analysis			
						Areas of peaks, mg. of paper		Ratios of peak areas	
Mole % Rb	Mole % Cs	Mg. of Rb	Mg. of Cs	Mg. calcd.	Mg. found	Rb	Cs	Rb/Cs	Cs/Rb
5.0	95.0	0.4	12.7	30.2	30.3	9.2	21.9	0.43	2.38
10.0	90.0	0.9	12.0	30.0	30.0	45.3	21.6	2.1	0.48
15.0	85.0	1.3	11.3	29.9	29.8	64.0	12.9	4.9	0.20
20.0	80.0	1.7	10.7	29.6	29.6	40.6	7.4	5.5	0.18
25.0	75.0	2.1	10.0	29.4	29.4	97.6	11.8	8.3	0.12
30.0	70.0	2.6	9.3	29.2	29.2	165.7	12.0	13.8	0.07

obtained. Since rubidium and cesium were the only metal ions present and complexed, their exact quantities could be calculated.

This analytical procedure was tested with rubidium in the range of 3.4 to 2.6 mg. and cesium in the range of 9.3 to 12.7 mg. The areas of the peaks given in Table I could be reproduced with a relative error of ±3%. Because of the low intensity of the cesium peak compared to the rubidium peak, the method appears to be practical only for high concentrations of cesium with rubidium.

From the calibration curves once plotted (*2*), the mole fractions of rubidium and cesium in a sample can be obtained. In addition if rubidium and cesium are the only metal ions complexed, their exact quantities can be calculated.

This method of analysis, employing suitable organic precipitation reagents, can be easily extended to other binary metal mixtures difficult to separate, such as zirconium-hafnium, columbium-tantalum, and molybdenum-tungsten.

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Catalyzed Copper–Copper Oxide Flame Reactions of Selected Organohalogens in the Presence of Methane and Air

SIR: The Beilstein copper oxide flame test for halogen has been a classical test for organic halogens. However, it is quite limited in its scope because of the volatility of many of the organic halogens (*2*). The contact time of the halogen on the copper oxide is too fleeting to be studied in our laboratory. Certain other compounds also cause a green color when given the Beilstein copper oxide flame test. Among those listed are quinoline, pyridine derivatives, organic acids (*3*), urea, and copper cyanide (*1*).

During the course of our studies of gas chromatography we devised a 5-foot coil of 7-mm. borosilicate glass tubing with a drawn opening of approximately 1 mm. for the burner tip so that the exit gas could be burned. We placed a 6-inch coil of number 18-gauge copper wire, 1 inch long, $\frac{1}{2}$ inch in diameter, consisting of 12 turns placed into the tip of the drawn glass exit, and we passed dry, deodorized methane (natural gas) through the 5-foot coil of glass tubing and simply lighted the exit gas. The flame height was adjusted to about 1 inch and was allowed to burn until all foreign substances were removed. The flame then burned smoothly with a characteristic faintly blue color, similar to a well adjusted Bunsen burner. Both copper and copper(II) oxide were present in the flame.

One-microliter samples or 1-mg. solid samples were introduced into the glass coil at a T joint where the organohalogen samples were picked up by the methane carrier gas and burned in the copper wire coil. The following observations were recorded:

1. Methyl iodide was introduced into the above described system and wet starch paper was held in the dark green flame which gave a positive test for iodine (I_2).

$$R\text{-}I + CH_4 + O_2 \rightarrow I_2 + CO_2 + H_2O$$

2. Ethylene dibromide was introduced in a similar manner and wet starch–KI paper gave a positive test for iodine which was displaced by bromine (Br_2). Here we noted a brilliant blue tip on the copper wire coil. This observation was made using bromobenzene and several other organic bromides.

$$R\text{-}Br + CH_4 + 2O_2 \rightarrow Br_2 + H_2O + CO_2$$

$$2KI + Br_2 \rightarrow 2KBr + I_2$$

3. Ethylene dichloride was introduced into the system in a similar manner and the halogen imparted a light green color to the flame and again iodine was displaced from wet starch–iodide paper.

$$R\text{-}Cl + CH_4 + O_2 \rightarrow Cl_2 + CO_2 + H_2O$$

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

4. Trifluoroacetic acid (CF_3COOH) was injected into the above system. Its subtle green flame was examined for products as follows:

a. Wet blue litmus turned red.

b. A hanging drop slide of distilled water held over the flame indicated etching.

$$Na_2SiO_3 + 6HF \rightarrow SiF_4 + 2NaF + 3H_2O$$

$$CaSiO_3 + 6HF \rightarrow SiF_4 + CaF_2 + 3H_2O$$

c. A hanging drop slide of 5% silver nitrate and dilute ammonium hydroxide solution held over the flame gave a white precipitate.

$$AgNO_3 + HF \xrightarrow{(NH_4OH)} HNO_3 + AgF$$

d. Similarly a hanging drop slide of 0.5*M* calcium chloride solution ($CaCl_2$) gave a gelatinous precipitate.

$$CaCl_2 + 2HF \rightarrow 2HCl + CaF_2$$

e. Carbon dioxide was found using a gas chromatograph.

$$R\text{-}F + CH_4 + O_2 \rightarrow HF + CO_2$$

The color of this flame was distinctly different from the other halogens (*1*). Difluoroethene (CF_2CF_2) and *sym*-tetrafluoroethane gave the same flame tests, evolving CO_2 and HF as combustion products.

We have been using this technique rather than the sodium fusion method to test for organohalogens.

It was possible to modify the Cu–CuO, methane oxidation technique for microtests for boron, nitrogen, phosphorus, and sulfur in the limited number of organic compounds we studied.

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Simple Variable-Temperature Sample Inlet for Beckman GC-2 Gas Chromatograph

SIR: Lowry (*1*) in a recent paper in this journal described a device (solid sample injector) he designed to overcome tailing and poor resolution which he found while analyzing fatty acid esters with a Beckman GC-2 gas chromatograph hydrogen flame accessory. This same problem was encountered in this laboratory (Figure 1*A*) and may be characteristic of these instruments. The solution offered below requires no custom fabrication, uses commercially available components, and can be installed in a short time.

The temperature of the stock inlet was found to be about 210° C., apparently not a sufficiently high temperature to ensure adequate vaporization. Attempts to increase the temperature of the standard sample inlet with insulation were unsuccessful.

The standard inlet was replaced by a special preparative inlet (Beckman No. 45429). This unit is designed to vaporize large samples for eventual fraction collection, and is heated by a high-density 550 W cartridge heater operated at 110 volts for short periods through a timer. The temperature rise of the heater is about 10° C./second. Operation of the heater for 12 to 14 seconds prior to injection of the sample yields an inlet temperature of about 260° C., and the chromatogram seen in Figure 1*B*.

Although the separation was excellent and tailing was practically nonexistent, the effectiveness of this procedure was nullified by the appearance of a "peak" next to the solvent peak, which would prevent analysis of fatty acid esters shorter than palmitate. Occasionally, unknown peaks would appear in other positions in the chromatogram. These "peaks" apparently represented traces of impurities deposited in the special inlet which were vaporized each time the inlet reached its maximum temperature. All attempts to remove these impurities both by solvent extraction and by repeated heating were unsuccessful.

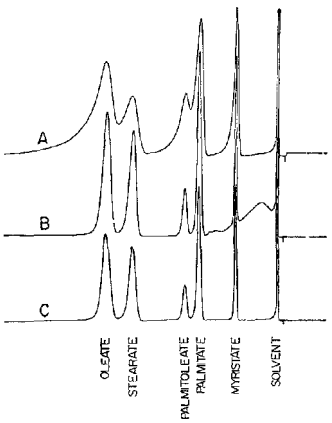

Figure 1. Chromatograms of fatty acid methyl esters

Operating conditions: column, 6 ft. × 1/8 inch, 20% DEGS on Chromosorb W. Column temperature, 175°C. Flow rate, 50 ml. He/minute. Split ratio, 1:1. Air pressure, 7 p.s.i.; hydrogen pressure, 4 p.s.i. Samples, 0.2 μl. 10% solution fatty acid methyl esters in acetone (purchased from Applied Science Co., College Park, Pa.). Attenuation, ×2000

Excellent results were finally obtained by disconnecting the special inlet heater from the timer and operating the cartridge heater continuously through a variable resistance (Powerstat). A setting of 18 volts kept the inlet temperature between 260 and 270° C. and yielded chromatograms of which Figure 1*C* is typical. This system has been successfully used to chromatograph methyl esters of fatty acids prepared from lipoproteins, fish, and fish products. The long-chain polyunsaturated fatty acids in the latter show no decomposition due to the new inlet as shown by comparison with chromatograms obtained from other instruments.

In effect, this modification provides the GC-2 with a variable-temperature injection heater, which undoubtedly would prove useful in other applications as well.

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Determination of Vanadyl Porphyrins by Demetalation with Hydrogen Bromide–Formic Acid

SIR: Although the Groennings' method (*10*) has been widely applied in the quantitative determination of metalloporphyrins in fossil fuels, decomposition occurs in varying degrees depending upon the conditions imposed and the types of porphyrins involved (*14*).

EXPERIMENTAL

An amount of 0.005 to 0.2 μmole of a model vanadyl porphyrin, dissolved in 10 to 15 ml. of benzene or toluene, is placed in a 50-ml. round-bottomed flask together with 25 ml. of 97+% formic acid (Distillation Products, Rochester, N. Y.). The flask is attached to a Claisen head with ground glass joints. A gas-inlet tube, with the appropriate ground glass joint, to introduce N_2 or HBr is arranged so that a capillary reaches near the bottom of the flask. A T-unit with appropriate stopcocks is attached to the gas line using Teflon tubing and then connected to N_2 and HBr tanks. A water-cooled condenser is attached to the other Claisen head opening. Gases leaving the unit through the top of the condenser are carried into a trap containing mineral oil to inhibit backflow of the atmosphere and then into a water trap to dissipate HBr.

The unit is thoroughly flushed with N_2 (about 20 minutes) while the reaction flask is heated to 50° C. and maintained at that temperature. Then N_2 flow is stopped and anhydrous HBr (Matheson Coleman & Bell) is introduced at a rate sufficient to maintain observable agitation in the reaction flask for a period of 2–3 hours. The rate of input is decreased after the reaction mixture is saturated. The system is then flushed with N_2 again for 20 to 30 minutes while the reaction mixture is allowed to cool to room temperature. This operation is necessary to inhibit Br_2 formation resulting from atmospheric oxidation of HBr.

The benzene or toluene phase is separated from the acid layer, and the former is washed once with 15 ml. of 97+% HCO_2H. The combined acid solutions are neutralized with anhydrous NH_3. Water is added to the resulting mixture to dissolve precipitated salts. This solution is then treated in the manner described by Groennings (*10*). The purified porphyrin or porphyrin aggregate is analyzed spectrophotometrically (Beckman DK-2) by integration of the area under the Soret band (*13*).

Formyl fluoride was prepared by the method of Olah and Kuhn (*12*). Mesoporphyrin IX dimethyl ester was prepared (*2*) and metalated (*6*) with vanadyl sulfate. Etioporphyrin I was obtained by the two-step synthesis (*7*, *8*) from 3-ethyl-2,4-dimethylpyrrole (*9*)

and was converted into the vanadyl complex (*15*).

RESULTS AND DISCUSSION

The Groennings' method (*10*) in our hands provided very low recoveries of etioporphyrin I and mesoporphyrin IX dimethyl ester from their vanadyl complexes, although colorless, freshly prepared solutions of hydrogen bromide in glacial acetic acid were applied. Representative data are given in Table I. Varied reaction conditions did not permit higher recovery of porphyrins with the exception of that involving the introduction of hydrogen bromide gas into a heated mixture of the sample in acetic acid (*4, 5*). This method applied to vanadyl etioporphyrin I gave a higher recovery of the free porphyrin (Table I). Apparently, maintenance of the reaction solution with the maximum concentration of hydrogen bromide promotes demetalation.

Significantly better success was realized when formic acid was substituted for acetic acid. Since acids catalyze the dehydration of formic acid to liberate carbon monoxide, a sealed reaction container could not conveniently be applied. To circumvent this problem, a flow system operating slightly above atmospheric pressure was devised. Precautions were taken to minimize atmospheric oxidation of hydrogen bromide to form bromine. The many runs demonstrated that etioporphyrin I and mesoporphyrin IX dimethyl ester could be derived from their vanadyl complexes in amounts distinctly higher than obtained by the Groennings' method (*10*). The recovered porphyrins appeared to have a high degree of homogeneity as indicated by paper chromatography. A similar inspection of the comparable free porphyrins obtained in the Groennings' procedure suggested the presence of several compounds.

A series of runs was made at 50° C. varying reaction time. Periods less than 2 to 3 hours provided incomplete reaction but longer reaction times gave products which were less homogeneous. Limited studies with varying amounts of vanadyl etioporphyrin I demonstrated that the sample size of the metalloporphyrin may be altered within wide limits. Minimum amounts are determined by the limit of detectability in the spectrophotometric method used. The maximum amount for a reaction volume of some 40 ml. is of the order of 0.2 μmole of vanadyl etioporphyrin I. A larger sample was not completely demetalated under the conditions applied. Formyl fluoride in place of hydrogen bromide in formic acid demetalated 0.16 μmole of vanadyl etioporphyrin I to allow recovery of 49% of the free porphyrin.

Application of this procedure to several natural materials followed (Tables II and III). The course of the demetalation procedure was followed by determining Soret absorbance in the starting material and in the acid and hydrocarbon phases derived (*13*). A comparison of experiments 1 and 2 demonstrates that the recovery of porphyrins after 3- and 6-hour reaction periods is essentially the same. In experiment 3, the hydrocarbon phase obtained after a 3-hour reaction was reprocessed in the same manner. Some additional porphyrin may have been recovered but in an amount too small to be measurable because of high background absorbance. Using the figure of 40% recovery of porphyrins, a calculation of metalloporphyrin content in Boscan asphaltenes provides a figure of about 10 μmoles per gram, essentially the same as 11 μmoles per gram calculated (*13*) from data (*6*) obtained in the Groennings' method. Similarly, the determination of metalloporphyrins in Wilmington crude oil by the hydrobromic–formic acid method gave a value of 0.39 μmoles per gram as compared to 0.42 μmoles per gram found by the Groennings' method (*6*). As previously described, the model metalloporphyrins were distinctly more efficiently demetalated with hydrobromic–formic acid. Thus, the metalloporphyrins contained in Boscan and Wilmington crudes must be more readily demetalated or are more stable to the prolonged action of hydrobromic–acetic acid.

Soret absorbance of the hydrocarbon phase was considerable following a 3-hour reaction period (experiment 1), but was decreased markedly follow-

Table I. Demetalation of Model Vanadyl Porphyrins

(Integral extinction coefficients in l. mμmole^{-1} cm.$^{-1}$: vanadyl etio I, 4.7×10^6; vanadyl meso IX, 4.5×10^6; etio I, 5.1×10^6; meso IX, 4.8×10^6.)

Substrate	Sample, μmoles	Method	Porphyrin recovered, %
Vanadyl etio I	0.132	(*10*)	19
Vanadyl meso IX	0.196	(*10*)	>5
Vanadyl etio I	0.132	HBr into CH_3CO_2H	50
Vanadyl etio I	0.132	HBr into HCO_2H	92
Vanadyl etio I	0.063	HBr into HCO_2H	91
Vanadyl meso IX	0.059	HBr into HCO_2H	83

Table II. Demetalation of Natural Metalloporphyrins

(Integral extinction coefficients in l. mμmole^{-1} cm.$^{-1}$: porphyrins in acid phase, 5×10^6; materials in hydrocarbon phase, 4.7×10^6)

Experiment No.		Soret absorbing material: In sample, μmoles/gram	In sample, μmoles	In acid phase, % of sample	In hydrocarbon phase, % of sample
1	Boscan asphalt	25[a]	0.13	40	38
2	Boscan asphalt[b]	25	0.13	41	2
3	Boscan asphalt	25	0.13	40	...
	Hydrocarbon phase from above	...	...	>5	5
4	Wilmington crude	1.35[a]	0.40	29	[c]

[a] Ref. *13*.
[b] Reaction time of 6 hours instead of 3 hours used in all other instances.
[c] High background did not allow determination.

