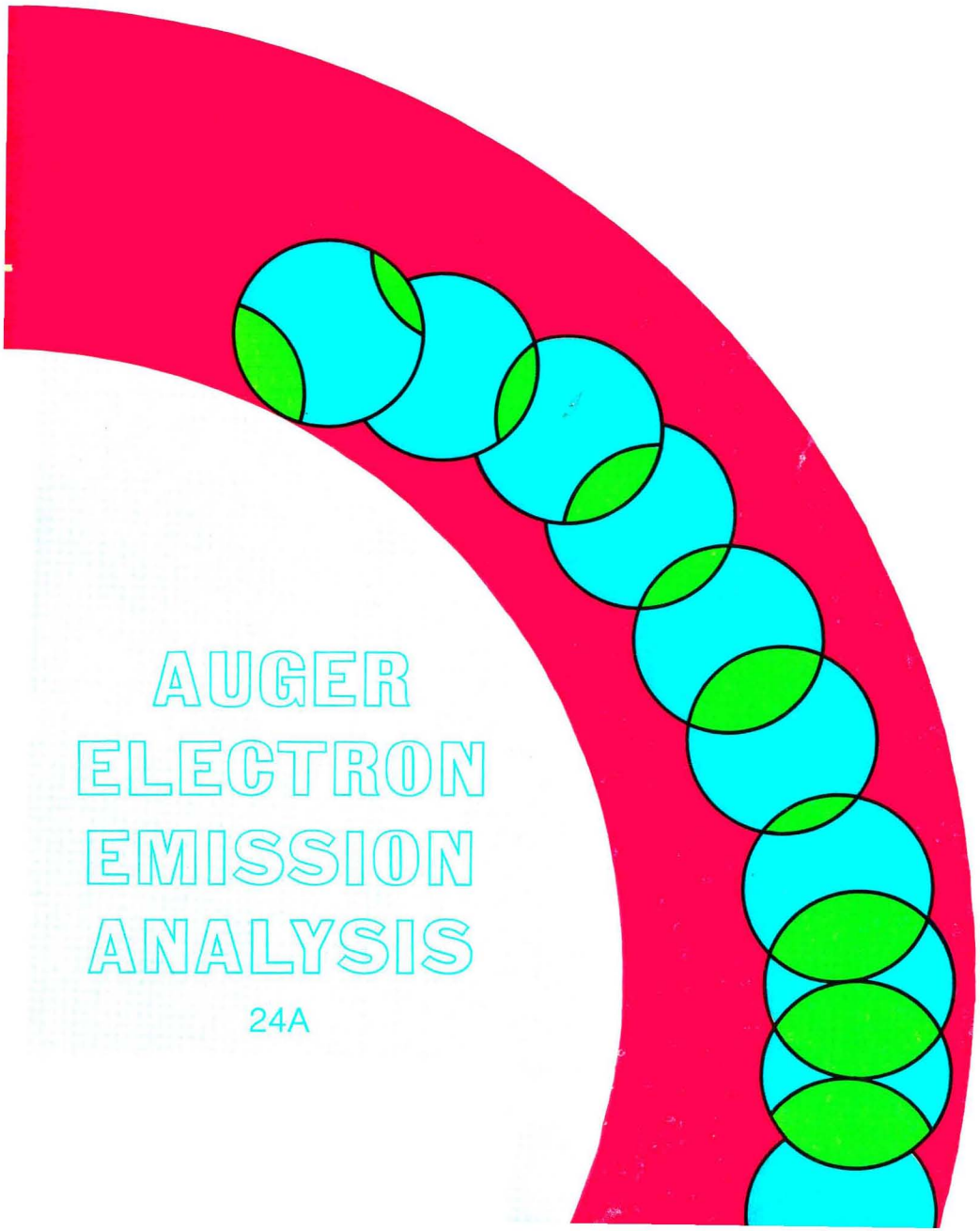
DECEMBER 1968

ANCHAM

ANALYTICAL CHEMISTRY



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24A

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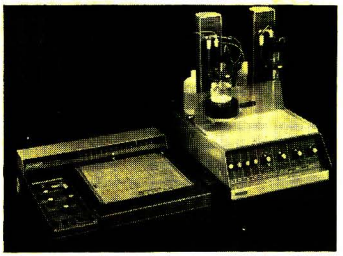
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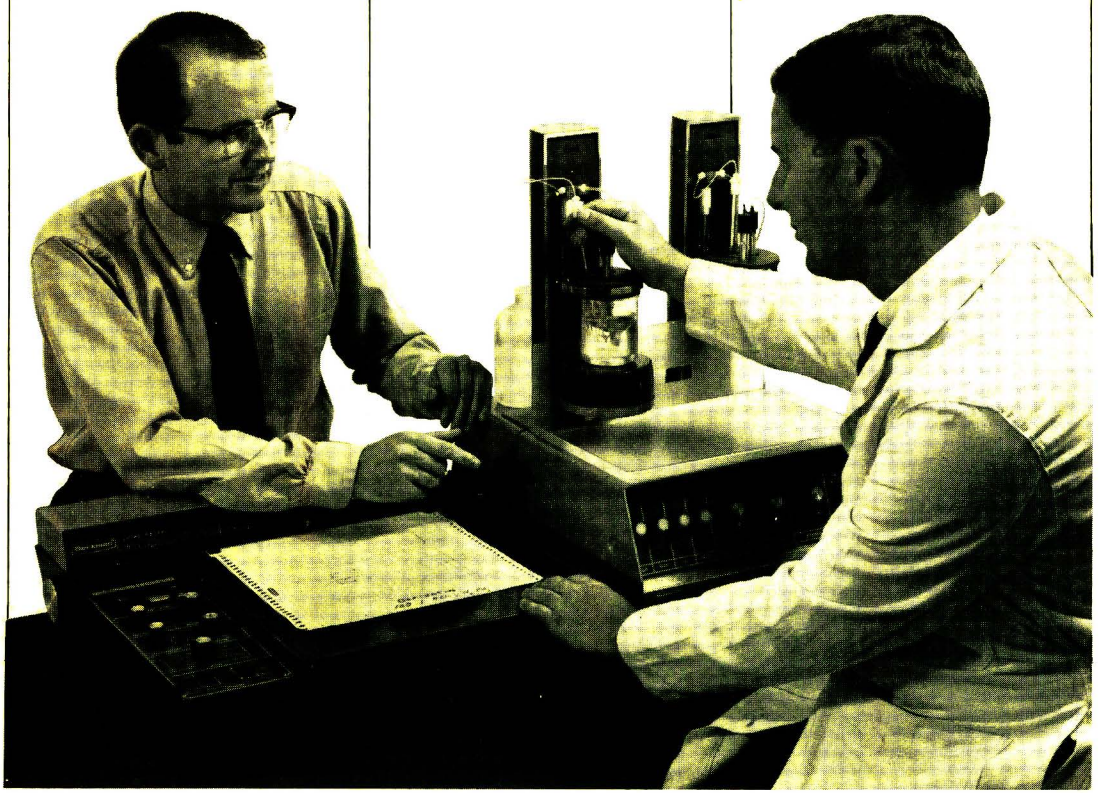
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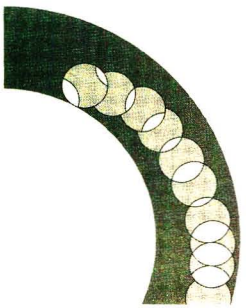
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VOLUME 40, NO. 14 DECEMBER 1968



Our colorful cover illustrates Auger electron emission analysis. For information on this method, see Report for Analytical Chemists, page 24 A.

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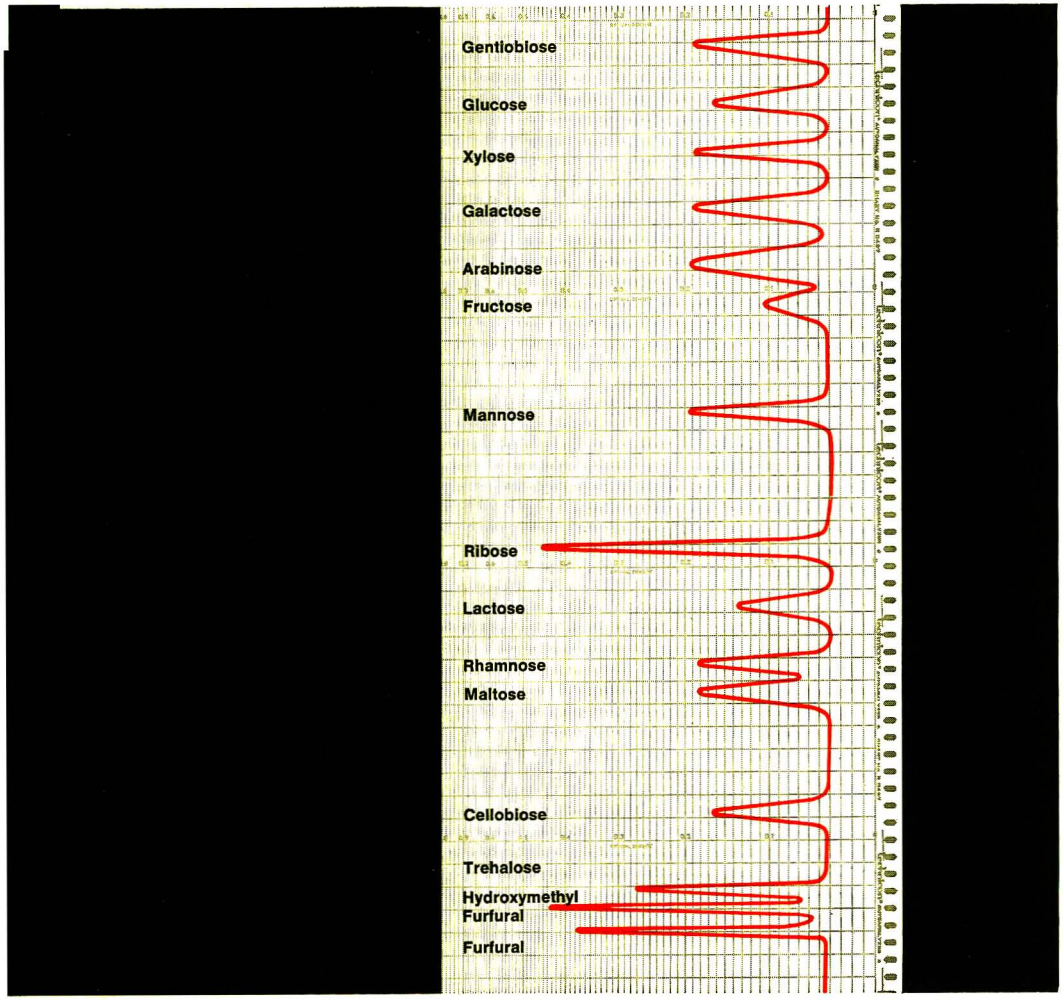
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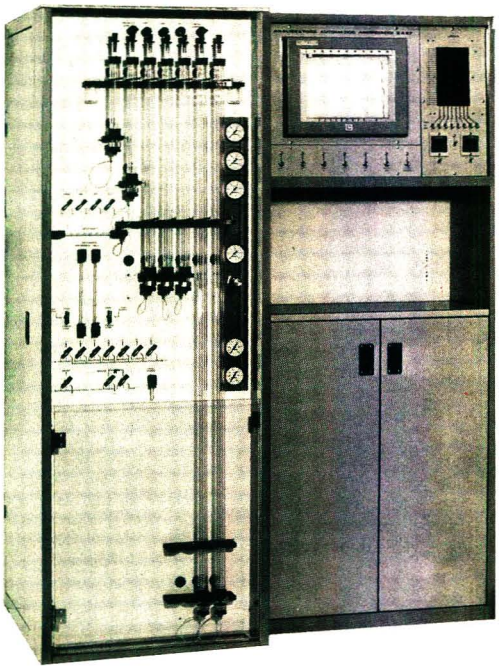
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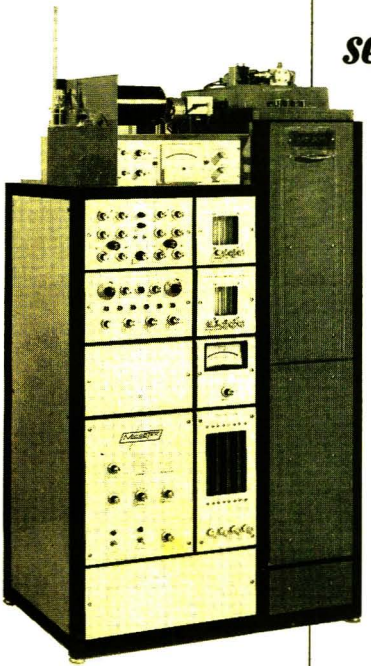
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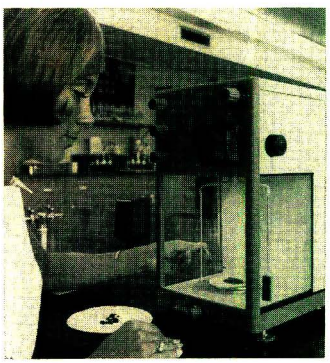
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HIGHLIGHTS OF THE SCIENTIFIC AND TECHNICAL ARTICLES IN THIS ISSUE

Analytical Applications of X-Ray Excited Optical Fluorescence Spectra: The Internal Standard Principle

An internal standardization principle is described that compensates for interference effects caused by impurities present at the ppm level in the host matrix.

EDWARD L. DeKALB, VELMER A. FASSEL, TAKESHI TANIGUCHI, and T. R. SARANATHAN, Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010

Anal. Chem. 40, 2082 (1968)

Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry

A reduction–aeration procedure is employed to produce and introduce mercury vapor into a closed system where the absorption of the 2537 Å line is measured in a quartz windowed cell.

W. RONALD HATCH and WELLAND L. OTT, Falconbridge Nickel Mines Limited, Metallurgical Laboratories, Thornhill, Ontario, Canada

Anal. Chem. 40, 2085 (1968)

Enhancement of Zirconium Atomic Absorption by Nitrogen-Containing Compounds and Its Use in the Determination of Ammonia

Nitrogen-containing compounds acting as Lewis bases enhance the absorption of zirconium in the nitrous oxide–acetylene flame. A practical application is the determination of ammonia in biological material.

A. M. BOND, Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria, Australia 3052, and J. B. WILLIS, Division of Chemical Physics, CSIRO Chemical Research Laboratories, P. O. Box 160, Clayton, Victoria, Australia 3168

Anal. Chem. 40, 2087 (1968)

High Resolution Mass Spectral Photoplate Data Acquired and Reduced with a Real Time Remote Time-Shared Digital Computer

The procedure and the data presented illustrate the accuracy obtained by direct on-line communication between a microdensitometer–comparator system measuring photoplates and a remote digital computer which is involved in decision making during the data acquisition step.

D. M. DESIDERIO JR., and T. E. MEAD, American Cyanamid Co., Stamford Research Laboratories, Stamford, Conn. 06904

Anal. Chem. 40, 2090 (1968)

Photometric Determination of Substances in Presence of Strongly Interfering Unknown Media

The method of changing parameters, which yields results with an accuracy that is dependent upon the precision of the measuring device used, is introduced for the determination of substances in the presence of interfering media.

ADAM SHATKAY, Isotope Department, The Weizmann Institute of Science, Rehovoth, Israel

Anal. Chem. 40, 2097 (1968)

Time Resolution in Spark Source Mass Spectrometry

The electronics necessary for pulse synchronization, instrumental requirements, a method of data reduction, and preliminary results of a study of the time variance of the ion beam emanating from an rf spark source are discussed.

C. A. EVANS, JR., and G. H. MORRISON, Department of Chemistry, Cornell University, Ithaca, N. Y. 14850

Anal. Chem. 40, 2106 (1968)

Studies on the Anion Exchange Behavior of Carboxylic Acids and Phenols

Conclusions are drawn regarding the ion exchange behavior of carboxylic acids and phenols by a study of their sorption by a macroreticular anion exchange resin over a wide range of pH in aqueous–organic solvent mixtures.

JAMES S. FRITZ and AKIRA TATEDA, Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010

Anal. Chem. 40, 2115 (1968)

Copper(II) Oxidation of Thioureas in Acetonitrile

The oxidation of a series of thioureas by copper(II) in acetonitrile and the nature of the intermediates formed in the oxidation process are reported.

DAVID A. ZATKO and BYRON KRATOCHVIL, Department of Chemistry, University of Wisconsin, Madison, Wis. 53706

Anal. Chem. 40, 2120 (1968)

Mixed-Metal Hydroxycarboxylic Acid Complexes. The Chromium(III) Inhibition of the Solvent Extraction of Indium(III)

Hydroxycarboxylic acids both showing and not showing the inhibitory effect of chromium on the extraction of indium are presented, as well as data indicating that complexes of several of these acids with more than one kind of metal can have high stability.

T. W. GILBERT, Chemistry Department, University of Cincinnati, Cincinnati, Ohio, and LEONARD NEWMAN and PAUL KLOTZ, Brookhaven National Laboratory, Upton, N. Y.

Anal. Chem. 40, 2123 (1968)

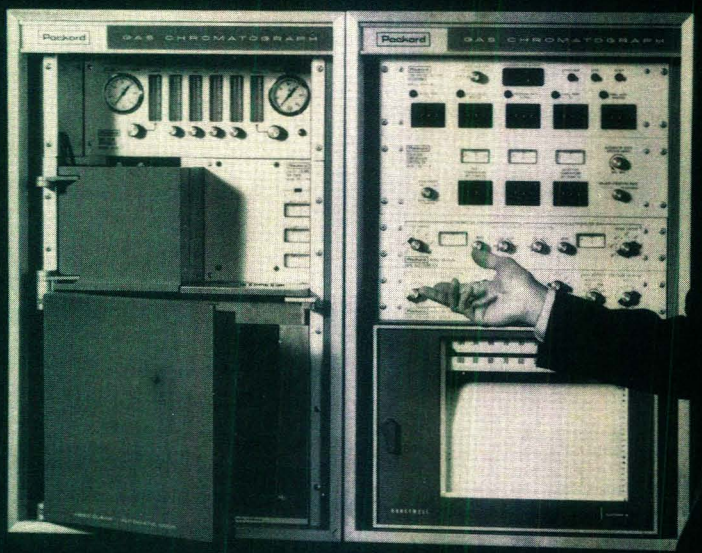
New Extraction Chromatographic Method for Rapid Separation of Americium from Other Transuranium Elements

Extraction chromatography with a Teflon-HDEHP column is used to separate Am(V), obtained through an oxidation–reduction sequence, from Cm(III), other actinide (III, IV, VI) ions, lathanide (III, IV) ions, and other metal ions.

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

Anal. Chem. 40, 2130 (1968)

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Vapor-Programmed Thin-Layer Chromatography, A New Technique for Improved Separations

The apparatus described provides for more efficient control of the vapor processes during development. Closely related substances which are inadequately separated by classical TLC techniques can now be identified through the use of vapor-programmed TLC.

ROKUS A. de ZEEUW, Laboratory for Pharmaceutical and Analytical Chemistry, State University, Antonius Deusinglaan 2, Groningen, The Netherlands

Anal. Chem. 40, 2134 (1968)

2,6-Dichloroquinone-4-Chloroimide as a Reagent for Amines and Aromatic Hydrocarbons on Thin-Layer Chromatograms

A survey of the range of utility of 2,6-dichloroquinone 4-chloroimide is reported. Amines, other nitrogen and oxygen compounds, and hydrocarbons were investigated as well as several chromatographic variables.

JOSEPH H. ROSS, Indiana University, South Bend, Ind. 46615

Anal. Chem. 40, 2138 (1968)

Resolution and Optimization in Gel Filtration and Permeation Chromatography

Included among the factors discussed are plate height and optimum velocity, temperature, and solvent, optimum pore size and retention based on geometric similarity, and examples of resolution as related to molecular size differences.

J. CALVIN GIDDINGS, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Anal. Chem. 40, 2143 (1968)

Visual Titrimetric Determination of Total Reactivity and Differentiation of Trialkylaluminum and Dialkylaluminum Hydride in Mixtures

Aluminum trialkyl and aluminum dialkyl hydride can be determined either in mixtures or separately by titration with pyridine using phenazine as the indicator.

DONALD E. JORDON, Research and Development Department, Continental Oil Co., Ponca City, Okla.

Anal. Chem. 40, 2150 (1968)

Resolution of C_4 to C_{12} Petroleum Mixtures by Capillary Gas Chromatography

The present study determines the resolution of the hydrocarbons which occur in the C_4 to C_{12} portion of nonolefinic petroleum by using a mixture of squalane + Kel-F_{40} as the substrate.

PHILIP MERCHANT, JR., Dow Chemical Co., Pilot Plant Laboratory, Texas Division, Freeport, Texas

Anal. Chem. 40, 2153 (1968)

Rapid Separation by Carbon Number and Determination of Naphthene and Paraffin Content of Saturate Petroleum Distillates up to 185 °C

Type 13X molecular sieve is used for the separation. The influence of temperature and column length has been examined and the conditions necessary for analysis and collection of the separated naphthene and paraffin components have been established.

J. V. BRUNNOCK and L. A. LUKE, The British Petroleum Company Limited, BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, England

Anal. Chem. 40, 2158 (1968)

Pyrolysis-Gas Chromatography of Hydrocarbons

This paper is an attempt to form standard methods for the reporting of PGC data analogous to that used in reporting mass spectra. The results of the vapor phase pyrolysis of 83 different hydrocarbons are reported.

DALE L. FANTER, JOHN Q. WALKER, and CLARENCE J. WOLF, Research Division, McDonnell Douglas Corp., St. Louis, Mo. 63166

Anal. Chem. 40, 2168 (1968)

Improved Techniques for Corrosive Fluoride Gas Chromatography

A column based on fluorocarbon oil, techniques for more sensitive analysis of reactive fluoride compounds, and a stepped-up column arrangement which speeds up an analysis without storage of fractions are described.

W. S. PAPPAS and J. G. MILLION, Laboratory Division, Oak Ridge Gaseous Diffusion Plant, Union Carbide Corp., Nuclear Division, Oak Ridge, Tenn.

Anal. Chem. 40, 2176 (1968)

Electrochemical Reduction of Beta-Diketones in Dimethylsulfoxide

Dibenzoylmethane (DBMH) and other β-diketones are electrochemically reduced with DMSO as the solvent. The acidity of the species formed, the neutral enol, results in complex electrochemical behavior because of the formation of radicals.

RAYMOND C. BUCHTA and DENNIS H. EVANS, Department of Chemistry, University of Wisconsin, Madison, Wis. 53706

Anal. Chem. 40, 2181 (1968)

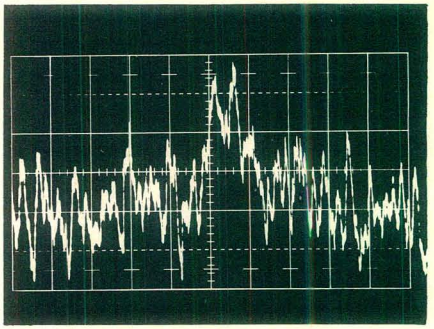
Effect of Static Magnetic Field on Direct Current Polarography

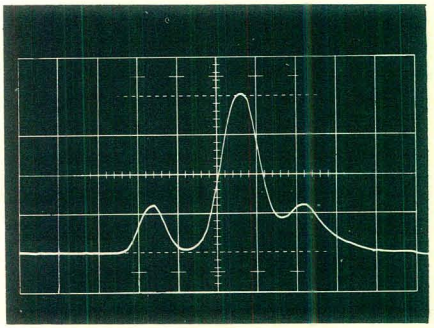
The theory of magnetohydrodynamics is used to explain, in terms of the retardation of tangential motion of the mercury surface, the mechanism of the effect of magnetic field on the second kind of maxima.

SHIZUO FUJIWARA, YOSHIO UMEZAWA, and TERUHIKO KUGO, Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo, Japan

Anal. Chem. 40, 2186 (1968)

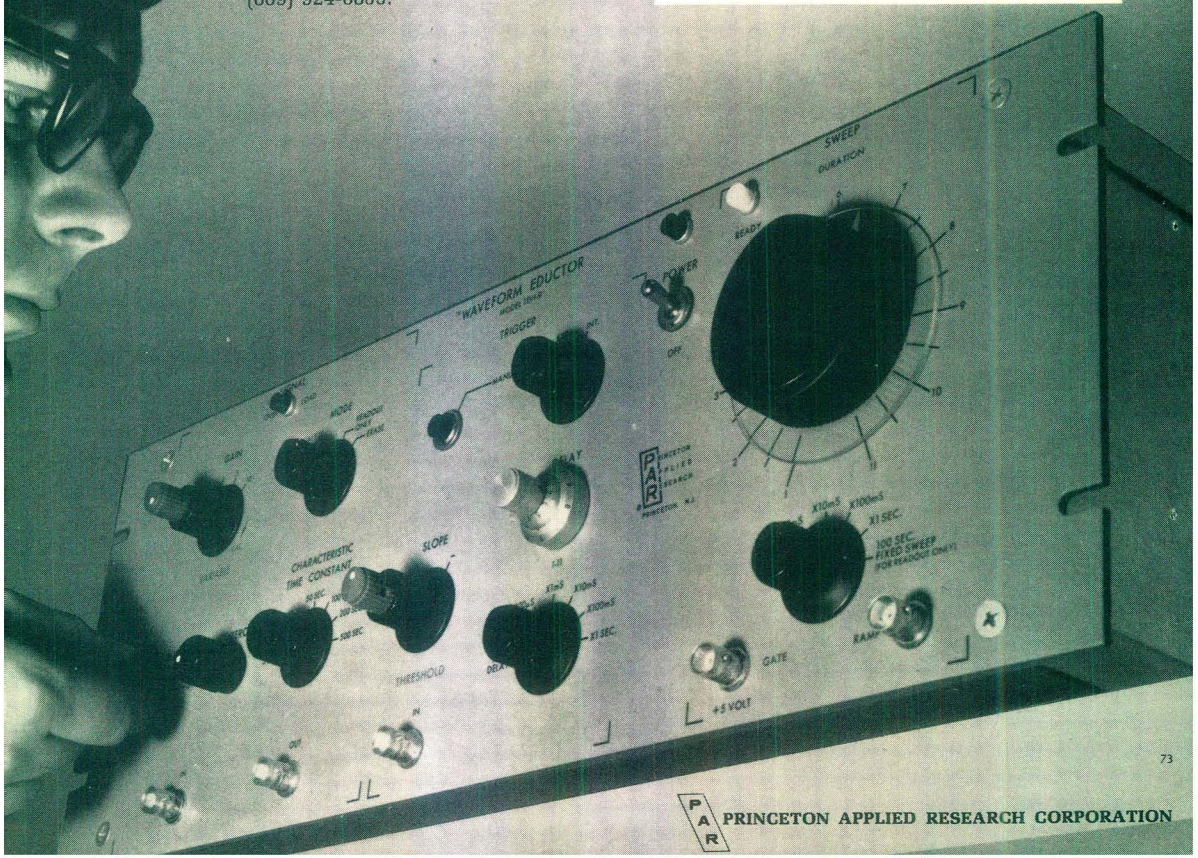
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C. L. GANTT, L. R. KIZLAITIS, D. R. THOMAS, and J. G. GRESLIN, Clinical Research Center, Department of Medicine, University of Illinois College of Medicine, Chicago, Ill. 60612

Anal. Chem. 40, 2190 (1968)

Separation of Paraffinic Classes in Petroleum Distillates on a Cross-Linked Dextran

The Sephadex LH-20 separation of branched paraffins from cycloparaffins is extended to wide-range petroleum fractions. Three other separations were also found to occur: condensed from noncondensed cycloparaffins, condensed cycloparaffins according to the number of rings, and separation of branched paraffins according to carbon number.

P. C. TALARICO, E. W. ALBAUGH, and R. E. SNYDER, Gulf Research & Development Co., Pittsburgh, Pa.

Anal. Chem. 40, 2192 (1968)

Quantitative Determination of Organic Halides in Dimethylsulfoxide

Organic halides are determined quantitatively by making use of their rapid reaction with base in DMSO. The excess base is determined by the Volhard method or by titration with standard acid.

JOE A. VINSON and JAMES S. FRITZ, Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010

Anal. Chem. 40, 2194 (1968)

Determination of Trace Copper in Petroleum Middle Distillates with Cuprizone

Copper is determined colorimetrically after complexing and extracting it with bicyclohexanone oxaldihydrazone. Methanol or another polar solvent is used for the extraction.

C. E. LAMBDIN and W. V. TAYLOR, Research and Technical Development, Texaco, Inc., P. O. Box 1608, Port Arthur, Texas 77640

Anal. Chem. 40, 2196 (1968)

Volumetric Determination of Alcohols in Aqueous Solution with Bromine Chloride

Micro amounts of either a primary or secondary alcohol in an aqueous solution can be determined quantitatively by oxidizing the alcohol with bromine chloride and titrating the excess bromine chloride iodometrically.

KAZUO KONISHI, YOSHIHIRO MORI, HIROH INOUE, and MACHIKO NOZOE, Industrial Research Laboratories, Kao Soap Co., Ltd., 1334 Minatoyakushubata, Wakayama-shi, Japan

Anal. Chem. 40, 2198 (1968)

Quantitative Analysis of Amines *via* Amine Boranes

The method involves treatment of an amine with an excess, but measured volume, of a standardized solution of diborane in tetrahydrofuran. Excess diborane is decomposed by the addition of water or alcohol, and the liberated hydrogen is measured.

ROBERT E. LYLE and EVERETT W. SOUTHWICK, Department of Chemistry, University of New Hampshire, Durham, N. H. 03824

Anal. Chem. 40, 2201 (1968)

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Chemical Microscopy of 10-Methylacridiniumchloride. Reactions with Platinum Metals and Gold

The addition of a 0.2*M* solution of 10-methylacridiniumchloride in 1*M* HCl to acid solutions of the chlorides of several precious metals at low concentrations causes the separation of micro crystals of characteristic shapes and optical properties.

HAROLD F. SCHAEFFER, Department of Chemistry, Westminster College, Fulton, Mo. 65251

Anal. Chem. 40, 2202 (1968)

Submicro Sampling and Solvent Extraction System for Rapid Gas Chromatographic Determination of Blood Alcohol

The sampling procedure used in this study is based upon the Unopette sampling system. Many of the cumbersome manipulative steps associated with sample preparation for gas chromatographic analysis are eliminated by using this procedure.

RONALD H. LAESSIG, Department of Preventive Medicine, State Laboratory of Hygiene, University of Wisconsin, Madison, Wis.

Anal. Chem. 40, 2205 (1968)

Determination of Amphetamine by Ultraviolet Spectrophotometry

Cerium oxidation of amphetamine in aqueous HCl results in a hexane soluble product which absorbs ultraviolet radiations. The procedure is specific for the β-phenylethylamine group.

JACK E. WALLACE, JOHN D. BIGGS, and SHELDON L. LADD, Forensic Toxicology Branch, USAF Epidemiological Laboratory, Lackland Air Force Base, Tex. 78236

Anal. Chem. 40, 2207 (1968)

Spectrophotometric Determination of Microgram Amounts of Tantalum with Victoria Blue B

Tantalum forms a ternary ion-associated complex with Victoria Blue B and fluoride in hydrofluoric acid–sulfuric acid medium. The complex is extracted into benzene and the tantalum determined spectrophotometrically.

G. F. KIRKBRIGHT, M. D. MAYHEW, and T. S. WEST, Chemistry Department, Imperial College, London, S.W. 7, England

Anal. Chem. 40, 2210 (1968)

Determination of Bisphenol A and Impurities by Gas Chromatography of Their Trimethylsilyl Ether Derivatives

Bisphenol A and the major, high-boiling impurities in bisphenol A are reacted with bis(trimethylsilyl)acetamide to form the corresponding trimethylsilyl ether derivatives which are analyzed gas chromatographically by using a flame ionization detector.

L. E. BRYDIA, Chemicals and Plastics, Union Carbide Corp., Bound Brook, N. J. 08805

Anal. Chem. 40, 2212 (1968)

Indirect Spectrophotometric and Atomic Absorption Spectrometric Methods for Determination of Thiocyanate

These methods, for the determination of 0.1 to 15 ppm of thiocyanate, are based on the formation of the dithiocyanatodipyridine copper(II) complex which is extractable with chloroform.

RICHARD S. DANCHIK and D. F. BOLTZ, Department of Chemistry, Wayne State University, Detroit, Mich. 48202

Anal. Chem. 40, 2215 (1968)



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Electroanalytical Determination of Molecular Fluorine in the Atmosphere

An instrument is described for measuring the concentration of atmospheric fluorine. The measurement is accomplished coulometically when air is bubbled into a lithium chloride solution containing a silver anode and platinum cathode.

SAMUEL KAYE and MICHAEL GRIGGS, General Dynamics Convair, San Diego, Calif.

Anal. Chem. 40, 2217 (1968)

Correspondence

An Alternative Combustion Technique for Tritium Scintillation Counting

T. H. VICKERS, Krebsforschungsinstitut der Universität, 1090 Wien, Austria

Anal. Chem. 40, 2219 (1968)

Automated Structure Elucidation of Several Kinds of Aliphatic and Alicyclic Compounds

SHIN-ICHI SASAKI, Miyagi University of Education, Aoba, Sendai, Japan, HIDETSUGU ABE, Department of Chemistry, Tohoku University, Katahira, Senadi, Japan, TATSUMI OUKI, MASAYOSHI SAKAMOTO, and SHUKICHI OCHIAI, Japan Electron Optics Laboratory, Akishima, Tokyo, Japan

Anal. Chem. 40, 2220 (1968)

Aids for Analytical Chemists

Simple Tuning Device for Microwave Tapered Matching Cavity

CARL A. BACHE and DONALD J. LISK, Pesticide Residue Laboratory, Cornell University, Ithaca, N. Y. 14850

Anal. Chem. 40, 2224 (1968)

Simplified Method of Preparing Column Materials for Gas–Liquid Chromatographic Separation of Some Pesticides

C. E. MENDOZA, K. A. McCULLY, and P. J. WALES, Research Laboratories, Food and Drug Directorate, Department of National Health and Welfare, Ottawa 3, Ontario, Canada

Anal. Chem. 40, 2225 (1968)

Calibration of the Methanol and Glycol Nuclear Magnetic Resonance Thermometers with a Static Thermistor Probe

ANTHONY L. VAN GEET, Department of Chemistry, State University of New York, Buffalo, N. Y. 14214

Anal. Chem. 40, 2227 (1968)

Use of a Primary Beam Filter in X-Ray Fluorescence Spectrometric Determination of Trace Arsenic

JOHN T. GILMORE, Chevron Research Company, Richmond, Calif.

Anal. Chem. 40, 2230 (1968)

Determination of Trace Contaminants in Air by Concentrating on Porous Polymer Beads

FREDERICK W. WILLIAMS and MERLE E. UMSTEAD, Fuels Branch, Chemistry Division, Naval Research Laboratory, Washington, D. C. 20390

Anal. Chem. 40, 2232 (1968)

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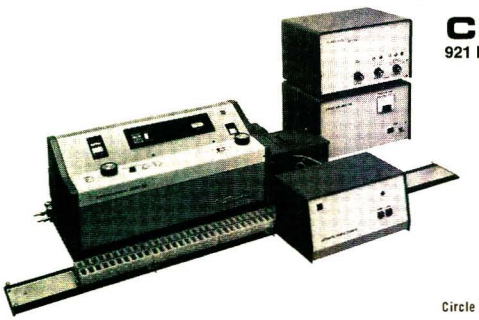
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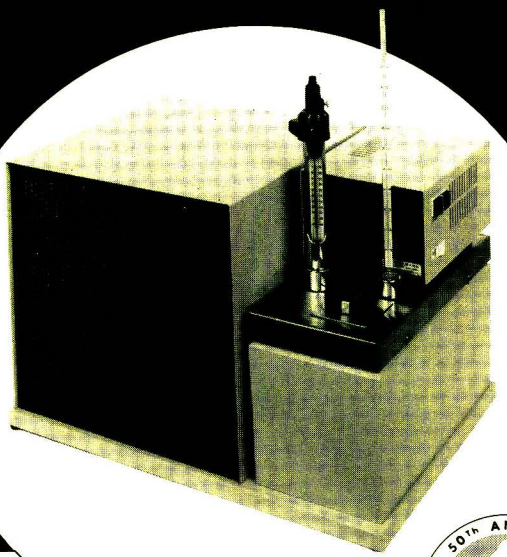


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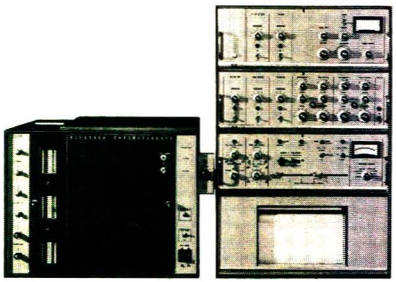
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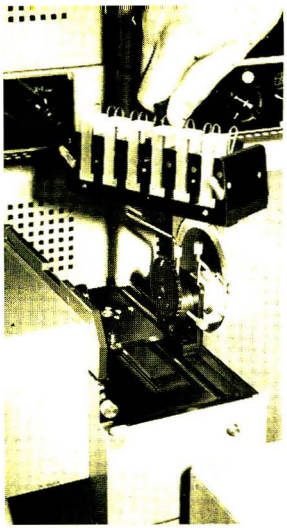
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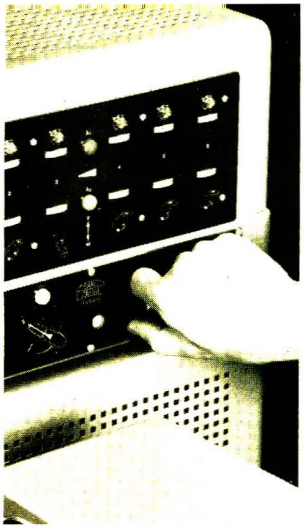
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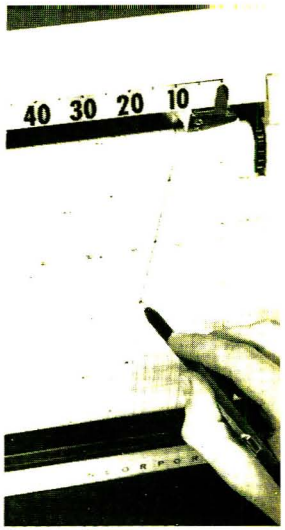
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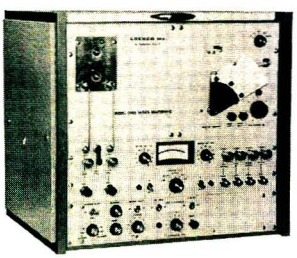
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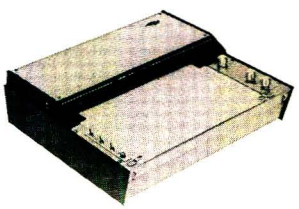
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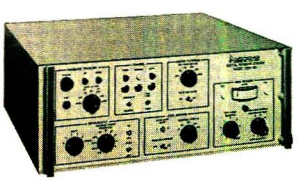
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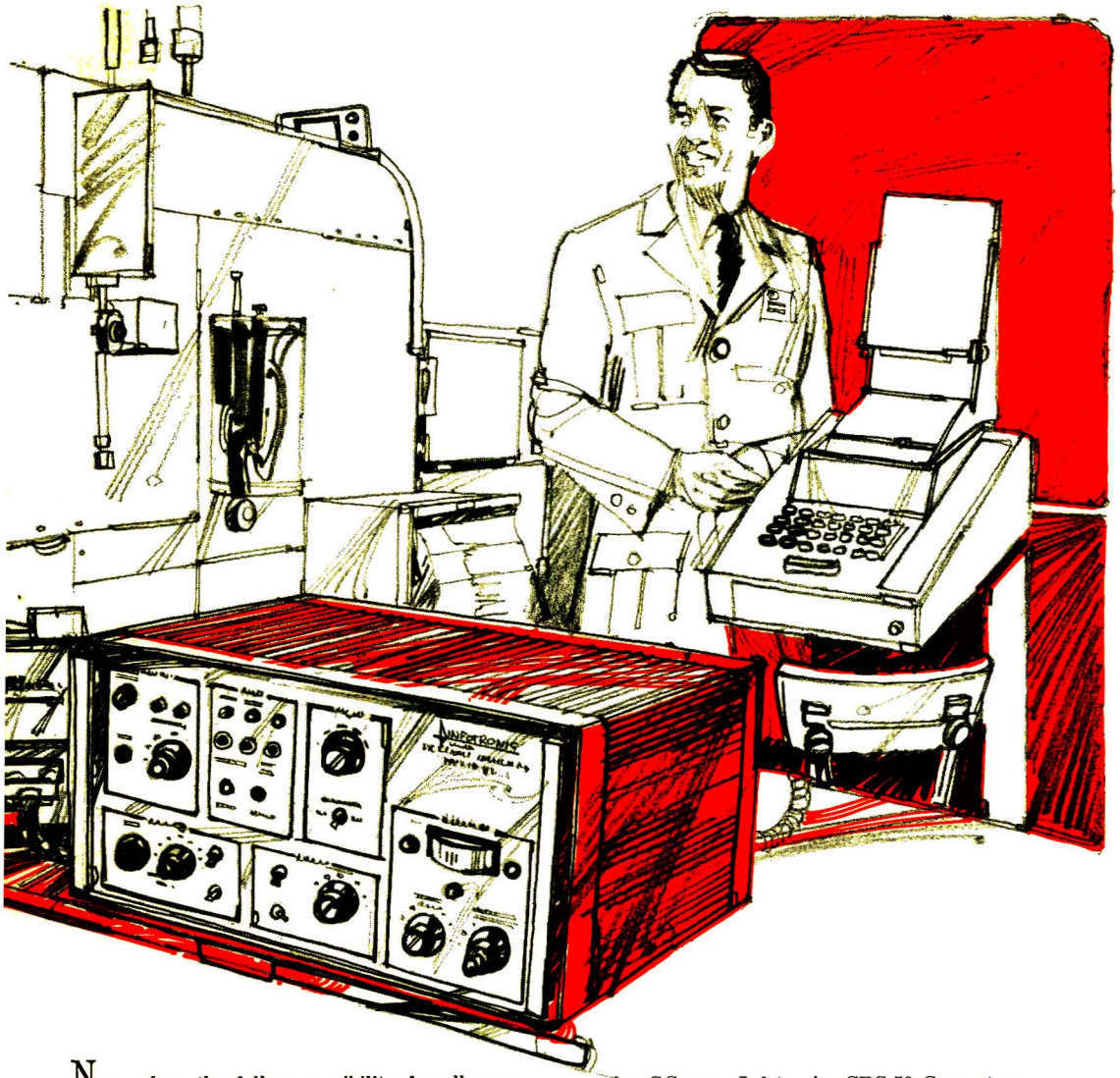
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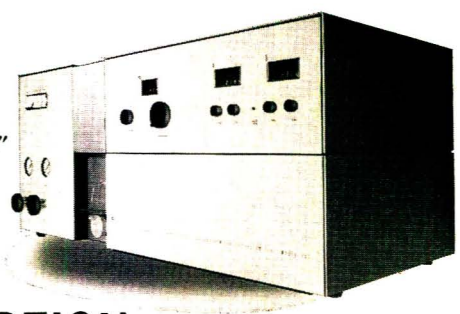
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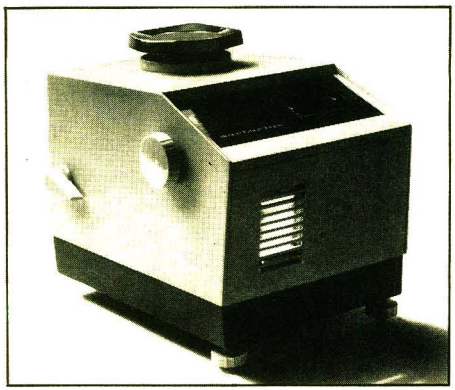
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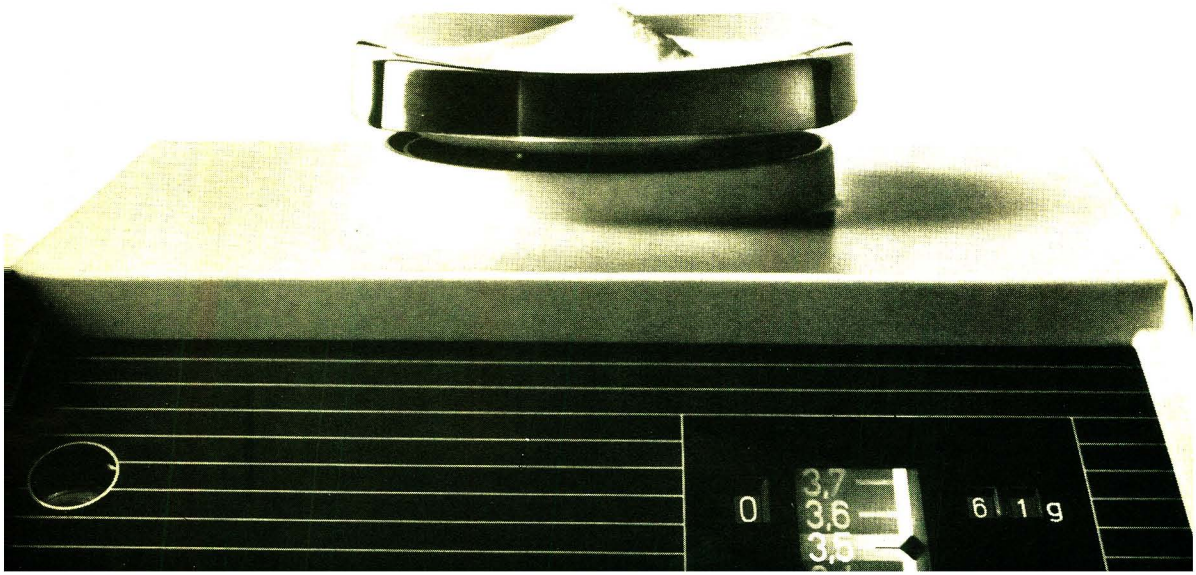
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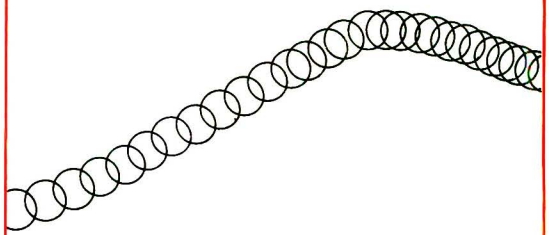
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AUGER ELECTRON EMISSION ANALYSIS

Lawrence A. Harris
Research and Development Center
General Electric Company
Schenectady, New York



ANALYTICAL SCIENTISTS are becoming increasingly aware of the advantages, usefulness, and potential applications of various forms of electron spectroscopy, especially in the area of surface analysis. Recent articles in this journal, for example, have noted the advantages of low energy electron diffraction (LEED) (*1*) and electron spectroscopic chemical analysis (ESCA) (*2*). The latter method of particle spectroscopy is closely related to the method discussed here, with the exception that X-ray excitation produces photoelectric as well as Auger emission of electrons.

Auger electrons, with energies characteristic of the emitting atom, have been known for quite some time (*3–6*), but it has only been recently that dramatic steps have been taken to move spectroscopic detection of the electrons, with a concomitant indication of the elements associated with various peak energies, toward a reliable analytical procedure.

The Auger electron spectroscopic procedure described herein possesses several real advantages:

- Light elements are more readily detected
- Equipment required is of modest size and cost
- The method is nondestructive
- Extremely thin layers on the surface of solids can be detected
- The method is sensitive

On the other side of the coin, the method requires a vacuum and freedom from organic material contamination, and detection of heavier elements becomes difficult. However, since X-ray methods are available for the heavier elements, this last disadvantage does not detract from the overall usefulness of the method, and Auger electron emission should take its place among the sensitive methods for elemental detection (and quantitative determination, as improvements are made).

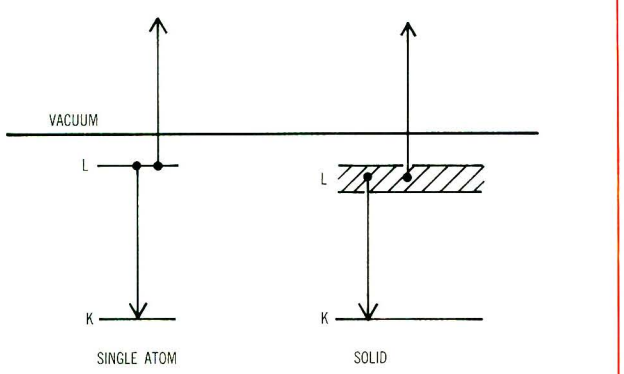


Figure 1. Schematic of the Auger process

The Method

Figure 1 shows, in a simplified schematic way, the essential nature of the Auger process with which we are concerned. We postulate that an atom has been ionized in one of its inner shells, either by electron or photon irradiation. The excited atom rearranges itself by filling the ionized shell with an electron from a higher energy orbit and by releasing the energy of the transition. This energy may be carried off either by a photon or by another electron, the Auger electron. In either case the energy released is characteristic of the parent atom and may be used to identify it.

X-ray fluorescence has been a standard method of analysis for a long time, but the probability of

X-ray emission from an excited atom, that is the x-ray fluorescence yield, decreases sharply as the atomic number drops. This makes X-ray analysis of light elements more difficult than for heavier elements. However, the drop in fluorescence yield implies a corresponding rise in the Auger yield, so that it seems reasonable to look at the energy distribution of emitted electrons when light elements are involved (and for other elements, too, since Auger electron emission is a comparatively high probability process). The presence of peaks in the distribution at certain characteristic energies implies the presence of the corresponding atoms in the emitting material. This is a form of particle spectroscopy, which we have called *secondary electron spectroscopy*. Although the principle is not new, until very recently it has received little attention except for the work of the Swedish group under Siegbahn (*2, 7*), and that of Burton Henke in this country.

To observe the Auger peaks in the secondary electron distribution, we must excite the material, sort the secondaries according to energy, and detect them. The arrangement used to do this is shown in Figure 2. This is basically the same scheme as that used by Lander, Harrower, and others, but our equipment uses a 127° electrostatic analyzer and an electron multiplier to compensate for the small fraction of secondaries sampled by the analyzer. A multiple sample holder is incorporated for experimental convenience.

The electrons are sorted according to energy by slowly sweeping the deflection voltage applied to the curved analyzer plates. This type of analyzer has a narrow energy "window" which is swept across the energy range of interest, and which broadens linearly with the energy location of the "window."

Figure 3 shows three typical distribution curves obtained in this way from a beryllium sample, using three different primary energies.

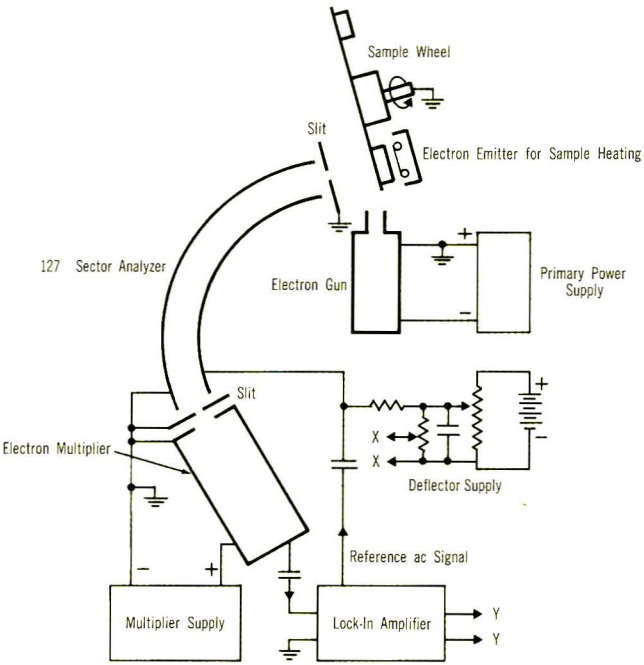


Figure 2. Apparatus used for measuring Auger emission

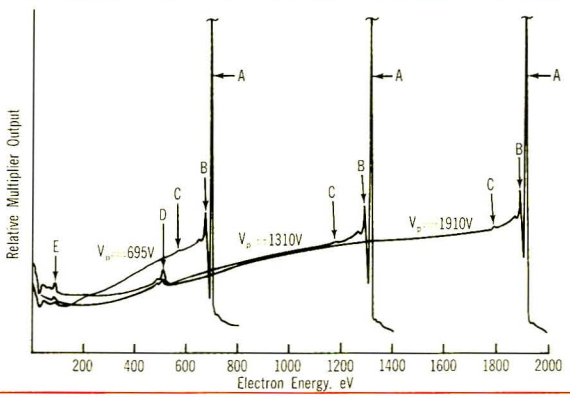


Figure 3. Energy distribution curves for a beryllium sample (three different primary energies)

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The high sharp peaks, labeled A, are reflected primary peaks. They were used as convenient calibrations for the horizontal energy scale. The peaks labeled B and C are due to plasma losses and interband transitions and are thus spaced fixed energies below the primary energy. The peaks labeled D and E, which occur at energies independent of primary energies, are the Auger peaks for oxygen and beryllium, respectively. These are the peaks in which we are most interested.

It is noted that the expected large peak in the distribution due to slow secondaries has been suppressed. This was done by not accelerating the secondaries between the sample and the first dynode of the multiplier, so that slow electrons generate few secondaries at the first dynode. Even with this suppression of an important part of the background, it is evident that the Auger peaks are small bumps on quite a large background and are, therefore, difficult to detect and characterize with accuracy. To make the Auger peaks more prominent with respect to the slowly varying background, we obtained the derivative of the distribution curve with respect to energy.

Figure 2 also shows the circuit devised to take the derivative electronically. An ac signal from the lock-in amplifier is superimposed on the slow dc sweep of the analyzer deflection plate voltage. The corresponding fluctuations in the output of the electron multiplier are fed back to the lock-in amplifier, where they are correlated with the perturbing signal, and the filtered output is recorded. This output signal is proportional to the slope or derivative of the energy distribution curve.

Of course, other analyzer arrangements can be used for Auger analysis. In particular, it has been demonstrated by others that low energy electron diffraction apparatus with spherical grids lends itself well to this purpose.

The advantage gained by differentiating is illustrated in Figure 4, which shows the distribution and the derivative. The background is

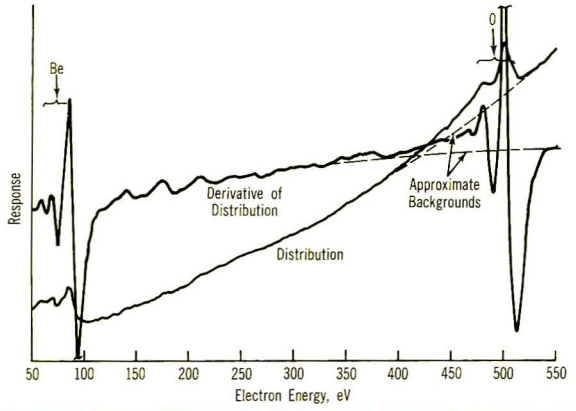


Figure 4. Energy distribution curve and derivative of the curve for a beryllium sample

(Courtesy Journal of Applied Physics)

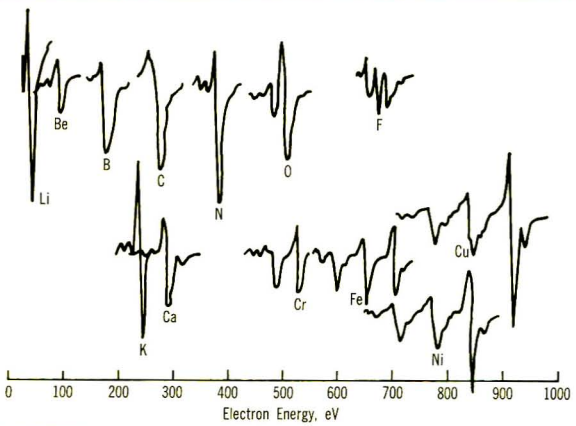


Figure 5. Differentiated Auger lines for typical light elements

flattened considerably in the derivative curve and the more rapidly varying Auger peaks stand out distinctively enough to show their structure.

Typical Auger Patterns

Typical Auger lines from various elements, as they appear in differentiated form, are shown in Figure 5. This composite of a number of Auger lines for various elements shows shapes and positions on the energy scale, although amplitudes are not in any definite relation to each other. In the top row are the single, well separated lines of the lighter elements. These lines are due to *KL* transitions and correspond quite nicely with tabulated X-ray energies. There are, however, some minor differences due to the energy Auger electrons must lose in escaping from the material, and the Auger lines are relatively broad because of the double uncertainty of the origins within a band

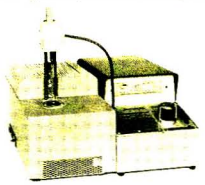
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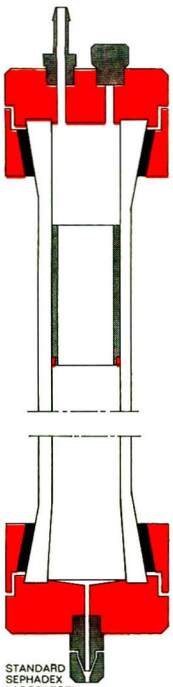
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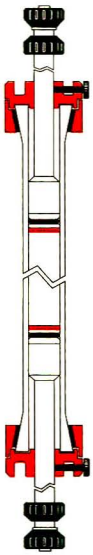
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of both the downward and upward electrons involved in the Auger process.

The spectra of a number of somewhat heavier elements appear in the lower row. These lines are due to *LM* transitions and also tend to correlate with X-ray energies, but some lines are beginning to appear which the selection rules for photon emission forbid. The selection rules must be relaxed for the radiationless Auger process. As the atomic number increases, the spectra become more complex and overlapping occurs, for example, between the copper and nickel spectra. The growing complexity in the spectra, which reflects the growing complexity of the atomic subshell structure, is shown in Figures 6-8. These spectra are for germanium, molybdenum, and tungsten with iron and carbon impurities.

Information on location of Auger peaks is summarized in Figure 9. Virtually all the elements have readily identifiable features between 50 and 1000 eV because the various possible transitions tend to overlap in this range. Although Auger analysis is most effective and easiest for the light elements, it can also be used for heavy elements. In this case, because of the extra lines not tabulated in X-ray data, empirical determinations must be made from previously recorded

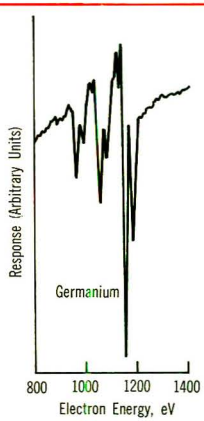


Figure 6. Auger spectrum for germanium

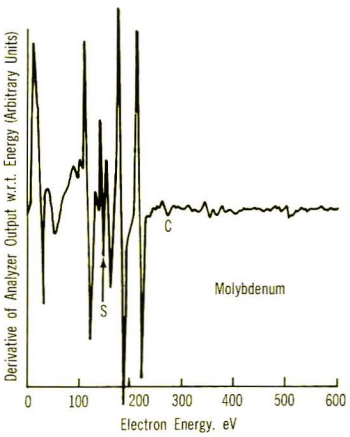


Figure 7. Auger spectrum for molybdenum

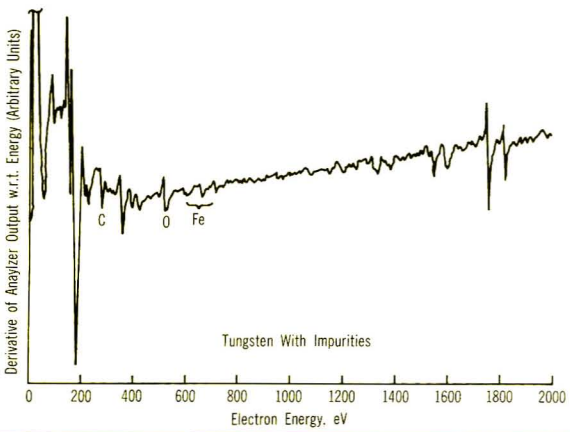


Figure 8. Auger spectrum for tungsten with impurities

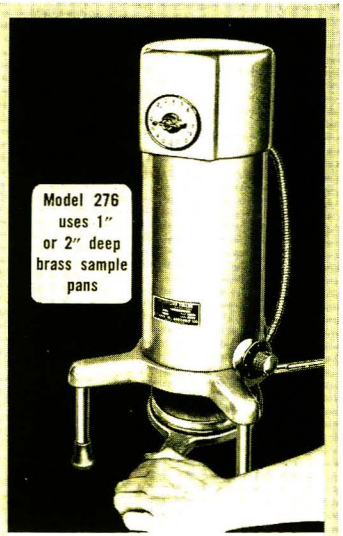
spectra of known materials. It is appropriate to explore other questions regarding Auger determinations: Is the measurement a quantitative one, how sensitive is it, how deep is the examined layer, and what are possible applications?

Surface Studies

It is expected that Auger electrons observed by this method must originate within relatively few atomic layers of the surface.

While the primary beam may excite Auger emission deeper within the material, it is highly unlikely that these electrons could escape without some scattering, thereby losing their identity as part of an Auger peak. In fact, it is found that extremely superficial layers of one material on a surface may completely hide the Auger emission from the substrate beneath. One example which occurred in the very beginning of this work was the prevalence of a large carbon peak in all measurements made in a presumably well trapped oil-pumped

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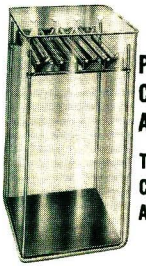
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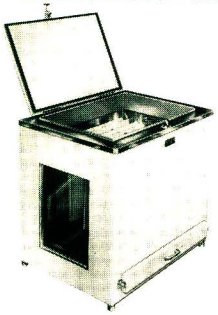


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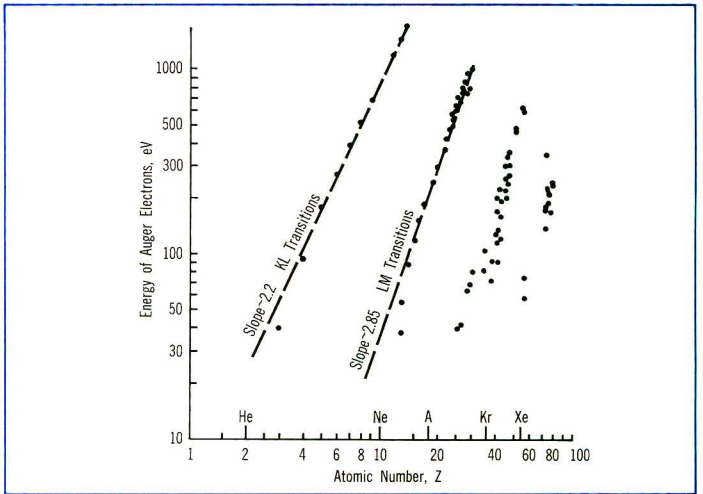


Figure 9. Maximum negative derivatives of Auger electron energies plotted against atomic numbers
(Courtesy Journal of Applied Physics)



LAWRENCE A. HARRIS *was born in Toronto in 1923. He received a B.A.Sc. from the University of Toronto (1946) and S.M. and Sc.D. degrees from M.I.T. (1948 and 1950, respectively). He taught electrical engineering at the University of Florida (1950–51) and was on the faculty of the University of Minnesota from 1951 to 1955. Since 1956 Dr. Harris has been a physicist at the Research and Development Center of General Electric Company in Schenectady, New York.*

system. The characteristic features of a beryllium substrate were barely visible only after argon sputtering of the sample to remove the organic layer (*8*). Successive runs were taken after sputtering, and it was revealed that a buildup of carbon or polymer had taken place under the electron beam. After these tests, there was no visible evidence of these layers on the samples, so the surface layer could not have been more than a few tens of angstroms thick. This rather indirect evidence is confirmed by many other indirect results. Recent work by Palmberg and Rhodin (*9*) at Cornell University has put this estimate of observed depth at a few atomic layers.