Table III. Demetalation of Metalloporphyrins in Sample Derived from Boscan Asphaltenes by Solvent Extraction

(Integral extinction coefficients in l. mμmole^{-1} cm.$^{-1}$: sample and materials in hydrocarbon phase, 4.7×10^6; porphyrins in acid phase, 5×10^6)

Extracting solvent	Soret absorbing material: In sample, μmoles/gram	In sample, μmoles	In acid phase, % of sample	In hydrocarbon phase, % of sample
Acetone	81.4	0.076	63	30
Acetic acid	47.7	0.053	76	32
2-Methoxyethanol	40.8	0.13	76	27
Ethanol	38.2	0.053	75	...
1-Butanol	26.3	0.057	65	39
2-Propanol	20.3	0.044	53	26

ing a 6-hour one (experiment 2). This change was observed without a corresponding increase in porphyrin recovery. The usual Groennings' procedure (*10*) subjects the materials responsible for the absorbance to a reaction period of about 48 hours. These conditions would likely be more severe than the 6-hour reaction of experiment 2, and thus any residual Soret absorbance in the hydrocarbon phase would be totally lost.

Extraction of Boscan asphaltenes with varying solvents might be expected to remove different ratios of metalloporphyrins and other materials exhibiting Soret absorbance. Although concentration of Soret-absorbing materials varied considerably in these extracts, the relative percentages of porphyrins and other Soret-absorbing materials not extracted by acid, were appreciably more constant (Table III). These observations suggest that the two types of compounds present in Boscan asphaltenes have similar solubility characteristics.

The hydrocarbon solution containing the materials not extracted by acid, subsequently washed to remove bromine and hydrobromic acid, is green in appearance to the eye. The absorption spectrum of a chromatographed concentrate, dissolved in chloroform, exhibits peaks at about 550, 566, and 590 mμ in the visible range, and a Soret band at 416 mμ. The suggestion of the presence of a peak near 590 mμ in the spectra of many crudes has been made recently by Constantinides (*1*), Dean and Whitehead (*3*), and Hodgson (*11*). Investigation directed toward the separation and the characterization of the types of components in the "green material" is in progress.

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Nicotinylhydroxamic Acid Chelates of Uranium and Titanium(IV)

SIR: Hydroxamic acid chelates are important as analytical reagents, and the search for new systems is a continuing one. One such hydroxamic acid, nicotinylhydroxamic acid, has been found to form several chelates. Of these, the Mn(III), Fe(III), and V(V) systems have been reported by Dutta (*1*), and the Mo(VI) system by Rowland and Meloan (*2*). This communication is to complete the series by reporting on uranium(UO_2^{+2}) and titanium[Ti(IV)], the remaining two ions which appear to have possibilities as analytical reagents.

EXPERIMENTAL

Titanium. Titanium(IV) formed a yellow solution over the pH range 3 to 9 when mixed with nicotinylhydroxamic acid with a pH of 9 providing the maximum absorption. The absorption maximum occurred at 380 mμ. Job's method of continuous variations was applied to this system and the results indicated a 4:1 (ligand to metal) chelate at pH 8 at 380 and 500 mμ. The molar absorptivity is 4900.

Table I. Beer's Law Applied to Titanium(IV)

Moles/liter of Ti(IV)	Absorbance
4×10^{-6}	0.013
8×10^{-6}	0.035
1.2×10^{-5}	0.054
1.6×10^{-5}	0.071
2.0×10^{-5}	0.091
4.0×10^{-5}	0.193
8.0×10^{-5}	0.393
1.2×10^{-4}	0.587
1.6×10^{-4}	0.770

Table I shows the results of a Beer's law study using a 5:1 ligand to metal ratio in solution. The molar absorptivity is 1990.

Uranium. Uranium(UO_2^{+2}) formed a yellow solution over the pH range 3 to 11 with the region 6 to 8 the most favorable for the chelate formation. The wavelength of maximum absorption was 380 mμ. Continuous variations studies were made at 380 mμ and 440 mμ and the results showed a 2:1 (ligand to metal) chelate at pH 7. Since the uranium chelate formed a pink color at more acidic pH's a continuous variations study was made at pH 3. The results indicated a mixture of 1:1 and 2:1 species.

Table I indicates the results of a Beer's law study using a 5:1 ligand to metal ratio in solution. The useful range could be extended if a larger ligand to metal ratio was used.

Table II. Beer's Law Applied to UO_2^{+2}

Moles/liter of UO_2^{+2}	Absorbance
4×10^{-6}	0.002
8×10^{-6}	0.005
1.2×10^{-5}	0.010
1.6×10^{-5}	0.022
2.0×10^{-5}	0.027
4.0×10^{-5}	0.057
8.0×10^{-5}	0.142
1.2×10^{-4}	0.230
1.6×10^{-4}	0.308
2.0×10^{-4}	0.396

DISCUSSION

Interferences. Interfering ions are the same as those reported by Dutta (*1*) and Rowland and Meloan (*2*).

Extraction. Extraction studies were made using 0.01*M* chelate solutions at pH's of 3, 6, and 9. No solvent was found that would extract the chelate. Those tried were benzene, bromoethane, carbon tetrachloride, chloroform, diethyl ether, diisobutyl ketone, ethyl acetate, ethyl benzoate, heptaldehyde, *n*-hexanol, isoamyl alcohol, Skelly B, and toluene.

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Use of Anhydrous Cobaltous Bromide as a Standard in Cobalt Analysis

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FOSTER AND WILLIAMS (*1*) studied cobalt sponge, cobalt wire, and five cobalt compounds as primary standards in cobalt analysis, by using the phosphate method. They recommend chloropentamminecobalt(III) chloride, $[Co(NH_3)_5Cl]Cl_2$; hexamminecobalt(III) chloride, $Co(NH_3)_6Cl_3$; and potassium cobalt(III) cyanide, $K_3[Co(CN)_6]$, as primary standards. These authors (*2*) described a very accurate method of determining 24.2 to 241 mg. of cobalt by precipitating cobalt ammonium phosphate, weighing cobalt pyrophosphate, and also determining the filtrate cobalt ion spectrophotometrically with nitroso-R salt. The first cobalt compound was used as the primary standard in the methods research (*2*). However, anhydrous cobalt(II) bromide was not studied as a standard.

The method of Lingane, Lingane, and Morris (*4*), in which cobalt is weighed as $K_3Co(NO_2)_6$, was chosen for determining cobalt in mixtures of cobalt, copper, and nickel compounds, because the method is rapid and accurate. Lingane (*3*) states that if the precipitation is begun with the cobalt and the potassium nitrite solutions both at 100°, and the mixture is allowed to cool to 25°, the composition of the $K_3Co(NO_2)_6$ precipitate will be very close to stoichiometric. The error will be less than 0.1 mg. of cobalt for 20 to 175 mg. of cobalt. The original directions (*4*) were followed. Anhydrous cobalt(II) bromide was used in our laboratories as a standard to determine the recoveries of cobalt ion by this method (*4*).

Cobalt(II) bromide was prepared by the reaction of reagent cobalt carbonate with excess 34% hydrobromic acid, followed by evaporating the solution to a small volume, filtering the crystals, and recrystallizing from deionized water. The $CoBr_2$ was dried at 150° C. and held in a vacuum desiccator at reduced pressure before weighing. An amount of 7.4382 grams of the anhydrous green $CoBr_2$ was dissolved in deionized water, diluted to 1 liter, and mixed. A 25-ml. aliquot was equivalent to 50.10 mg. of Co^{+2}.

Table I gives the recoveries of 50.1 to 200.4 mg. of Co^{+2}, weighed as $K_3Co(NO_2)_6$. The cobalt determinations, by the same method, of four of the mixtures of cobalt, copper, and nickel compounds are shown in Table II. In the double precipitations of potassium cobaltinitrite, the first precipitate was dissolved through the sintered glass crucible with 3 to 5 20-ml. portions of boiling 11.5*M* hydrochloric acid by applying gentle suction. The crucible was washed with 100 ml. of boiling deionized water, the combined solution was evaporated to dryness twice; the cobalt(II) chloride was dissolved with 0.03 ml. of 11.5*M* hydrochloric acid and deionized water, and potassium cobaltinitrite was precipitated as directed.

Table I. Determination of Cobalt Recoveries, Weighed as $K_3CO(NO_2)_6$

Co, mg. Taken (as $CoBr_2$)	Co, mg. Found (corr.)	Co, mg. Taken (as $CoBr_2$)	Co, mg. Found (corr.)
50.10	50.16	50.10 Co^{+2} +	50.24
50.10	49.99	30.0 Ni^{+2}	50.22
	Av. 50.08		50.23
100.20	99.51	100.20 Co^{+2} +	100.09
100.20	99.43	40.0 Ni^{+2}	99.99
	Av. 99.5		100.0
200.40	198.1	200.40 Co^{+2} +	198.61
200.40	198.0	30.0 Ni^{+2}	198.34
	Av. 198.0		198.5
$CoCO_3$			
105.0	51.13		
105.0	51.04		
	Av. 51.09 (48.66% Co)		

Table II. Determination of Cobalt in Mixtures of Cobalt, Copper, and Nickel Compounds, Weighed as $K_3CO(NO_2)_6$

Co-Cu-Ni sample No.	Single pptn., no sepn. Co found, mg. (corr.)	Co, %	CuS sepn., single pptn. Co found, mg. (corr.)	Co, %	CuS sepn., double pptn. Co found, mg. (corr.)	Co, %
2	16.70	8.35	59.19	8.22	...	...
	16.67	8.34	59.12	8.21	...	...
	Av.	8.34		8.22		
3	18.12	9.06	98.54	8.96	...	...
	18.02	9.01	98.35	8.94	...	...
	Av.	9.04		8.95		
4	52.08	17.36	69.34	17.33	69.32	17.33
	51.90	17.30	69.34	17.33	69.29	17.32
	Av.	17.33		17.33		17.33
10	Not detd.	...	66.05	27.52	65.65	27.35
		...	65.92	27.47	65.46	27.28
			Av.	27.50		27.32

ACKNOWLEDGMENT

R. W. Whealy graciously supplied the mixtures of cobalt, copper, and nickel compounds which were analyzed.

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Silver Chloride Disk Technique for Infrared Spectra of Aqueous Polymer Suspensions

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APPLICATION of aqueous polymer suspensions to potassium bromide pressed disks for preparation of qualitative infrared spectra is sometimes complicated by the water solubility of the disk. Water insoluble silver chloride or Irtran plates (Eastman Kodak Co.) are expensive and are time-consuming to maintain in perfect condition, especially when it is desirable to cure the polymer on the plate. The use of silver chloride windows is reported in the literature (*1*, *2*, *6*) and special techniques using silver chloride have been published (*3–5*, *7*, *8*).

Many of the inherent difficulties of using and maintaining silver chloride for infrared spectrometry can be eliminated by the preparation of low cost, disposable pressed disks from powdered silver chloride using the type of die commonly employed for preparation of potassium bromide pellets. A spectrum may be prepared directly from a wet film of an aqueous suspension applied to the disk, or from a film dried on the disk. The choice depends upon the speed required in obtaining the spectrum and the interpretation that is to be gained.

EXPERIMENTAL

Reagent grade powdered silver chloride, screened through a 60-mesh Tyler sieve was dried in a vacuum oven for 48 hours at 80° C. A paper retaining ring (Spex Industries, Inc.) was placed inside a 13-mm. die and about 300 mg. of powder was spread on top of the ring. The die was centered in a 20-ton hydraulic press and evacuated for one minute while under one-ton gauge pressure. The disk was then pressed at 12.5 tons gauge pressure.

At a somewhat higher cost suitable disks were also prepared from 10-mm. squares cut from a silver chloride pressed plate (Barnes Engineering Co., ATR-SP-1) normally used for preparing attenuated total reflectance spectra. The corners of the square were cut off to permit insertion into the die.

All parts of the die that come in contact with silver chloride should be kept highly polished with crocus cloth. These parts must also be kept clean and dry to avoid corrosion and to prevent the disk from sticking to the metal surfaces. The silver chloride must be protected from light at all times to minimize discoloration.

Transmittance spectra were first obtained on wet polymer films applied to a silver chloride disk, or in the case of less viscous resins, sandwiched between two disks. Then, after curing the sample on a disk at 80° C. for 30 minutes in a vacuum oven, the spectrum was rerun. All spectral curves were prepared on a Perkin-Elmer Model 21 double-beam infrared spectrophotometer, with use of a grating type variable beam attenuator (Barnes Engineering Co., BA-1) for reference beam compensation. A slit program of 927 was used with gain 5.6, response 1, suppression 2, and speed of 3 microns per minute with recorder chart scale of 2 cm. per micron.

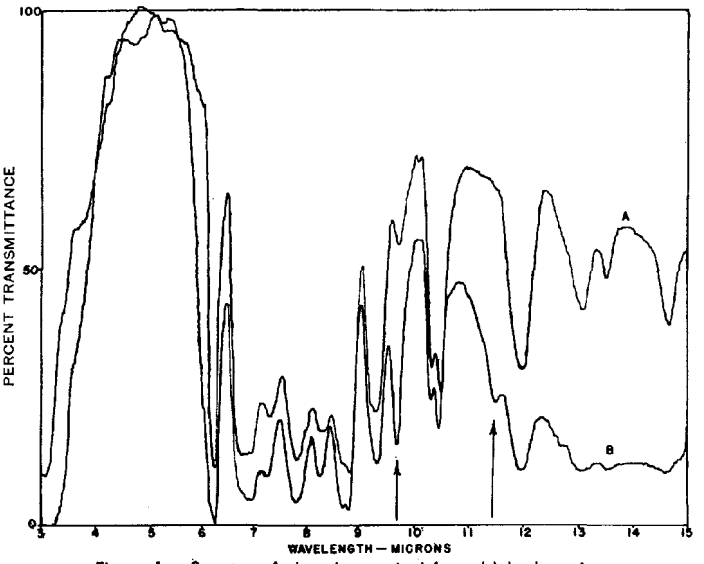

Figure 1. Spectra of phenol-resorcinol-formaldehyde resin

A. Dry. B. 45% water solution between two AgCl disks

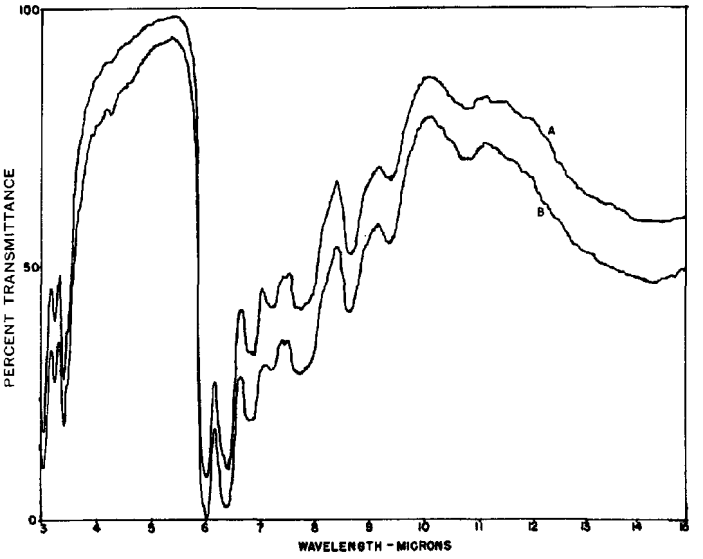

Figure 2. Spectra of polyamide resin

A. Dry. B. Wet film cast from 49% water solution on single AgCl disk

DISCUSSION

The silver chloride disks prepared by this technique were only slightly pink in color and completely transparent. Blank disks without reference beam compensation could be adjusted to give a baseline at greater than 90% transmittance between 3.5 and 15 microns with the aid of the 100% transmittance adjustment. Full compensation was easily obtained by placing a similar silver chloride disk in the reference beam. Storage between layers of polyurethane foam protected from light lengthened the useful life of the disk.