Quantitative Determinations

Sensitivity to surface conditions has caused great difficulty in establishing quantitative measures of the method's sensitivity. Since specimen preparation techniques such as chemical etching, sputtering, and heating commonly cause the surface concentrations of impurities to differ from those in the bulk, it is difficult to characterize a two component surface without some other independent technique.

It is here that Weber and Peria (*10*), by combining LEED measurements with Auger analysis, have established a clear measure of sensitivity and, indeed, have established that the measurement is quantitative. As a result of this work it is known that as little as one or two per cent of a monolayer of one species on another can be detected.

Before this had been established, we had suspected sensitivities in this range, again on the basis of indirect evidence. For example, we could detect the difference in carbon between a sample of electrolytic iron and one known to have 40 ppm of carbon. Since both samples underwent the same rather violent cleaning treatments, we cannot say that the surface carbon concentration truly corresponded to the known bulk concentration. Additional insight to the sensitivity of the method is provided by some of the following applications.

Applications

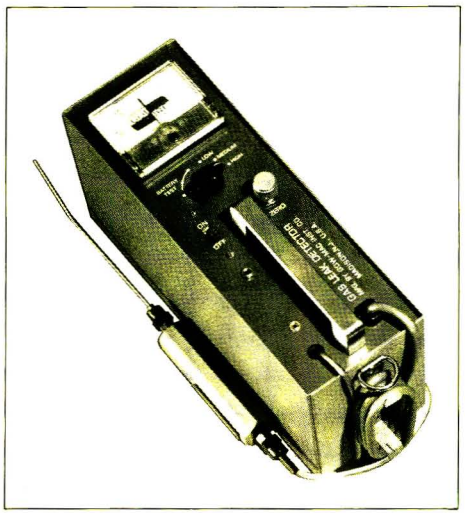
Certainly, one of the most obvious applications of a sensitive technique of surface analysis is the identification of contaminants on surfaces. Figure 8 illustrates that the tungsten spectrum also had carbon and iron lines present. That spectrum was taken from a tungsten anode of an X-ray tube known to have contaminants. However, these impurities had previously defied identification by the more common methods, and identification of the impurities by secondary electron spectroscopy led to changes in the preparation of the material.

Similarly, phosphorus has been identified as a residue of a plating procedure which has since been modified.

Surface contamination can be particularly troublesome in semiconductor technology. Here, too, sources of contamination have been pinpointed, and further work on such problems is planned.

One source of contamination can be the very solvents used to rid materials of other forms of dirt. Auger analysis is sensitive enough to reveal differences in the residues left by various solvents. Figure 10

The Unspoiler.

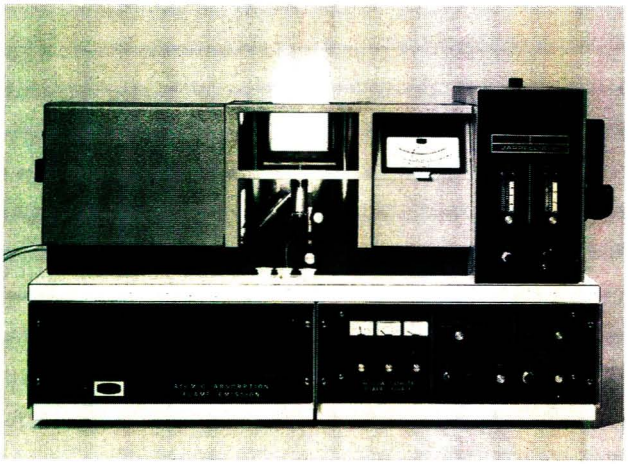


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shows what is left on nickel blanks identically processed except for different final rinses in acetone, trichloroethylene, and distilled water. The differences in such elements as sulfur, carbon, nitrogen, and chlorine may be important, depending on how and where the cleaned material is to be used.

Since changes in surface concentrations can be readily observed, Auger analysis is a useful tool for observing thermally induced migration, such as dissolution of surface layers into the bulk, segregation of bulk impurities at the surface, or migration of species over a surface. Nickel provides some interesting examples. A nickel sample freshly loaded into the system generally has carbon and oxygen residues. By secondary electron spectroscopy we have shown that heating the nickel in vacuum removes much of the oxygen, probably by desorption of oxygen and water and decomposition of nickel oxide. It also removes carbon either by evaporating organic residues or by dissolving the carbon residue from decomposed organic films. But while oxygen and carbon are removed from the surface, sulfur accumulates there. A series of experiments (*11*) shows that this sulfur is in fact due to segregation of the bulk impurity at the surface. *This segregation enhances the detection sensitivity markedly.* The sample on which these measurements were made contained sulfur *at a level of 3 ppm.* Similar segregation tendencies may be responsible for our being able to detect a number of different impurities. Incidentally, sulfur readily migrates to the surface of many metals with the application of only slight heating. Among metals commonly showing this growth of surface sulfur are iron, nickel, copper, titanium, niobium, tantalum, molybdenum, tungsten, and others.

This ability to study surface segregation promises to be useful in metallurgical studies. The mechanical properties of various alloys are often dependent on grain boundary segregation of certain constituents. If one can establish a connection between grain boundaries and surface segregation, then the observa-

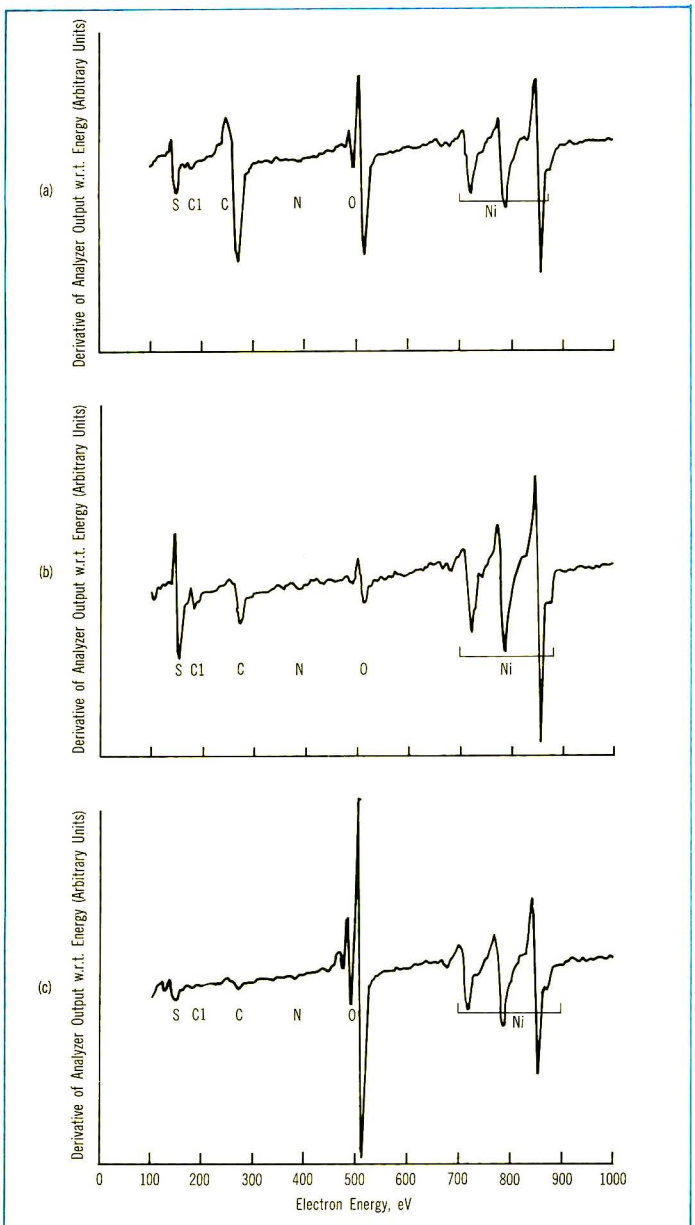
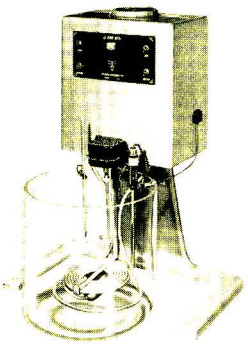


Figure 10. Auger electron energies for various solvents used on nickel blanks (a) acetone (b) trichloroethylene (c) distilled water

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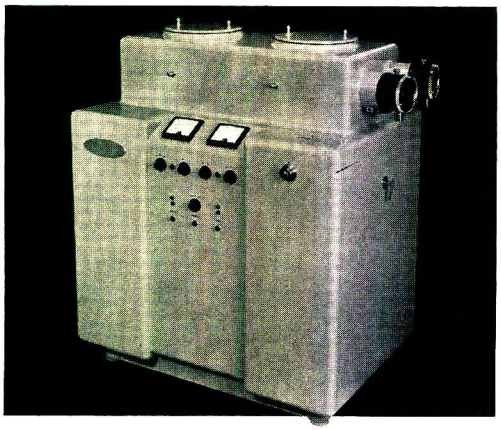
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tion of surface segregation by Auger emission can throw light on what happens at the inaccessible grain boundaries. Another approach is to examine intergranular fracture surfaces for concentrations of different species.

Auger analysis has also been used for such diverse purposes as identification of coatings on bearing surfaces, detection of carbon evaporation from a thorium dispenser cathode, determination of polarity of SiC crystals, and measurement of differences in mercury content of various lamp electrodes.

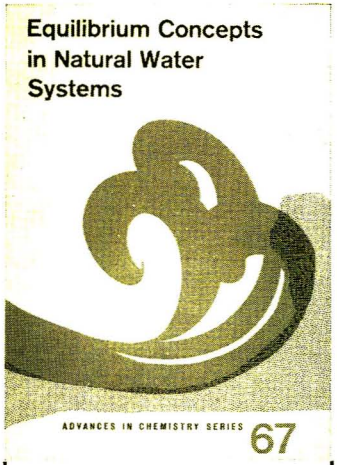
Future of the Method

In summary, Auger analysis is a nondestructive tool for identifying extremely small quantities of surface constituents. It is a method that can be applied almost as a routine laboratory technique because the equipment and vacuum conditions required are modest.

Although Auger analysis has been used primarily as a qualitative analytical method, its usefulness will be greatly enhanced when it can be extended to quantitative determinations and, hopefully, will tell us something of the chemical states of the atoms detected. There is no doubt that the important combination of Auger and LEED techniques will do much to provide the solid quantitative understanding necessary for these ends.

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(11) L. A. Harris, *ibid.*, **39**, 1419 (1968).



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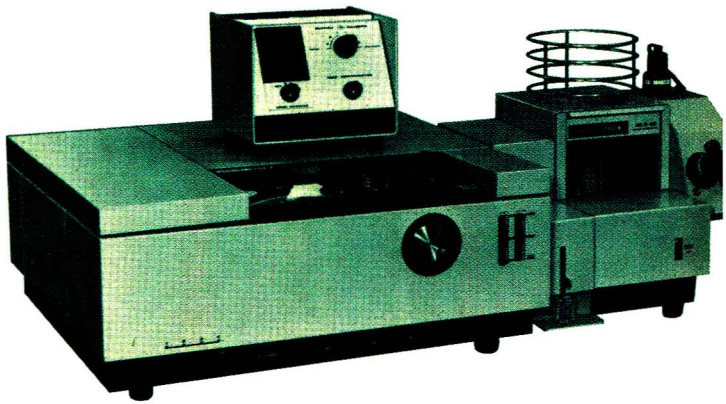
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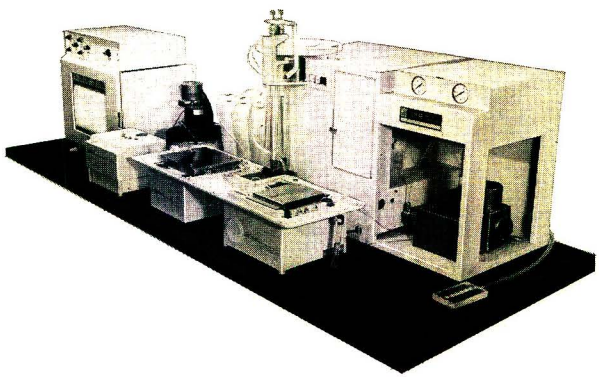
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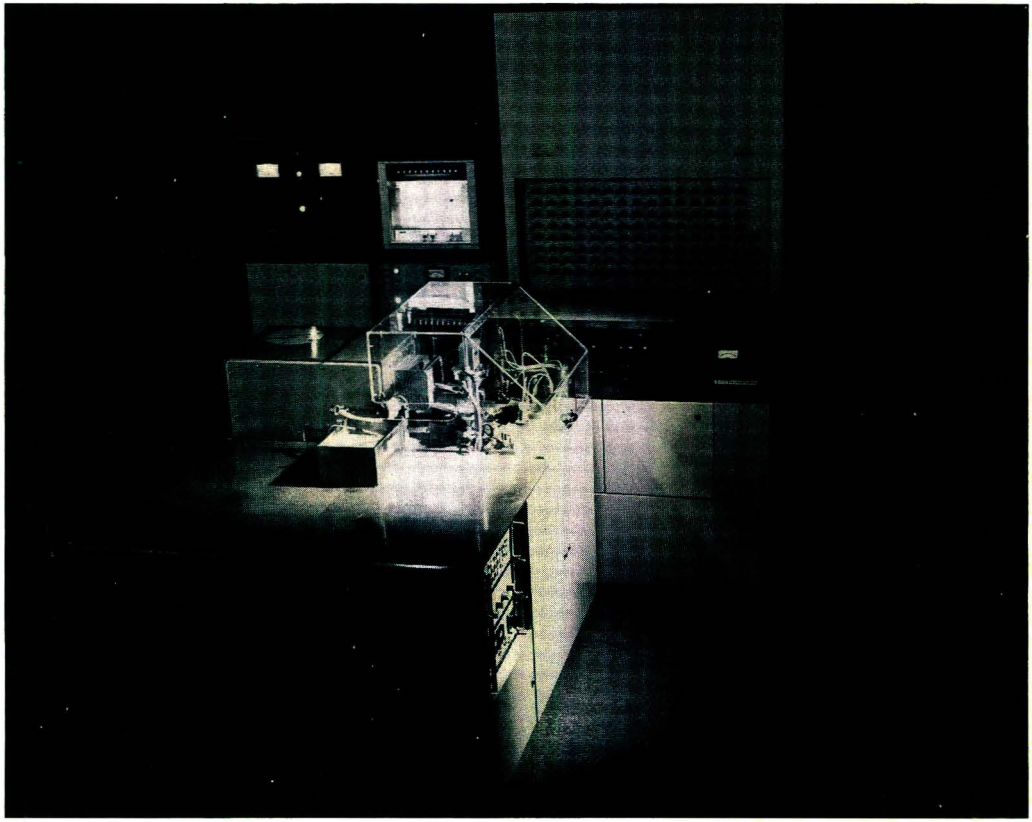
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The first few issues of ANALYTICAL CHEMISTRY in 1969 will contain articles on the Josephson effect and its application to sensitive galvanometers and infrared detectors by Dr. J. Matisoo of International Business Machines, and on instrumentation for kinetics measurements by Dr. Harry Mark of the University of Michigan and Theodore Weichselbaum and William H. Plumpe, Jr. of Sherwood Medical Industries, Inc.

ANALYTICAL CHEMISTRY hopes that this emphasis on measurement systems will encourage analytical chemists to broaden and deepen their knowledgeability in closely related disciplines and to stimulate the cross-fertilization of ideas and provoke original and useful thinking in analytical problem solving. Readers are invited to make suggestions of potentially interesting topics and authors for this continuing feature.

Glenn L. Booman is a research chemist in the Analytical Chemistry Branch of Idaho Nuclear Corporation at the Atomic Energy Commission's National Reactor Testing Station located near Idaho Falls, Idaho. He received his B.A. (mathematics) in 1951 from Western Washington College and his Ph.D. (analytical chemistry) in 1954 from the University of Washington. Before transferring to Idaho Nuclear in 1966, he was with Phillips Petroleum Company at the same location. Dr. Booman's interests are in electroanalytical chemistry, electrochemical kinetics, and analytical instrumentation. He has been active in the application of operational amplifier and digital techniques to electroanalytical instruments and has contributed papers on the construction and theory of operation of such instruments involving feedback control. Dr. Booman is presently Chairman of the Idaho Section of ACS.



Robert L. Bowman, M.D., is Chief of the Laboratory of Technical Development, National Heart Institute, National Institutes of Health, Bethesda, Maryland, where he has been developing instrumental methods since 1951. His contributions include instruments for spectrofluorometry, gas chromatography, chloride titrimetry, ultramicro methods, and artificial organs. He received his M.D. degree from New York University College of Medicine in 1942, and after internship and military service held medical research appointments at New York University Medical School before coming to National Institutes of Health. He was recipient of the American Chemical Society Award in Chemical Instrumentation in 1967.

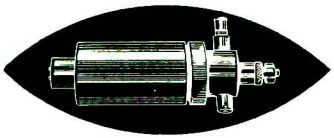


Jonathan W. Amy was born in Delaware, Ohio, in 1923. His formal education includes a B.A. from Ohio Wesleyan, in 1948, and M.S. and Ph.D. degrees from Purdue University in 1950 and 1955. Since that time he has remained on the chemistry department staff at Purdue to establish a program in chemical instrumentation. This program includes spectroscopic service laboratories, instrument construction, modification, and repair. An "instrument library" has been established for use by the department in both teaching and research. Consultation services are offered for both the staff and students on instrumental and experimental problems. Short courses have been offered on new instrumental techniques. This group has also worked closely with new staff members in establishing research programs. Special research interests have included molecular spectroscopy, gas chromatography, mass spectrometry, and data handling. Dr. Amy has served as a consultant in chemical instrumentation and as a member of the board of directors of several companies and laboratories.



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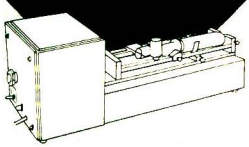


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Jack W. Frazer is in charge of analytical chemistry operations at Lawrence Radiation Laboratory, Livermore, California. He was born in 1924 in Forest Grove, Oregon, and served as a pilot with the Army Air Force during World War II. He received a B.S. in chemistry from Hardin-Simmons University in 1948, and was a chemist with Los Alamos Scientific Laboratory 1948–53. Mr. Frazer has been at Lawrence Radiation Laboratory since 1953. His principal interests are computer automation in analytical chemistry, development of analytical methods involving gas analyses, and inorganic syntheses.



Howard V. Malmstadt received a B.S. degree from the University of Wisconsin in 1943. After two years as a Radar Officer for a division of destroyers in the Pacific, he returned to the University of Wisconsin where he earned an M.S. degree (1948), a Ph.D. degree (1950), and remained for a year as a postdoctoral research associate. He joined the University of Illinois in 1951 and was made a full professor in 1961. He was a Guggenheim Fellow in 1960 and was the 1963 winner of the ACS Award in Chemical Instrumentation. He was the 1964 national chairman of the ACS Analytical Division and is on the Advisory Council of College Chemistry. His major areas of research are in time-resolved spectroscopy, short-time phenomena in sparks, laser plumes and flames, fast reaction-rate methods, and automation. He is the author or coauthor of more than 70 technical publications and the book, "Electronics for Scientists."



William F. Ulrich received his B.S. degree (1949) from Southern Illinois University and Ph.D. degree (1952) from the University of Illinois. From 1952 to 1956, he was an analytical chemist with Shell Development Co. in Houston, then joined Beckman Instruments, Inc., where he is Manager, Applications Research in the Scientific Instruments Division. He has published over 30 papers, mostly on absorption spectroscopy. In 1962 he was Chairman of the Southern California Section of the SAS and served as Meeting Chairman for the 1st Annual Pacific Conference on Spectroscopy. Currently, he is a member of ASTM Committee E-13 and the SAMA Subcommittee on Atomic Absorption. He is a Councilor for the Orange County Section of the ACS and National Treasurer of the Society for Applied Spectroscopy.



Analytical Chemistry Summer Fellowship Program

The Division of Analytical Chemistry of the American Chemical Society announces its Summer Fellowship Program for 1969. These fellowships, awarded by the Division and sponsored with the aid of several industrial organizations and scientific groups, support summer research for students in analytical chemistry. They carry a stipend of $800 plus tuition and fees. In 1967, five such fellowships were awarded; the successful nominees were: James G. Connery, St. John's University; William C. Flythe, Howard University; John D. Gorsuch, Massachusetts Institute of Technology; Gary Horlick, University of Illinois; and Gary R. Wiley, Illinois Institute of Technology.

The number of fellowships to be awarded in 1969 will depend upon the number and strength of applications received and upon the extent of financial support received from divisional members and other organizations. Summer Fellowships were awarded in 1968 in the names of the Eastern Analytical Symposium, the Division of Analytical Chemistry, the Society for Analytical Chemists of Pittsburgh, Consolidated Electrodynamics Corp./Bell and Howell, and personal contributors to the Division.

For eligibility, students must have completed at least one academic year of graduate study, and must be engaged in research on a subject appropriate for publication in ANALYTICAL CHEMISTRY. Also, only those students who are not terminal graduate students will be considered—i.e., the graduate student must return for at least one quarter or semester of further gradu-

ate study following the summer of his fellowship. Although the research would normally be a continuation of that already in progress, the student might desire to participate in a special summer research project elsewhere, for example, in a government laboratory.

Nominations should be made by the student's research supervisor, and should be accompanied by a completed application blank (to be filled in by the student), transcripts of the student's undergraduate and graduate records, and a statement of 250 words or less describing the research program proposed for the summer of the fellowship. The student shall request one more supporting letter of recommendation besides that of his research supervisor (the original nomination of the research supervisor shall constitute his recommendation.) Application blanks are available from, and all material concerning the nomination should be submitted to: Dr. James C. White, Oak Ridge National Laboratories, Oak Ridge, Tennessee 37830. Deadline for receipt of all information is February 1, 1969.

A special award committee will announce the recipients of the fellowship on March 15, 1969.

Members of the Division of Analytical Chemistry are urged to make voluntary contributions to the Division Secretary in support of this program. In addition, the Division invites the cooperation of industrial and other sponsors to support an entire fellowship (which will be named for or by the sponsor at his request). Details on sponsorship may be obtained by writing to Dr. White.

The Summer Fellowship Program is intended to foster the development of the next generation of analytical chemists and to attract to the ranks of analytical chemistry the finest young minds in our universities. The magnitude of the program and the extent of its success will be determined by the degree to which it is assisted financially and by the number of outstanding candidates who are encouraged to apply.

Winter Gordon Research Conferences

The Winter Gordon Research Conferences will be held January 20 to 31, 1969, in Santa Barbara, Calif., at the Miramar Hotel. Subjects of concern this year are electrochemistry, January 20 to 24, and polymers, January 27 to 31. Isaac Trachtenberg is Chairman of the sessions on electrochemistry; Fred Anson is Vice Chairman. The polymer conferences are chaired by Charles L. Segal; Jack R. Knox is Vice Chairman.

The scheduled part of the conference on electrochemistry is given below.

Attendance at the conferences is limited. Those interested in attending or those wishing more information on the meetings should write to Alexander M. Cruickshank, Director, Gordon Research Conferences, University of Rhode Island, Kingston, R. I. 02881.

ELECTROCHEMISTRY

Isaac Trachtenberg, Chairman

Monday, Jan. 20

Kinetics of Active Metal Electrodes. J. P. G. Farr, University of Birmingham, England

Bioelectrochemistry

Electron Transfer in Biology. Britton Chance, University of Pennsylvania

Electron Tunneling in Photosynthesis. D. C. DeVault, University of Pennsylvania

Tuesday, Jan. 21

Dynamic Analysis of Porous Electrodes. A. A. Pilla, United States Army Electronics Command

Influence of Electrode Structure on Operation of Porous Gas Electrodes. E. A. Grens, University of California, Berkeley

Photoelectrochemistry. D. L. Maricle, American Cyanamid Co.

Photoemission from Mercury Electrodes. R. deLevie, Georgetown University

Wednesday, Jan. 22

Theory and Application of Disc and Ring-Disc Electrodes. John Albery, Oxford University, England

Some Recent Applications of Ring-Disc Electrodes. Stanley Bruckenstein, University of Minnesota

Open Session

Thursday, Jan. 23

Theory and Application of Disc and Ring-Disc Electrodes (continued). A. C. Riddiford, University of Victoria, Canada; E. A. Yeager, Case Western Reserve University

Application of Digital Computers to Electrochemistry. D. M. Mohilner, Colorado State University

Discussion

Digital Computer Analysis of Double Layer Measurements. D. M. Mohilner, Colorado State University

Digital Simulation of Electrochemical Processes. Stephen F. Feldberg, Brookhaven National Laboratory

The Computer as an Electrochemical Instrument. George Lauer, North American Rockwell Corp.

Friday, Jan. 24

Electrical Double Layer in New Solvent Systems. R. Payne, United States Air Force, Cambridge Research Laboratories

Electrode Kinetics in Non-aqueous Solvents. J. N. Butler, Tyco Laboratories

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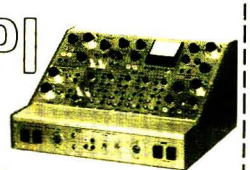
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LSU Symposium Program

The program for the Louisiana State University Twenty-Second Annual Symposium on Modern Methods of Analytical Chemistry is given below. The meeting will be held January 20 to 23 at Baton Rouge, La. Further information is available from James W. Robinson, Dept. of Chemistry, Louisiana State University, Baton Rouge, La. 70803

Nuclear Quadrupole Resonance Spectroscopy. Edward G. Brame, Jr., E. I. duPont de Nemours and Co., Bldg. 353, Room 18, Wilmington, Del. 19898

Electron Microscopy. H. Fernandez-Moran, Department of Biophysics, University of Chicago, Chicago, Ill. 60637

Recent Developments in Solvent Extraction. Henry Freiser, Department of Chemistry, The University of Arizona, Tucson, Ariz. 85721

Differential Scanning Calorimetry. Allan P. Gray, Analytical Department, The Perkin-Elmer Corp., Norwalk, Conn. 06852

Photoelectron–Spectroscopy. David M. Hercules, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139

Problems in Environmental Trace Analysis. David N. Hume, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139

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Below is a report on the activities of the Analytical Division of IUPAC. The large number of projects under investigation should be of interest to readers of ANALYTICAL CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

The Analytical Chemistry Division is administered by the Division Committee, the present members being:

PROFESSOR P. W. WEST, **U.S.A.** *President*
PROFESSOR W. KEMULA, **Poland** *Vice-President*
PROFESSOR I. P. ALIMARIN, **U.S.S.R.**
PROFESSOR R. BELCHER, **U.K.**
PROFESSOR C. DUVAL, **France.**
PROFESSOR L. ERDEY, **Hungary.**
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PROFESSOR D. N. HUME, **U.S.A.**
PROFESSOR H. KAISER, **Germany.**
MR. R. W. FENNELL *Secretary, Materials Department, Royal Aircraft Establishment, Farnborough, Hants., U.K.*

The bulk of the scientific work of the Division is done by the seven Commissions, whose terms of reference are the study of topics of international scientific or technical significance requiring agreement, regularisation, standardisation or codification with the sphere of their respective expertise.

Brief summaries of the work currently being done by these Commissions follow. Requests for further information or suggestions for future projects should be addressed to the appropriate Commission Secretary or, in case of doubt, to the Division Secretary.

Commission 1. Analytical Reactions and Reagents

Chairman:
PROFESSOR H. MALISSA
Institut für Analytische Chemie und Mikrochemie
Technische Hochschule,
Getreidemarkt 9,
A-1060 WIEN, Austria.

At the present time, this Commission is concerned entirely with standardisation of analytical methods required by the European Economic Community with whom IUPAC has a working agreement.

Commission 2. Microchemical Techniques and Trace Analysis

Chairman:
DR. W. SCHÖNIGER (Switzerland)
Secretary:
DR. R. LÉVY
Service central de Microanalyse du CNRS,
2, Rue H.-Dunant,
94 Thiais, France.

Studies are being carried out, on an international basis, on the elemental analysis of organic materials, in particular:

a) carbon and hydrogen, especially in compounds containing heteroelements
b) fluorine
c) nitrogen, based on the Dumas method
d) metals, excluding simple residue procedures.

In addition, known sources of errors in microanalysis are being collated and studies being made on the purification of chemicals used for micro and trace analysis and on mass absorption coefficients used in electron beam microanalysis.

Laser-Raman, and Rapid Scan UV and Process Control UV Analysis. D. O. Landon, Spex Industries, Inc., 3880 Park Ave., Metuchen, N. J. 08840

Contribution of Gel Permeation to Polymer Analysis. John C. Moore, The Dow Chemical Co., B-1214 Bldg., Freeport, Texas 77541

Atomic Absorption Flame Emission Spectrometry for Major Constituents. Theodore C. Rains, U.S. Department of Commerce, National Bureau of Standards, Washington, D. C. 20234

Applications of Resolved Spectroscopy. David W. Steinhaus, University of California, P. O. Box 1663, Los Alamos, N. M. 87544

Third Toronto Symposium on Thermal Analysis

The Toronto Section of the Chemical Institute of Canada will hold its Third Symposium on Thermal Analysis at "The Inn on the Park," Toronto, Canada, February 25 to 26, 1969. The meeting will feature three half-day sessions with in-depth presentations from 10 well-known scientists in areas devoted to: Frontiers in Thermoanalytical Techniques; Quantitative Thermal Analysis; and Frontiers in Thermoanalytical Applications.

A fourth half-day session will contain a series of short reports on new methodology. At the banquet, the second Mettler Award in Thermal Analysis

(*Continued on page 45 A*)

Commission 3. Analytical Nomenclature

Chairman:
PROFESSOR R. BELCHER (U.K.)
Secretary:
PROFESSOR T. S. WEST,
Department of Chemistry,
Imperial College,
Kensington,
London, S.W.7, U.K.

Internationally acceptable nomenclature, definitions and symbols are being sought in the following areas of analytical interest—

a) liquid-liquid distribution (solvent extraction)
b) automatic analysis
c) ion exchange
d) chromatography
e) scales of working
f) mass spectrometry
g) contamination phenomena in analytical precipitation.

The Commission is also compiling a list of trivial names of analytical reagents and examining the need for primary standards other than acid-base standards. Other projects under consideration are the concept of a selectivity index and the presentation of analytical methods for publication.

Commission 4. Spectrochemical and Other Optical Procedures

Chairman:
PROFESSOR H. KAISER (Germany)
Secretary:
PROFESSOR V. A. FASSEL,
Department of Chemistry,
Iowa State University,
Ames, Iowa 50010, U.S.A.