Some examples of the spectra obtained from polymer films on silver chloride disks are shown in Figures 1 and 2. They illustrate that even in the presence of some residual water good definition is obtained. The wet resorcinol resin (Figure 1) was sandwiched between two silver chloride disks and retained practically all of its original 45% water throughout the 4-minute scan. A rescan of the same sample within 10 minutes gave intensities almost identical to the original. The resin was still easily identified from the spectra of the wet film.

Similar types of resins were easily distinguished from wet film spectra as long as the O—H stretching vibration was not the only criterion of identification. Polyamide *vs.* urea-formaldehyde and phenol-formaldehyde *vs.* phenol-resorcinol-formaldehyde were good examples.

The silver chloride disk technique also lends itself well to rapidly determining qualitative and semiquantitative changes taking place in resins as a result of curing. The qualitative change is well illustrated in the resorcinol resin spectra. In comparing the dry and wet spectra, note the intensity decrease in the dry spectra at the 9.6- and 11.4-micron bands. These bands originate from the methylol hydroxyl C—O stretching vibration and the C—H out-of-plane bending vibration associated with the aromatic ring, respectively.

The low cost and the ease of preparing silver chloride disks allow disposal after each use. However, if wet polymer films were washed off the disk, it could be reused four to five times before scratching and darkening necessitated disposal.

ACKNOWLEDGMENT

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Porous Glass as an Adsorbent for Thin Layer Chromatography

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POROUS GLASS has been used as a chromatographic medium in gas-liquid chromatography (*2*, *8*) and in liquid-solid chromatography (*3*) in the form of plates (1 inch × 4 inches × 1/16 inch). To the latter, electrophoresis techniques have been applied (*1*). It was pointed out that porous glass (Corning Glass Works, Code 7930) possesses desirable properties for chromatographic use, such as its extremely porous structure, uniformity of pore size, large surface area, inert inorganic nature, and optical transparency. The last property mentioned applies only when the porous glass is used in the form of plates.

Porous glass plates gave well defined separations of water-soluble inks (*3*) using aqueous developers; however, when organic solvents were used as eluents, the resolution was much poorer, and 10 to 20 times longer development times were required. It was necessary to pretreat the porous glass plates with an acidic fluoride solution or heat them in absolute methanol before using organic liquids of low dielectric constant as eluents.

We have found that porous glass can be used as an adsorbent for thin layer chromatography (TLC) to circumvent these disadvantages. Porous glass was ground to a mesh size 200 to 250 and mixed with plaster of Paris of the same mesh size in a ratio of 87 to 13, porous glass to plaster of Paris. The new adsorbent was applied to the plates in the same manner as described by Stahl (*7*). The thickness of the coating was 0.012 inch. The chromatograms were dried at room temperature, followed by heating to 130° C. for 3 hours to activate them, and then stored in a desiccator.

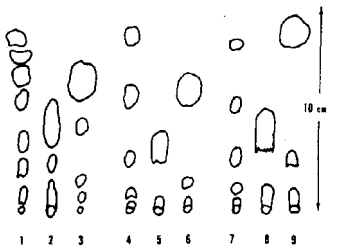

Figure 1. The development of three waxes, beeswax, 1, 4, 7; bayberry wax, 2, 5, 8; and spermaceti, 3, 6, 9; is compared on three different thin layer adsorbents, porous glass, 1–3; silica gel G, 4–6; and aluminum oxide G, 7–9

The same eluent was used: petroleum ether (b.p. 38°–49°)/ethyl ether = 95/5 (v./v.)

In several cases a superior separation was achieved on thin layer chromatograms with porous glass as adsorbent, compared to silica gel G and aluminum oxide G. Often more spots appeared and the corresponding R_f values were greater, using the same developer (see Figure 1). These spots were equally or more distinct. Partition chromatography is operative even with nonpolar solvents such as petroleum ether–ether. Since the pore and particle size of the adsorbent can be controlled, one is capable of changing the conditions of separation. It was furthermore observed that faint spots were darker on the porous glass chromatograms than on silica gel G after the plates were charred with chromic-sulfuric acid and then heated at 150° C.

Powdered glass (about 300 mesh) has previously been adapted to thin layer chromatography (*4–6*); however, it does not possess the desirable properties of porous glass, such as its large surface area, its uniform pore size, and the ability to be able to control the pore

size (*8*). Therefore, it appears that powdered porous glass as an adsorbent for thin layer chromatography is superior in separation and sensitivity in some cases to the other well established adsorbents.

This method of using porous glass for a TLC adsorbent is in many ways preferable to using porous glass plates. First, polar and nonpolar organic solvents and aqueous developers were used successfully as developers. Second, the development times of the new adsorbent were comparable to those for silica gel G and aluminum oxide G. A typical separation of beeswax on silica gel G took 17 to 20 minutes compared with 39 to 43 minutes with the porous glass adsorbent, development distance being 10 cm. To develop amino acids with phenol–water (75:25) took 5 hours in both cases.

In the new method described, spots can be eluted and further analyzed as is common in thin layer chromatography. Therefore, this method is much more versatile than the use of porous plates.

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A Rapid-Scan Far Ultraviolet Spectrophotometer for Monitoring Gas Chromatograph Effluent

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A BECKMAN DU spectrophotometer has been modified to scan the wavelength interval 1600 to 2100 A. in 6 seconds with a resolution better than 1 A. By utilizing a double-size prism, unmodulated light in a single-beam mode, and a shortened optical path, this instrument has a gain in energy about 10 times that of the far ultraviolet Beckman DK spectrophotometer previously used for monitoring gas chromatographic effluents (*1*). It may be used for conventional single-wavelength absorption measurements in the far ultraviolet region or for scanning wavelength intervals. A special wavelength drive and synchronized gain circuit compensates for background energy variation with wavelength. This instrument is particularly suited to monitoring effluent emerging from a gas chromatograph. The repetitively-recorded spectra may be used to identify eluting components as well as to discriminate among sample components unresolved by the chromatograph.

INSTRUMENTATION

The instrument used was a Beckman DU spectrophotometer modified for operation in the far ultraviolet region by employing a synthetic quartz prism, MgF_2-coated mirrors, hydrogen lamp with Suprasil window, 7200 Photomultiplier Detector, a special wavelength drive, gain attenuation circuit, and 19-inch radius of curvature slits. The entire optical path was purged with nitrogen. Gas chromatographic effluent was conveyed to a 1-cm. optical path silica cell in the spectrophotometer by means of a heated $^1/_8$-inch tube. A Sanborn recorder provided the readout. The spectrophotometer was used in the single-beam mode with unmodulated light.

The effective luminosity of this instrument is about 10 times that of the far ultraviolet Beckman DK spectrophotometer by virtue of the shorter optical path, fewer reflections, larger prisms, and unmodulated radiation. Limiting resolution is 0.15 A. at 1640 A., as shown in Figure 1, an emission spectrum of the Beckman 94055 hydrogen lamp.

This resolution in the far ultraviolet region can be achieved using a full length ($^1/_2$-inch) slit when using slits with a radius of curvature of 19 inches. At wavelengths longer than 2200 A., this slit curvature impairs resolution. The slit function at limiting resolution is slightly skewed. Scattered light at 1700 A., using the continuum emission of the hydrogen lamp, is under 0.2%.

A special single-turn 360° cam with a linear rise, but nonlinear readout, was constructed to drive the prism repetitively through the wavelength region 1600 to 2100 A. A synchronous motor and gear cluster permits this wavelength region to be scanned in periods from 6 to 600 seconds.

The detected intensity of the hydrogen lamp decreases about 500-fold on going from 2100 to 1600 A. If single-beam absorption spectra are to be portrayed throughout this region, either the gain of the amplifier or the slit width of the monochromator must be varied to maintain a reasonably constant background signal. In this instrument a special variable-gain circuit has been coupled to the wavelength drive. Maximum attenuation occurs at the long wavelength end of the scale. This simple circuit holds the background constant within ±5% from 2100 to 1750 A. Below this wavelength the recorded hydrogen background signal decreases rapidly as shown in the first cycle of Figure 2. The discrete emission lines around 1650 A. from the hydrogen lamp can be seen.

The 98% response time, 0.01 second, of the instrument is limited by the recorder. At 1800 A. the dispersion of the monochromator is 4.2 A./mm. Typical slit widths are 0.20 mm. resulting in a resolution of 0.84 A. at 1800 A. At the maximum scanning speed of 6 seconds, the spectrum in the neighborhood of 1800 A. was scanned at the rate of 83 A. per second or 100 bandwidths per second (0.20 mm. slit). This corresponds to 1 bandwidth per period yielding a tracking error of 12% (*2*). For purposes of spectrum identification this recording fidelity is adequate. Measurements of concentration are made at fixed wavelengths and no appreciable tracking error is observed.

For this study a Beckman GC-2A gas chromatograph was used with a 6-foot column of Apiezon L on C-22 firebrick. The column was maintained at 100° C. A heated $^1/_8$-inch copper tube conveyed the gases from the chromatograph to a 1-cm. absorption cell in the spectrophotometer. This cell was made from far ultraviolet transmitting silica and had a volume of 1.5 cc. At the entrance of this cell a small flange was placed in the flow path to create turbulence in the cell, thereby reducing channeling. This cell was not heated and only highly volatile samples were used in this study. A heated cell could be readily designed.

The recorder used was a Sanborn Model 60-1300 dual channel high-speed recorder. One channel was coupled to the load resistor of the 7200 photomultiplier detector through the variable gain circuit and the other was coupled to the thermal conductivity bridge through a ground isolation circuit. Chart speeds of 1 and 100 mm. per second were used. Carrier gas

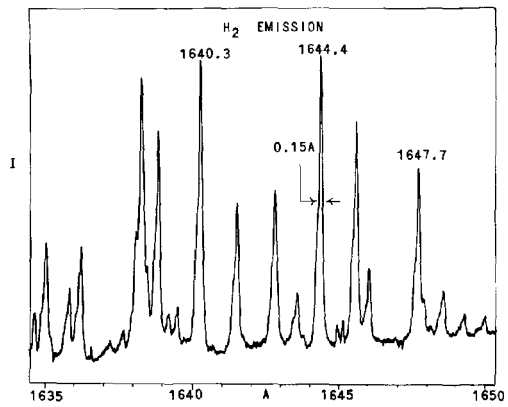

Figure 1. Hydrogen emission spectrum at the limiting resolution of the spectrophotometer

Slits, 0.03 × 12 mm.

(helium) flow rate was 123 cc. per minute and approximately 2 seconds lapsed for the sample to pass from the thermal conductivity bridge to the optical absorption cell.

PERFORMANCE

Three modes of operation are possible with this instrument assembly. The wavelength can be fixed and the transmittance of the gas stream can be recorded as a function of time; the wavelength can be scanned repetitively as the sample components emerge; or sample components can be trapped in the sample cell and their spectra can be scanned at leisure.

To demonstrate the performance of this apparatus, a 7-component mixture of volatile liquids was prepared. This mixture consisted of the following compounds in the given volume percentages; acetone 10%, methyl iodide 10%, *n*-hexane 10%, ethyl iodide 10%, benzene 20%, 2-propyl iodide 20%, and 1-propyl iodide 20%. The components emerged from the column in the above order. The thermal chromatogram of this mixture exhibited approximately equal peak heights for each of these components.

Figure 2 shows portions of the repetitively scanned spectra of the eluting components of the above 7-component mixture. The abscissa of these spectra are simultaneously wavelength and time. The period of each wavelength scan is 6.3 seconds. Thus in the 5½ minutes required for the components to elute from the column, 52 separate spectra were obtained. Only

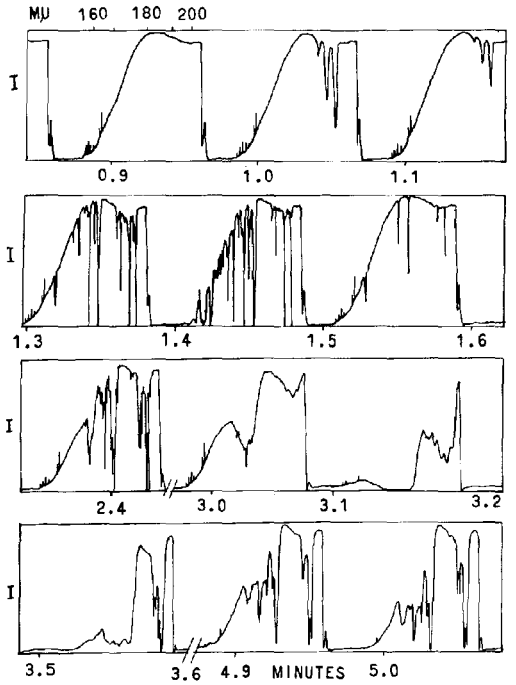

Figure 2. Selected repetitively-recorded far UV spectra of chromatographic effluent

portions of the total record with significant information are shown here.

The first component, acetone, emerged about 0.98 minute after insertion in the column. Consequently, the first wavelength cycle shown in Figure 2 represents the compensated background energy spectrum of the hydrogen lamp. A wavelength scale overlays this cycle. The next cycle shows the characteristic spectrum of acetone with its three pronounced absorption bands at 1860, 1910, and 1950 A. The three scan cycles between 1.3 and 1.6 minutes all show the methyl iodide vapor spectrum. In all cases, components were spread over three or more cycles. The wavelength scale for each cycle can best be estimated from this methyl iodide spectrum. A double-beam transmittance spectrum of this compound may be found in Figure 2 of reference (*3*). The absorption bands showing near or complete absorption in the cycle beginning at 1.38 minutes, occur at wavelengths of 1700, 1763, 1796, 1830, 1971, and 2016 A.

Ethyl iodide emerges after about 2.4 minutes. Its characteristic spectrum readily distinguishes it from methyl iodide.

Benzene, eluting at 3.0 minutes, exhibits a particularly intense absorption band at 1791 A. and a group of weaker bands around 2000 A.

The spectra of the two propyl iodides are sufficiently different to permit ready identification. Other iodides have been studied. These spectra are all distinguishable from one another until the number of carbon atoms attached to the iodide atom exceeds 6. In general, organic components—with the exception of certain aromatic and highly symmetrical compounds—containing more than 6 atoms, exhibit broad absorption bands. However, the number of compounds, inorganic as well as organic, possessing fewer than 7 carbon atoms and exhibiting a characteristic far ultraviolet absorption, is very large. Almost all of these compounds are amenable to purification in a gas chromatograph.

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Oscillometric Titrations of Air-Sensitive Substances

R. E. Cuthrell and J. J. Lagowski, Department of Chemistry, The University of Texas, Austin 12, Texas

In the course of an investigation of acid-base equilibria in nonaqueous solvents and the formation of coordination compounds in acetonitrile and in benzene (*2*), it became necessary to conduct oscillometric titrations on systems that were either hydroscopic or reacted with atmospheric constituents. Although oscillometric cells of various designs have been described (*1*, *3*), none was readily adaptable for titrations in an inert atmosphere. Accordingly, the capacitor-type titration cell illustrated in Figure 1 was constructed. The design of this cell is unique in that mercury is used both for the capacitor plates and to provide electrical contact. This design permitted more vigorous cleaning and drying procedures than are possible with the commercially available cells since the mercury could be removed prior to these operations. Very efficient horizontal and vertical motion of the cell contents was effected by a stirrer which impelled the liquid through a side arm by-pass tube. The stirrer was mounted through a precision ground-glass bearing lubricated with silicone oil and was driven by a compressed air motor. Titrant was introduced into the cell by a micrometer syringe inserted through a rubber serum cap which closed a short tube extending from the body of the cell. Several cells of this type have been constructed with volumes varying from 5 to 10 ml. It was possible to dry these cells in a vacuum oven after cleaning, load them in an inert atmosphere box, and conduct oscillometric titrations reproducibly on moisture-sensitive substances.

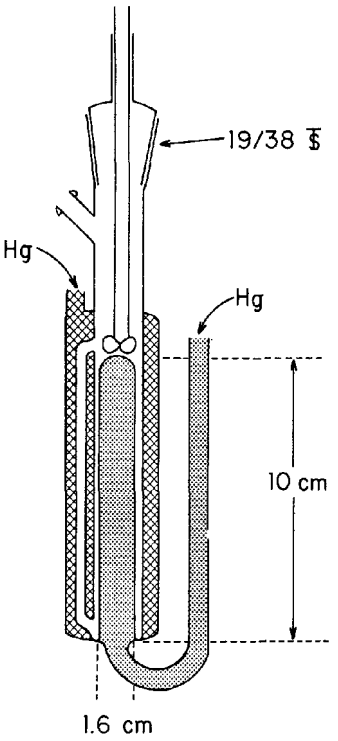

Figure 1. Oscillometric titration cell

The cell was used with a Sargent Model V oscillometer equipped with a cell compensator and was shielded during the course of a titration by a grounded copper cylinder; electrical contact was provided to the oscillometer by shielded coaxial connectors. It was necessary to maintain the same relative position of the oscillometer, cell compensator, and cell throughout the course of a titration as well as to exclude air bubbles from the mercury filling the cell; a variation of either of these factors during a titration leads to erratic results.

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Drop-Time Trigger for Synchronization of Delay and Timing Circuits with Drop-Rate of Dropping Mercury Electrode

R. C. Propst and M. H. Goosey, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, S. C.

We have designed a simple transistorized drop-time trigger to detect the instant a drop is detached from the capillary of the dropping mercury electrode (DME). The trigger was developed for use in a multipurpose instrument similar in principle to the one described by Underkofler and Shain (*3*), and has many potential applications where it is desirable to measure the electrolysis current at the DME at precise and reproducible intervals late in the life of each drop.

Drop-time triggers are utilized in instruments for square wave (*2*), incremental deviative (*1*), and oscilloscopic polarography to supply trigger pulses to auxiliary delay and timing circuits each time a drop falls from the DME. Several drop-time triggers based on different operating principles are described in the literature; however, the most successful design is based on monitoring the sudden increase in impedance of the DME each time a drop is detached from the capillary. This principle is utilized by Barker (*2*) in his square wave polarograph and the trigger provides positive operation regardless of the faradaic current flowing in the DME circuit. The drop-time which we describe also incorporates this principle.

A schematic of our drop-time trigger is shown in Figure 1. Transistor Q_1 is utilized in a series-tuned 250-KC oscillator circuit that is sensitive to a capacitance load. The double layer capacitance at the DME is sufficient to load the circuit and prevent oscillation except at the instant a drop is detached. Transistor Q_2 is employed as an emitter follower to provide a low impedance

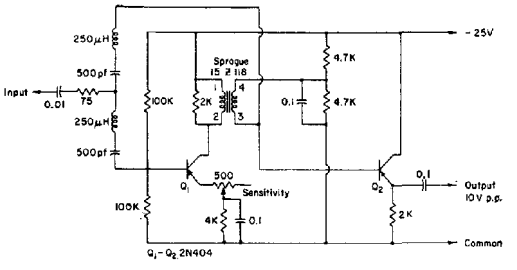

Figure 1. Drop-time trigger

output and to isolate the output from the oscillator circuit.

The drop-time trigger was evaluated in a square wave polarograph based on operational amplifiers. The polarograph utilized a conventional three-electrode, potential control circuit, and a 1 K ohm isolation resistor was installed between the output terminal of the potential control amplifier and the counter electrode to isolate the input of the drop-time trigger from the output of the operational amplifier. The output of the drop-time trigger was connected to a conventional transistorized monostable multivibrator. The sensitivity control of the drop-time trigger was adjusted so that a burst of oscillations occurred each time a drop was detached from the DME. The sensitivity adjustment was not critical; and once adjusted, the trigger operated reliably regardless of the current flowing in the DME circuit.

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Information contained in this paper was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

A Spring Microbalance for Magnetic Susceptibility, Adsorption, and Thermogravimetric Studies

L. N. Mulay and L. K. Keys, Materials Research Laboratory, Pennsylvania State University, University Park, Pa.

THE BASIC classical and induction methods and their modifications for measuring magnetic susceptibility, including those related to nuclear magnetic resonance, have been critically reviewed by one of us (L.N.M.) (*5*, *6*, *8*). A survey of these methods shows that the Faraday method provides by far the most convenient technique for measuring the magnetic susceptibility of dia-, para-, and ferromagnetic samples. A review of balances and force measuring devices is given by Gordon and Campbell (*1*) and this indicates several advantages of the helical spring method for measuring small forces. McBain (*4*) discusses especially an advantage in eliminating any significance attaching to the "dead space" in adsorption studies.

Generally in the handling of a McBain (*4*) type adsorption balance or a similar Faraday type magnetic balance using quartz helical springs, considerable difficulty is experienced in placing the sample at a given position, where any changes in its weight can be conveniently observed within the span of a measuring microscope. The conventional bellows usually allows positioning over as limited a range as 1 cm. Samples varying widely in weight naturally require a larger range of adjustment both initially and during the course of a measurement. Some unique constructional and operational details of a microbalance are described below for studies on magnetic susceptibility, adsorption, and thermogravimetry, and for measuring small changes in susceptibility occurring during these processes.

INSTRUMENTATION

Figure 1 shows the balance which consists of a helical quartz spring suspended from a bellows assembly, a main sample-adsorption (or thermal decomposition) chamber, and an inlet gas system. A photograph of this assembly appeared in a review article (*8*), which shows the general setup of the apparatus. A special bellows assembly for sample positioning was constructed from bellows (approximately 2-cm. o.d., 7.5 cm. long with a total extension of 5 cm., obtainable from Servometer Corp., Clifton, N. J.); a short section of borosilicate glass pipe (about 2.5-cm. i.d., 20 cm. long) using a retainer ring, brass bonnet, and seat (obtainable from Kopp Scientific Co., New York, N. Y.); and a vertical screw with a very fine pitch (0.625-cm. diameter, 15 cm. long, 16 threads per cm.). Any gyrational motion of the brass cylinder at the base of the bellows assembly during the travel of the vertical screw was avoided by allowing the cylinder to slide through a sleeve machined from a plastic rod to give a

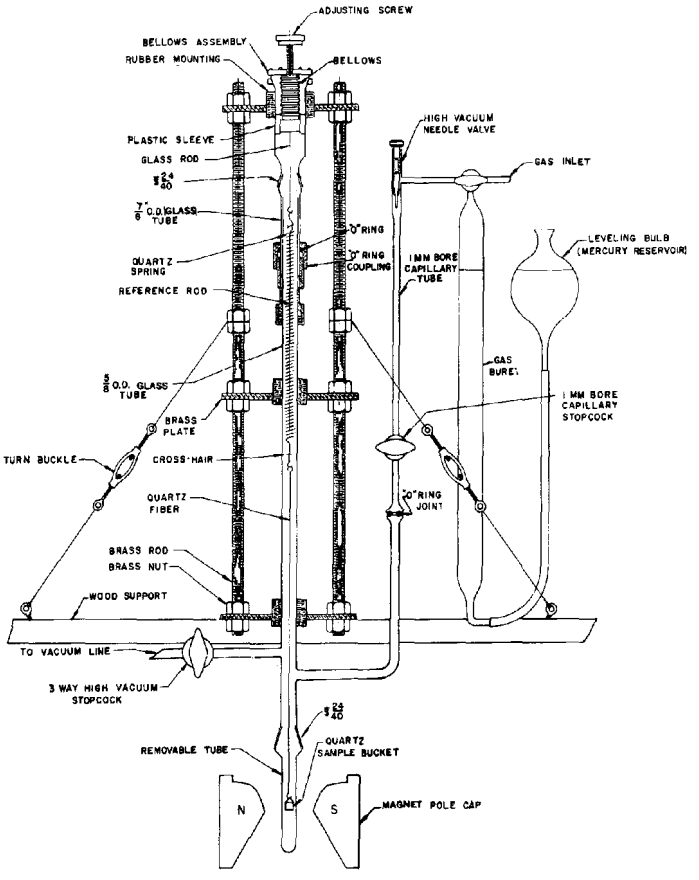

Figure 1. Helical-spring microbalance for studies on magnetic susceptibility (Faraday method), adsorption, and thermogravimetry, and for measuring changes in magnetic susceptibility during adsorption and thermal decomposition

Table I. Thermogravimetric and Thermomagnetic Data for $CuSO_4:5H_2O \rightarrow CuSO_4:1H_2O + 4H_2O$

Temp.	Wt. of sample, gram	Observed weight loss in moles of H_2O	Expected formula	Susceptibility per gram observed χ_g ($\times 10^{-6}$ c.g.s. units)	Molar susceptibility χ_m ($\times 10^{-6}$ c.g.s. units)	Observed in χ_m, $\Delta\chi_M$ ($\times 10^{-6}$ c.g.s. units)	Moles[a] of H_2O needed to cause $\Delta\chi_m$
25° C.	0.25437		$CuSO_4:5H_2O$	5.860	1129.6[b]		
		~4				−49	≃4
100° C. ($p = 10^{-6}$ mm. of mercury)	0.17675		$CuSO_4:1H_2O$	6.632	1178.4		

[a] Calculated on the basis that $\chi_{m(H_2O)} = -12.9 \times 10^{-6}$ c.g.s. units.

[b] Since $\chi_M = \frac{1}{T + \theta}$ according to Curie-Weiss law, this molar susceptibility (for $CuSO_4:5H_2O$) is expressed at 100° C. for comparison with the observed value for $CuSO_4:1H_2O$ at the same temperature.

snug fitting arrangement similar to a piston and chamber system. This was lubricated with a small amount of stopcock grease, which provided smooth motion of the bellows. At the base of the bellows, a glass rod (2-mm. diameter) with a hook was attached from which a quartz spring and a bucket were suspended.

A provision for a coarse positioning of the sample was also introduced by a telescoping arrangement of two concentric glass tubes using two "Veeco type C" O-ring couplings (about 1.6- and 2.0-cm. i.d., Vacuum Electronics Corp., Plainview, N. Y.), which were soldered together. The entire assembly was vacuumtight to pressures of 10^{-7} mm. of mercury. When the sample was removed, the spring pulled the fiber up into the chamber, thus making its retrieval very difficult. With this special telescoping arrangement, the coupling could be loosened, the fiber lowered to the position where the sample could be replaced, and then raised to the desired position and tightened. The sample is then accurately positioned by adjusting the vertical screw on the bellows.

The sample was aligned and positioned in the correct region of the magnetic field by observing the position of the crosshair at the bottom of the spring through a microscope (32× magnification, No. 72905 Gaertner Scientific Co., Chicago, Ill.). This microscope was attached to a vertical mechanical stage which could be adjusted over a range of 5 cm. with an accuracy of 0.002 mm., using a micrometer drum for measuring deflections of the spring. The sample could be centered in the pole gap in the desired region of the magnetic field by adjusting the 4 turn buckles which controlled the tilting of glass chamber and spring assembly. Commercially available cathetometers can be used also for the same purpose.

The quartz bucket was cylindrical in shape, about 0.8-cm. diameter, 0.5 cm. tall and weighed about 0.3 gram. This was adequate to hold a few milligrams of the sample. The quartz buckets and springs of varying sensitivity were obtained from Worden Laboratory, Houston, Texas. A typical spring used for paramagnetic measurements had a sensitivity of 1 mm. per 2 mg., a maximum load capacity of 1200 mg., an extension of 600 mm. and a helix diameter of 8 mm. A reference rod was provided inside the spring to correct for any changes in the length of the spring due to temperature variations.

A Newport type A water cooled electromagnet with a matching power supply was used (Newport Instruments Co., Newport Pagnell, Buckinghamshire, England; obtainable in U. S. A. from Cryotronics Co., High Bridge, N. J.). In order to obtain the best field characteristics, special pole caps were made for the magnet according to the specifications of Heyding, Taylor, and Hair (*2*). These pole caps provide almost a 1-cm. region of constant force in a pole gap of about 4 cm., with less than 1% variation. This region is found experimentally by placing any sample (the empty quartz bucket itself may be used as a diamagnetic sample) at different positions (about 0.5 mm. apart) along the vertical axis in the field with respect to any arbitrary starting point and making a plot of deflection observed on application of the field *vs.* the position of the sample.

TYPICAL RESULTS AND DISCUSSION

General procedures for magnetic susceptibility measurements have been described elsewhere (*6*, *10*). Using sucrose as a reference (*10*) ($\chi = -0.566$) the following specific susceptibilities (all in units of 10^{-6} c.g.s. units) were obtained: KCl (−0.517); KBr (−0.379); SiO_2 (−0.492); NaCl (−0.496). These are in excellent agreement with those reported in the literature (*3*).

Measurements on $CuSO_4:5H_2O$ provide a good example for the application of our microbalance for thermogravimetric and thermomagnetic analysis. The data in Table I show a loss of four molecules of water when $CuSO_4:5H_2O$ is heated from 25° to 100° C. under vacuum (10^{-6} mm. of mercury). The same conclusion can be also drawn from the susceptibility data based on a difference between the molar susceptibilities. The change in susceptibility is due not only to loss of water molecules but also to a change in paramagnetism of the sample. The latter factor is easily accounted for by calculating theoretically the susceptibility for the entire $CuSO_4:5H_2O$ at 100° C., on the assumption of Curie-Weiss law. Experiments below room temperature show the Weiss constant to be negligibly small (*9*) ($\theta = 1°$). The difference in molar susceptibilities between this value and the one actually observed at 100° C. after dehydration corresponds to about 4 molecules of water, χ_m for H_2O being taken as -12.9×10^{-6} c.g.s. units.

In another application the apparatus was also used for studying the adsorption of oxygen on γ-aluminina and for studying the changes in magnetic susceptibility during adsorption. The magnetic measurements indicate the formation of a dimeric O_4 species with a very small magnetic susceptibility. This work is reported separately (*7*).

ACKNOWLEDGMENT

We wish to thank R. Myers (Lehigh University), J. S. Long (University of Louisville), and Harry Burrell (Interchemical Corp.) of the Paint Research Institute for their encouragement.