The Commission is concentrating its efforts on nomenclature, symbols and usage in atomic spectrochemical analysis. The first part of its report, dealing with atomic emission spectroscopy, is being finalised and work is proceeding to cover:

a) flame atomic absorption and atomic fluorescence spectroscopy
b) X-ray fluorescence spectroscopy (including X-ray microprobe techniques)
c) excitation source descriptions and parameters
d) terms and concepts related to rigorous determination of detection limits.

Pending the standardisation of concepts and procedures for establishing detection limits, a project on the compilation of lists of minimal detectable concentrations is in abeyance.

Commission 5. Electroanalytical Chemistry

Chairman:
PROFESSOR I. M. KOLTHOFF (U.S.A.)
Secretary:
DR. P. ZUMAN,
Department of Chemistry,
University of Birmingham,
P.O. Box 363,
Birmingham 15, U.K.

The purification and purity of solvents and reagents of interest in electroanalytical chemistry is a continuing project of the Commission. Other projects include:

a) the compilation of physico-chemical data in non-aqueous media
b) the production of polarographic data cards and critical evaluation of polarographic procedures
c) studies on solid electrodes
d) the revision of tables of oxidation-reduction potentials.

Commission 6. Equilibrium Data

Chairman:
PROFESSOR Y. MARCUS (Israel)
Secretary:
DR. F. J. C. ROSSOTTI,
Inorganic Chemistry Laboratory,
South Parks Road,
Oxford, U.K.

The Commission is actively engaged on the compilation and revision of data under the following headings:

a) stability constants
b) distribution and solubility constants
c) ion-exchange equilibrium constants
d) stability constants of complexes

Commission 7. Analytical Radiochemistry and Nuclear Materials

Chairman:
DR. G. B. COOK (U.K.)
Secretary:
DR. W. W. MEINKE,
National Bureau of Standards,
Chemistry Division,
Washington, D. C. 20234, U.S.A.

Studies are being made on:

a) the purity of commercial radioactively labelled preparations
b) the use of radioactive methods in analytical chemistry
c) national regulations for the use of small quantities of radioisotopes
d) reference materials for activation analysis

The limits of reliability in the analysis of nuclear materials and the results of an intercomparison of laboratory methods for the determination of uranium are being studied. Multilingual nomenclature and basic reference reports are also being studied.



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will be presented. Additional events at the symposium include meetings of the North American Society for Thermal Analysis (NATAS) and exhibits of thermoanalytical instrumentation.

For details and registration forms, write to Dr. H. G. McAdie, Ontario Research Foundation, Sheridan Park, Ontario, Canada.

Symposium on Ion-Selective Electrodes

The present and future capabilities of ion-selective electrodes will be discussed at a Symposium on Ion-Selective Electrodes at the National Bureau of Standards, Gaithersburg, Md., January 30 to 31, 1969. The symposium, sponsored by the Bureau, will consist of 10 invited papers and will review the theory, characteristics, methodology, and applications of these electrochemical sensors. Round-table discussion and question periods at the close of each session will provide a forum for the interdisciplinary exchange of information. The papers and discussions will be published by NBS as a state-of-the-art monograph. Further program and registration information is available from Dr. Richard A. Durst, Room B326, Chemistry Bldg., National Bureau of Standards, Washington, D. C. 20234, Tel: (301) 921-2860.

Scheduled Courses in Analytical Techniques

Information is given in the following order: date, name of course, location of course, professional person(s) in charge of course, and/or sponsoring organizations and *Contact* (numbers in parentheses refer to addresses and telephone numbers given at the bottom of the list of scheduled courses).

Dec. 2 to 5—Characterization of Organic Coatings. The Summit Hotel, New York, N. Y. *Contact:* Program Design, Inc., 3645 Warrensville Center Rd., Cleveland, Ohio 44122. Tel: (216) 283-1160

Dec. 2 to 6—Mass Spectrometry—Principles & Applications. Hopatcong, N. J. F. Gollob. *Contact (1)*

Dec. 2 to 6—Two Separate Courses: Infrared Interpretation, Part I; Gas Chromatography. Philadelphia, Pa. Sadtler Research. *Contact (2)*

Dec. 9 to 13—Two Separate Courses. Infrared Interpretation, Part II; Nuclear Magnetic Resonance. Philadelphia, Pa. Sadtler Research. *Contact (2)*

Dec. 11 to 13—Gas Chromatography. San Francisco, Calif. *Contact:* Frank Owen, Varian Aerograph, 2700 Mitchell Dr., Walnut Creek, Calif. 94598

Jan. 3 to 5—Spectrometric Identification of Organic Compounds. Albany, N. Y. Robert M. Silverstein, G. Clayton Bassler. ACS. *Contact (3)*

Jan. 10 to 12—Spectrometric Identification of Organic Compounds. St. Louis, Mo. Robert M. Silverstein, G. Clayton Bassler. ACS. *Contact (3)*

Jan. 13 to 15—Basics of Instrument Systems & Modules for Chemical Analysis. Hopatcong, N. J. Nelson Alpert. *Contact (1)*

Jan. 13 to 17—Measurement of the Appearance of Properties of Materials. Marriott Twin Bridges Motor Hotel, Washington, D. C. *Contact:* Hunterlab, 9529 Lee Highway, Fairfax, Va. 22130. Tel: (703) 591-5310

Jan. 17 to 18—Basic Gas Chromatography. New York City Area. Harold M. McNair, James Miller. ACS. *Contact (3)*

Jan. 20 to 22—Operational Amplifiers. Hopatcong, N. J. Galen Ewing. *Contact (1)*

Jan. 22 to 24—Analog Computers. Hopatcong, N. J. Galen Ewing. *Contact (1)*

Jan. 25 to 28—Molecular Characterization of Polymers. Cleveland Ohio. F. W. Billmeyer, Jack B. Kinsinger, J. P. Kratohvil. ACS. *Contact (3)*

Jan. 27 to 31—Electronics for Scientists and Engineers (Basic). Hopatcong, N. J. Saul Ritterman. *Contact (1)*

Jan. 27 to 31—Spectral Interpretation Workshop. Hopatcong, N. J. A. J. Diefenderfer; David A. Aikens. *Contact (1)*

Jan. 29 to 31—Gas Chromatography. Atlanta, Ga. *Contact:* Bernie Jagielski, Varian Aerograph, 3939 Hillcroft Ave., Suite 180, Houston, Texas 77027

Feb. 7 to 9—Spectrometric Identification of Organic Compounds. New York City Area. Robert M. Silverstein, G. Clayton Bassler. ACS. *Contact (3)*

Feb. 10 to 12—Thermal Methods of Analysis. Washington, D. C. W. W. Wendlandt, Ilya M. Sarasohn, E. L. Simons, or A. E. Newkirk. ACS. *Contact (3)*

Mar. 24 to 25—2nd Annual Modern Practice of Chromatography. Drexel Institute of Technology, Philadelphia, Pa. *Contact:* J. G. Nikelly, Philadelphia College of Pharmacy and Science, Philadelphia, Pa. 19104

Apr. 1—Internal Reflection Techniques. Apr. 2—Gas Chromatography/Infrared Techniques. Holiday Inn, Darien, Conn. *Contact:* Wilks Scientific Corp., South Norwalk, Conn. 06856. Tel: (203) 838-4537

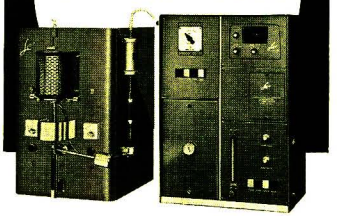
[1] Center for Professional Advancement, P. O. Box 66, Hopatcong, N. J. 07843. Tel: (201) 398-7110

[2] Sadtler Research Laboratories, Inc., 3316 Spring Garden St., Philadelphia, Pa. 19104. Tel: (215) 382-7800

[3] Education Office, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Tel: (202) 737-3337

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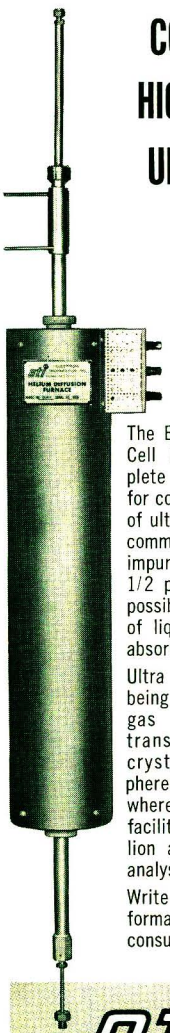
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CALENDAR OF EVENTS

Dec. 4 to 7	**Southeastern Regional ACS Meeting.** Tallahassee, Fla. *Contact:* Earl Frieden, Department of Chemistry, Florida State University, Tallahassee, Fla.
Dec. 5 to 7	**Southwestern Regional ACS Meeting.** Austin, Texas. Includes Analytical Chemistry Sessions. *Contact:* Donald M. Carlton, c/o Tracor, Inc., 6500 Tracor Lane, Austin, Texas 78721
Dec. 12	**Computers in the Analytical Chemistry Laboratory.** Holiday Inn, Houston, Texas. *Contact:* Donald K. Atwood, Esso Production Research Co., P. O. Box 2189, Houston, Texas 77001. Tel: (712) NA 2-4222, Ext. 2610
Dec. 12	**American Microchemical Society.** Willy's Restaurant, 166 William St., New York City. "Chemical Microstandards." David H. Freeman, NBS. *Contact:* L. M. Brancone, Lederle Laboratories Div., American Cyanamid Co., Pearl River, N. Y. 10965
Dec. 26 to 29	**Ninth Seminar on Electrochemistry.** Karaikudi, India. *Contact:* Shri B. A. Shenoi, Ninth Seminar on Electrochemistry, Central Electrochemical Research Institute, Karaikudi-3 (Madras State), India
Dec. 26 to 31	**135th Annual AAAS Meeting.** Dallas, Texas. *Contact:* American Association for the Advancement of Science. Dept. R, 1515 Mass. Ave., N. W., Washington, D. C. 20005

Coming Events

Jan. 20 to 23—Fifth International Symposium on Advances in Chromatography. Las Vegas, Nev. *Contact:* Albert Zlatkis, Department of Chemistry, University of Houston, Houston, Texas 77004. Page 57 A, Nov.

Jan. 20 to 23—Louisiana State University Twenty-Second Annual Analytical Symposium on Modern Methods of Analytical Chemistry. Baton Rouge, La. *Contact:* James W. Robinson, Dept. of Chemistry, Louisiana State University, Baton Rouge, La. 70803. Page 42 A, Dec.

Jan. 20 to 31—Gordon Research Conference on Electrochemistry. Miramar Hotel, Santa Barbara, Calif. *Contact:* Alexander M. Cruickshank, Dept. of Chemistry, University of Rhode Island, Kingston, R. I. 02881. Page 41 A, Dec.

Jan. 30 to 31—Symposium on Ion-Selective Electrodes. Washington, D. C. *Contact:* Richard A. Durst, Room B326, Chemistry Bldg., National Bureau of Standards, Washington, D. C. 20234. Tel: (301) 921-2860, page 45 A, Dec.

Feb. 2 to 7—ASTM Winter Meeting. Denver Hilton Hotel, Denver, Colo. *Contact:* American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103

Feb. 13 to 15—Fourth Mid-Atlantic Regional ACS Meeting. Sheraton-Park Hotel, Washington, D. C. *Contact:* Richard H. Jacquith, University of Maryland, College Park, Md. Page 62 A, Aug.

Feb. 21 to 24—Twentieth Annual Meeting American Academy of Forensic Sciences. Drake Hotel, Chicago, Ill. *Contact:* Lt. Irwin G. Haviland, Chicago Police Dept., Crime Laboratory Division, 1121 South State St., Chicago, Ill. 60605

Feb. 25 to 26—Third Toronto Symposium on Thermal Analysis. The Inn on the Park, Toronto, Canada. Sponsor: Toronto Section, Chemical Institute of Canada. *Contact:* H. G. McAdie, Ontario Research Foundation, Sheridan Park, Ontario, Canada. Page 43 A, Dec.

March 2 to 7—Twentieth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. Cleveland, Ohio. *Contact:* Gerald L. Carlson, Carnegie-Mellon University, Mellon Institute, Pittsburgh, Pa. 15213. Page 59 A, Sept.

Mar. 13 to 14—First Annual Symposium on Automated, High-Resolution Analyses in the Clinical Laboratory. ORNL. Sponsors: Oak Ridge National Laboratory; National Institute of General Medical Sciences. *Contact:* Charles D. Scott, Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tenn. 37830. Page 59 A, Nov.

Mar. 13 to 14—Automation and Data Processing in Clinical Chemistry. Hannover, Germany. Sponsor: German Society of Clinical Chemistry. *Contact:* Dr. I. Trautschold, Medizinische Hochschule Hannover, Klinische Biochemie, 3000 Hannover, Osterfeldstrasse 5, Germany.

Mar. 25 to 29—LABEX International 1969. Earls Court, London, England. *Contact:* UTP Exhibitions, Ltd., Racquet Court, Fleet St., London, E.C. 4, England. Page 61 A, Nov.

Apr. 13 to 18—157th National ACS Meeting. Minneapolis, Minn. Includes Analytical Division Sessions. *Contact:* Fred McLafferty, Cornell Univ., Ithaca, N. Y. 14850

Apr. 14 to 16—Fourth National ISA Instrument Maintenance Management Symposium. Statler-Hilton Hotel, Detroit, Mich. *Contact:* A. T. Upfold, Polymer Corp., Ltd., Sarnia, Ontario, Canada

May 1 to 2—Metrochem '69. Hilton Hotel, New York City. Sponsors: New York and North Jersey Sections, ACS. *Contact:* George Heinze, Johnson and Johnson Research Center, New Brunswick, N. J. 08903

May 4 to 9—Spring Meeting Electrochemical Society. Commodore Hotel, New York City. *Contact:* The Electrochemical Society, 30 East 42nd St., New York, N. Y. 10017

May 12 to 15—20th Annual Mid-America Symposium on Spectroscopy. Sheraton-Chicago Hotel, Chicago, Ill. *Contact:* Richard L. Terry, Sinclair Research, Inc., 400 East Sibley Blvd., Harvey, Ill. 60426. Tel: (312) 468-9300, Ext. 503. Page 61 A, Nov.

May 17 to 25—International Chemistry Exhibition; XX International Congress—Chemistry Days 1969. Milan, Italy. Sponsor: Federation of Scientific and Technical Associations. *Contact:* Federazione Delle Associazioni Scientifiche e Tecniche, 20121 Milan, Via Marcona 49, Italy

May 18 to 23—17th Annual Conference on Mass Spectrometry and Allied Topics. Sheraton-Dallas Hotel, Dallas, Texas. Sponsor: ASTM Committee E-14. *Contact:* J. M. McCrea, Applied Research Laboratory (73), U. S. Steel Corp., Monroeville, Pa. 15146. Page 47 A, Dec.

May 26 to 30—XV Colloquium Spectroscopicum Internationale. Madrid, Spain. *Contact:* E. Arsensi Alvarez-Arenas, Serrano, 119, Madrid-6, Espana

June 5 to 6—Third Great Lakes Regional ACS Meeting. DeKalb, Ill. Includes Analytical Chemistry Sessions. *Contact:* Richard C. Bowers, Northern Illinois University, DeKalb, Ill. 60115

June 5 to 11—Fifth International Meeting of Forensic Sciences. Toronto, Canada. *Contact:* Frank L. Wilson, Dept. of the Attorney General, Parliament Bldg., Toronto 2, Canada

June 12 to 13—24th Annual Northwest Regional ACS Meeting. University of Utah, Salt Lake City, Utah. Includes Analytical Chemistry Sessions. *Contact:* Edward M. Eyring, Dept. of Chemistry, University of Utah, Salt Lake City, Utah 84112

June 22 to 27—ASTM 72nd Annual Meeting. Chalfonte-Haddon Hall, Atlantic City, N. J. *Contact:* American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103

July 14 to 18—International Conference on Atomic Absorption Spectroscopy. Sheffield, England. *Contact:* A.A.S. Conference Secretary, Society for Analytical Chemistry, 9/10 Savile Row, London, W.1, England Page 49 A, July

July 15 to 18—Meeting on NMR Spectroscopy. Birmingham, England. *Contact:* The Chemical Society, Burlington House, London, W.1, England

July 21 to 25—International Symposium on Analytical Chemistry. Birmingham, England. Sponsors: SAC and IUPAC. *Contact:* D. M. Peake, 61 Lodge Rd., Walsall, Staffordshire, England. Page 57 A, Aug.

Aug. 31 to Sept. 4—International Conference on Calorimetry and Thermodynamics. Warsaw, Poland. *Contact:* H. Kehiaian, Secretary, Organizing Committee, Institute of Physical Chemistry, Polish Academy of Sciences, P. O. Box 49, Warsaw 42, Poland.

Sept. 7 to 12—158th National ACS Meeting. New York City. Includes Analytical Division Sessions. *Contact:* Fred McLafferty, Cornell University, Ithaca, N. Y. 14850

Sept. 8 to 13—Seventh International Congress of Clinical Chemistry. Geneva, Switzerland. *Contact:* VIIth International Congress of Clinical Chemistry, Palais des Expositions, 1211 Geneva 4, Switzerland. Page 93 A, Feb.

Oct. 5 to 10—Fall Meeting Electrochemical Society. Statler Hilton Hotel (also Sheraton Cadillac), Detroit, Mich. *Contact:* The Electrochemical Society, 30 East 42nd St., New York, N. Y. 10017

17th Annual Conference on Mass Spectrometry

The officers of ASTM Committee E-14 will sponsor the 17th Annual Conference on Mass Spectrometry and Allied Topics to be held May 18 to 23, 1969, at the Sheraton-Dallas Hotel, Dallas, Texas. In addition to contributed papers, the conference will feature two invited lectures and four symposia on Thermal Analysis—Mass Spectrometry; Collisions of Electronically Excited Atoms and Molecules; Ionization Cross Section Data; and Geo- and Cosmo-Applications of Mass Spectrometry. Further information on this meeting is available from J. M. McCrea, Applied Research Laboratory (73), U. S. Steel Corp., Monroeville, Pa. 15146.

Industry Items

Beckman Instruments, Inc., has formed a wholly-owned subsidiary in Austria. **Beckman Instruments, G.m.b.H.,** Vienna, Austria, will direct the marketing of the company's scientific, medical, and industrial instruments. This is Beckman's ninth foreign subsidiary.

A new firm, **Environmental Development, Inc.,** will offer consultation and research services to industry and all levels of government. The corporation is staffed by specialists in air and water pollution, marine biology, oceanography, occupational medicine, and meteorology. Offices of the company are at 1000 Vermont Ave., N.W., Suite 209, Washington, D. C. 20005.

Orion Research, Inc., 11 Blackstone St., Cambridge, Mass. 02139, has completed acquisition of **Sage Instruments, Inc.,** White Plains, N. Y. Orion is a manufacturer of electrochemical sensors and advance instrumentation for digital data analysis and printout; Sage makes laboratory pumps, cinemicrographic apparatus, and related equipment.

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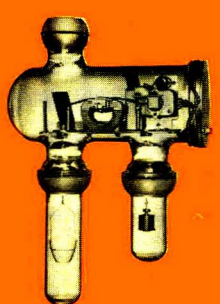
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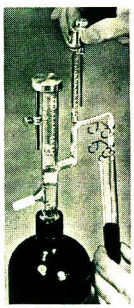
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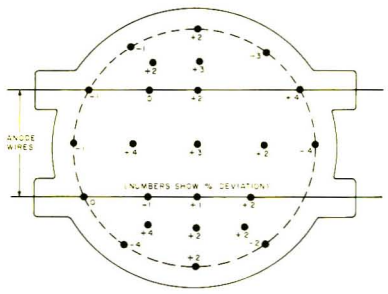
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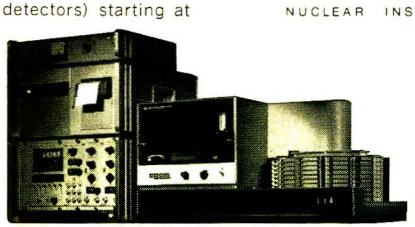
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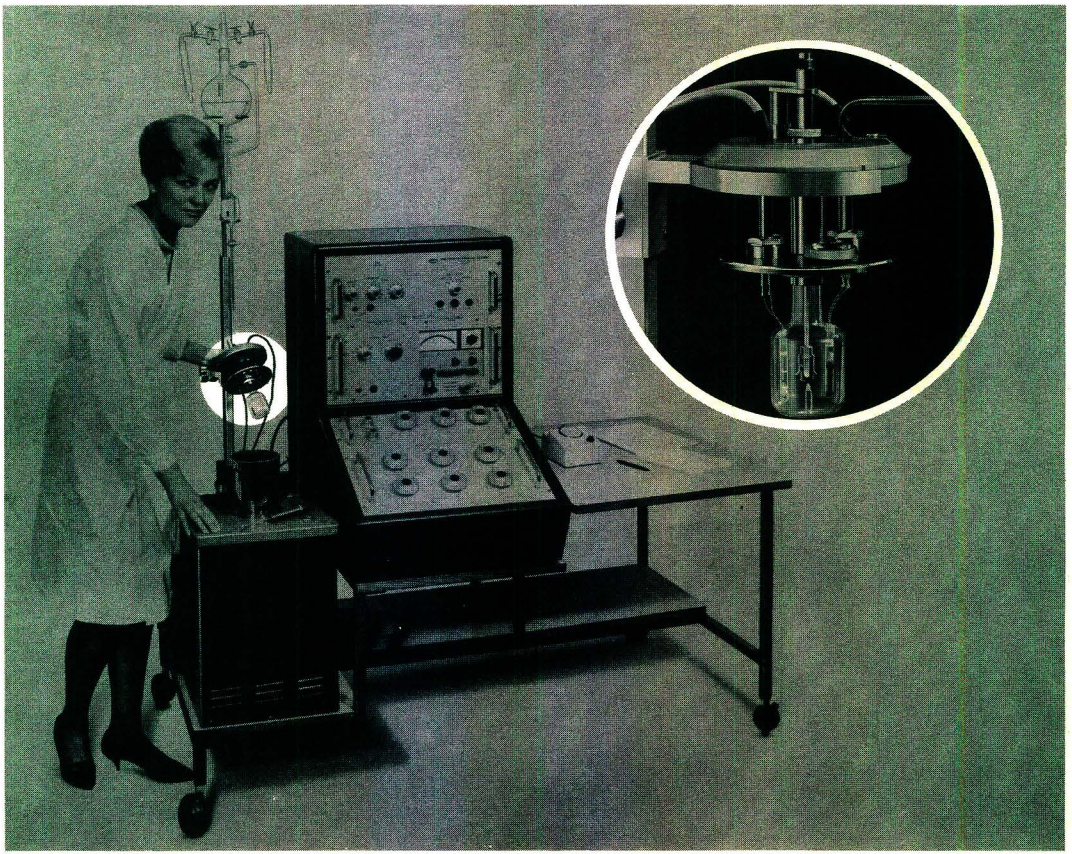
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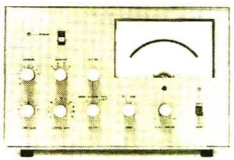
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The atomic absorption spectrophotometer for chemists who frustrate easily.

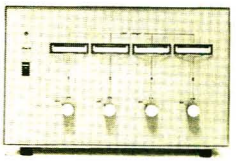
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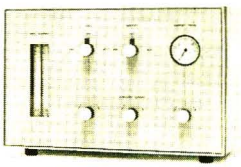
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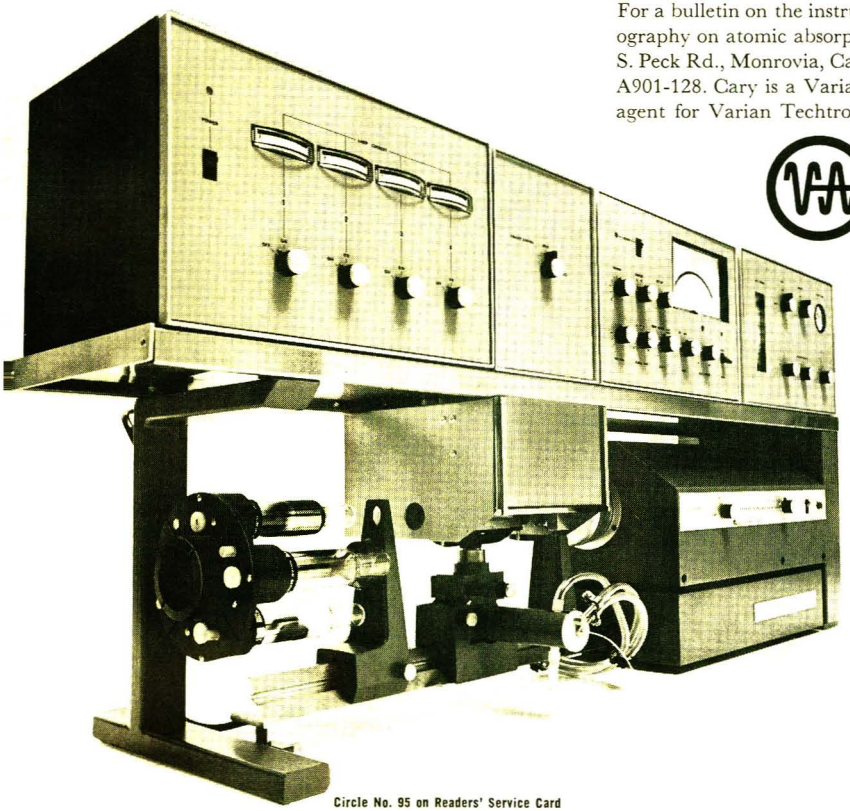
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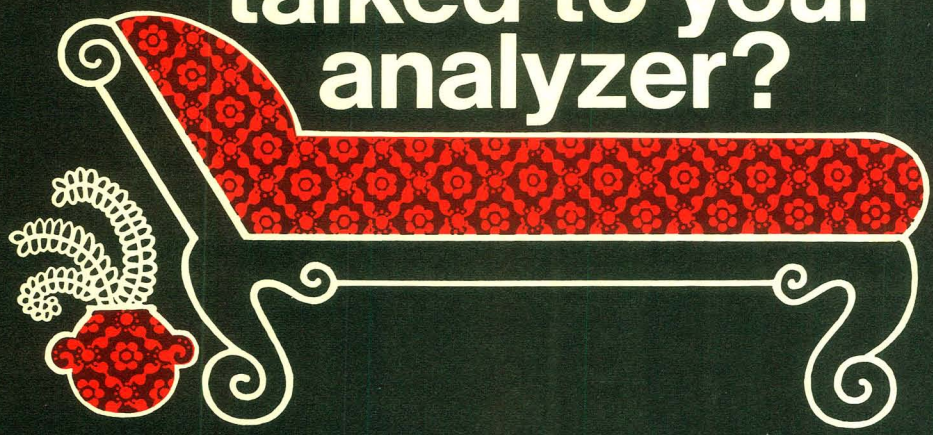
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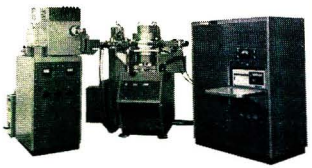
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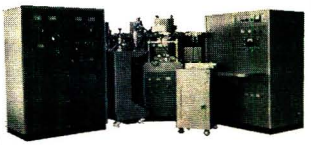
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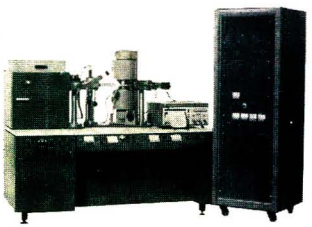
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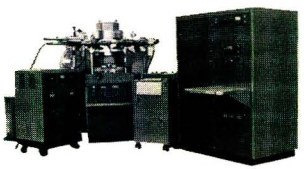




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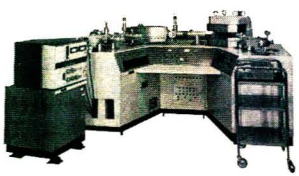
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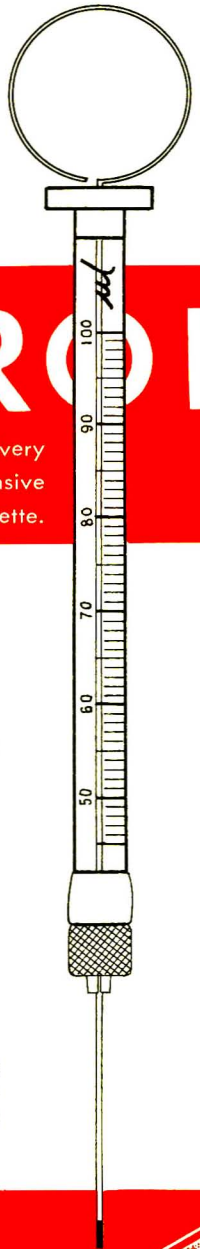
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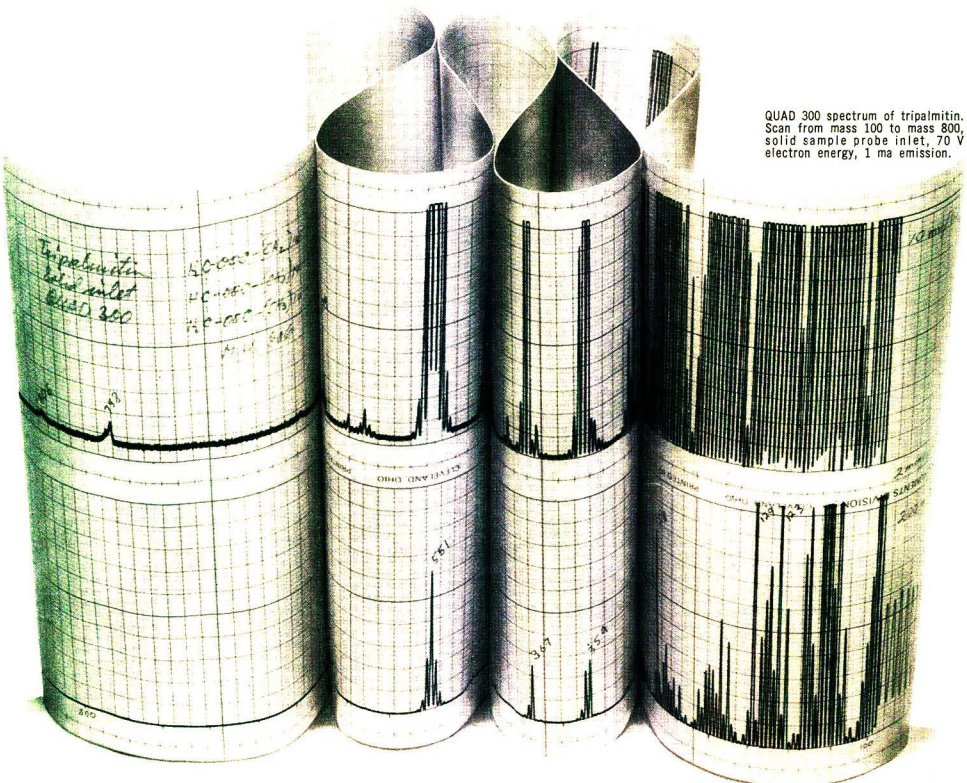
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Air Pollution. Vol. II. Analysis, Monitoring, and Surveying. *Second Edition. Arthur C. Stern, Editor. xix + 684 pages. Academic Press, Inc., 111 Fifth Ave., New York, N. Y. 10003. 1968. $35*

Reviewed by Edward F. Ferrand, Bureau of Technical Services, Dept. of Air Pollution Control, 51 Astor Place, New York, N. Y. 10003

This three-volume work is meant to provide a summary of existing knowledge about air pollution to the rapidly increasing, heterogeneous audience to whom this subject is an important concern. Volume II covers the sampling, analysis, measurement, and monitoring of air pollution and is intended as a reference on the chemical analysis of pollutants. Because it is the result of contributions from many authors working independently, some overlapping has occurred. For the same reason, because the field is growing rapidly but has few well-established domains, the points of view and preferences of the individual authors tend to be emphasized.