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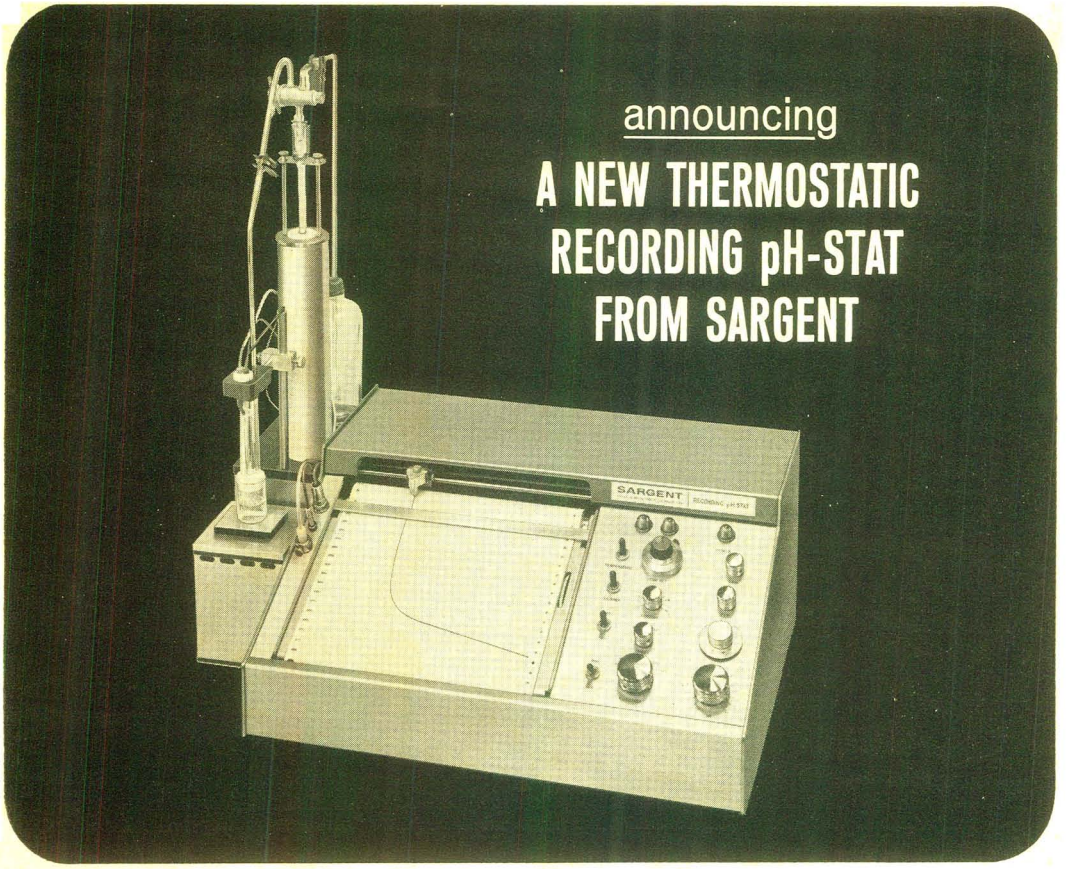
WORK supported by a predoctoral fellowship (to L.K.K.) from the Paint Research Institute and by the U. S. Atomic Energy Commission through Contract AT-(30-1)-2581.



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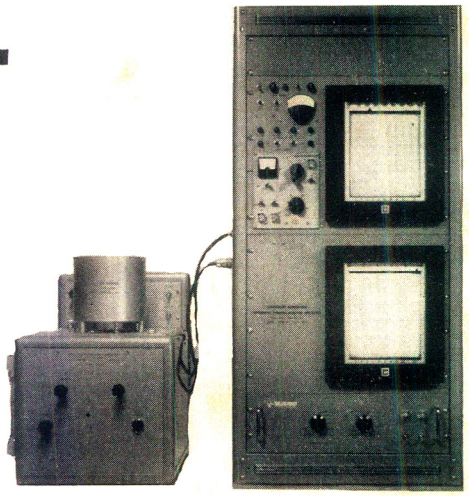

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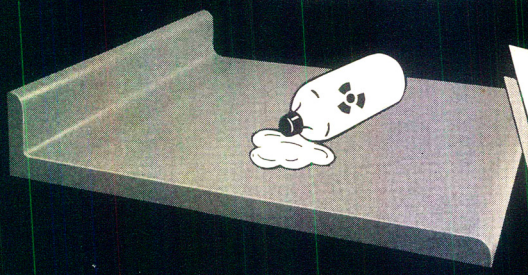

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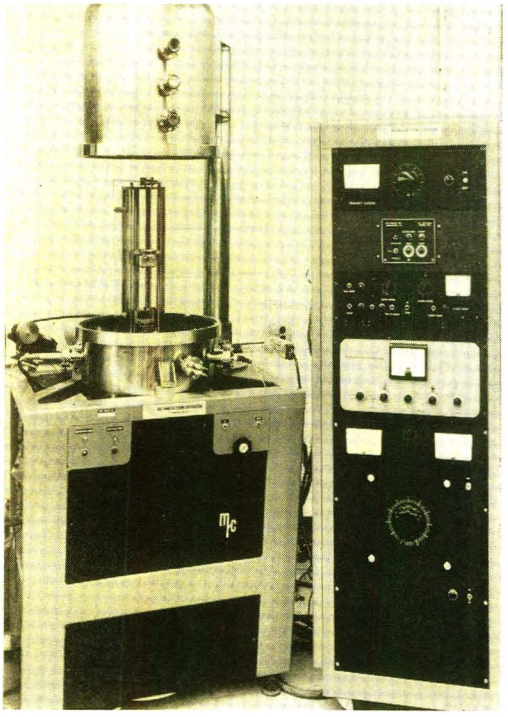

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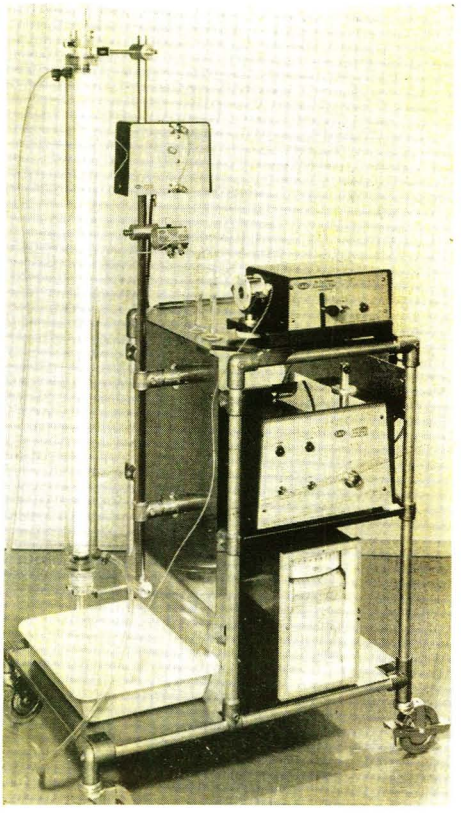


The ReCyChrom 4900 is a new type of column apparatus intended for fractionating complex solutions of substances by gel filtration. The system is equally applicable to analytical and to preparative separations. With the system the sample is passed many times through the same column. The effective height of the bed is thereby increased greatly without extremely long columns, with their well-known disadvantages, being used. Components which cannot be resolved either on simple chromatographic columns of moderate length or by other methods such as electrophoresis and ultracentrifugation are often separated easily by this technique. LKB Instruments, Inc., 4840 Rugby Ave., Washington 14, D. C. **402**

Ozone Meter

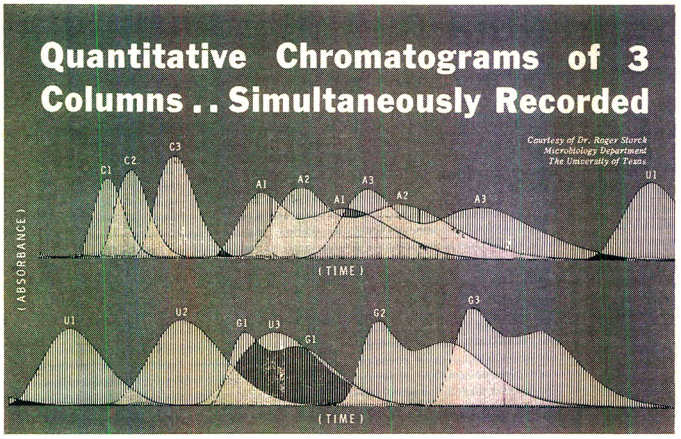
The Model H-81 ozone meter measures ozone concentrations in carrier gas from 0 to 80 milligrams per liter. The instrument operates independently and requires no chemicals. It has no drift, gives an 100% response in 30 seconds, and has an accuracy of $\pm 1^1/_2\%$ over full scale. Operating pressure range is 0–15 p.s.i.g., operating temperature range is 35–110° F., and gas sampling rate is 20 liters per hour. The Welsbach Corp., Westmoreland and Stokley Streets, Philadelphia, Pa., 19120. **403**

Enzymatic Analyzer

A direct reading enzymatic analyzer for blood urea nitrogen has been introduced. With no wet chemistry, incubation, reagent preparation, nor installation time required, the portable unit will analyze for blood urea nitrogen in less than two minutes, using a sample size of 0.05 ml. or less of whole blood or serum. The method is based on the rate of development of electrical conductivity from the conversion of urea to ammonium carbonate by the enzyme urease. Laboratory Equipment Corp., St. Joseph, Mich. **404**

Research Osmometer

The Hi-Precision research osmometer features repeatability of 0.2 milliosmol. The osmometer can be read in millidegrees, milliosmols, or milliosmosity. A special bath temperature controller and sample handling system in addition to the increased sensitivity lead to increased precision. The major application of the instrument is in the determination of total body water by deuterium dilution as well as other dilution studies where small changes are important. Advanced Instruments, Inc., 45 Kenneth St., Newton Highland, Mass. **405**



A contribution of the Gilford 2000 Multiple Sample Absorbance Recorder is in the determination of the nucleotide composition of DNA and RNA. For example, in the complete separation of four ribonucleotides shown above, three columns were eluted with formic acid and sequentially monitored. On this chart, divided into two segments because of space limitations, the recording is on a time-sharing basis with three channels for the samples, and one for the baseline. Here, the samples were handled at a rate of 2 to 3 ml per hr. by a set of four 1 cm path length Gilford Flow Through Cuvettes. The cuvettes were sequentially positioned by the Automatic Cuvette Positioner, and the baseline maintained at zero by the Gilford Automatic Blank Compensator.

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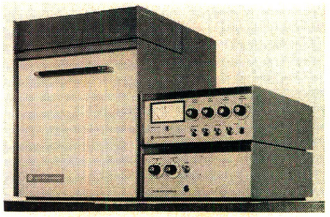

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Differential Thermal Microanalyzer

The Thermal Differential Micro Analyzer Model M-1 features a semimicro probe for samples ranging up to 5 mg. and/or an optional micro probe for samples of a few μg. Samples are placed inside the thermocouples. Temperature ranges from ambient to 1250° C. An interchangeable low temperature oven is available for operation on the −150° C. to +200° C. range. A simplified programmation is provided. Differential temperature is recorded by means of an ultrasensitive low internal resistance galvanometer and an electro-optical spot follower. Sensitivities of up to 40 in./° C. can be achieved. Temperature recording is made on standard strip chart recorders. Bureau de Liaison, 113 Rue de L'Université, Paris, France. **407**

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it has 1-2-3 speeds
IT COSTS JUST $97.00

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It's ideal in size and design for lab and pilot work and in production for fluid mixing, blending, solids suspension and dispersion. You'll find it helpful for studies in mass transfer and heat transfer.

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MIXING EQUIPMENT Co., Inc.,160-m Mt. Read Blvd., Rochester 3, N.Y. In Canada: Greey Mixing Equipment Ltd., 100 Miranda Avenue, Toronto 19, Ont. In Europe: Lightnin Mixers Ltd., Poynton, Cheshire, England.

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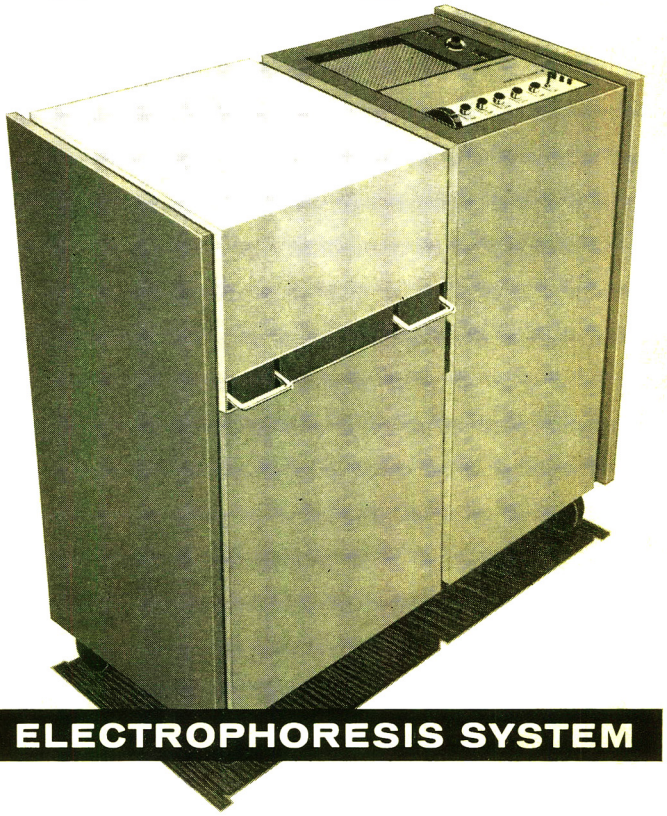

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A power operated mortar and pestle assembly has been developed for the chemical or spectrographic laboratory. The apparatus includes a mortar and pestle made of carefully hardened Graph-Mo tool steel with the pestle shank reduced to take either the electric hammer or the air hammer. With this arrangement, a white iron, for example, can be crushed for carbon and/or sulfur analysis in 30 seconds. Harry W. Dietert Co., 9330 Roselawn Ave., Detroit, Mich. 48204. **408**

The Redox-Con-Trol is a flexible and versatile instrument developed for the control, analysis, and investigation of a wide range of electrochemical reactions. The instrument can be used as a constant voltage source at any voltage from 0 to 120 volts. It can serve as a constant current source for currents up to 30 amperes. The instrument can be used to perform oxidations at constant anode potentials from 0 to 6 volts. The Redox-Con-Trol performs reduction at constant cathode potentials from 0 to 6 volts and is capable of plotting applied voltage and current vs. reference potential. Melpar, Inc., 3000 Arlington Boulevard, Falls Church, Va. 22046. **409**

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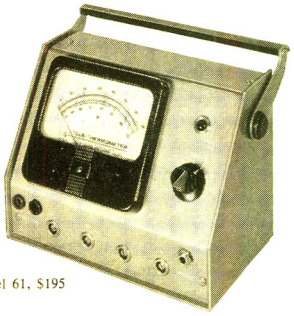

Model 61, $195

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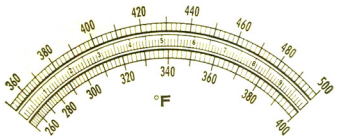

Accuracy is ±3°F over most of range. Readability and reproducibility better than 1°F.

The Model 61 is battery operated and completely portable. Convenient recorder jacks provide 0-160 MV full scale output. The full line of YSI Tele-thermometers includes single and multi-channel instruments for precise temperature measurements from −200° to +260°C.