With few exceptions this volume cannot be used as a laboratory manual, nor should it be expected to serve as such considering the range covered. It is the most convenient source for anyone searching for a comprehensive view of the problems and procedures encountered in measurements in the air pollution field. It also serves well as a starting point for an investigator embarking into research in an unfamiliar area. Unfortunately, studies are not covered equally well in all chapters.

Some authors discuss and emphasize recent studies more than do others. Although in some cases the difference can be attributed to the nature of the subject matter, it is recommended that the coverage of the reference be examined before embarking on a detailed study of each chapter. The abstracts published by the Air Pollution Control Association are a valuable adjunct to such study.

In view of the influence that this work will have upon the air pollution field, it is fortunate than an attempt is made to recommend units for reporting air pollution measurements. The problem is vexing enough to merit treatment in a separate chapter together with recommendations for nomenclature, standards, and calibrations.

Air quality data has developed its own variations of statistical analyses and presentation which could have received more detailed and unified treatment. In view of the importance that new generations of monitoring instruments will have, more attention might have been given to developments in this direction.

This volume represents an important contribution to the air pollution field. In spite of its relatively high cost, it definitely belongs in the library of anyone who has more than a passing interest in the quality of the air environment. In this connection it should be noted that this volume is concerned with many topics beyond the analysis of the atmosphere and of emissions. These analyses lead to social applications intended for the control of air pollution. The techniques connected with these applications are an important part of this work.

The Mass Spectra of Organic Molecules. *J. H. Beynon, R. A. Saunders, A. E. Williams. ix + 510 pages. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 10017. 1968. $34*

Reviewed by Seymour Meyerson, Research and Development Department, American Oil Co., Whiting, Ind. 46394

In view of the many important contributions by Beynon and his associates to the mass spectrometry of organic compounds, the publication of this book ought to constitute a major event for workers in the field. But circumstances ordained otherwise. The subject matter almost exactly duplicates that of another book with a similar title, "Mass Spectrometry of Organic Compounds," by Budzikiewicz, Djerassi, and Williams (BDW), which came out a year earlier. Especially in view of the high price of the present volume, almost twice that of BDW, the prospective purchaser will think twice before placing his order, and his decision is likely to hinge on a comparison of the two books. For the worker who already owns a copy of BDW, does Beynon's book contain enough additional useful information to justify buying it, too? The answer is not an unequivocal yes.

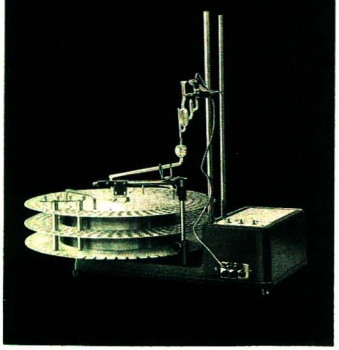
In at least one important respect, that of timeliness, the present book runs a poor second. Only 14 literature references, or 2.5% of the total, are dated 1966, 1967, or in press. In BDW, despite the earlier publication date, 350 references, or 37% of the total (however, references in BDW are listed separately for each chapter, and the total therefore includes much duplication), fall in this category. The large number of typographical errors and careless or inaccurate statements in the present book is inconsistent with the high standards that readers have come to expect from both the authors and the publisher. One suspects that they may have grown panicky at seeing themselves so thoroughly scooped by BDW and cut short their normal editing and proofreading procedures. Similarly, the fear that their sales would suffer from the poor showing vis-a-vis BDW may have been a factor in setting the price so high. Even the feeding of paper stock into the printing presses seems to reflect a last-minute rush. Pages 39–102, 263–278, 327–342, and 375–390 of my copy are printed on high-gloss paper; the rest of the book is on matte.

However, the picture is far from one-sided. The senior author has been in this game for over twenty years, and the breadth and depth of his and his associates' experience give a tone and a quality to their book that are not readily attained by relative newcomers to the field. By comparison, BDW has something of the flavor of a catalog, whereas the present book is a series of lecture-discussions. Many classes of compounds are accorded extensive treatments that go well beyond that of BDW. The text is illustrated with large numbers of problems, approached on a highly pragmatic basis and discussed in great detail.

The reader will come away from this book cognizant of a great number of empirical correlations between mass spectra and molecular structures, many of them not well explored or understood, but nonetheless useful in structure identification. For example, the spectra of 6- and 7-methylquinolines, although generally quite similar, differ sharply in relative intensities at masses 89 and 90; in perfluoroparaffin spectra, the most abundant ion at each carbon number is $C_nF_{2n+1}^+$ except for n equal to one less than the number of carbons in the original molecule, where it is $C_nF_{2n-1}^+$. Odd bits of useful information are scattered through the discussions of various compound types. For example, pentaborane rapidly dehydrogenates in the instrument, but this problem can be avoided by 5 minutes' pretreatment of the sample-handling system with ammonia.

Finally, a semi-philosophical comment is perhaps in order. Concepts and terminology borrowed from physical-organic chemistry have proved of inestimable value in rationalizing mass spectra and in popularizing mass spec-

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trometry among organic chemists, but at a price. Their glib use all too often produces arguments that are far more satisfying to the writer than to the reader in search of understanding. The sparsity of such jargon in Beynon's book is at times a disadvantage, but most of the time it is refreshing.

Substoichiometry in Radiochemical Analysis. *Jaromir Ruzicka, Jiri Stary. ix + 151 pages.* **Vol. 30. International Series of Monographs in Analytical Chemistry.** *Pergamon Press, Inc., 4401 21st St., Long Island City, N. Y. 11101. 1968. $7*

Reviewed by G. W. Leddicotte, Research Reactor Facility, University of Missouri, Columbia, Mo.

The ideas promoted by the authors of this monograph provide an interesting approach to the use of the potentials of nuclear science methodology in the determination of substoichiometric amounts of the elements. Chapter 5 is the most meaningful chapter in the monograph. It has an excellent source of sensitive, specific, and rapid methods of analysis for at least 23 elements, many of which are important to researchers concerned with trace substance research interests. In almost all instances, an analyst can easily adapt these methods for use in the assay of almost any type of sample material. Chapter 4 offers some useful information on the general techniques applied in the methods described in Chapter 5. However, no attempt is made to reference any of this general information, much of which has been ably documented in detail elsewhere by the authors.

With respect to the rest of the book, this reviewer finds that it contains better than average material; however, the manner in which this information is presented makes it difficult to achieve a rapid comprehension of the authors' intents. It would appear to have been more practical to review and generally discuss the nuclear methods being considered,—i.e., activation analysis, isotope dilution, and radiometric—in a single chapter and then elaborate upon the principles and separation techniques that could be used in carrying out the substoichiometric determination by a particular technique. For example, in Chapters 2 and 3, the authors give a few paragraphs about specific techniques and then immediately propose theories on separation techniques—e.g., solvent extraction of metal chelates—so that the prime intent of each chapter is somewhat overshadowed by material which could be best presented as a separate topic.

Although it would be desirable to have a more favorable format for this introductory material and certain other portions of the monograph (especially Chapters 6, 7, and 8), the monograph is a potentially valuable aid to any analyst. It provides him with unique ideas on how to use certain nuclear methods of analysis for trace element determinations.

Analysis of High-Purity Materials. *I. P. Alimarin, Editor. xviii + 584 pages. Daniel Davey & Co., Inc. 964 Asylum Ave., Hartford, Conn. 06105. 1968. $20.25*

Reviewed by G. H. Morrison, Department of Chemistry, Cornell University, Ithaca, N. Y. 14850

In no other field of modern science and technology has the requirement of high purity been more stringent than in the area of semiconductor materials. In order to improve the technology of the preparation of semiconductor materials and their compounds and to produce high-quality semiconductor devices with predetermined properties, it has been necessary to develop methods for the determination of impurities with detection limits as low as 10^{-6}–10^{-8}%.

The book under review is an English translation of the original Russian edition, "Metody Analiza Veshchestv Vysokoi Chistoty," published in 1965. It represents a collection of procedures developed in a number of institutes of the Academy of Sciences of the USSR and other departments for the determination of trace impurities in high-purity materials used in radioelectronic and semi-conductor technology.

The introductory articles, which describe the position reached in the USSR in the control of the purity of different materials, have been written by their leading experts in the field. Subjects discussed include control of high-purity materials, potential developments of modern analytical methods, improvement in their sensitivity and accuracy, and experimental techniques to be adopted when working with high-purity materials.

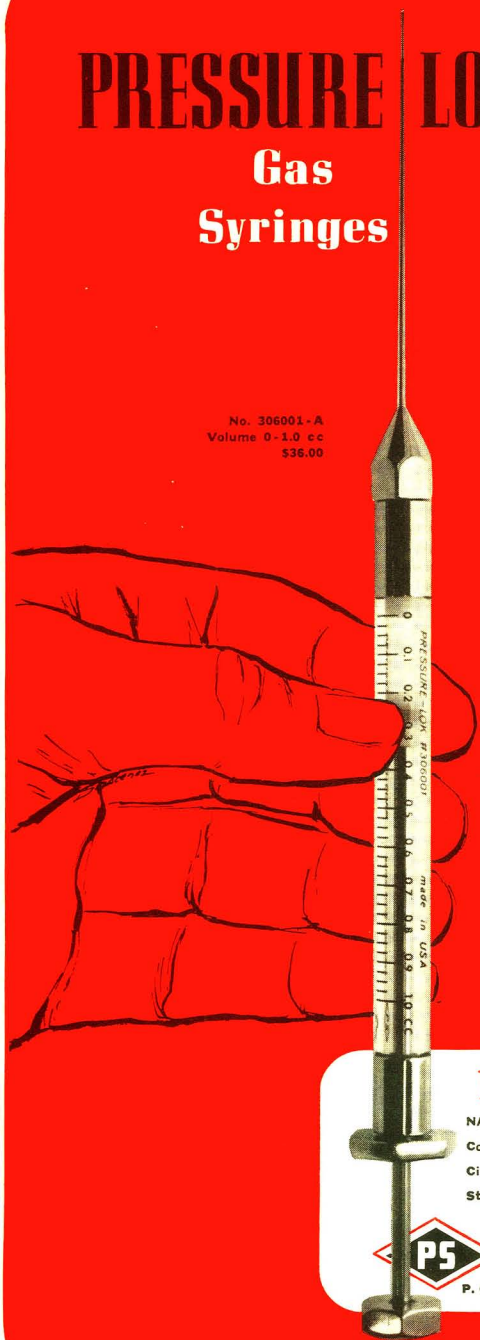
Detailed procedures are given for the determination of trace impurities in silicon and its compounds, germanium and its compounds, gallium, indium, thallium, arsenic, antimony, compounds of the $A_{III}B_{V}$ type, phosphorus, aluminum, lead and its compounds, bismuth and its compounds, tin, zinc, cadmium, sulfur, selenium, tellurium, boron, iodine, graphite, compounds of the $A_{II}B_{VI}$ type, and reagents.

According to a translator's note, in many instances, industrial routine analyses in the Soviet Union are carried out by specially trained technicians rather

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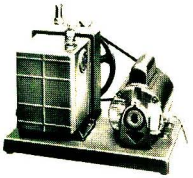
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than by graduate chemists. This accounts for the fact that the description of analytical procedures given in this book is found to contain much detail, partly repetitive, which would seem to be stressing the obvious, but is really intended not to leave any room for doubt as to the correct procedure to be followed.

The techniques of trace analysis covered in this book reveal the state of the art in the USSR as of 1965. A majority of the procedures involve chemical preconcentration and separation followed by colorimetric or spectrophotometric determination of individual trace elements. Also quite prominent are chemical preconcentration–emission spectrographic methods for survey analyses. To a lesser extent activation analysis, polarographic, and luminescent methods are employed, all accompanied by the necessary enrichment and/or separation steps to achieve adequate sensitivity or freedom from interferences. It is interesting to note that although continuous reference in the book is made to the great potential of spark source mass spectrometry for the analysis of high-purity materials, only very limited use is made of this valuable technique, presumably due to the non-availability of instruments. Also, noticeably absent are flame emission and atomic absorption methods.

This book is a welcome addition to the growing list of authoritative texts on trace analysis. Although it is restricted to the analysis of semiconductor materials, it provides considerable detail of great value to the practicing analyst concerned with this demanding field.

The book is written in a clear and straightforward manner and the Israel Program for Scientific Translations is to be congratulated for the high quality of the translation. The only annoyances encountered by the reviewer were the absence of a subject index and the frequent use of the word "etalon" for "standard" in this English edition.

New Books

Proceedings of the International Conference on Luminescence, Budapest, 1966. Vol. 1. Vol. 2. *G. Szigeta, Editor. 2165 pages. Akadémaiai Kiadó, Budapest V., Alkotmany U. 21., Hungary. 1968. $72*

These two volumes contain in English the papers presented at the International Conference on Luminescence which was held in Budapest in 1966. The three introductory lectures by Prof. Garlick, Prof. Levshin, and Prof. Seitz are in both English and Russian. The subject matter of the conference encompassed general problems of luminescence, the problems of organic and inorganic luminescent materials, especially of oxides and sulfides and rare earth metal compounds, the phenomena of injection luminescence, solid state lasers, and the application of luminescence.

Inorganic Qualitative Analysis: A Short Course for Introductory Chemistry. *2nd Edition. Richard B. Hahn, Frank J. Welcher. viii + 326 pages. D. Van Nostrand Co., Inc., 120 Alexander St., Princeton, N.J. 08540. 1968. $6.40*

This book was written as a text for Freshman chemistry where qualitative analysis is offered in the laboratory portion of the latter part of general chemistry. Changes made over the first edition include a complete reorganization of the theoretical sections, and substantial revisions in the chapters on chemical equilibrium, chemical kinetics, and ionics. A new chapter deals with oxidation-reduction.

Experimental Procedures in Elementary Qualitative Analysis. *Esmarch S. Gilreath. vii + 115 pages. McGraw-Hill Book Co., 330 W. 42nd St., New York, N. Y. 10036. 1968. Paperbound. $3.25*

This text has been designed for use in schools where a separate course on qualitative analysis has been abandoned and a simplified scheme of analysis is used within the laboratory exercises of general chemistry. The analytical procedures within the cation scheme are based on the Fresenius system of analysis, but they have been greatly altered in terms of efficiency and simplicity. The anion-analysis scheme is adapted from one developed by J. T. Dobbins and H. A. Ljung [*J. Chem. Educ.* **12**, 586 (1935)].

Analysis and Characterization of Oils, Fats and Fat Products. Vol. 2. *H. A. Boekenoogen, Editor. ix + 681 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N. Y. 10016. 1968. $26.50*

The first volume of this series appeared in 1964. Volume 2 contains seven articles on various aspects of fat analysis and author and subject indexes. Titles of the articles and their authors follow: Mass Spectrometry in Fat Analysis by Einar Stenhagen; Measurement of Oil Colour by Maurice Naudet and Elie Sambuc; Paper and Thin-layer Chromatography in Fat Chemistry by Peter Vogel and Theophil Wieske; Analysis of Glycerides

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and Composition of Natural Oils and Fats by G. Jurriens; The Determination of the Position of Double Bonds in Fatty Acids by P. Haverkamp Begemann; The Chemistry and Analysis of Olive Oil by Jaime Gracian Tous; and The Determination of Vitamins and Carotenoids in Fats by G. Brubacher.

Of special interest to all those who deal with the assessment of the quality of edible oils is the chapter on olive oil, which takes up 293 pages of this volume and which is an extremely detailed consideration of all the analytical problems connected with the criteria used in evaluating olive oils of various origins.

Peptides and Proteins. *D. T. Elmore. xi + 154 pages. Cambridge University Press, 32 East 57th St., New York, N. Y. 10022. 1968. Clothbound, $6; Paperbound, $2.75*

This book is designed to give the advanced undergraduate student in chemistry an insight into the field of proteins. Most of the book is devoted to the structural and synthetic aspects of protein chemistry. Actually, much of the book is devoted to discussions of methods for the isolation and separation of peptides and proteins and the determination of structure. Chapters are also included on the macromolecular properties and structures of proteins, the chemical synthesis of peptides, the biosynthesis of proteins, and importantly, the relationships between structure and biological activity of peptides and proteins.

A New Dictionary of Chemistry. *L. Mackenzie Miall; D. W. A. Sharp, Editors. ix + 638 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N. Y. 1968. $14*

The form of the fourth edition of this book remains substantially the same as that of earlier editions. The dictionary is not intended for the expert but should be of use to those who need information in chemical fields outside their own specialities.

Methods of Biochemical Analysis. Vol. 16. *David Glick, Editor. vii + 446 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N. Y. 10016. 1968. $16.50*

This volume of the biochemical analysis series contains the following chapters: The Isotope Derivative Method in Biochemical Analysis by J. K. Whitehead and H. G. Dean; Bioluminescence Assay: Principles and Practice by B. L. Strehler; Utilization of Automation for Studies of Enzyme Kinetics by M. K. Schwartz and Oscar Bodansky; Enzymatic Synthesis and Hydrolysis of Cholesterol Esters by G. V. Vahouny and C. R. Treadwell; Determination of Histidine Decarboxylase Activity by R. W. Schayer; The Estimation of Total (Free + Conjugated) Cathecholamines and Some Catecholamine Metabolites in Human Urine by H. Weil-Malherbe; and The Automated Analysis of Absorbent and Fluorescent Substances Separated on Paper Strips by A. A. Boulton.

The book also contains subject and author indexes and a cumulative index for Volumes 1–16.

Organic Scintillators. *Donald L. Horrocks, Editor. 422 pages. Gordon and Breach, 150 Fifth Ave., New York, N. Y. 10011. 1968. $40. (20% discount for payment in advance)*

This book contains the Proceedings of the International Symposium on Organic Scintillators held at Argonne National Laboratory, June 20 to 22, 1966. The papers are grouped under headings designated as Theory and Mechanisms: Energy Transfer, Quenching Studies, Lifetime Studies, and Triplet, Exciton and Other Studies; Applications; and Other Recent Advances.

Advances in Mass Spectrometry, Vol. 4. *E. Kendrick, Editor. xvi + 971 pages. The Institute of Petroleum, 61 Cavendish St., London, W.1., England. 1968. £10.0.0*

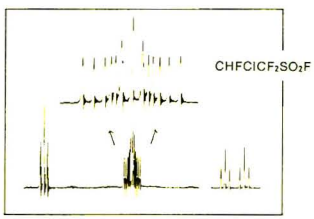
This volume contains the papers and discussions of the Mass Spectrometry Conference organized by a joint committee from ASTM E-14, the Hydrocarbon Research Group, AG Massenspektroskopie der DPG, and GAMS and held in Berlin, September 1967. There were 83 papers presented at this meeting. The book contains an author index but not a subject index.

Glassblowing for Laboratory Technicians. *R. Barbour. xv + 245 pages. Pergamon Press, Inc., 44-01 21st St., Long Island City, N. Y. 11101. 1968. $5*

The beginning chapters of this book cover fully the glassblowing requirements of the City and Guilds of London Institute syllabus 119 for laboratory technician's work. Subsequent chapters delve rather completely into the art of glassblowing including discussions of hazards, needs of the workshop, annealing, glass-to-metal seals, glassblowing, vacuum techniques, and interchangeable ground-glass joints, and stopcocks.

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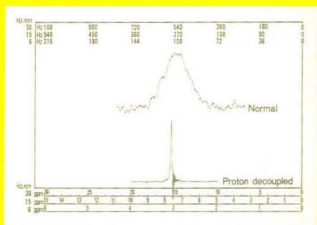
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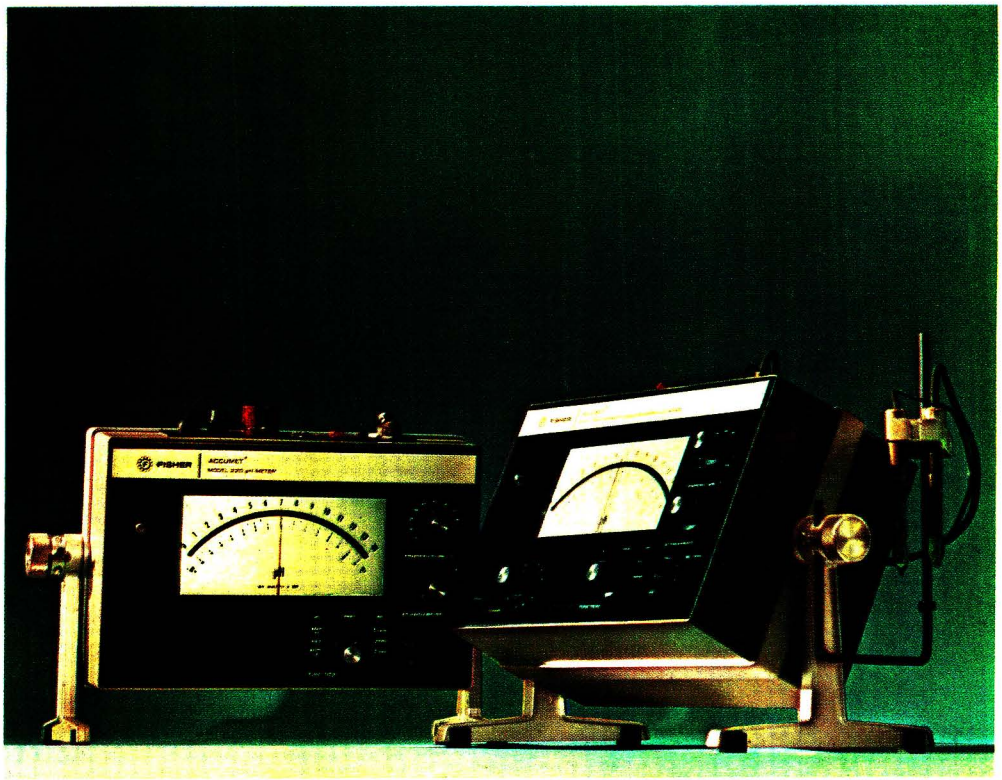
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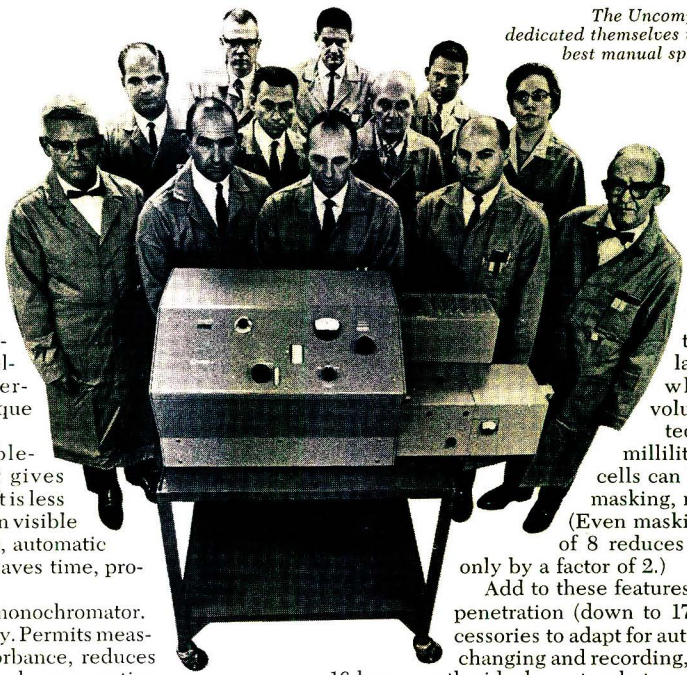
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THE EDITORS' COLUMN

O doubtful names which are like the true names, what errors and anguish have you provoked among men!"

—Book of Crates, Berth.
M. A., iii, p. 50

This quotation, which introduces Part I of M. P. Crosland's book "Historical Studies in the Language of Chemistry," illustrates the great difficulties in understanding writings in the science of chemistry, even from the times of alchemy. Regardless of the elegance of our scientific research, it is important to preserve and to build upon the inherent beauty and practicality of our scientific language. A scientist without an intelligent grasp of the language of his field is apt to find himself at a great disadvantage in communicating both within and without his area of specialty.

With ideas such as the foregoing in mind, the Division of Analytical Chemistry of the American Chemical Society has decided to revitalize its Committee on Nomenclature. The question might arise as to the need for such a group, particularly in light of active committees on analytically-oriented nomenclature sponsored by such bodies as the International Union of Pure and Applied Chemistry and various subcommittees of the American Society for Testing and Materials.

It is certainly not the intent of the Analytical Division Committee to usurp the functions of or to duplicate the efforts of these other committees. However, it is clear that the Division Committee can serve in at least two important areas: (1) It can advise the editors of analytical science journals concerning acceptable nomenclature and terminology, especially when new developments cause new terms

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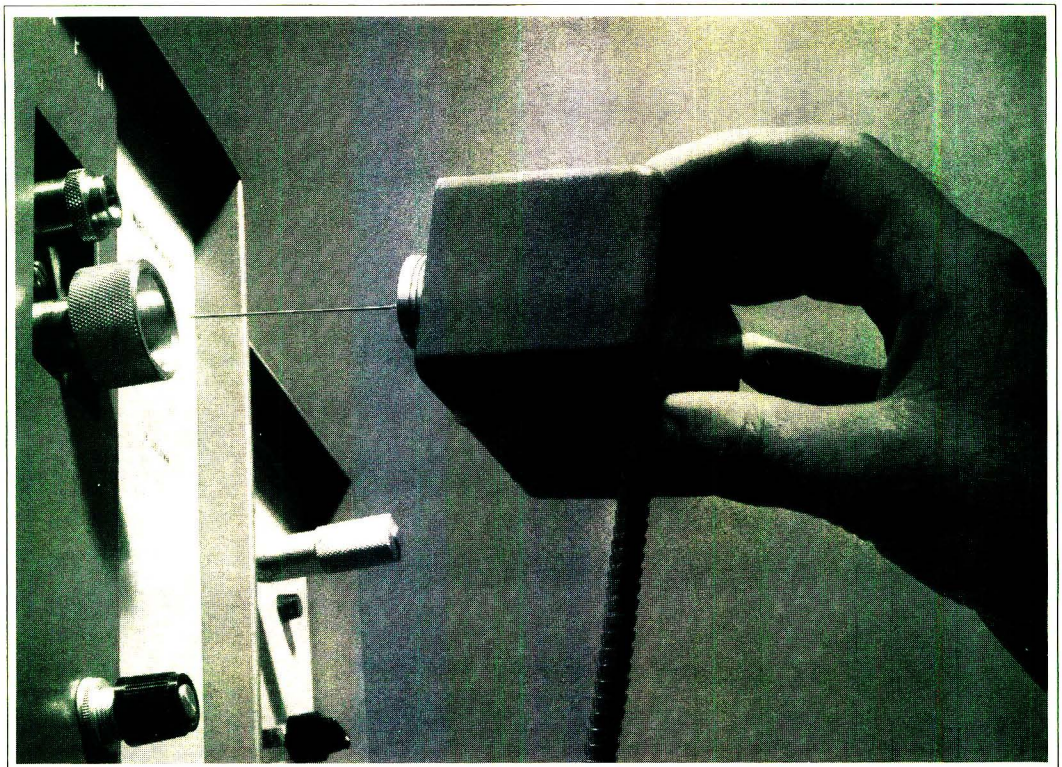
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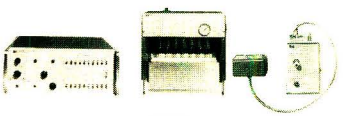
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to come to light. In the writer's firsthand experience, for example, a large number of inquiries have been received in the recent past concerning proper use of the terms "gel filtration chromatography" and "gel permeation chromatography." (2) The Division Committee can participate more actively in the workings of the American Chemical Society's Committee on Nomenclature by bringing the viewpoints and problems of analytical chemists to the attention of nomenclature representatives of other branches of chemistry.

Journal editors are often called upon for decisive action *vis-a-vis* a nomenclature problem in a pending publication. All too often an expert must be consulted and a more-or-less subjective judgment be quickly made about the suitability or appropriateness of a term. There is inherent hazard in such action, because publication of a new term for the first time is tantamount to creation of an authoritative aura of acceptance of the term. If a mistake has been made, the battle to right the wrong might assume epic proportions.

There is certainly much nomenclature that should be in the province of, and capture the attention of, analytical chemists. Although we are late in asserting any dominance in this area, the time is ripe for effective participation. In this regard it is hoped that the analytical scientists who read this column will take advantage of the opportunity provided by revitalization of the Division. Committee to come forth with their ideas on the use and misuse of terms, suggestions for individual terms to be discussed and acted upon, and ideas for fruitful areas of development by the Committee. Correspondence should be addressed to:

John K. Crum, Chairman
ACS Analytical Division Nomenclature Committee
c/o ANALYTICAL CHEMISTRY
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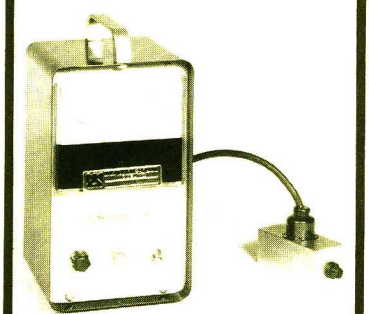
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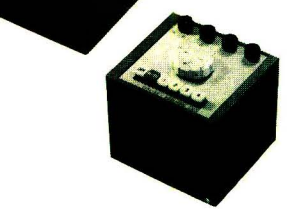
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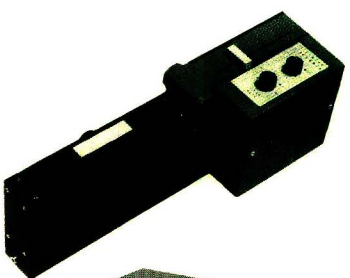
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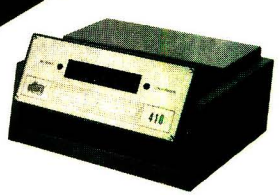
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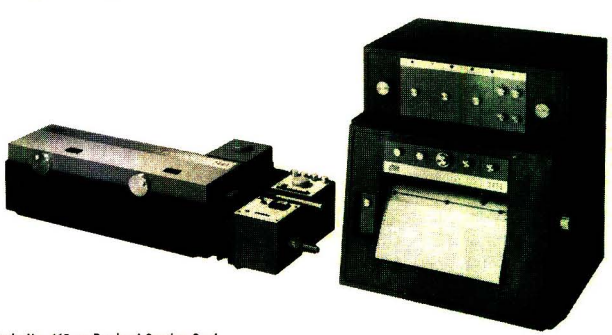






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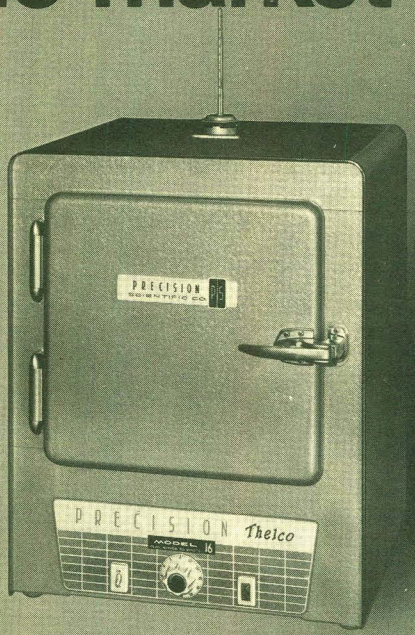
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IMC Consolidates Its Analytical Capability

FIFTY YEARS of growth have brought International Minerals & Chemical Corporation from a small mining company to a large diversified organization with research interests which span almost all areas of the life and physical sciences. As the company interests expanded, it became increasingly desirable to consolidate all its research activities at one central location.

The new Growth Sciences Center was designed to meet the needs of such a unification of research effort. Occupied in late 1966, the Center at Libertyville, Illinois, consists of six buildings on 296 acres of rolling farm land twenty-six miles north and west of the company's world headquarters in Skokie, Illinois. Libertyville is approximately one hour from the Chicago loop, providing an easy choice of the metropolitan cultural environment of Chicago or the recreational areas of the lake regions of northern Illinois and Wisconsin. Two golf courses border the property, and a private lake at the site is being developed for employee use.

The four-story research and development building is the largest single unit of the complex and contains 84,800 square feet. Here the biological sciences group is engaged in problems which range from molecular biology to the development of biological insect control agents. Research in the plant sciences is augmented by more than 125 acres of experimental fields, greenhouses, and growth chambers where plant growth regulators, germination enhancers, plant nutrient research, and cropping systems are studied.

Theoretical and practical applications of the physical sciences form a third division of IMC's research effort. Physical, inorganic, and organic chemists, mineralogists, geologists, and engineers phase their efforts from studies of molecular phenomena to scale-up in the Development Engineering facilities.

This concentration of research has made it necessary to develop a versatile analytical facility which is capable of servicing not only the chemical and biological needs of the corporate research programs, but also the technical problems of the many IMC production locations throughout the United States.





Growth Sciences Center, Libertyville, Ill., shown with night lights. The new $6.5 million research facility is the largest in the fertilizer industry and will enable IMC to double its research efforts. Shown is the administration building and the three-story research and development center

The equivalent of one entire floor of the Research and Development building is devoted to the Analytical and Technical Services Department. The analytical laboratories, headed by Dr. Graham A. Stoner, have been expanded to accommodate the increased requirement for services. Nearly 65 professionals and technicians at the Growth Sciences Center are employed in the Analytical and Technical Services department.

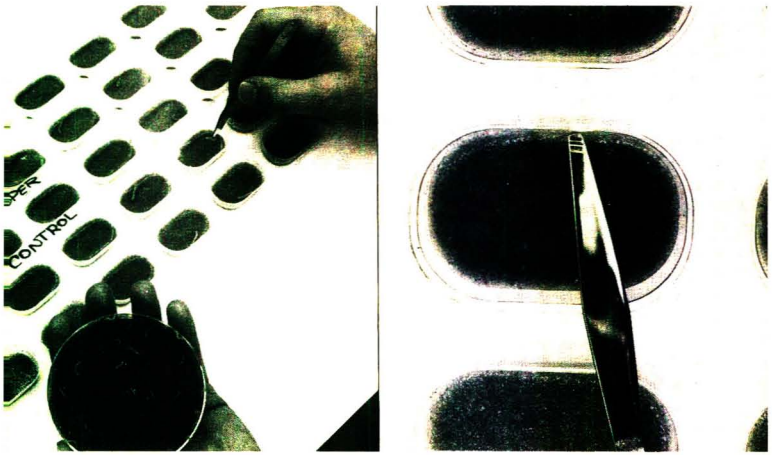
The analytical laboratories are divided into four groups: Analytical Chemistry, Analytical Biology, Technical Services, and Quality Control. Each is responsible for analytical and problem-solving skills for the overall research program, as well as for technical services to outlying IMC production locations.

It is not uncommon for one or more chemist(s) to work with production personnel on complex plant problems. The quality control group assumes overall responsibility for the performance of 10 fertilizer blending plants throughout the United States. The technical services group encounters problems of a varying nature which range from extensive investigations at various plant locations to the solution of customer service problems originating from the corporate sales staff. One such problem developed into a two-year research project during which many of the unit operations performed at one

IBM 1800 computer with a 16K core serves on a time-shared basis as an instrument monitor and as an ordinary computer. A direct reading spectrograph, several AutoAnalyzers, and three atomic absorption spectrometers are currently being interfaced directly to the computer. Thousands of routine analytical results can be calculated, tabulated, and reported automatically. The computer is also used for infrared searches, solution of complex mathematical problems, and to simulate experimental research conditions



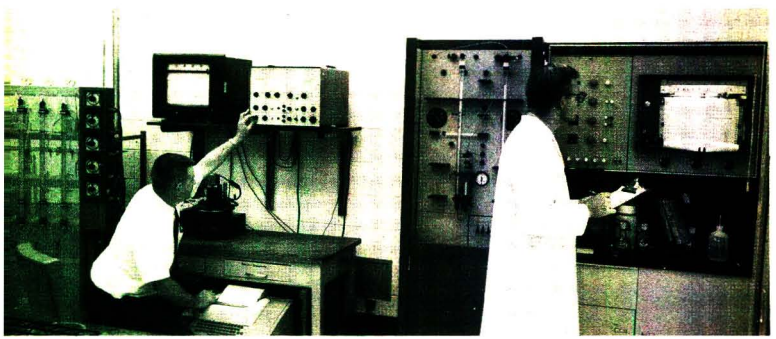
Analytical instrument laboratory, which is both temperature and humidity controlled, is centrally located within the analytical complex. The instruments here are available for use by all analytical personnel. One entire laboratory (not shown) in the analytical complex is devoted to atomic absorption analysis. About 2000 analyses are performed each day on five continually operated units. Each unit has digital readout device



Insect assay, before and after, is shown above. Standard jelly tray containing a nutrient medium is blended with a particular pesticide under study. One-day-old larvae are placed into each of the 50 cavities and the entire tray is covered with a Mylar film. After five days incubation, the number of dead larvae affords a measure of the effectiveness of the pesticide



Balance room has three-tiered lazy-susan table positioned strategically among balance tables so that five chemists can weigh from the same bottle without moving from balance



Two amino acid analyzers are used for the analysis of protein hydrolysates. Both analyzers are coupled to the Infotronics Model 12AB digital integrator and teletypewriter. One of the five chromatography columns from the Technicon unit on the left has been converted to an anion exchange resin for automatic sugar analysis

production site were simulated on a micro scale in the analytical laboratories, sometimes using radioactive tracers. As a result of these studies, significant changes in the plant processing system gave major improvements in plant operation. This is only one example of the versatility of this group which receives samples ranging from ham, fish, and other food products to fertilizers, insecticides, and ore samples submitted by geological prospecting teams.

The analytical chemistry section performs all types of chemical analyses and also has its own method development section. The plant and soil analysis section, for example, performs tens of thousands of plant tissue and soil analyses per year. These samples are requested by IMC field agronomists in their continuing effort to help growers achieve better fertilizer usage. A direct reading emission spectrograph is now being installed to handle this large number of samples.

IMC is a pioneer in the field of biological insecticides, and entomologists and microbiologists in the analytical biology group are engaged in rearing many different insect cultures on a routine basis. These cultures are then used for insect assay work and as experimental material by research entomologists. Since a biological insecticide has no chemical "handle," all analytical and quality control work must be done against the actual target insect. This requires extensive and completely equipped facilities and a versatile scientific staff such as that assembled at the Growth Sciences Center.

As a result of one particular analytical investigation, an enzyme reagent was developed for the rapid determination of gamma aminobutyric acid. The technique was so simple and accurate that the reagent is now offered as a special product marketed through the Analytical Department. The sales of this enzyme have been so encouraging that a series of analytical enzymes are now being developed. Dr. Stoner points out that, in this way, the department can defray part of its overhead.

An extensive program is currently in progress which will tie many of the analytical instruments into a central computer facility which is being installed at the Growth Sciences Center. The immediate plans call for interfacing a direct reading spectrograph, five atomic absorption spectrometers, and three AutoAnalyzers to the computer system, all on a "live-time" basis. Through time-sharing, it is anticipated that a 25% increase in sample output can be achieved with the present personnel.

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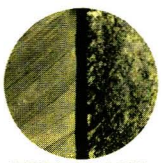
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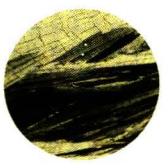
The instrument operates over the range of $-20°$ to $+300°C$, temperatures suitable for study of fusion phenomena of virtually all organic



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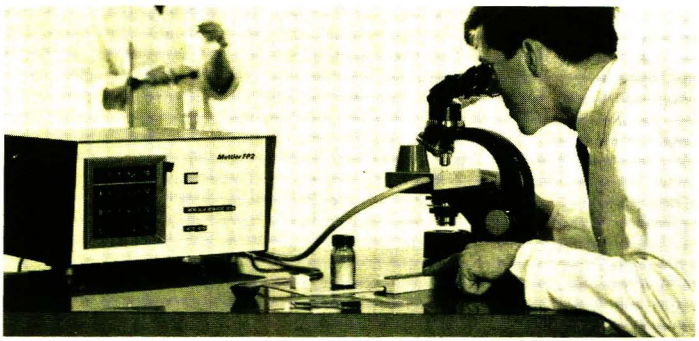
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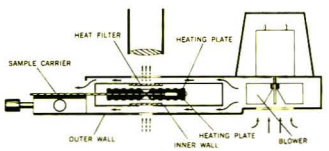
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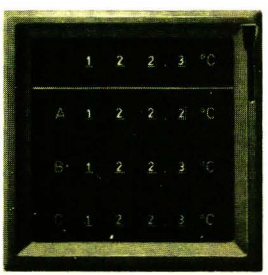
Mettler FP-2 is usable with any standard laboratory microscope



Schematic of sample chamber

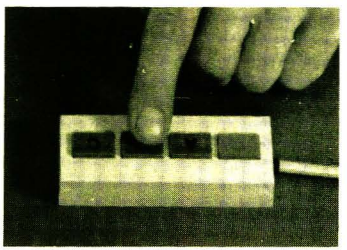
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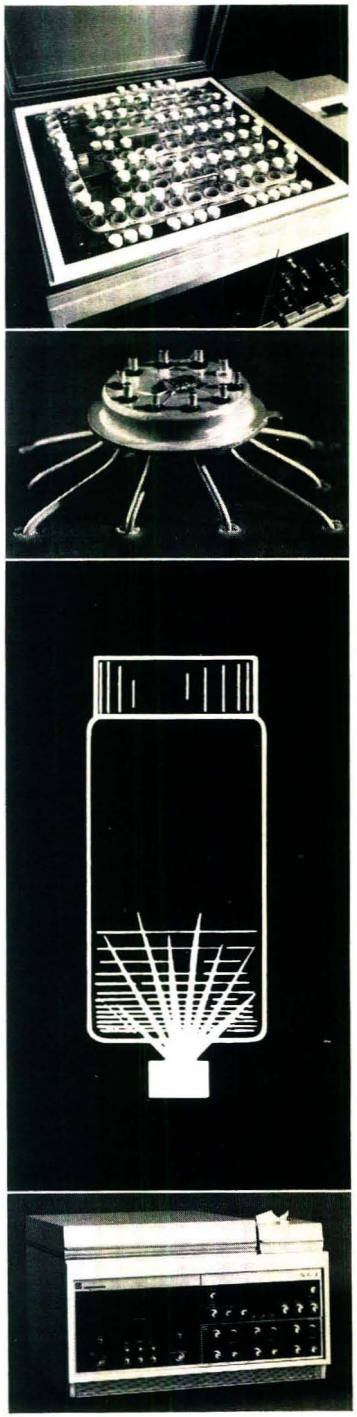
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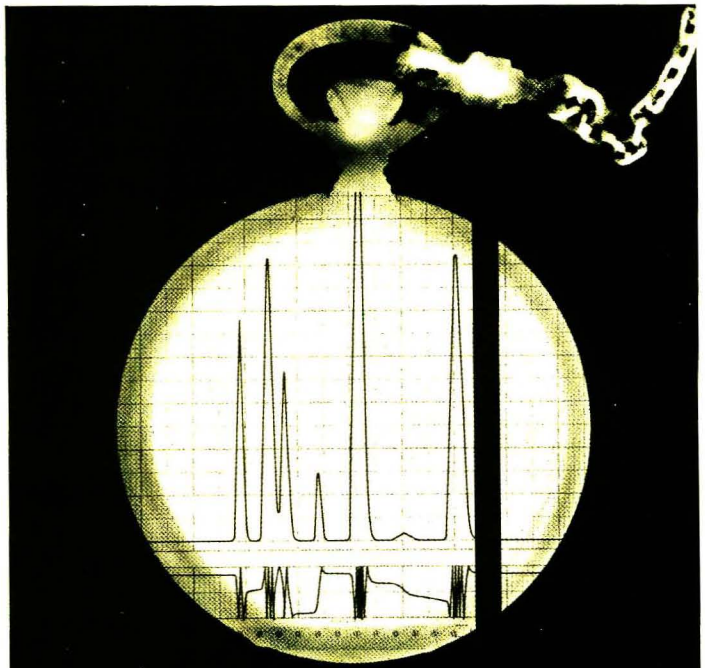
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INSTRUMENTATION



BY RALPH H. MÜLLER

Techniques of Electron Spectroscopy for Chemical Analysis Offer Challenge to Conventional Spectroscopy

WE ARE INDEBTED to Howard M. Bedell of 1269 Druid Rd. E., Clearwater, Fla. 33516, for further information on Electron Spectroscopy for Chemical Analysis (ESCA) and closely related techniques. Bedell, a physicist, has had a long and distinguished career in applied spectroscopy and as Regional Manager of McPherson Instrument Corp., at 530 Main St., Acton, Mass. 01720, has devoted much time to the exploitation of ESCA developments. McPherson is in production of two models, one limited to the study of gases and a larger, general purpose instrument. He informs us that the McPherson Corp. has been made the exclusive distributor of the book, "ESCA" by Kai Siegbahn *et al.*, published by Almquist and Wiksells of Stockholm.

Earlier studies on electron spectrometry, such as those of Lassettre, Berman, Silverman, and Krasnow, *J. Chem. Phys.*, **40**, 1232 (1964), afforded precise measurements of inelastic collision cross sections in helium, carbon monoxide, and oxygen.

A *Technical News Letter* from the National Bureau of Standards of August 1968 reports briefly on an impact spectrometer found valuable in trace analysis. It states that the instrument, called an electron impact spectrometer, developed four years earlier for research in atomic physics, has recently shown great potential in the fields of chemical trace analysis. By the use of the spectrometer, such hard-to-distinguish compounds as carbon monoxide can now be detected in concentrations as low as 15 parts per million. The instrument's high resolution and sensitivity should make it valuable for trace analysis and in the detection and control of air pollution. Its full capabilities are being investigated in a joint program of NBS and the National Aeronautics and Space Administration, Langley Research Center. As developed by J. A. Simpson, C. E. Kuzatt, and S. R. Mielczarek of the NBS Institute for Basic Standards, its operation depends on the collision of electrons with gas atoms or molecules. Upon impact, the collision electrons transfer their energy to the electrons bound within the atom, which are thus raised from the stable state to an excited energy level. The spectrometer disperses the collision electrons according to their energies after impact and the resultant energy corresponds to the optical absorption spectrum of the gas. In a study of the atmosphere, the naturally occurring argon and helium in the sample (approximately 0.2 nanogram and 0.2 picogram, respectively) were detected. In less favorable conditions where interference is a problem, as in detecting carbon monoxide in air, contaminants on the order of 10 parts per million have been detected. Simpson reports that, with a new design, 0.01 ppm may be detected.

The electron impact spectrometer possesses a number of advantages over other analytical instruments. For example, in comparison with a mass spectrometer, it is smaller, lighter in weight, and, at least for atoms and simple molecules, it is less susceptible to interference between constituents of mixtures. For example, in the case of nitrogen and carbon monoxide, there are differences in the molecular weight occurring in the third decimal place which constitutes a real problem in the mass spectrometer but not in the impact spectrometer. Also, the problem of identifying the parent compounds from their fragments does not arise.

The comparison with optical absorption methods is highly instructive. The electron impact spectrometer covers an enormous range because the energy losses which are measured correspond to optical wavelengths ranging from the X-ray to the visible region. Also, the response is linear rather than exponential with concentration, hence the sensitivity is greatly improved and the spectra are easier to interpret. References pertinent to this development are: *NBS Tech. News Bull.*, **48**, No. 4, 64–68 (April 1964): Absorption spectrum of SF_6 in the far ultraviolet by electron impact, *J. Chem. Phys.*, **44**, No. 12, 4403–4404 (June 1966); and Electron monochromator design, *Rev. Sci. Instr.*, **38**, No. 1, 103–111 (Jan. 1967).

Dr. William J. Campbell has very kindly sent us a copy of his review paper with James R. Brown: X-ray Absorption and Emission, ANAL. CHEM., **40**, No. 5, 364 R (1968). These and several related topics are discussed in detail. The report on the general subject contains 695 references. He discusses low energy X-rays, excitation by heavy particles, Auger and photoelectrons, and ESCA. Dr. Campbell, who is a supervisory research chemist at the Bureau of Mines, College Park, Md. 20740, states that he expects delivery of a combined LEED–Auger spectrometer in December. It is being designed for them by Varian Associates and when combined with a low voltage, high current X-ray tube for excitation of photoelectrons will provide the capability of LEED, Auger, and photoelectron spectroscopy on a sample surface that can be heated up to 1000 °C and exposed to a variety of atmospheres.

ESCA and its closely related techniques are being studied and examined in all quarters of the scientific world, following the monumental contribution from Sweden. We hope Mr. Bedell will find it possible to report on centers of interest and activity—he seems to know just about everyone who is interested or working on the subject. We have heard enthusiastic comment on the talks given by Dr. David Hercules of M.I.T. and are looking forward to his formal lecture at the twenty-second Annual Louisiana State University Symposium on Analytical Chemistry next January.

The essential antiquity of the subject has been pointed out by Siegbahn and others and its delayed development is easily understood in view of the great experimental difficulties in making electrical measurements of electron energies with a precision comparable to the optical equivalent so easily obtained by spectroscopy. The professional spectroscopist knows that the first resonance line of mercury has a wavelength of

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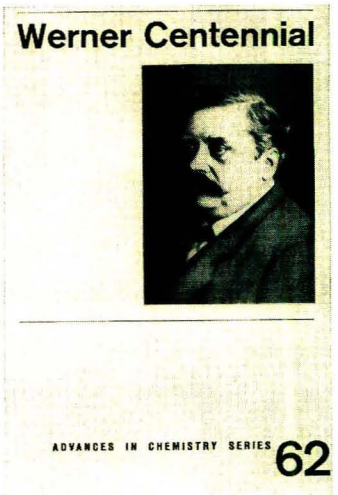
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2536.519 Å but has to be wary of V, Fe, Rh, Bi, P, Ta. Indeed, a Pt line only 1/20 the intensity of the Hg line has a wavelength of 2536.49 Å. The other neighbors differ by only 1 or 2 tenths of an Å. Anyone who wishes to plug these values into $Ve = h\nu$ can note the minute potential differences in V associated with these transitions. Also, the Auger electrons representing a nonradiating transition are unique because the resources of optical spectroscopy are fruitless.

Our interest and present excitement over the recent developments goes back to more than 40 years. Our postdoctoral studies at the Institute of the late James Franck at Göttingen were at a time when he was concerned with other important problems and hardly liked to be reminded of the simple but epochmaking experiment which he and Gustav Hertz had made in 1914. In bombarding mercury vapor with electrons of controlled velocity, they had noted the inelastic impact at 4.9 volts and properly identified as the excitation energy leading to the emission of the first resonance line of Hg at 2537 Å. This was the first experimental demonstration of the validity of quantized energy levels in the atom as postulated by Bohr a year earlier. Although Franck and Hertz jointly and singly determined many other critical impact values, the subject soon became of great interest and, in the hands of Bergen Davis, Foote, Mohler, and K. T. Compton, was soon established as a firm relationship between electrical excitation and optically established energy values, leaving no apparent extensions of further profit.

It soon became accepted that real precision was to be gained from the spectroscopic data and not from electrical measurements. The superb achievements of modern spectroscopy from the X-ray region out to microwaves can well be regarded as a *fait accompli*. What more could be asked for certainty and precision? We have continued to ask, and bore our friends, with the question, "What more can be learned electrically about flames, arcs, sparks, and luminous gases?" The unquestioned advantage of optical methods may be put bluntly, "Seeing is believing." To do these things electrically is obviously doing it the hard way, but now genius has prevailed and we have a potent challenge to conventional spectroscopy. It should convince the most doubtful that the phenomenological studies are still useful and all progress does not depend upon computers. Once more, it confirms the dictum of the inventor and designer, "Never let well enough alone."



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*U.S. Patents No. 3,245,665; No. 3,306,829

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Advisory Panel for Instrumentation

AFTER MANY YEARS of successful operation in the able hands of our Contributing Editor, Dr. Ralph H. Müller, the Instrumentation column will take a new form beginning with the January 1969 issue. Invited articles from outside contributors will cover a wide variety of subjects related to chemical instrumentation. The topics will range from descriptions of developments from the research frontiers of physics through specially constructed components or equipment for research measurements to modifications or design features in commercial instrumentation. Dr. Müller will continue as editor of this feature and will add commentary to the contributed articles as he deems appropriate.

One page 39A of this issue, an announcement is being made of the formation of a new Advisory Panel for Instrumentation. Initial membership on the Panel consists of six well-known authorities in various aspects of analytical instrumentation, Jonathan W. Amy, Glenn L. Booman, Robert L. Bowman, Jack W. Frazer, Howard V. Malmstadt, and William F. Ulrich. We are deeply indebted to this outstanding group, which during the past year has consulted by telephone, correspondence, and personal meetings with the editorial staff, and has helped to formulate policy and to recommend topics and authors for the invited contributions. It is anticipated that membership on the Panel will be on a rotating basis, so that we can call upon the advice of a wide circle of experts over a period of years without imposing unduly upon the efforts of any individual scientist.

We are eagerly looking forward to an exciting new feature which we confidently expect will play an increasingly significant role in keeping analytical chemists abreast of developments in this most important area in the years to come.



Analytical Applications of X-Ray Excited Optical Fluorescence Spectra: The Internal Standard Principle

Edward L. DeKalb, Velmer A. Fassel, Takeshi Taniguchi,[1] and T. R. Saranathan[2]

Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010

The intensities of X-ray-induced optical fluorescence emitted by trace concentrations of various rare earth elements in a suitable matrix are shown to be enhanced by low concentrations of residual impurities, and to be suppressed by somewhat higher concentrations of the same impurities. A variety of other operational variables, such as the time and temperature course of the sample ignition, the degree of absorption of H_2O and CO_2, and drifts in power output of the X-ray tube and in the detector response sensitivity, can also influence the fluorescence intensities. It is shown that the use of an internal standard will satisfactorily compensate for many of these effects.

THE SHARP-LINE optical fluorescence spectra emitted by ions of the rare earth elements when certain matrices are irradiated by X-rays (*1–3*) have recently been applied to the quantitative determination of fractional ppm amounts of Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, and Yb in Y_2O_3 and Gd_2O_3 matrices (*4, 5*). In the analytical papers by Linares, Schroeder, and Hurlburt (*4*) and by Cosgrove, Oblas, Walters, and Bracco (*5*) no mention is made of the sensitive dependence of fluorescence intensities on the kind and amount of residual impurities present in the host. Under ultraviolet excitation conditions, such dependence is commonly observed (*6–8*). Our studies of fluorescence emission under X-ray excitation conditions have clearly demonstrated that the emitted intensities are markedly influenced by other impurities present at the ppm level in the host matrix. In this paper, a description of these and other interference effects is given, and a technique for internally compensating for these effects on the fluorescent emission is outlined.

[1] Present address, Asahi Chemical Industry Co., Ltd., Tokyo, Japan.

[2] Present address, B.A.R.C., Trombay, Bombay-74, India.

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EXPERIMENTAL FACILITIES AND PROCEDURES

Apparatus. The experimental equipment employed is similar to that described by Linares *et al.* In our facility the X-ray source consists of a Machlett OEG-50 tungsten-target X-ray tube driven by a Norelco power supply. A sample chamber, an exploded view of which is shown in Figure 1, provides for the completely safe exchange of samples even though the X-ray tube (*a*) continues in operation at full power. During activation of the sample in this chamber, a small access door (*b*) is blocked in the closed position by a large lever (*c*). To exchange samples, the lever and an attached shutter (*d*) are rotated so that the X-ray beam is completely interrupted before the door can be raised. The sample is accurately and reproducibly positioned at an angle of 45° to the incident X-ray beam through the use of a vee-way mounting block (*e*) and mating sample holder (*f*). The optical path is inclined at an angle of 45° to the sample surface, and at 90° to the X-ray beam. A quartz lens focuses an image of the fluorescing sample onto the entrance slit of a 25-cm focal length grating spectrometer.

The entrance and exit slits of the spectrometer are set at 100 nm, and the spectrum is scanned at the rate of 200 Å per minute. The fluorescent radiation is detected with an S-20 response, fused silica-window photomultiplier (RCA 7268). The photocurrent is amplified (Keithley Model 417 Picoammeter) and recorded with a two-pen strip-chart recorder. One of the pens is one tenth as sensitive as the other, which permits a greater range of spectral intensities to be recorded during a single scan of wavelength. For the observation of some of the data reported in this paper, such as those shown in Figures 2–6, the photomultiplier voltage was adjusted to bring the photocurrents of the various spectral lines into an appropriate range for optimal plotting of the data.

Sample Preparation. All samples were prepared by combining dilute HNO_3 solutions of the various elements, followed by evaporation, dehydration, and ignition at appropriate

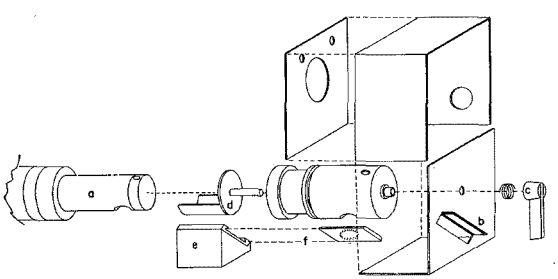


Figure 1. Diagram of the disassembled excitation chamber

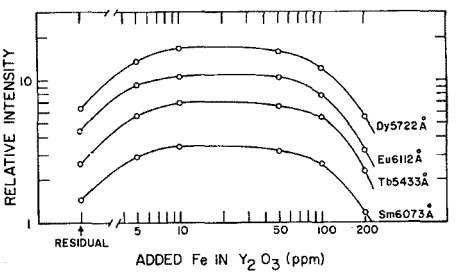


Figure 2. Effect of iron addition of the fluorescent emission of 200 ppm of Sm, Eu, Tb, and Dy in Y_2O_3

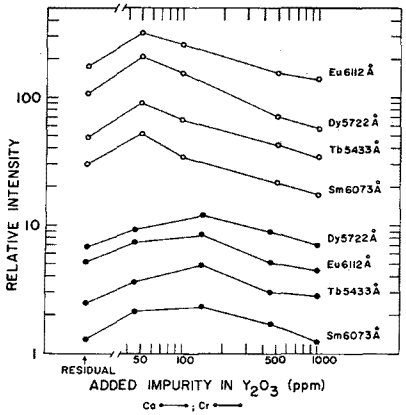


Figure 3. Effect of chromium and calcium additions on the fluorescent emission of 200 ppm of Sm, Eu, Tb, and Dy in Y_2O_3

temperatures. An oxalic acid precipitation was avoided because incomplete precipitation, which could significantly alter the rare earth concentrations at trace levels, has been reported (*9*). The ignited oxide was ground to a fine powder and then pressed into an aluminum planchet with the aid of a hydraulic press.

EXPERIMENTAL RESULTS AND DISCUSSION

Figures 2 and 3 show the intensity behavior of the optical fluorescent emission of 200 ppm of Sm, Eu, Tb, and Dy in a highly purified Y_2O_3 host, with the addition of increasing amounts of iron, chromium, or calcium. The enhancements observed at the lower concentration additions, which may be greater than a factor of two, are indeed surprising. We can offer no explanation for this enhancement effect. The

(9) M. M. Woyski and R. E. Harris, in "Treatise on Analytical Chemistry," Part II, Vol. 8, Interscience, New York, 1963, p 29.

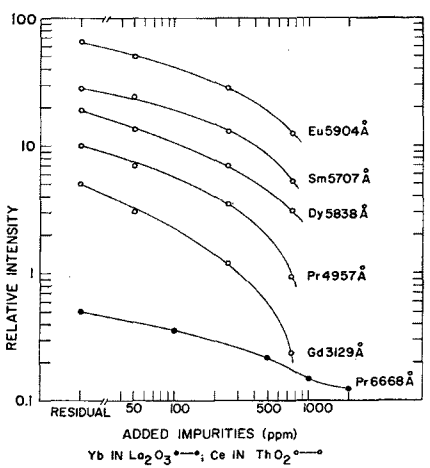


Figure 5. Effect of ytterbium addition on the fluorescent emission of 40 ppm of Pr in La_2O_3, and of cerium addition on the florescent emission of 2 ppm Pr, 3 ppm Sm, 1 ppm Eu, 0.5 ppm Gd, and 5 ppm Dy in ThO_2

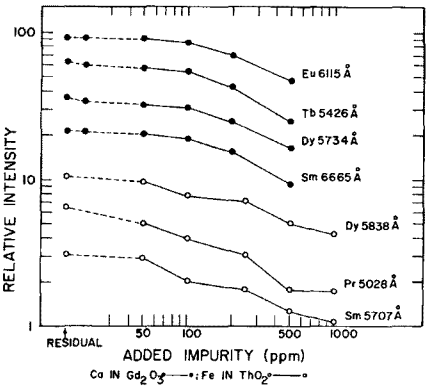


Figure 4. Effect of iron addition on the fluorescent emission of 2 ppm Pr, 3 ppm Sm, and 5 ppm Dy in ThO_2, and of calcium addition on the fluorescent emission of 100 ppm of Sm, Eu, Tb, and Dy in Gd_2O_3

validity of these observations was substantiated by repeated experiments which yielded essentially similar results. For several other Y_2O_3 matrices, a degree of enhancement lower than that shown in Figures 2 and 3 was observed. Whether these hosts contained a higher total non-rare earth impurity content has not been unequivocally established. Figure 4 shows essentially similar depressions of the fluorescence emission for Pr, Sm, and Dy in a ThO_2 matrix as the iron impurity level is increased, and for Sm, Eu, Tb, and Dy in a Gd_2O_3 host as the calcium impurity level is varied. Since these experiments may have been performed at total non-rare earth impurity levels greater than those for which enhancement may be observed, we have chosen to use dotted lines to extend the curves below 50-ppm impurity additions.

Linares *et al.* (*4*) have indicated that spurious results arising from energy transfer mechanisms between rare earth ions should not be expected at concentrations below 0.1 atomic per cent. Also, Cosgrove *et al.* (*5*) have provided experimental evidence that interactions of this type were not operative in an Y_2O_3 host when rare earth ion dopant levels of 100 ppm were investigated. However, our experimental results show that dopant concentrations of ytterbium or cerium at levels less than 100 ppm can markedly reduce the fluorescent emission of Pr in La_2O_3 or of Pr, Sm, Eu, Gd, and Dy in ThO_2 hosts. These observations are shown in Figure 5.