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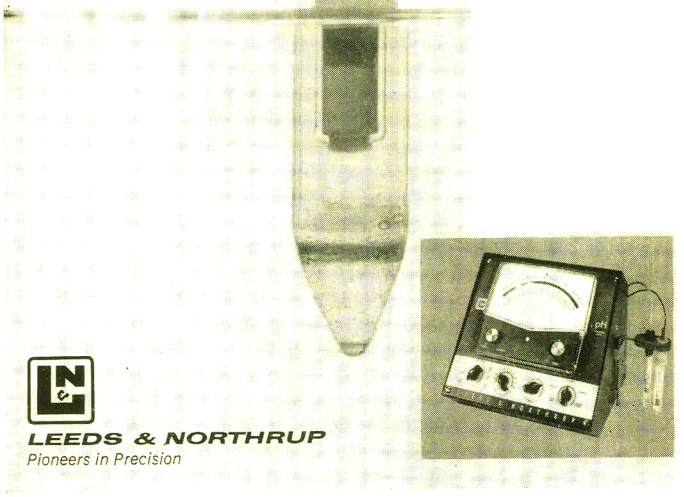

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J-401

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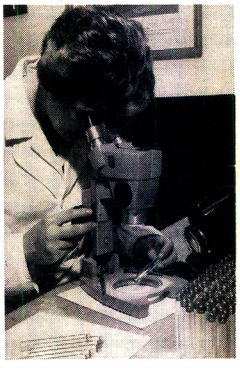

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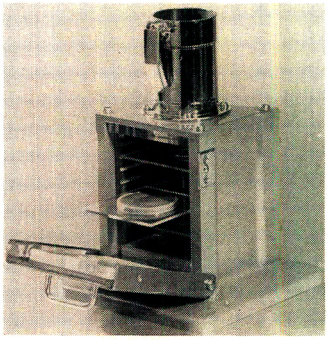
NEW PRODUCTS

Process Chromatographic Programmer

A new process chromatographic programmer, the Model 620 Composition Transmitter, is designed to monitor the key components of process streams. It was developed specifically for a closed-loop, process control chromatographic system. The 620 features trend readout with single-stream, dual-component capability. This system is suited for petroleum, petrochemical, and chemical applications where high reliabilitiy is essential for control of fractionation columns. Beckman Instruments, Inc., 2500 Harbor Boulevard, Fullerton, Calif. **410**



The Model EA-11 is a probe mount for more precise geiger and scintillation counting of alpha, beta, and gamma radiation. The mount is made of cast aluminum and includes a detector holder clamp system for varying the distance of the probe from the sample. It has an internal 7-position shelf system which provides fixed geometries between probe and sample. Three sample trays provide the stand with the ability to handle 1″ and 2″ planchets, odd size samples, and standard absorbers. This internal shelf system is completely surrounded by ⅜″ of clear plastic which minimizes the effect of Bremsstrahlung caused by radiation from the sample. Nuclear Supplies, Inc., P. O. Box 312, Encino, Calif. **411**

Vacuum Ultraviolet Spectrophotometer

A fully automatic recording vacuum ultraviolet spectrophotometer provides double-beam absorption in the vacuum ultraviolet region down to 584 A. The system includes use of helium, argon, krypton, and xenon sources and offers a predisperser, as well as ratio-readout electronics. Jarrell-Ash Co., 590 Lincoln St., Waltham, Mass. **412**

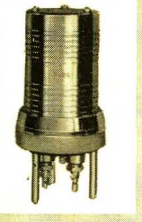
PARR
OXYGEN BOMBS

1101 **360 ml.**

Most Parr calorimeters are equipped with this double valve bomb or its single valve counterpart, No. 1102. Both are widely used for general purpose calorimetry; also for determining sulfur, chlorine, arsenic and other elements in combustible solid or liquid samples.

1104 **240 ml.**

This is the heaviest and strongest of all Parr oxygen bombs. It is designed to withstand the high pressures and shock forces developed when testing explosives and high energy fuels in Parr oxygen bomb calorimeters. It has gas inlet and release valves similar to No. 1101.



1106 **340 ml.**

This bomb is used for high precision calorimetry and for tests requiring flushing or evacuation before or after firing. It is offered in the inverted style as shown, also in an upright model, No. 1105. Both can be equipped with platinum fittings and liner.

1003 **360 ml.**

This is a special purpose bomb used primarily for burning samples in fluorine instead of oxygen. It can be made of nickel, Monel or other alloys. Gas inlet and outlet connections are made through valves built into a one-piece head.

1004 **320 ml.**

This is a special purpose bomb used in rotating bomb calorimeters. It can be made for either oxygen or fluorine combustions, and can be equipped with a full set of platinum fittings and a platinum liner. There are two needle valves in the one-piece head.

Ask for the new issue of Specification 1100 describing these and other Parr oxygen bombs.

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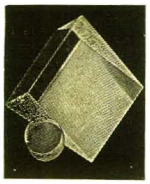

Materials available include lithium fluoride, calcium fluoride, barium fluoride, sodium fluoride, sodium chloride, potassium chloride, potassium bromide, silver chloride, KRS-5, KRS-6, thallous chloride, thallous bromide, cesium bromide and cesium iodide. Special crystals can be custom grown to customer 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.

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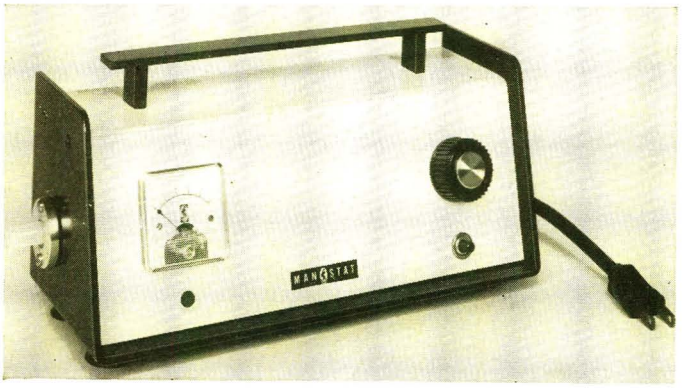

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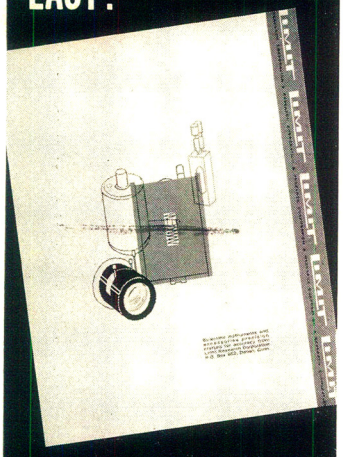

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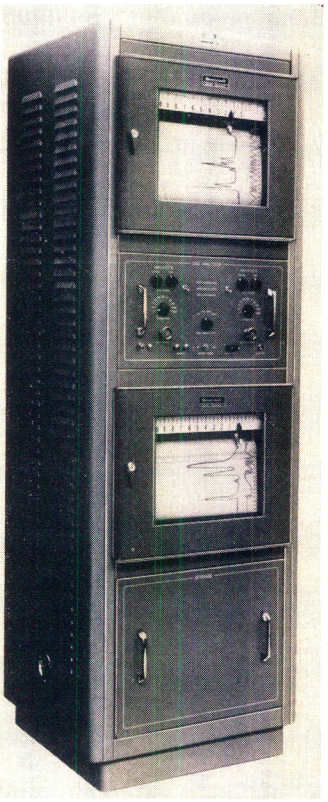
NEW PRODUCTS

Pulverisette shown was exhibited at the recent ACHEMA in Frankfort. This new grinding mill uses centrifugal action and either agate or tungsten carbide bowls for pulverizing hard materials. A safety switch and lucite cover are included with this Fritsch equipment. Schuco Scientific, 250 West 18th St., New York 11, N. Y. **413**



The Atmospheric Analyzer is a gas chromatograph developed for the separation and detection of all normal atmospheric components. This system may be used to analyze the atmosphere in environmental test chambers and effluents from a wide range of chemical and biological reactions. Melpar, Inc., 3000 Arlington Boulevard, Falls Church, Va. 22046. **414**

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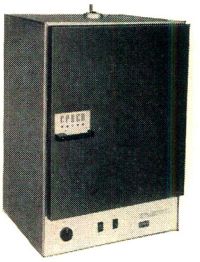

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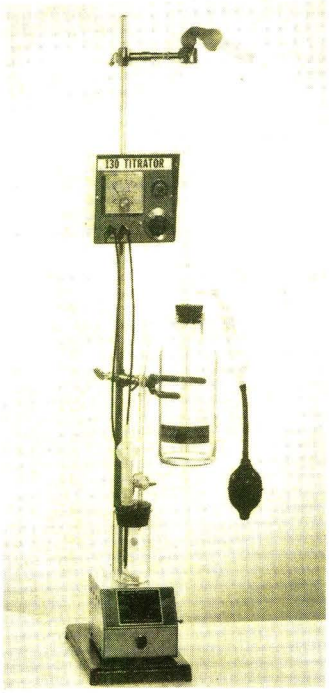

Moisture determination apparatus which uses the Karl Fischer titration principle, the Model 130 titrator, is available. Using 1-gram liquid or solid samples, the unit will detect 0.01% to 100% moisture and, with the addition of a microburet accessory, it will indicate 0.001% moisture. The titrator may be used for accurate moisture content determination in foodstuffs, petroleum products including jet fuels, paints, vegetable oils, sugars and syrups, pharmaceuticals, explosives, soaps, and many other types of material which prohibit visual titration. Harris & Co., 624 Peach St., Lincoln, Neb. **416**

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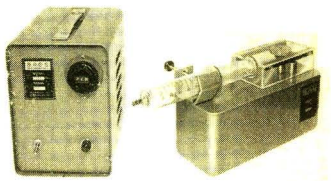

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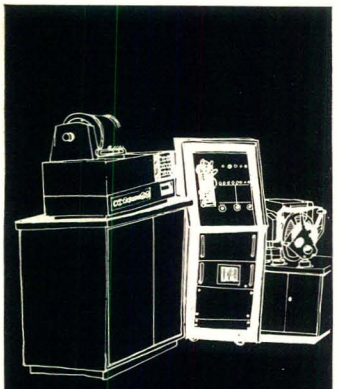

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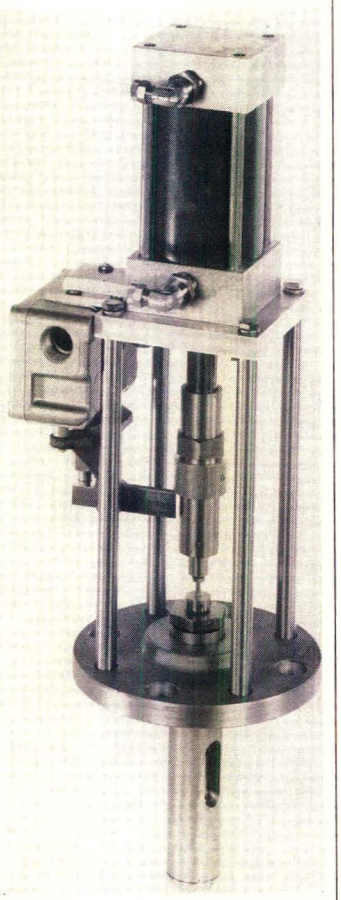
NEW PRODUCTS

Thermal Conductivity Detector

A new micro-filament detector expands the high performance usefulness of thermal conductivity detection for small bore packed or capillary columns. It offers the high drift stability of filament type detectors in addition to providing high sensitivity over a wide temperature range. The detector is particularly useful for columns having diameters below $^1/_8$" i.d. The body provides single reference and sample cells to minimize cell volume. Special arrangements involving four elements can also be supplied. Loenco, Inc., 2092 N. Lincoln Ave., Altadena, Calif. **417**



Viscometer measuring element, Model M20, for closed systems can be installed in a pipe line or in any process reactor or vessel. It can be installed in any position and, consequently, can be used either in a vertical or horizontal section of a pipe line or in the top, side, or bottom of any process vessel. Norcross Corp., Dept. #N73, Newton, Mass. 02158. **418**

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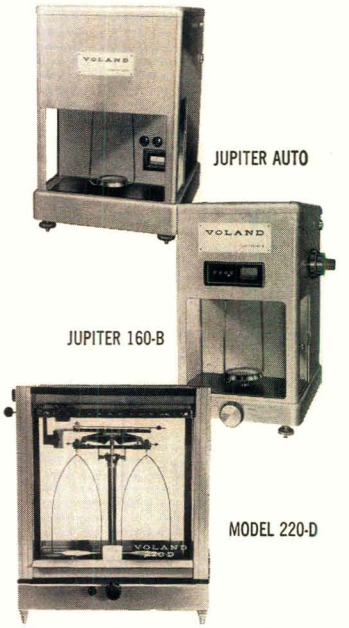

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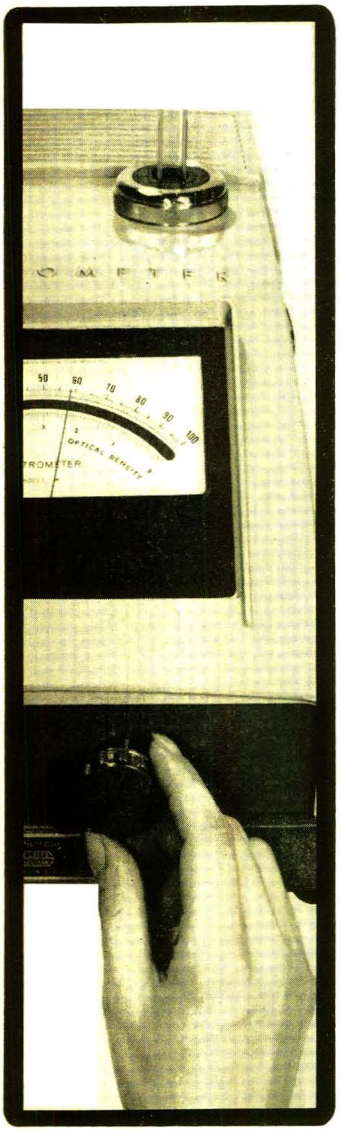

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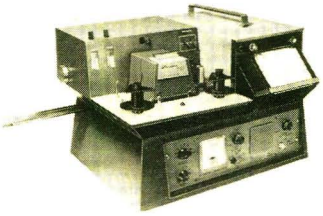

A new, automatic radiochromatogram scanner, the Model RSC-363, records the exact location and intensity of separated, low-energy beta emitters on paper strips and glass plates used in thin-layer chromatography, and also scans emitters of higher energy used in thick gel applications. The scanner uses 3 separate gas flow detectors: two for 4-pi scanning of paper strips, and one for thick gels and glass plates. It offers window or windowless operation, variable collimation, automatic event marker, automatic gas and power shutoff, and a background of about 12 counts per minute. Atomic Accessories, Inc., 811 West Merrick Rd., Valley Stream, N. Y. **419**

Portable electronic infrared instrument for analyzing and recording constituents of gases, vapors, or liquids, the Carbochek, is used to detect the desired component present in a chemical or petrochemical process stream. It will respond to within 90% of the final reading in five seconds and is accurate within ±2% of the full scale. Lindberg/Hevi-Duty Marketing Service, 2450 West Hubbard St., Chicago, Ill. 60612. **420**

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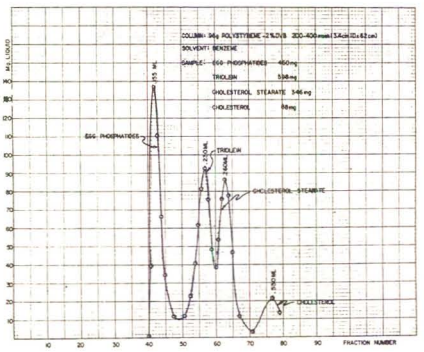

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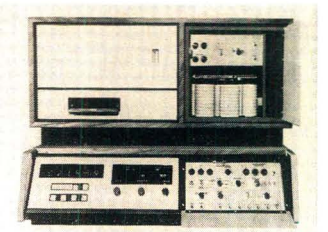
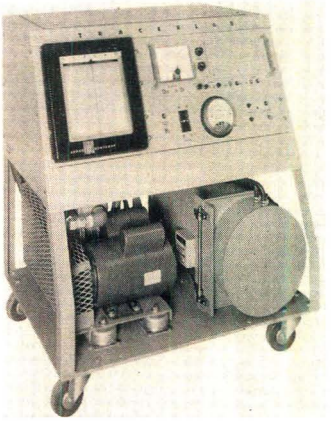
NEW PRODUCTS