APPLICATION OF THE INTERNAL STANDARD PRINCIPLE

The typical enhancement–suppression effects illustrated in Figures 2 to 5 imply that precise knowledge of the nature and concentrations of all impurities is a prerequisite for quan-

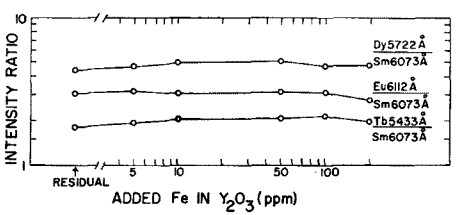


Figure 6. Effect of iron addition on intensity ratios of fluorescent emissions using Sm as the internal standard. The sample contained 200 ppm of Sm, Eu, Tb, and Dy in Y_2O_3

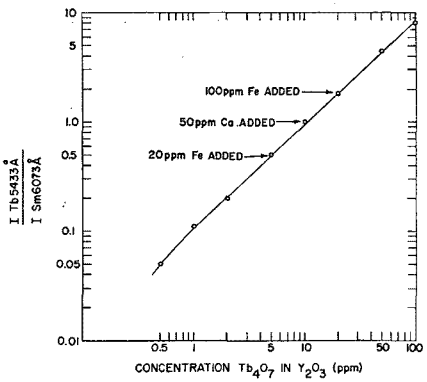


Figure 7. Typical analytical curve using 50 ppm of Sm as the internal standard

titative analytical applications of these spectra. Fortunately, this is not so. A characteristic exhibited by both the enhancement and suppression effects so far observed is the nearly parallel behavior of the intensities among the rare earths. Thus, though the individual relative intensities undergo wide excursions, the intensity ratios remain essentially invariant. These observations immediately suggest the application of the internal standard principle (*10*) so widely used in optical emission spectroscopy to these radiations as well. The merit of employing intensity ratio measurements to compensate internally for impurity enhancement or depression effects is excellently illustrated in Figure 6, where the same data in Figure 3 are replotted as the relative intensity of Eu, Tb, and Dy with reference to the Sm emission. A typical application of the internal standard principle is shown in Figure 7. For this application, the Y_2O_3 host was doped with 50 ppm Sm before the evaporation–dehydration–ignition preparation steps were undertaken. The amount of Sm added was far above the concentration normally found in ion-exchange column–purified Y_2O_3 when either EDTA or citric acid is used as the chelating eluant (*11*). Although two

(10) W. Gerlach, "Foundation and Methods of Chemical Analysis by the Emission Spectrum," Chap. V, Adam Hilger, London, 1929.

(11) D. B. James, J. E. Powell, and F. H. Spedding, *J. Inorg. Nucl. Chem.*, **19**, 133 (1961).

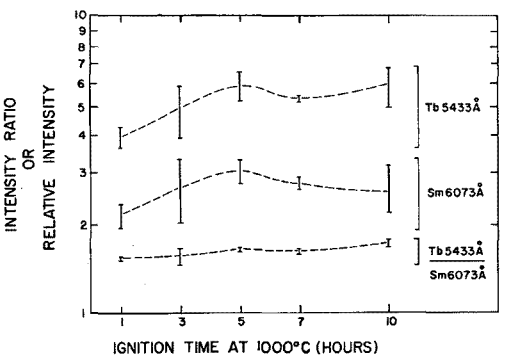


Figure 9. Effectiveness of internal standardization in compensating for both day-to-day fluctuations and the effect of ignition time on net intensities of separately prepared Y_2O_3 samples containing 10 ppm Tb and 50 ppm Sm

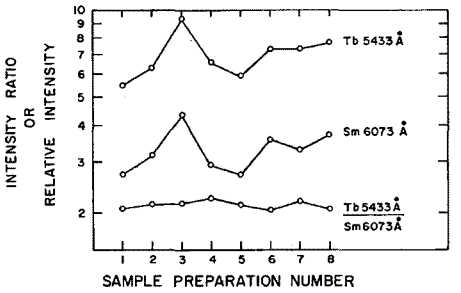


Figure 8. Effectiveness of internal standardization in compensating for day-to-day fluctuations in net intensities of separately prepared Y_2O_3 samples containing 10 ppm Tb and 50 ppm Sm

of the standard samples were deliberately doped with iron, and one with calcium, the working curve is essentially straight over the concentration range studied. Similar calibrating curves have been prepared and successfully utilized for the routine quantitative determination of Eu, Gd, Tb, and Dy in highly purified Y_2O_3.

The emission intensities of X-ray induced optical fluorescence spectra are also dependent on the time and temperature course of the ignition, on the degree of absorption of H_2O and CO_2, and on drifts in power output of the X-ray tube and in the detector response sensitivity. Linares *et al.* (*4*) have already observed that measurement of intensity ratios compensated for day-to-day variations in the emission intensities caused by differences in details of preparation. (After this manuscript was submitted for publication, the paper by Burke and Woods (*12*) came to our attention. Burke and Woods also observed that the emission intensities were strongly dependent on the details of preparation of the crystalline host and that measurement of internal standard intensity ratios compensated for this effect.) The effectiveness of the internal standard principle in compensating for these run-to-run and day-to-day variations is illustrated in Figure 8. For these experiments eight identical samples were prepared and analyzed on different days, with all operating conditions maintained as nearly constant as possible. Although the standard deviations in intensity of both the terbium and samarium fluorescent lines are greater than 16%, the intensity ratio of the pair is much less variable, with only a 4% standard deviation.

A similar study on the effect of ignition time is shown in Figure 9. The study was run twice on different days, to provide two data points for each ignition period. Again, it is clear that internal standardization has compensated for the effects of both time of ignition and day-to-day variations in net fluorescent emission intensities.

The internal standardization principle described in this paper has also been applied in a quantitative procedure for the determination of fractional ppm amounts of several rare earths in reactor grade thorium metal (*13*). This analytical method will be described in a subsequent communication.

RECEIVED for review July 9, 1968. Accepted September 16, 1968.

(12) W. E. Burke and D. L. Woods, Conference on Applications of X-Ray Analysis, Denver, Colo., Aug 1967.

(13) T. R. Saranathan, V. A. Fassel, and E. L. DeKalb, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 1968, Paper #267.

Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry

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The procedure outlined describes an extremely sensitive and accurate method for the determination of mercury down to 1.0 ppb in solution. This procedure has been applied to nickel and cobalt metal as well as rock samples and soil samples containing organic materials. The sample is taken into solution by an oxidizing acid attack. Mercury is then reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a quartz absorption cell of an atomic absorption spectrophotometer where its concentration is measured. The procedure is free from interferences due to organic matter or other volatile constituents of the sample. Large amounts of easily reducible elements must be absent from the solution.

THE following method for the determination of mercury in solution employs a simple reduction–aeration procedure to produce and introduce mercury vapor into a closed system where the absorption of the 2537Å line is measured in a quartz windowed cell.

Several spectrophotometric reagents have been employed for the determination of traces of mercury (*1*). Of these, dithizone is the most popular because it exhibits a high sensitivity. Many elements interfere and various separations and complexing agents are required in the analysis of materials containing heavy metals.

Conventional atomic absorption techniques using a flame lack the sensitivity that is required for trace analytical work (15 ppm for 1% Abs). Addition of a reducing agent to the solution improves the sensitivity slightly.

Several instruments are available for the atomic absorptiometric determination of mercury vapor (*2*, *3*). These range from small portable units to the elaborate instruments used for very low concentrations of mercury. The mercury vapor is produced by direct heating of the sample, thus limiting their application to solid samples.

The following procedure requires a commercial atomic absorption spectrophotometer with an otherwise simple apparatus to obtain extremely sensitive and accurate results for mercury down to 1.0 ppb in solution. The procedure is described for nickel and cobalt analysis, and has also been applied to rock analysis and soils containing organic matter. The method should find applications in biological analysis, where traces of mercury are present in aqueous solutions.

EXPERIMENTAL

Excellent results have been obtained in the determination of mercury by the procedure of Kimura and Miller (*1*) who employ an aeration step in the separation of mercury prior to its determination with dithizone.

Attempts were made to measure the mercury aerated from various solutions by passing the vapor through a quartz-windowed cell. The effects of different acids and several reducing agents were investigated. The presence of hydrochloric acid caused high absorbance values which may be due to its high mercury content (*4*). Aeration was satisfactory from dilute perchloric acid as well as dilute nitric and sulfuric acid solutions. Hypophosphorous acid is suitable for reduction of the mercury but contributes a small blank value. For nickel and cobalt samples, nitric and sulfuric acid were found most satisfactory with stannous sulfate as reducing agent. Reduction was carried out in a sodium chloride–hydroxylamine sulfate medium. Very low blank values were observed using these reagents.

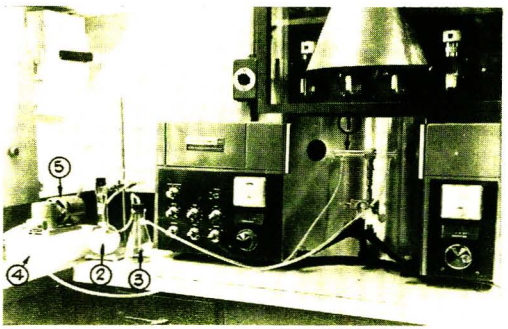


Figure 1. Apparatus used

(1) Absorption cell
(2) Reaction flask
(3) Flask containing drying agent
(4) Disconnect for bleeding mercury from system
(5) Neptune Dyna-Pump

Apparatus. ATOMIC ABSORPTION SPECTROPHOTOMETER. Perkin-Elmer Model 303 equipped with Automatic Null Recorder Readout. Other commercial units having an open sample presentation area to mount the absorption cell could be used.

MERCURY HOLLOW CATHODE LAMP. Westinghouse WL-22847, argon filled.

RECORDER. Sargent Model SRL used in the logarithmic mode for direct absorbance measurement.

ABSORPTION CELL. Constructed from borosilicate glass tubing, 25-mm o.d. × 15 cm. The ends were ground perpendicular to the longitudinal axis and quartz windows (25-mm diameter × 2-mm thickness) were cemented in place. Gas inlet and outlet ports were attached approximately 2 cm from each end.

VARIAC, 0 to 130 volts, for controlling pump speed.

NEPTUNE DYNA-PUMP, Model 3. The pump was disassembled, valves and diaphragm were removed, and all metallic surfaces were sprayed with a clear plastic to resist corrosion. When dry, the unit was reassembled.

AERATION TUBING. Borosilicate glass of 5-mm i.d.

SUCTION FILTRATION FLASK containing 10 grams of magnesium perchlorate.

The apparatus is assembled as shown in the accompanying

(1) Y. Kimura and V. L. Miller, *Anal. Chim. Acta*, **27**, 325 (1962).
(2) W. W. Vaughn and J. H. McCarthy Jr., *U. S. Geol. Survey Prof. Paper* **501-D**, pp D 123–127 (1964).
(3) A. R. Barringer, Institution of Mining and Metallurgy, **75**, *Bull No.* **714**, May (1966).
(4) E. B. Sandell, 3rd Ed., "Colorimetric Determination of Trace Metals," Interscience, New York, 1959, p 625.

Table I. Variation in Mercury Vapor Absorbance with Time

Time, seconds	Absorbance
0	0.000
24	0.108
48	0.198
72	0.245
96	0.268
120	0.282
144	0.290
168	0.292
192	0.292
216	0.292
240	0.292

Table II. Calibration and Analysis of Nickel and Cobalt Samples

Sample	Hg added, μg	Absorbance	Hg found, μg	Parts per billion
Blank	0.00	0.002		
Blank	0.30	0.090		
Blank	0.60	0.175		
Blank	1.00	0.268		
Blank	2.00	0.440		
Nickel (1.0 g)	0.00	0.040	0.12	120.0
Nickel (1.0 g)	1.00	0.305	1.16	
Cobalt (1.0 g)	0.00	0.020	0.07	70.0
Cobalt (1.0 g)	1.00	0.270	1.03	

photograph. Tygon tubing is used for passage of the mercury vapor with a disconnect in the line for bleeding mercury from the closed system.

The cell is aligned in the light beam by the use of two 2-inch by 2-inch cards. Twenty-five-millimeter holes are cut in the middle of each card and placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

Reagents. STANNOUS SULFATE, 10% w/v solution in 0.5*N* sulfuric acid.

SODIUM CHLORIDE, 30% w/v solution.

HYDROXYLAMINE SULFATE, 25% w/v solution.

SODIUM CHLORIDE–HYDROXYLAMINE SULFATE SOLUTION. Transfer 60 ml of the 25% hydroxylamine sulfate and 50 ml of the 30% sodium chloride solutions to a 500-ml volumetric flask and dilute to the mark with water.

POTASSIUM PERMANGANATE, 5% w/v solution.

STANDARD MERCURY SOLUTION, 0.100%. Dissolve 0.1354 gram of mercuric chloride in 100 ml of 1*N* sulfuric acid. From this solution prepare by dilution a 0.001% solution in 1*N* sulfuric acid. Dilute solutions should be prepared fresh daily.

Instrument Settings. Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer with Automatic Null Recorder Readout

Lamp Current	10 mA
Wavelength	2537 Å (UV)
Slit Setting	3
Scale	X1
Noise Suppression	2

Recorder Settings
Logarithmic Mode
Scale Selector—mV
Range—10 mV
Chart Speed 0.5 inch per minute

Calibration. Transfer aliquots of the standard mercury solution containing 0.2 to 2.0 μg of mercury to 250-ml round-bottom flasks. Add 25 ml of 18*N* sulfuric acid and 10 ml of 7*N* nitric acid to each and dilute to 100 ml.

Treating each sample individually, add 20 ml of the sodium chloride–hydroxylamine sulfate solution, followed by 10 ml of the stannous sulfate solution. Immediately attach the flask to the aeration apparatus forming a closed system. Turn on the circulating pump and adjust the aeration rate using the Variac.

The absorbance value will increase and reach a constant value within a period of 3 minutes. Open the system at the disconnect and continue the aeration until the absorbance returns to its minimum value. The absorbance readings thus obtained are plotted against micrograms of mercury to establish the calibration curve.

Absorbance values obtained on aeration of 1.1 μg Hg from solution are given in Table I. A maximum value is reached after 3 minutes at a circulation rate of approximately 2 liters per minute.

Procedure. Transfer 1.0 gram of nickel or cobalt metal to a 250-ml round-bottom flask. Add 10 ml of 7*N* nitric acid and dissolve without the application of heat. Add 25 ml of 18*N* sulfuric acid and dilute to 100 ml. Cool to 20 °C and add 20 ml of mixed sodium chloride–hydroxylamine sulfate solution. Add 10 ml of stannous sulfate and immediately attach to the aeration apparatus. Aerate the solution according to the directions given under "calibration curve" obtaining the absorbance of the mercury vapor.

A variation of this procedure is used for the analysis of rock samples.

Treat 1 to 4 grams of finely-ground material with 25 ml of concentrated sulfuric acid in a 250-ml round-bottom flask. Carefully make three, 1-ml additions of 50% hydrogen peroxide solution to the flask, allowing sufficient time for the decomposition of peroxide between additions. Heat the flask gently to decompose any remaining peroxide. Cool to 20 °C.

(5) M. Fleischer, *Geochim. Cosmochim. Acta*, **29**, 1271 (1965).

Table III. Results Obtained on U.S.G.S. Rocks[a] and Falconbridge Secondary Rock Standard "A"

	Mercury—Parts per Million			
Sample	Proposed method	Neutron activation (5)	Atomic absorption (2)	Dithizone spectrophotometry[b]
G-1	0.11; 0.08	0.34	0.13	0.090; 0.070; 0.095
W-1	0.18; 0.18	0.17	0.34	0.17; 0.16
Falconbridge Secondary Rock Standard "A"	0.36; 0.33; 0.36; 0.36; 0.39; 0.33; 0.32[c]			

[a] Standard Rock Samples—Granite (G-1) and Diabase (W-1) issued by the United States Geological Survey.
[b] Analysis performed at Falconbridge, Thornhill.
[c] Mean 0.35
Standard deviation 0.024

Carefully add 100 ml of water and 5% potassium permanganate solution until a permanent pink color is obtained. Cool the solution to 20 °C and continue as in the above procedure adding the hydroxylamine sulfate–sodium chloride solution and the stannous sulfate solution.

RESULTS AND DISCUSSION

The values obtained in establishing the calibration curve and the results obtained from the analysis of nickel and cobalt samples are given in Table II.

Table III lists the values obtained on U. S. Geological Survey rocks•G-1 and W-1 using the modified procedure. Results obtained in this laboratory using the dithizone procedure of Kimura and Miller (*1*) and other available data are also shown.

Also shown in Table III are the results of seven determinations performed on a finely-ground rock sample used as a secondary standard. From these data the precision of the method was calculated.

There are few interferences under the conditions described. The procedure cannot be applied to metal samples such as copper, which is easily reduced, thus preventing the complete aeration of mercury. Large amounts of elements such as tellurium, which are easily reduced to their elemental state, cause low results by coprecipitating some of the mercury. Usually this interference can be detected by visual inspection of the solution after the addition of stannous sulfate. Normally these elements are not present in sufficient quantity to cause interference.

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Enhancement of Zirconium Atomic Absorption by Nitrogen-Containing Compounds and its Use in the Determination of Ammonia

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The absorption by zirconium atoms in the nitrous oxide–acetylene flame is enhanced in the presence of many nitrogen-containing compounds which can act as Lewis bases. For ammonia the magnitude of this enhancement is proportional to the concentration of base over the range 1×10^{-4} to $5 \times 10^{-3}M$ and can be used to determine ammonia in the absence of phosphate and of certain nitrogen-containing compounds. When interfering species are present the method can be used, after prior distillation of the ammonia, to replace spectrophotometric methods which require considerable time for color development. The analytical usefulness of the enhancement technique is demonstrated by the determination of ammonia in biological systems.

AMOS AND WILLIS (*1*) observed that fluoride ion enhanced the absorption by zirconium atoms in the nitrous oxide–acetylene flame, and Bond and O'Donnell (*2*), while investigating this effect as a method for determining fluoride, found that ammonium ion interfered by causing an enhancement similar to that produced by fluoride. This suggested that the atomic absorption technique might be applied to the determination of ammonia and be a useful supplement to existing methods, most of which require prior distillation of the ammonia and time-consuming color development before making spectrophotometric measurements (*3*).

In order to investigate further the principles behind the enhancement of zirconium absorption by ammonia, a range of other nitrogen-containing compounds was also investigated.

EXPERIMENTAL

Ammonium chloride (B.D.H. "AnalaR" quality) and zirconium oxychloride octahydrate (B.D.H. "L.R." quality, 98.5% ex. Cl analysis) were assumed to be stoichiometric. Other nitrogen-containing compounds were of analytical reagent grade wherever available, and if any doubts existed about purity the materials were purified by distillation or recrystallization, as appropriate.

Atomic absorption measurements at the 3601.2Å line of zirconium were made with an AA-4 or AA-100 atomic absorption spectrophotometer (Varian Techtron Pty. Ltd., North Springvale, Victoria 3170, Australia) fitted with a 50- × 0.5-mm slot burner for use with nitrous oxide–acetylene mixtures. Absorption was measured in a fuel-rich, slightly luminous flame having an interconal zone about 30 mm high.

ENHANCEMENT OF ZIRCONIUM ABSORPTION BY NITROGEN-CONTAINING COMPOUNDS

Figure 1 shows the effect of a number of nitrogenous compounds on zirconium absorption. The absorbance at first increases linearly with the concentration of compound, and then flattens out to a plateau when the molar ratio of nitrogenous compound to zirconium exceeds a value of about four. The solutions measured contained $0.8M$ hydrochloric acid to keep the nitrogenous compounds in solution and $0.006M$ potassium chloride to suppress the ionization of zirconium, which is appreciable in the nitrous oxide–acetylene flame (*4*). Table I shows the results of semi-quantitative survey of a wider range of compounds; in general, the most basic compounds show the strongest enhancement of zirconium absorption, which seems to depend principally on the availability of an unshared electron-pair at the nitrogen atom.

(1) M. D. Amos and J. B. Willis, *Spectrochim. Acta*, **22**, 1325, 2128 (1966).
(2) A. M. Bond and T. A. O'Donnell, ANAL. CHEM., **40**, 560 (1968).
(3) I. M. Kolthoff and P. J. Elving, "Treatise on Analytical Chemistry," Part II, Vol **5**, Interscience, New York, 1961, pp 279–85.
(4) D. C. Manning, *Atomic Absorption Newsletter*, **5**, 127 (1966).

Table I. Enhancement of Zirconium Absorption by Nitrogen-Containing Compounds

Compound	pK_b[a]	Magnitude of enhancement[b]
Inorganically substituted ammonias		
NH_3	4.75	3
$NH_2 \cdot NH_2$	5.77	3
$C_6H_5 \cdot NH \cdot NH_2$	8.79	3
$HO \cdot NH_2$	7.97	2
Aliphatic amines		
$CH_3 \cdot NH_2$	3.36	3
$(CH_3)_2 \cdot NH$	3.28	3
$(CH_3)_3 \cdot N$	4.26	3
$C_6H_5 \cdot CH_2 \cdot NH_2$	4.63	3
$(C_2H_5)_4N^+ Br^-$		0
Aromatic amines		
$C_6H_5NH_2$	9.42	2
$C_6H_5 \cdot NH \cdot CH_3$	9.30	2
$C_6H_5 \cdot N(CH_3)_2$	8.94	2
$p\text{-}NH_2 \cdot C_6H_4 \cdot NH_2$	7.96	2
2:4:6-Triaminotoluene		2
α-Naphthylamine	10.08	2[c]
Heterocyclics		
C_5H_5N	8.77	3
Quinoline	9.20	3
2-Hydroxyquinoline		3
8-Hydroxyquinoline	9.21	3
N-methylnicotinamide iodide		0
Aminoacids		
$o\text{-}NH_2 \cdot C_6H_4 \cdot COOH$	11.85	0
$p\text{-}NH_2 \cdot C_6H_4 \cdot COOH$	11.64	0
$HOOC \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$		0
$H_2N \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$		0
$H_2N \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$	5.05	1
$(HOOC \cdot CH_2)_2 \cdot N \cdot CH_2 \cdot CH_2 \cdot N \cdot (CH_2COOH)_2$		0
Miscellaneous		
$(NH_2)_2CO$	13.82	3[d]
$(NH_2)_2C{:}NH$		3
$CH_3 \cdot CO \cdot NH_2$	12.60	0
$p\text{-}NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH_2$		3
$CH_3 \cdot CN$		0
NaSCN		0
$CH_3 \cdot C(NOH) \cdot C(NOH) \cdot CH_3$	12.6	0

[a] Values in aqueous solution at 20 or 25 °C, mostly from reference (*5*).
[b] Measured as far as possible with solutions containing 0.020*M* Zr and 0.8*M* HCl. The figures 0, 1, 2, and 3 correspond to enhancement of the zirconium absorption plateau by 0.00, 0.00–0.05, 0.05–0.1, and >0.1 absorbance units, respectively.
[c] Low solubility makes magnitude of enhancement somewhat uncertain.
[d] This compound is readily and rapidly hydrolyzed to ammonia.

It is unlikely that the enhancement is due to improved atomization brought about by deflagration in the flame of particles of organic materials, both because the concentration of organic compound is so low (<0.1*M*), and because the effect seems highly specific for certain types of nitrogenous compound.

The enhancement of zirconium absorption can probably be explained in the following way. In aqueous media, even in the presence of 2*M* hydrochloric acid, Zr(IV) exists as oxyzirconium polymeric species such as $[Zr_4(OH)_8]^{8+}$ (*6*), so that in the absence of other materials the droplets of solution will dry out in the flame to particles of highly aggregated ZrO_2. This compound has a melting point of about 2700 °C, and is not very efficiently atomized even in the nitrous oxide–acetylene flame.

Now zirconium is a reasonably strong Lewis acid, as evidenced by its ability to form adducts with weakly basic organic oxygen compounds, such as esters and alcohols, as well as with amines. Bradley and Thomas (*7*) have prepared a number of compounds of zirconium with amines in which four nitrogen atoms are linked to an atom of zirconium; these compounds are characterized by their relatively high volatility, and are all monomeric rather than polymeric. It is reasonable to assume that when a zirconium solution containing a nitrogenous Lewis base is sprayed into the flame the zirconium can form metal–nitrogen compounds during the drying-out process, and these will be more volatile and more efficiently atomized than the zirconium oxide particles formed in the absence of nitrogenous compounds. It is unlikely that zirconium–nitrogen compounds can exist in the solution sprayed into the flame, as the high concentration of hydrochloric acid will ensure that all the nitrogen atoms are protonated and hence not available to form bonds to the zirconium.

Titanium and hafnium, which are chemically similar to zirconium, also show enhanced atomic absorption in the presence of nitrogen-containing compounds, but iron, cobalt, nickel, and copper have been reported by Hartlage (*8*) to show *reduced* absorption in the presence of amines, in air–acetylene though not in nitrous oxide–acetylene flames. Hartlage's experiments, however, were conducted with very high concentrations of amine in ethanolic solution, so that it is difficult to compare the results with those of the present work. Likewise, the two-fold enhancement of lanthanum oxide band emission in the presence of 1–2% ammonium chloride reported by Poluektov and Nikonova (*9*) probably calls for a different explanation from that given here for the enhancement of zirconium absorption.

Figure 2 shows that the presence of nitrogenous compounds has no effect on the height in the flame at which the maximum concentration of zirconium atoms occurs. It also indicates that high in the flame the absorption is independent of the presence of nitrogenous compound. This behavior is similar to that observed for other interferences in the nitrous oxide–acetylene flame (*10*), and is probably caused by the decomposi-

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(10) J. A. Bowman and J. B. Willis, ANAL. CHEM., **39**, 1210 (1967)

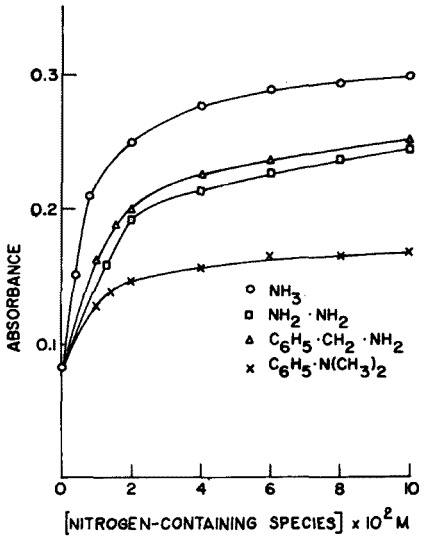


Figure 1. Effect of nitrogen-containing compounds on the absorption of Zr 3601.2 Å

Solutions contain 0.015*M* Zr, 0.006*M* KCl, and 0.8*M* HCl

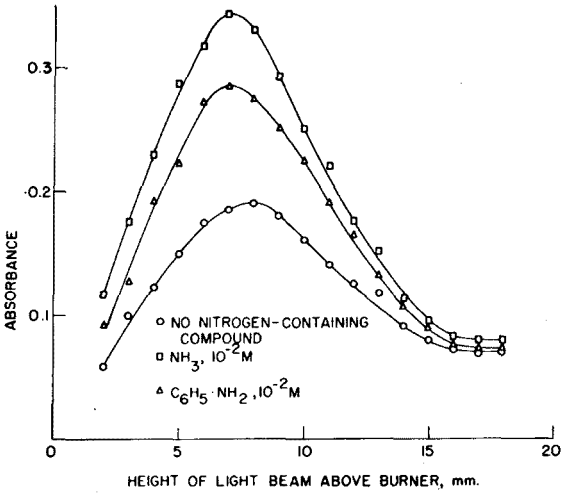


Figure 2. Relation between zirconium absorption and height of light beam in flame

Solutions contain 0.015*M* Zr, 0.006*M* KCl, and 0.8*M* HCl

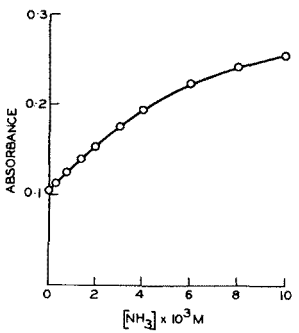


Figure 3. Typical calibration curve for determination of ammonia

Solution is 0.020*M* in Zr and 1*M* in HCl

tion of the zirconium–nitrogen compounds and by a close approach to equilibrium in the reaction of zirconium with oxygen under the conditions prevailing high in the flame.

DETERMINATION OF AMMONIA

For the lowest concentrations of ammonia a solution containing about 0.005*M* zirconium in 0.1–3 *M* hydrochloric acid is used, while for higher ammonia concentrations (0.001–0.01*M*) zirconium concentrations up to 0.02*M* are suitable. Standards are prepared by adding ammonium chloride to cover the required concentration range of ammonia, and 0.006*M* potassium chloride is incorporated if readily ionizable metals are present in the samples. Use of the scale expansion facility of the AA-4 instrument is advantageous at low ammonia concentrations. Figure 3 shows a typical calibration curve.

Phosphate interferes with the determination of ammonia by precipitating the zirconium, but other anions, such as nitrate and sulfate, only depress the zirconium absorption at concentrations about 100 times that of the ammonia. Fluoride enhances the absorption in the same way as does ammonia, but because the effects are additive it is possible to compensate for this interference by adding an excess (0.01*M*) of fluoride to both sample and standard solutions. The effect of alkali metals, which enhance zirconium absorption by suppressing its ionization in the flame, is overcome as mentioned earlier by adding excess potassium chloride to both sample and standard solutions.

Table II. Results of Analysis of Ammonium Nitrate Solutions

Solution No.	Concn of NH_3, *M*	Concn found by atomic absorption, *M*
1	1.00×10^{-2}	$1.08, 1.06, 0.94 \times 10^{-2}$
2	1.00×10^{-3}	$1.03, 1.12, 1.17 \times 10^{-3}$
3	1.00×10^{-4}	$0.9, 1.2, 1.1 \times 10^{-4}$

The precision of the method is limited chiefly by the noise level of the nitrous oxide–acetylene flame. Results of typical determinations are shown in Table II.

Attempts were made to determine ammonia directly in mitochondria samples prepared by the method of Hird and Marginson (*11*), but the results were unsatisfactory because of the presence of phosphate. However, the atomic absorption method was found suitable after separating the ammonia by distillation as described by these authors, but collecting it in hydrochloric rather than sulfuric acid. Considerable time was saved in analysis by atomic absorption because there was no need to wait for the development of the indo-

(11) F. J. R. Hird and M. A. Marginson, *Arch. Biochem. Biophys.*, **115**, 247 (1966).

phenol color required in the method of Hird and Marginson. The limit of detection of ammonia, however, was found to be superior in their method, but in all other aspects results obtained by the two methods were equivalent.

CONCLUSIONS

Nitrogen-containing compounds which can act as Lewis bases enhance the absorption of zirconium in the nitrous oxide–acetylene flame, probably through the formation of relatively volatile and easily atomized compounds containing zirconium–nitrogen bonds. This enhancement can be used in the determination of such nitrogenous compounds, and its practical application in the determination of ammonia in biological material has been demonstrated.

The work suggests that ammonium chloride might well be used, in place of the highly toxic and corrosive hydrofluoric acid, to enhance zirconium absorption in the determination of this metal by the atomic absorption technique.

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High Resolution Mass Spectral Photoplate Data Acquired and Reduced with a Real Time Remote Time-Shared Digital Computer

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A system is described that combines an automatic comparator–densitometer to read transmission values every 0.5 micron and a medium size, high speed, time-shared digital computer connected via a direct cabling system to transmit high resolution mass spectral photoplate data. The digital data are processed by a machine language data acquisition program resident in the computer, and those data above a threshold are stored on a disk file. While the comparator slews back to begin reading another exposure, the computer transfers the acquired data from the disk to a magnetic tape. This procedure is repeated until all spectra of interest are transmitted and stored sequentially on magnetic tape. The data are reduced at the computer operator's convenience. A FORTRAN program reads the peaks into memory, calculates peak centers and areas, resolving unresolved doublets by a nonlinear least squares procedure, calculates masses, elemental compositions, and prints an element map and a "low resolution spectrum" and a list of all elemental compositions found. Data are presented illustrating the accuracy of mass and intensity determinations with this system.