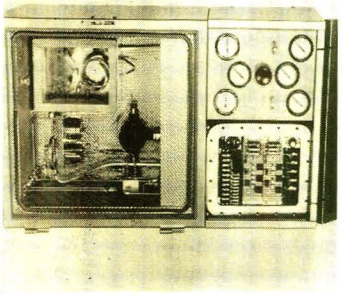
Widebeta II radioactivity counting system offers low background counting with a wide dynamic range for measuring alpha and beta radioactivity. The instrument permits automatic printout of alpha/beta ratio and beta/beta ratio. Push button controls are included and the system automatically displays sample number, time of day, counting time, counts, count per minute, and percentage counting error. Beckman Scientific and Process Instruments Division, 2500 Harbor Blvd., Fullerton, Calif. 92634. **421**



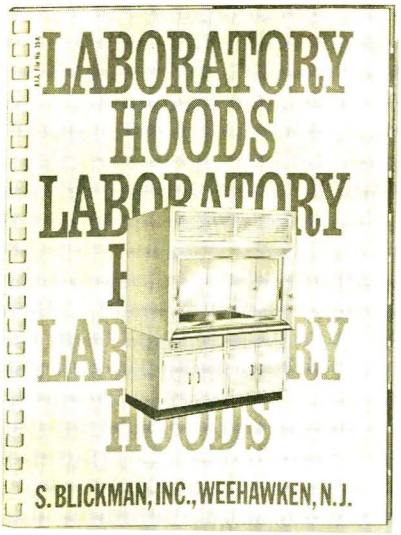
Radioiodine effluent monitor, the MIP-5B, features a triple filter capable of collecting volatile, particulate, and compound forms of iodine-131 with an efficiency in excess of 98%. The monitor features a gamma scintillation detector that is shielded for operation in high background count areas. The scintillation detector, located in front of the triple filter elements, develops a pulse-rate output proportional to be accumulated activity. The monitor is capable of detecting 10^{-10} μc./cc. iodine-131 within minutes. Radioiodine build-up is displayed on a large meter for direct readout and the reading is recorded on a strip chart recorder. The MIP-5B also contains high activity alarm and loss of flow alarms. Tracerlab, 1601 Trapelo Road, Waltham 54, Mass. **422**

Mercury Vapor Lamp

The Nikon MFL-100, a mercury vapor lamp for acridine orange and other blue-green fluorescence techniques, has been developed to meet the demand for a modestly priced lamp that can bring such microscopy techniques within the capabilities of routine office procedure. The MFL-100 can be used with any high quality microscope, and requires no other equipment. It is equipped with a 100-watt GE mercury vapor arc bulb and Corning 5113 exciter filter, which provides the correct spectral characteristics for blue-green fluorescence. Wratten 15 (G) blue-absorption filters are furnished for insertion into the eyepieces for the acridine orange technique. Instrument Division, Ehrenreich Photo-Optical Industries, Inc., 111 Fifth Ave., New York 3, N. Y. **423**



The Model 550 chromatographic analyzer features two independent temperature zones; solid state proportional temperature controls; and high velocity, forced air circulation and mixing. A modularly designed companion Model 525 programmer has multichannel disk programming and photoelectric solid state switching. These units are available for process gas chromatography analysis. The Model 550 includes a basic outer oven capable of operating between 50° and 250° C. with control to ±0.05° C. The instrument has an optional inner zone which permits temperatures as low as 0° C. or 100° C. below outer oven temperature. Microvolume sample valves handle gas volumes from 25 μl. and liquid volumes from 0.5 to 25 μl. with reproducibility better than ±0.1%. Available detectors include four-element hot-wire thermal conductivity; micro thermistor thermal conductivity; hydrogen flame ionization; and gas density balance. Mine Safety Appliances Co., 201 North Braddock Ave., Pittsburgh, Pa. **424**



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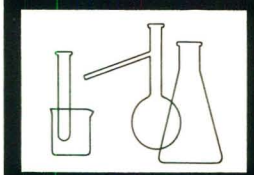

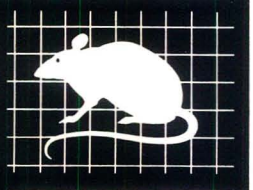

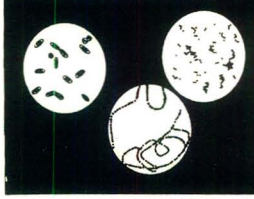

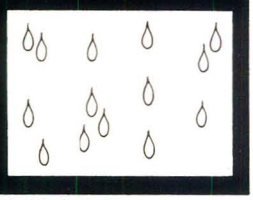

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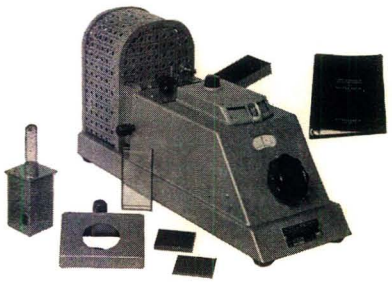

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Gas Chromatography Stationary Phases

New stationary phases available include benzylamine adipate which is used for the analysis of aqueous solutions of the lower fatty acids and organosilicon polymers EGSS-X and EGSP-Z, formerly only available as coated packings. Applied Science Laboratories, Inc., P. O. Box 140, State College, Pa. **502**

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Molybdosilicate Chemicals

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Single Crystals

Single crystals of high purity titanium, zirconium, and hafnium are now available. They are $^1/_4$ inch in diameter and 1 inch long. Materials Research Corp., Orangeburg, N. Y. **506**

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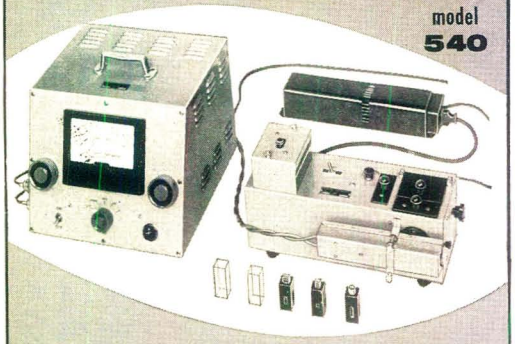

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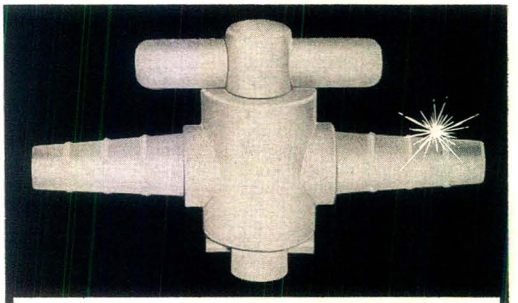

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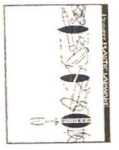

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MANUFACTURERS' LITERATURE

Ultraviolet Microcells. A 2-page sheet gives data and prices on short path length ultraviolet microcells available in the standard range 0.007 to 1.0 mm. Limit Research Corp., 557 Post Rd., Darien, Conn. **601**

Infrared Analyzers. Bulletin IR-4055, 8 pages, describes the Models IR 215, IR 315, and IR 415 infrared analyzers. Model IR 215 for laboratory use is a single compact unit, while the other two models designed for on-stream applications consist of two separate units: an analyzer section and an amplifier section. Beckman Scientific and Process Instruments Division, 2500 Harbor Blvd., Fullerton, Calif. 92634. **602**

Chromatography Items. Catalog No. 8, 24 pages, lists gas chromatography solid supports, stationary phases, packings, columns, syringes, and accessories. In addition, a section of thin layer chromatography lists a variety of adsorbents and a lipid section covers high purity lipids. Applied Science Laboratories, Inc., P. O. Box 140, State College, Pa. **603**

Lab Apparatus. A 20-page catalog, No. 64, illustrates and describes a wide range of laboratory burners and accessories, clamps, supports, tongs, and miscellaneous hardware. Humboldt Mfg. Co., 7300 W. Agatite Ave., (Norridge) Chicago, Ill. 60656. **604**

Gas Chromatograph. Bulletin 7032, 8 pages, describes the GC-4 chromatograph. This instrument has modular selectivity of components to give maximum flexibility and high performance. Beckman Scientific and Process Instruments Division, 2500 Harbor Blvd., Fullerton, Calif. 92634. **605**

Mass Spectrometer. A 12-page bulletin is devoted to the Model 21-130 laboratory mass spectrometer. This instrument, a cycloidal focusing mass spectrometer with a mass range from 2 to 230, is the principal instrument in the company's automated mass spectrometer/chromatograph system. Consolidated Electrodynamics Corp., 360 Sierra Madre Villa, Pasadena, Calif. **606**

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MANUFACTURERS' LITERATURE

Gas Chromatography Equipment. An 18-page brochure is a guide for evaluating and selecting gas chromatography equipment. Included in this bulletin are descriptions of the Series 810, 700, and 400 gas chromatographs. F & M Scientific Corp., Starr Rd. and Rt. 41, Avondale, Pa. 19311. **607**

Atomic Absorption Applications. A comprehensive bibliography of published literature on the applications of the atomic absorption technique for determination of trace metals is offered in an 8-page listing. Newsletter No. 16. Perkin-Elmer Corp., Main Ave., Norwalk, Conn. **608**

Diffractometer Control System. A 4-page bulletin describes the XDC-II which is an expandable automation system for x-ray diffractometry. This instrument is compatible with any neutron or single crystal x-ray diffractometer. Bulletin DB-132-1. Datex Corp., 1307 Myrtle Ave., Monrovia, Calif. **609**

Nitrogen Dioxide Instrument. The Model 725-11 nitrogen dioxide recorder is described in 3 pages. The system consists of two units, a nitrogen dioxide meter and strip chart recorder. Specifications and theory of operation are discussed. Mast Development Co., 2212 E. Twelfth St., Davenport, Iowa 52803. **610**

Chelometric Indicators. Technical Data TD-105, 35 pages, outlines procedures used for determining 29 metals by titration with EDTA. Properties of over two dozen of the most widely used chelometric indicators are also described. Fisher Scientific Co., 300 Fisher Bldg., Pittsburgh, Pa. 15219. **611**

Variable Gradient Mixer. A 4-page bulletin, No. 3-6000A, describes three different models of Varigrads, variable gradient mixers for column chromatography. Buchler Instruments, Inc., 1327 Sixteenth St., Fort Lee, N. J. **612**

Pure Materials. A 16-page catalog presents prices on spectrographically pure materials. Included are metals, compounds, and solutions. A laboratory certificate of analysis is included with all orders for these materials. Jarrell-Ash Co., 590 Lincoln St., Waltham, Mass. 02154. **613**

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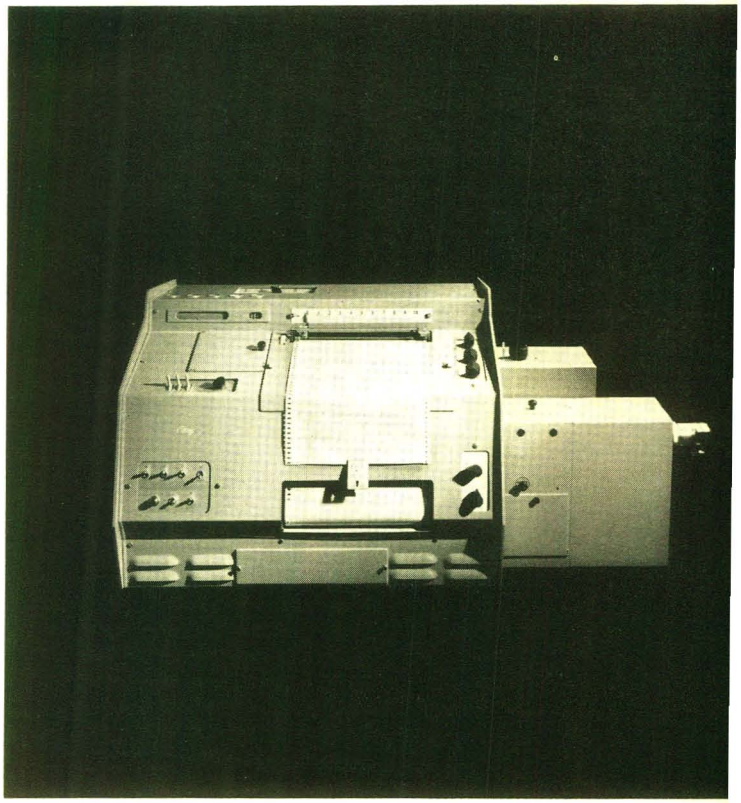

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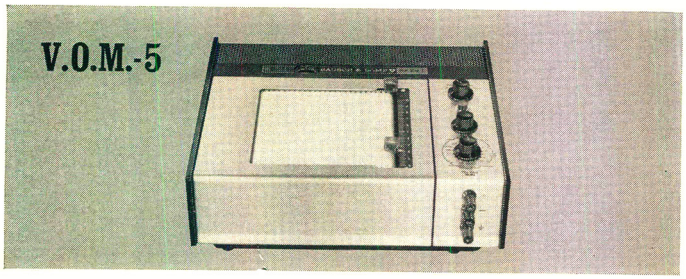

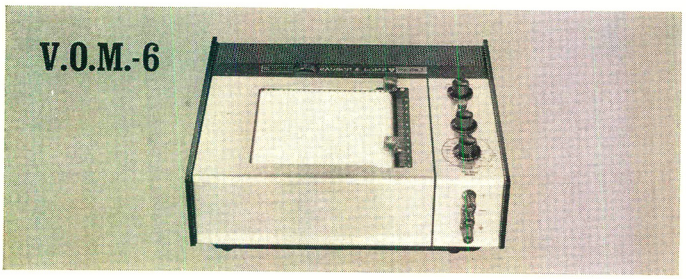

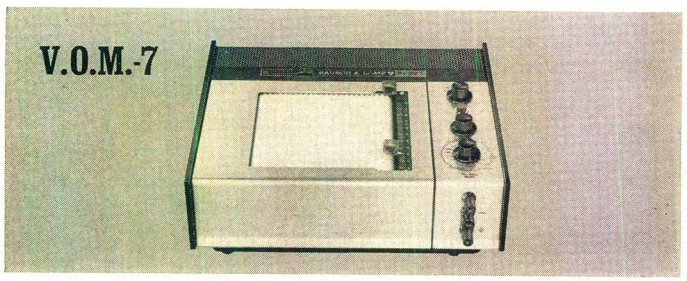

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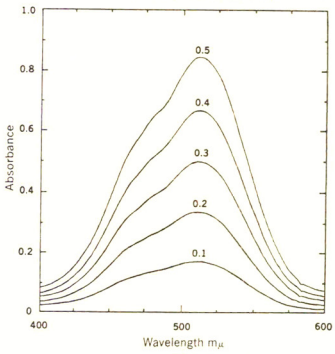

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MANUFACTURERS' LITERATURE

Electrobalance Techniques. Data sheet 10, 2 pages, describes recording Wilhelmy surface tension continuously and automatically. Data sheet 11, 22 pages, discusses making magnetic susceptibility measurements. Cahn Instrument Co., 15505 Minnesota Ave., Paramount, Calif. **614**

Laboratory Equipment. Catalog 65M contains 112 pages of information on metal laboratory equipment including base units, wall and counter storage cases, sink assemblies, titration tables, and other laboratory furniture items. Kewaunee Mfg. Co., 5090 S. Center St., Adrian, Mich. 49221. **615**

Miniature Piping Systems. A 4-page bulletin introduces 2-, 3-, and 4-way microvalves and accessories for the construction of miniature gas-tight piping systems. Hamilton Co., P. O. Box 307, Whittier, Calif. **616**

Column Chromatography. A 4-page Catalog 80A270 illustrates and describes column-type chromatographic equipment. Columns and end fittings as well as column extenders and eluent regulators are included. Fischer & Porter Co., Warminster, Pa. **617**

Radiochemicals. A 26-page catalog lists about 700 radiochemical compounds, a variety of precision reference sources, and describes the company's radioanalytical service. Chemtrac, 33 University Rd., Cambridge, Mass. 02138. **618**

Gas Chromatography Equipment. A 4-page bulletin describes various gas chromatographic supplies including a column packing device, pressure regulators, injection gaskets, etc. Illinois Instrument Group., Inc., 874 Third Ave., Des Plaines, Ill. 60016. **619**

X-Ray Analysis. A 4-page folder titled "X-Ray Analysis-Contemporary Industrial Tool," describes various x-ray analysis methods. Philips Electronic Instruments, 750 South Fulton Ave., Mount Vernon, N. Y. **620**

Pressure Vessels. An 8-page illustrated bulletin (No. 4700) describes small bombs and pressure vessels for general laboratory use. Parr Instrument Co., 211 53rd St., Moline, Ill. **621**

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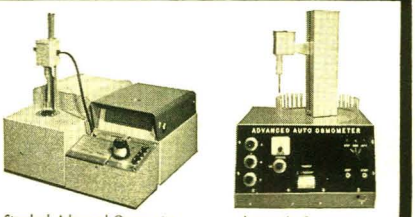

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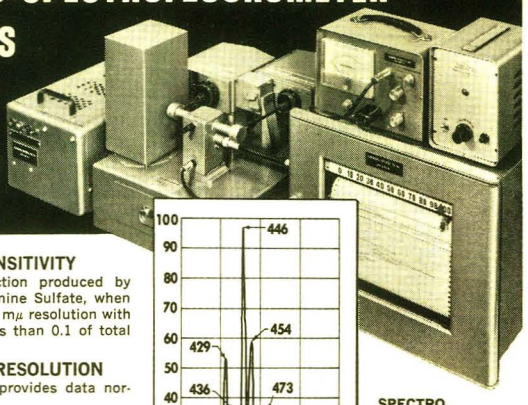

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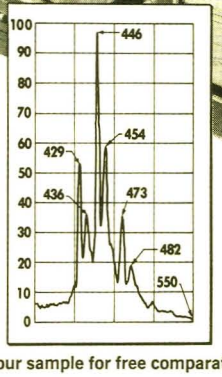

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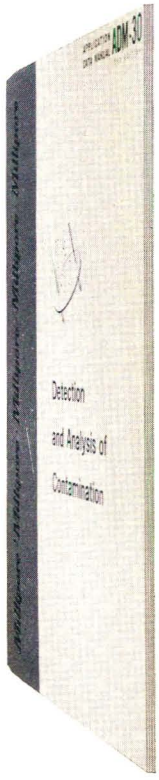

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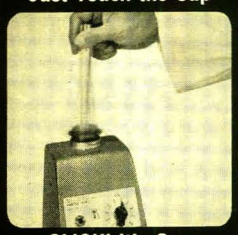

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MANUFACTURERS' LITERATURE

Hall Effect. A 4-page bulletin outlines the characteristics of the company's line of gaussmeters and three special probes—the High field, Magna-Probe, and differential probe and the full line of 12 miniaturized Hall effect devices. F. W. Bell, Inc., 1356 Norton Ave., Columbus, Ohio 43212. **622**

Spectrofluorometer. A 4-page bulletin describes a spectrofluorometer which has resolution to 1 mμ and wavelength accuracy to ± 2 mμ throughout the spectrum. Farrand Optical Co., Inc., Bronx Blvd. and E. 238th St., Bronx, N. Y. 10470. **623**

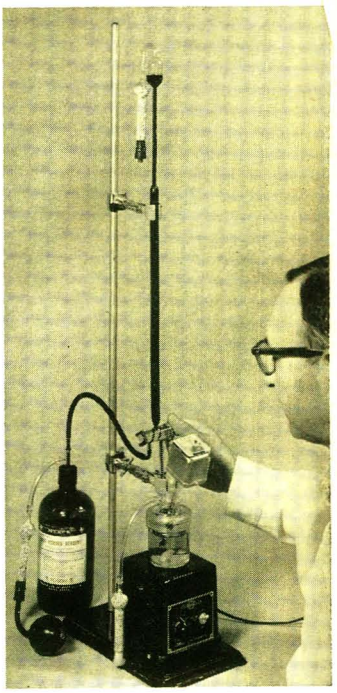
Oscillo Graph Recorders. A 12-page catalog describes 4-, 6-, and 8-channel recorders. All recorders in this line offer direct-carbon-transfer writing method and pen motors without permanent magnets. Esterline Angus Instrument Co., Inc., P. O. Box 24000, Indianapolis, Ind. 46224. **624**

Gas Chromatography Columns. A 4-page product data sheet gives prices and descriptions of custom-made columns and chromatographic packings with various combinations of solid support and liquid substrate. Fisher Scientific Co., 717 Forbes Ave., Pittsburgh, Pa. 15219. **625**

Chromatogram Scanner. A 6-page brochure illustrates and describes 1-channel, 2-channel, wide chart, and built-in integration models of the company's line of automatic chromatogram scanners. Vanguard Instrument Corp., P. O. Box 244, LaGrange, Ill. 60526. **626**

Polarography. A 4-page bulletin describes and illustrates the Mervyn Mark IV square wave polarographic analyzer. This British-made instrument is sensitive to concentrations as low as 1×10^{-8} molar. Matheson Scientific, 1735 N. Ashland Ave., Chicago, Ill. **627**

Testing Equipment. "Selected Listing of Testing and Laboratory Equipment for All Industries," 32 pages, includes 951 testing machines. Categories on physical testing include abrasion, hardness, moisture, impact, tensile, and 64 others. Testing Machines, Inc., 72 Jericho Turnpike, Mineola, L. I., N. Y. **628**



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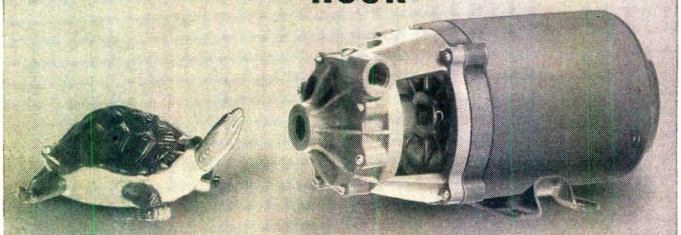

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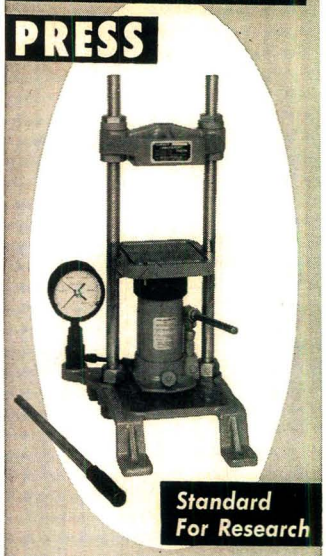

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MAUNFACTURERS' LITERATURE

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Company Periodicals

Requests for copies of the following publications, catalogs, etc., should be sent directly to the address shown. Business or professional letterheads are requested.

Lab-ORATORY. Vol. XXVIII, No. 3. This 16-page issue describes many laboratory items including analytical balances, vacuum ovens, chromatography supplies, ovens, hot plates, freeze drying equipment, etc., Schaar Scientific Co., 7300 W. Montrose Ave., Chicago, Ill.

Atomlight. No. 40. This 16-page issue contains articles on polyamino acids and on the use of tracers in the study of biogenic amine compartments. New labeled chemicals are also introduced in this periodical. New England Nuclear Corp., 575 Albany St., Boston, Mass. 02118.

What's New for the Laboratory. No. 54. This 20-page issue features 9 precision scales and includes a heavy-duty mixer, a laboratory hot plate with Pyroceram top, vacuum oven, automated oxygen analyzer, automatic pipets, plus many other laboratory items. Scientific Glass Apparatus Co., Inc., Bloomfield, N. J.

Barnes Engineering News. The September issue, 4 pages, contains an article which describes how ATR is used to reveal the composition of the adhesives of "sticky tapes." Other company products are discussed. Barnes Engineering Co., 30 Commerce Rd., Stamford, Conn. 06902.

GC Newsletter. Vol. 1 No. 3, This 8-page issue features an article on high speed analysis and also includes articles on simultaneous use of two gas chromatographic detectors, determination of the alcohol content of blood, and a simple method for check-out of an electron capture detector. Perkin-Elmer, Main Ave., Norwalk, Conn.

Cenco International News. Vol. 3, No. 1, This 8-page issue includes information on the company's line of new ovens, vacuum pumps, modular radiation lab, vacuum gauges, analytical balances, and other laboratory equipment. Cenco Instruments Corp., 2205 Lee St., Evanston, Ill. 60202.

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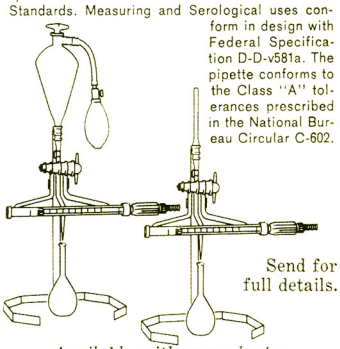

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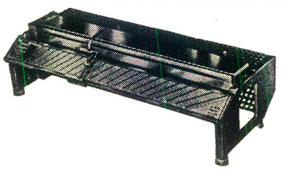

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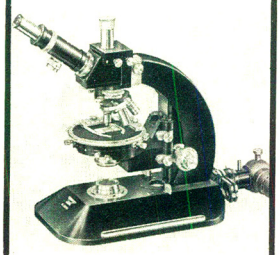

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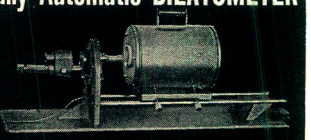

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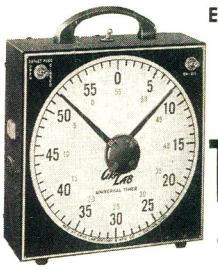

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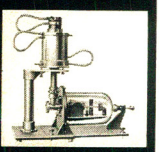

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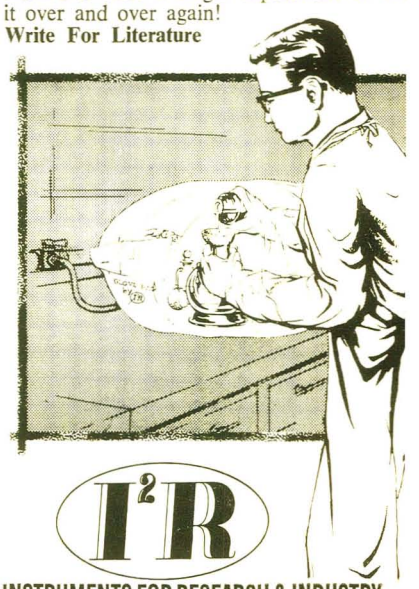

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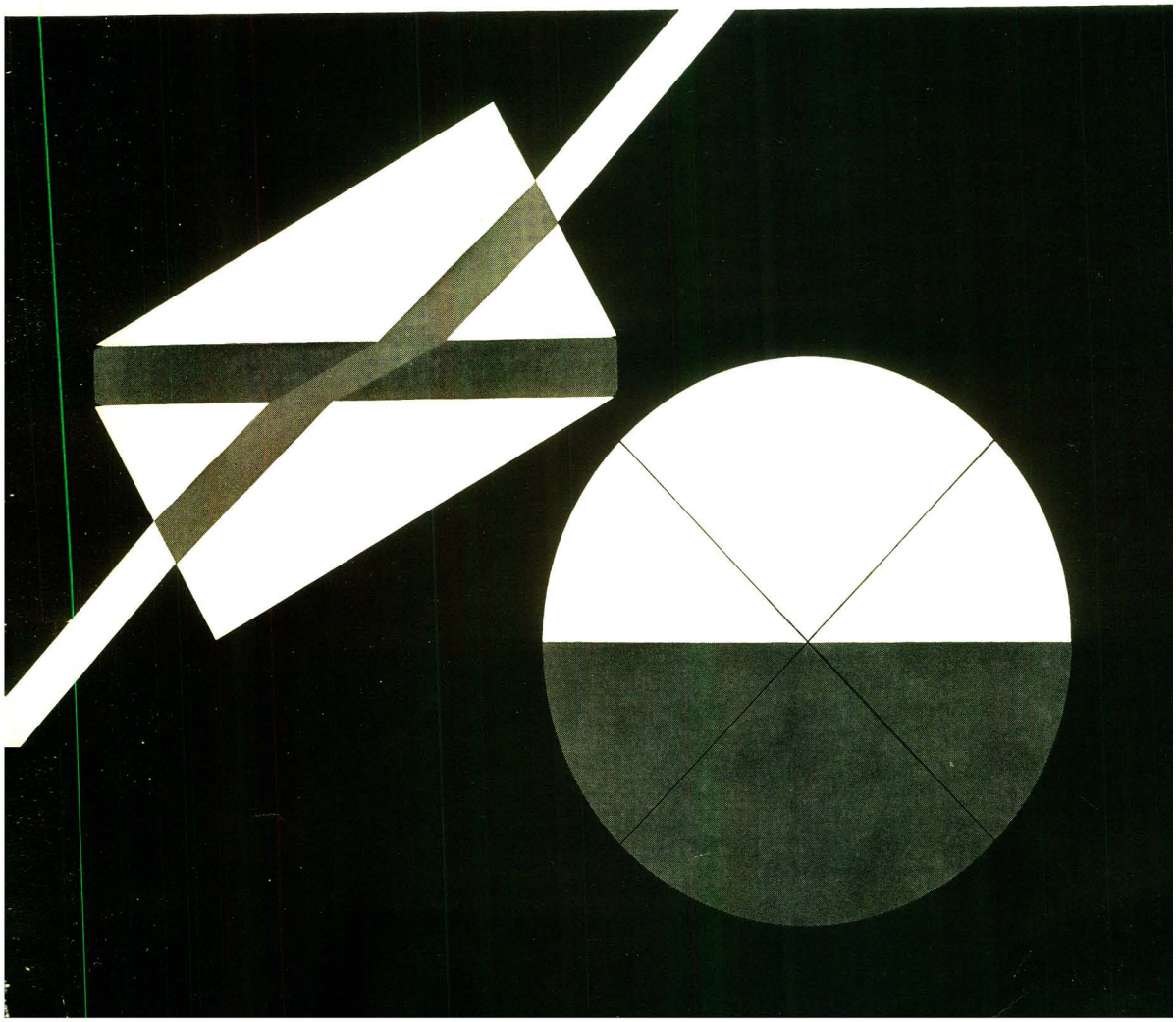

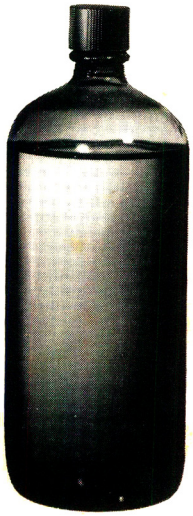

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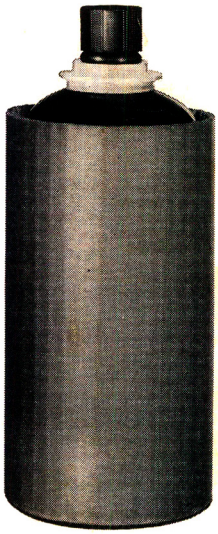

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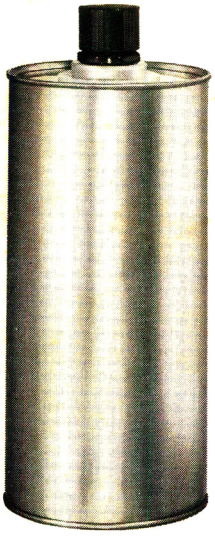

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