SINCE BEYNON (*1*) demonstrated that high resolution mass spectrometry can yield extremely useful information to an organic chemist, much work has gone into facilitating the acquisition and reduction of high resolution mass spectral data. The direct digital recording of high resolution mass spectral data onto magnetic tape was discussed by Merritt *et al.* (*2*). Analog recording was demonstrated by McMurray, Green, and Lipsky (*3*).

Obtaining data via photoplate recording has been shown by Biemann and Desiderio (*4–6*), McLafferty, Venkataraghavan, and Amy (*7*), Olsen (*8*), and Wadsworth and Tunnicliff (*9*). Quite recently Bowen *et al.* (*10*) and Burlingame, Smith, and Olsen (*11*) have shown the possibility of connecting a magnetically scanned spectrometer to a small, high speed computer.

Biemann *et al.* (*12*) have demonstrated a system that obtains data with an on-line computer located in the laboratory. The methods of acquiring the data and reducing the data are different in many respects from those described here and the distance over which data must be transmitted is minimal. This approach and the one described in this paper do, however, represent the terminal developmental step in the acquisition of data, namely, by direct communication with the computer. In both Biemann's system and our system, there is no intermittent storage of data during the acquisition step, and the computer acts in a decision-making capacity during this acquisition step.

A data reduction system was desired in this industrial laboratory to obtain high resolution mass spectral data from photoplates on a routine basis for confirming suspected structures or occasionally elucidating an unknown structure at a minimal cost to a chemist submitting a sample. In addition, a minimum amount of human intervention was desired along with both a maximum convenience to the comparator operator and a fast return of results. A microdensitometer–comparator connected remotely to an existing computer appeared to be the best design to achieve the above desiderata.

The data are reduced by specifically written curve analysis

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(1) J. H. Beynon, "Advances in Mass Spectrometry," J. D. Waldron, ed., Vol. I, Pergamon Press, New York, 1959.
(2) C. Merritt, P. Issenberg, M. L. Bazinet, B. N. Green, T. O. Merron, and J. G. Murray, ANAL. CHEM., **37**, 1037 (1965).
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(5) K. Biemann, P. Bommer, and D. M. Desiderio, *Tetrahedron Letters*, **26**, 1725 (1964).
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(9) P. Wadsworth and D. Tunnicliff, 18th Annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, March 1967.
(10) H. Bowen, T. Chenevix-Trench, S. Drackley, R. Faust, and R. Saunders, *J. Sci. Instr.*, **44**, 343 (1967).
(11) A. L. Burlingame, D. H. Smith, and R. W. Olsen, ANAL. CHEM., **40**, 13 (1968).
(12) C. Cone, P. Fennessey, R. Hites, N. Mancuso, and K. Biemann, 15th Annual Conference on Mass Spectrometry, Denver, May 1967.

and resolution programs employing well documented techniques and are converted to the convenient element map form in a manner described elsewhere (*4–6*).

EXPERIMENTAL

Description of Apparatus. The high resolution mass spectrometer used in this work is a Model 21-110B (CEC, Monrovia, Calif.) of a resolving power specification of one part in 31,800 with a 10% valley definition. The photoplates produced (2″ × 13.5″) contain up to 30 separate mass spectra.

The photoplates are read by a Gaertner comparator Model C9418 (Gaertner Scientific Corp., Chicago, Ill.). The linear range of plate travel is 380 mm with a cross motion of 90 mm. The optical slit is at an effective width of ≈1 micron on the photoplate. Since the objective lens is 6×, the slit is 6 microns in the slit plane. An RCA 931A photomultiplier tube is used. The motor drive unit has a continuously variable speed of from 0 to 125 mm/min, is automatically reversible, and has a control stability of better than 3%. However, this system is based on interrupts generated by the distance encoder and not on time-generated interrupts. Therefore, a stable speed is not necessary in this system.

A Datex optical encoder Model 03-507-9 (Datex Corp., Monrovia, Calif.) was attached to the lead screw of the comparator. Thus, each mm of travel of the stage (360 degree rotation of the lead screw) was divided into 2048 increments providing an accuracy of 0.488 microns (referred to hereafter as ½ micron). The optical encoder output is an 11-bit Gray Code word that is transmitted in a manner to be explained below.

The photomultiplier tube analog output is amplified by an Analog Devices Model 210 operational amplifier (Analog Devices, Cambridge, Mass.) and then converted to digital form by an SDS A/D converter. The A/D converter has a range of ±10 volts, and has an output of 10 bits plus a sign.

The existing computer in this laboratory is a time-shared SDS Model 930 digital computer (Scientific Data Systems, Santa Monica, Calif.) which is capable of foreground–background operation via a system employing a series of priority interrupts. The computer has a 24-bit word and a 16,384 word memory. The times for multiplication are 7.0 microseconds for fixed point and 147.0 microseconds for floating point. The times for addition are 3.5 microseconds for fixed point and 92.0 microseconds for floating point. The cycle time is 1.75 microseconds.

The apparatus used in this work is described here for the sake of completeness of the paper. A much more detailed explanation of the components of this system and the electronic manner of effecting the flow of data through the system is given in a companion paper (*13*).

Data Acquisition. The flow of information in the system is explained below and is illustrated in Figure 1. For time-shared operation, the photoplate is currently read by the comparator at a rate up to 30 mm/min. At a 30 mm/min data acquisition rate, a reduction of up to 25% in computer speed in performing background operations is experienced. For nontime-shared operation the system is capable of acquiring data at a rate up to approximately 100 mm/min. The system can be relatively easily switched from time-shared to nontime-shared mode and vice versa, if so desired.

The transmission determined by the photomultiplier and amplified, and the distance determined by the encoder are combined into one 24-bit computer word by the logic in the junction box. Every time the encoder changes position (each ½ micron), an interrupt is sent to the central processing unit (CPU) of the computer. The CPU returns another

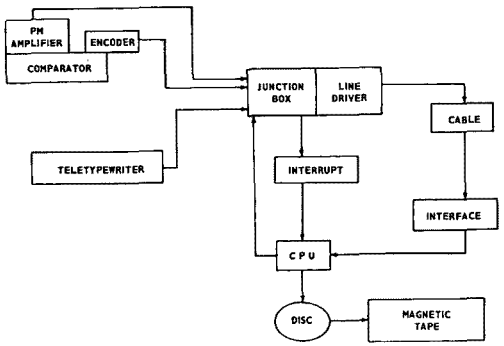


Figure 1. Block diagram of comparator–computer linkage

signal enabling the junction box to send the temporarily stored data. Appropriate line drivers amplify the signals and send the data through a 500-foot cable to an interface near the computer that accepts the parallel input data and converts the data to a form acceptable to the CPU.

Computer logic and programs resident in the computer determine whether each datum is above or below a preset threshold transmission value. If below threshold, the datum is discarded; if above, it is stored and checked to see if it is the first datum for a peak or one of the succeeding data. If it is the first datum, a flag is set in the 24-bit word and a second word is stored containing the background value for the individual peak and a continuously incremented whole mm counter. (The encoder transmits fractional rotations only; during acquisition, the computer maintains the integral mm of travel by incrementing a counter each time the encoder passes through zero.)

This process continues for all peaks on the photoplate. Each reading taken is stored in one computer word (the first reading generating an additional word) and these words are temporarily stored in a buffer area in core memory. When this buffer fills up with data, a second buffer is used and the first buffer's contents are transferred to a disk. After the second buffer is filled, the first buffer is filled again and the second buffer's contents are transferred. Each buffer consumes 128 words of storage. For nontime-shared operation each buffer consists of 4000 words of storage. This process continues until the photoplate is scanned over the desired range, and all data above the threshold are on the disk.

So that the complete transmission-distance envelope of the first peak can be determined, comparator travel must begin before the first peak of interest. It is then an easy matter for the computer to read the transmission at this point and consider this reading as the initial background. From this point, until the first peak is reached, each reading is checked to see if it is a maximum. The found maximum transmission is stored and considered the true background. After the first, and all succeeding peaks, a search is made for the minimum background (maximum transmission) value. The found backgrounds are weighted in a geometric fashion so that at any point the current background is weighted once, the preceding value one-half, its predecessor one-fourth, etc. This procedure follows a changing background on the photoplate well and guards against spurious scratches by imposing the requirement that only changes within a small voltage range (usually ± 300 millivolts) of the current background are employed in updating. The threshold value above which all data are accepted and below which all data are rejected is continuously updated by a preset amount above (smaller per cent transmission) the continuously changing background. The procedure for determining the threshold

(13) R. A. Herrmann and J. P. McNeill, unpublished data.

Table I. Example of Dialogue between Teletypewriter and Computer

```
READY TO GO
ENTER I.D. 80 CHR
TSANG R5398-124-1 61P19 71IH 8/15/67 1400 2092-07
ENTER BKGD DELTA     30
ENTER DELTA          100
ENTER START MM.      107
ENTER END MM.        320
ENTER 2ND. STDM MM 119.2131
ENTER INDEX STDMI    7
ENTER IMAP-0, 1      1
ENTER IDELI          3
ENTER MHET           0
ENTER JELEM          0
ENTER ELEMENTS AND MAXIMUM EXPECTED NUMBER
  FOR EACH
MORE    YES
C12
     50
MORE    YES
HI
     50
MORE  YES
N14
      2
MORE  YES
O16
      4
MORE  NO
TURN ON INTERRUPT SWITCH-START COMPARATOR
RUN COMPLETED-TURN OFF INTERRUPT SWITCH
```

acceptance value employing an updated background is illustrated in Figure 2.

An advantage to this system is seen by considering that in any system that acquires data off-line, the threshold is usually set at a fixed level by some appropriate input button or thumbwheel switches on the comparison logic electronic hardware. Unless provision is made for updating this value with extensive electronic hardware, this threshold will remain constant over the range desired to be measured. No trouble will be incurred as long as the photoplate fog level remains constant. If, however, the background is changed, either many useless sub-fog level points will be obtained or the medium to low intensity species will not be recorded. The first case would quickly exceed the capacity of any recording device, and the second case, in all probability, would lose some important fragment lines.

Before initiating plate travel, input parameters are sent to the computer with a teletypewriter located near the comparator. This input procedure is one of a "dialogue" nature with the computer. Previously written questions are asked by the machine language acquisition program and the comparator operator answers each question with a number. This stepwise procedure continues until the input parameters are fulfilled, and the computer instructs the operator to commence measurement. Table I is an example of one such dialogue and contains the identification, the permissible background fluctuation and the threshold (no decimal points, 0.30 and 1.00 volts, respectively), the starting and terminal mm of plate travel, the exact location of the second mass marker line, an index relating to the first mass marker line, a code denoting whether or not an element map is desired (a "low resolution" plot and a complete list of elemental compositions are always obtained), the number of milli-mass units within which all elemental compositions are found, the decrease in the maximum heteroatom content to account for mutually exclusive multi-isotopic elements, the number of elements not available on the disk (16 commonly encountered elements are always available on the disk),

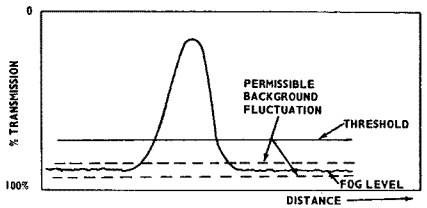


Figure 2. A typical peak illustrating the variations permitted on the fog level of the photoplate, and the threshold acceptance level

and the kinds and expected maximum number of those elements on the disk file. Messages are typed to inform the operator when to initiate and when to terminate plate travel.

Thus, at the end of the plate travel, the computer has stored on the disk the transmission-distance profiles of all peaks above the threshold level with each peak's data conveniently compartmentalized and easily recognized by succeeding programs. As the comparator slews back to begin reading another exposure, the computer transfers the acquired data onto a magnetic tape (SDS MAGPAK, $^1/_4'' \times 560'$). In this manner, a number of high resolution mass spectral photoplates can be scanned, their data sequentially stored on magnetic tape in minimal time and be readied for processing at a time convenient to the computer personnel.

In systems that place the photoplate data onto gapped magnetic tape, there is always the danger of losing a portion of the data while gapping the tape. In the system described here, there is an obvious advantage gained in this respect by compartmentalizing each variable length peak, storing the data onto the disk file, and at a later time and at a slower rate, placing the data onto magnetic tape. This procedure ensures that each and every reading taken at $^1/_2$-micron intervals will be used in calculating peak centers and areas.

Data Reduction. After several photoplate exposures have been scanned and the final data have been recorded on magnetic tape, a FORTRAN II chain program is loaded into the computer. While reading in distance values, the computer checks to see if any errors occurred in the acquisition step by knowing that each reading should be 1/2048 mm from the preceding one on the same peak. It should be noted, however, that in a million points, only a few points are dropped. Furthermore, this occurs only at the fastest speeds possible, and only on the initially fast-rising leading edge of a line's profile. Both factors combine to make this problem negligible. However, for the sake of complete insurance against any loss of data, the locations of any missing data are noted and these values calculated by a linear interpolation of adjacent values. In many months of operation, only once has a distance value been missing.

To determine the center line position and area of each peak, a two-step procedure was found necessary. The voltage reading (V) from the microdensitometer for each peak was well approximated by a Gaussian distribution once it was subtracted from the background reading (V_0)—i.e., $y = (V_0 - V)$ approximates a Gaussian distribution, where y is the ordinate of the transmission-distance profile. This function of the voltage was therefore used to determine peak centers. The areas under these curves, however, were not proportional to the relative intensities of each line because of the sensitometric properties of the photographic emulsion.

The following mathematical steps transform the voltages due to the transmission so that the relative areas on the photoplate correspond to the relative abundance of ions striking the plates. If we consider that transmission (T), optical density (OD), and the integrated energy (E) striking the photoplate over the region of linear response are related as follows:

$$OD = \log_{10}\left(\frac{1}{T}\right) = \log_{10}(a) + \gamma \log_{10}(E) \quad (1)$$

where a is an extrapolated intercept and γ is the contrast of the photographic emulsion, and that the voltage measured by the microdensitometer is proportional to the transmission, then one obtains:

$$\log_{10}\left(\frac{K}{V}\right) = \log_{10}(a) + \gamma \log_{10}(E) \quad (2)$$

where K is the proportionality constant. Rearranging terms, one sees that the energy is proportional (through C) to the following function of the voltage:

$$E = C\left(\frac{1}{V}\right)^{\frac{1}{\gamma}} \quad (3)$$

The energy (E_0) corresponding to the background fog transmission voltage (V_0) (which is unique for each peak as described in the section under Data Acquisition) is then subtracted from each transformed transmission value to give a more accurate measurement of the energy that has struck the photoplate at this $^1/_2$-micron interval:

$$E - E_0 = C \cdot \left[\left(\frac{1}{V}\right)^{\frac{1}{\gamma}} - \left(\frac{1}{V_0}\right)^{\frac{1}{\gamma}}\right] \quad (4)$$

In determining peak centers the computer transforms the data in each compartment to the form $y = V_0 - V$, where V_0 is the background (or fog level) for that set of data. If the peak consists of a single reading, *it* is assumed to be the peak center and the area is estimated by a rectangle of half-micron width and height given by Equation 4. If the peak consists of two points, an isosceles triangle with a base of one micron is fitted to estimate the peak center and the area is obtained by the trapezoid rule. When the number of points exceeds three and only one peak is present in the set of data, advantage is taken of the fact the log of the ordinates of a Gaussian distribution follow a quadratic curve. The location of the peak center is calculated by using this polynomial fit to a maximum of five points in the region of the peak.

One exception exists to the determination of peak centers from a quadratic fit. When there are more than 15 points, a test is made of the shape of the distribution by calculating its second, third, and fourth moments (μ_2, μ_3, and μ_4). If either (or both) of the ratios $\beta_1 = \mu_3/\mu_2^{3/2}$ or $\beta_2 = \mu_4/\mu_2^2$ (β_1 is a measure of the skewness of a peak, whereas β_2 is a measure of the kurtosis or "peakedness" of a peak) falls outside of prescribed limits, it indicates the presence of two or more unresolved peaks in the data. An iterative least squares procedure is then used to resolve the multiplet, fitting first two peaks and then adding an additional peak if the residual sum of squares indicates the need. In this way the resolving power of the mass spectrometer is increased.

In those cases where the data themselves pass through more than one maximum the same least squares procedure is used. When the valley between two peaks drops to less than 10% of the smaller peak it is arbitrarily treated as two singlets as the least squares fit would not contribute significantly to increasing the precision of the peak determination.

The area under multiplet curves resolved by the least squares procedure is divided in the following manner. Both the original data ($V_0 - V$) and the ordinates of the component peaks fitted by least squares are transformed by Equation 4. The trapezoid rule is then used to get the actual total area which is proportioned among the component peaks by the ratio of its fitted (transformed) area to the total fitted (transformed) area.

After all peak centers and areas have been calculated, the more intense peaks due to the reference compound, perfluorokerosene, are found via an extrapolation procedure, all intervening line positions converted to corresponding masses, and all masses known to be due to the reference compound are printed to illustrate the accuracy of this particular measurement. The remaining masses due to the compound of interest are converted to elemental compositions, and depending on the heteroatomic complexity, are either element mapped (*5*), or listed in tabular form. These procedures are explained in greater detail elsewhere (*4–6*).

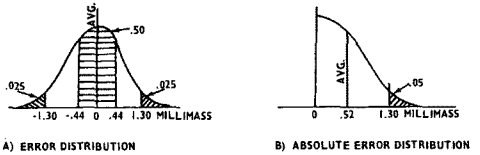


Figure 3. a. Error distribution of mass measurement, in millimass units. b. Absolute error distribution of mass measurement, in millimass units

DISCUSSION AND RESULTS

Determination of Mass. To test the precision and accuracy of mass determination using this system, data from 3 photoplates, each containing 2 exposures (2×10^{-11} coulomb and 4×10^{-11} coulomb) of a mixture of perfluorokerosene and hexachloropropene, were examined. The masses of 19 lines from each of these 6 exposures, arbitrarily chosen to cover the range in both relative intensity (5%–100%) and mass (m/e 70–250), were analyzed statistically for precision and accuracy of determination.

From these measurements the standard deviation of a mass determination was found to be 0.65 millimass unit. In other words, 95% of mass determinations should fall within a range of ±1.3 millimass units of their average value. This is equivalent to an average absolute deviation of 0.52 and a probable error of 0.44. The error distribution is depicted in Figure 3a and the absolute error distribution in Figure 3b. The values 0.5, 0.025, and 0.05 indicate the probability of falling in the indicated range. An analysis of variance of this data indicated no significant plate to plate component of error.

The values given above reflect reproducibility characteristics of the photoplate data. The accuracy of the mass determinations is reflected in the deviations of experimental from theoretical mass for the measurements described above and these deviations are listed with their masses in Table II. Of the individual average deviations none were significantly different from zero. The average of all deviations was 0.14 millimass unit and again showed no significant bias. Over the mass range covered, no apparent increase in error of mass determinations was observed with increasing mass.

Determination of Relative Abundance. In analyzing the precision and accuracy of relative abundance determinations, 4 alternate approaches were evaluated:

1. Using voltage readings (V) directly to calculate areas and relative intensities.
2. Using voltage readings transformed via the contrast function ($\gamma = 0.7$) to calculate areas and relative intensities.
3. Using an internal calibration compound, hexachloropropene (HCP), which corrects for the nonlinear photoplate response. Theoretical relative intensities for HCP employing the 211–219 multiplet which contains multichlorine isotopic peaks and covering a relative abundance range of 10^3 are used to calibrate the photoplate. By utilizing a plot of observed relative intensities *vs.* theoretical relative intensities for

Table II. Deviations (Experimental–Theoretical Mass) in Millimass Units for Representable PFK and HCP Masses

Mass	Relative intensity (means)	Exposure[a]	Deviations P_1	P_2	P_3	Av dev
72.966	73.2	E_1	0.1	−1.3	−0.1	−0.566
		E_2	−0.2	−1.7	−0.2	
83.935	49.2	E_1	0.9	0.2	0.0	0.417
		E_2	0.7	0.3	0.4	
92.996	93.2	E_1	0.4	0.2	−0.5	0.150
		E_2	0.8	0.3	−0.3	
99.995	216.0	E_1	0.8	0.1	0.5	0.400
		E_2	1.5	−0.1	−0.4	
105.938	154.0	E_1	−0.2	−0.4	−0.2	−0.317
		E_2	0.0	−0.6	−0.5	
106.421	76.0	E_1	0.5	0.2	0.3	0.083
		E_2	0.1	−0.6	0.0	
107.935	113.0	E_1	0.3	−0.7	−0.4	−0.133
		E_2	0.7	−0.8	0.1	
118.904	249.8	E_1	0.9	−0.3	−0.1	0.300
		E_2	0.1	0.3	0.9	
118.993	643.5	E_1	1.4	−0.1	0.0	0.650
		E_2	0.9	0.5	1.2	
120.901	103.5	E_1	0.9	0.1	−0.5	0.200
		E_2	0.5	−0.1	0.3	
130.992	738.5	E_1	0.3	0.0	1.8	0.316
		E_2	−0.2	−1.1	1.0	
142.904	175.2	E_1	0.7	0.2	−0.1	0.167
		E_2	0.1	0.6	−0.5	
150.997	48.0	E_1	−0.7	−1.0	0.6	−0.550
		E_2	−0.8	−1.6	0.2	
161.992	84.0	E_1	0.6	0.1	0.2	0.600
		E_2	1.1	1.2	0.4	
169.992	15.0	E_1	0.5	−0.9	0.4	0.133
		E_2	−0.1	0.1	0.8	
181.993	17.8	E_1	0.5	0.4	−0.8	0.583
		E_2	0.9	2.1	0.4	
212.841	994.2	E_1	−1.1	−0.2	0.0	−0.283
		E_2	−0.2	−0.2	0.0	
218.985	150.5	E_1	−0.4	0.2	−0.3	−0.083
		E_2	−0.3	0.6	−0.3	
247.811	83.7	E_1	0.2	0.3	0.2	0.616
		E_2	0.7	0.9	1.4	
					Av	0.141

[a] $E_1 = 4 \times 10^{-11}$ coulomb
$E_2 = 2 \times 10^{-11}$
P_1, P_2, and P_3 are 3 separate photoplates

HCP, all observed intensities of compounds of interest are corrected.

4. Using a combination of the γ transformation and HCP correction.

Since it was not possible to get reliable sensitometric data from the manufacturer which is pertinent to our application it was necessary to determine γ empirically. This was done by running a series of area determinations on three different photoplates using different γ's until the value was found which most nearly made the calculated areas of a series of standard lines proportional to their known abundances. The HCP 211–219 multiplet was used for this purpose. If the transformation worked perfectly, a log–log plot of the observed areas versus the theoretical abundances should fall on straight lines of slope one since if

$$\text{Abundance} = K \cdot \text{Area} \quad (5)$$

$$\log \text{Abundance} = \log K + \log \text{Area} \quad (6)$$

where K is a proportionality constant. At a value of $\gamma = 0.7$, the nearest approach to the ideal conditions was obtained. Two departures from ideality were observed. At low abundances, a significant portion of the area was lost due to not accepting data until a threshold level was exceeded. As peaks become larger this becomes insignificant. At the high end, areas again begin to understate abundance due to density saturation of the photographic plate—i.e., the end of the linear portion of the H and D curve has been reached.

To study the merits of the 4 approaches in determining relative abundance ratios, selected PFK lines were used. The electrical scan (low resolution) relative intensities of these lines were considered as theoretical values in calculating error

Table III. Relative Intensity Data for PFK Acquired from an Electrical Scan

m/e	Relative abundance	m/e	Relative abundance
93	175	162	88
100	320	169	454
112	49	181	433
119	1000	193	82
124	34	205	49
131	948	219	153
132	34	231	186
143	80	243	80
150	45	255	31
151	51	269	59
155	55	281	87

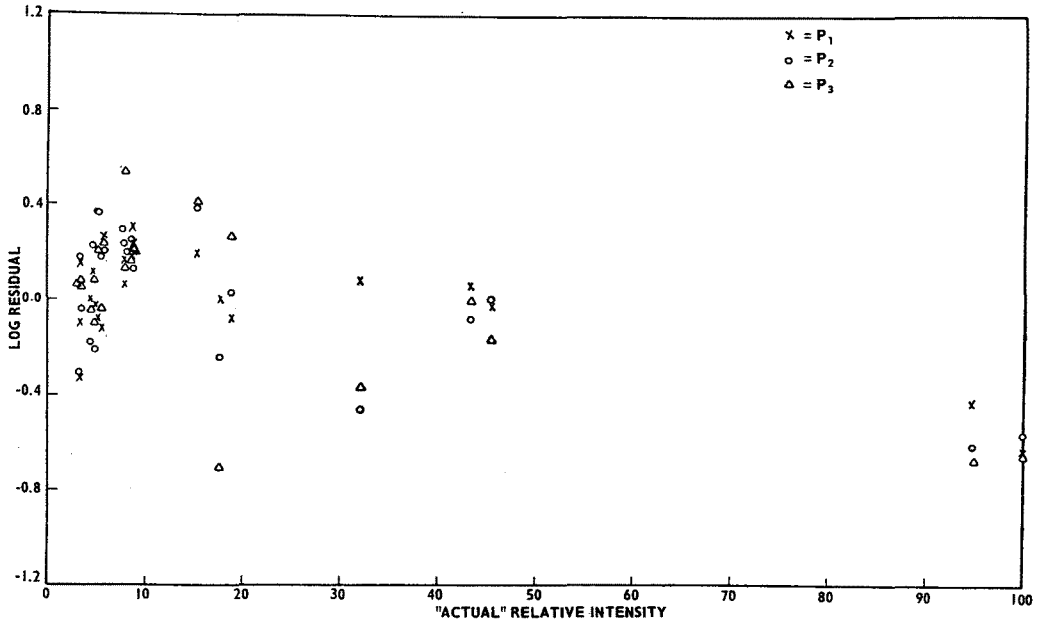


Figure 4. Plot of the logarithm of residuals of γ-transformed (no HCP correction) data *vs.* actual (electrical scan) relative intensities. Exposure = 2×10^{-11} coulomb

factors for the various approaches, and these theoretical values are presented for reference in Table III.

It is a recognized fact that PFK is a mixture of compounds of different volatilities. Therefore, the following precautions were employed to minimize this problem. The PFK samples were cooled with dry ice, then rapidly inserted via a Biemann probe (probe tip cooled with dry ice) into a constant temperature two-liter reservoir. A few second safter complete vaporization and temperature equilibration had occurred, as indicated by a constant ion beam (beam monitor signal), the sample ion beam was exposed to the photoplate. A gold leak is situated in the line leading from the reservoir to the ion source. All attempts were made to obtain the various photoplate exposures under similar conditions—i.e., the same timing sequence for sample introduction and the same temperatures of PFK (dry ice temperature prior to introduction), reservoir (200 °C), and ion source (200 °C). The electrical scan PFK theoretical relative intensities were acquired under similar conditions.

There is no question but that some fractionation occurs with mixtures of varying volatilities, even when extreme precautions are undertaken. However, by observing these precautions, the errors incurred in this comparison study of relative abundances are negligible compared with an error such as peak clipping which is caused by the threshold setting during data transmission. Also, 2 different exposures (2×10^{-11} and 4×10^{-11} coulomb) were examined independently for each of the methods tested, and the data were internally consistent for the pair of exposures. In other words, the trend observed in the data for one exposure was the same as observed in the other exposure, thus demonstrating that the relative abundance of peaks did not change significantly between sample introductions.

Table IV presents the 95% error factors involved in estimating the ratio of any two abundances and these factors reflect the combined error of the photographic process and the electrical scan, even though the latter are treated as "actual," or theoretical values. These estimates can be regarded as an extreme upper bound on the actual error of the automated photographic process. As shown in Table IV, statistical analysis of the data was done separately for each exposure, because even the relatively weak exposure of 4×10^{-11} coulomb showed some flattening of the larger peaks.

Table IV. Estimated 95% Level Error Factors for the Ratio of Two Abundances (*m/e* 93–281)

	Untransformed voltage data		γ Transformed data	
Coulombs	4×10^{-11}	2×10^{-11}	4×10^{-11}	2×10^{-11}
No HCP correction	7.1	6.3	2.8	2.3
HCP correction	2.4	2.0	2.4	1.9

The factors are interpreted in the following way. The factor of 2.0 for untransformed HCP corrected areas, for example, says that approximately 95% of the time the actual ratio of the abundances will lie between double or half the value obtained by taking the ratio of the experimental areas. Although this sounds excessive it must be recalled that this error is overstated by the electrical scan error and further that the 95% factor of 2 corresponds to a geometric average error factor of 1.33 and a probable error factor of 1.26. The latter implies that half the time the actual relative abundance will be within a range of 26% larger and approximately 21% smaller (complement of 1/1.26) than the reported values.

To investigate the possibility that the % error might not be constant over the whole range of intensities, the log residuals—

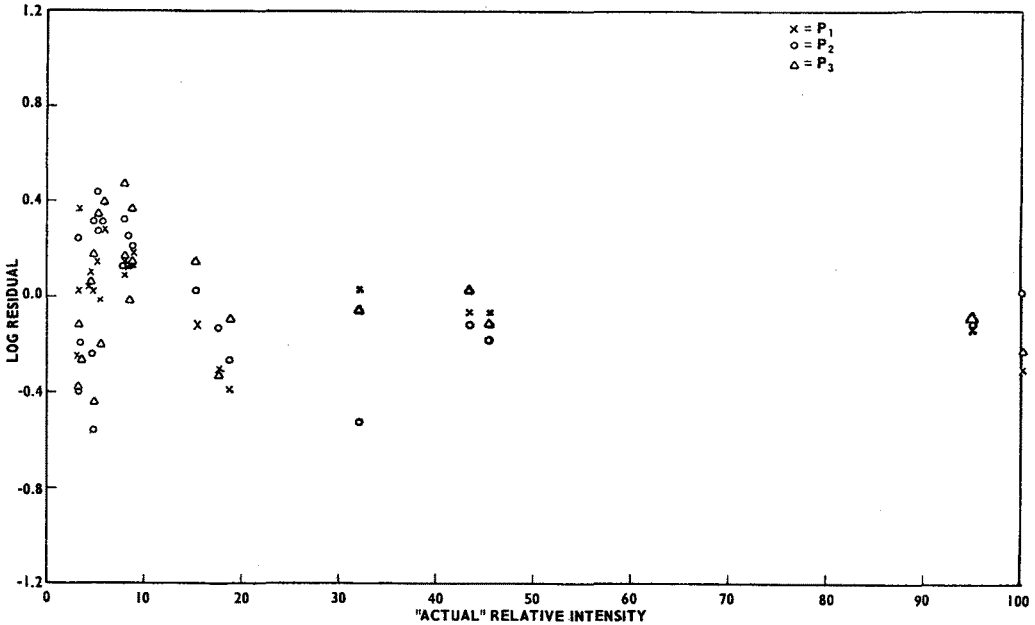


Figure 5. Plot of the logarithm of residuals for HCP corrected (no γ-transformation) data *vs.* actual (electrical scan) relative intensities. Exposure = 2×10^{-11} coulomb

i.e., log (K·Area) − log ("actual" relative intensities)—were plotted *vs.* the "actual" relative intensities. The plots for γ-transformed data (2×10^{-11} coulomb) and HCP corrected data (2×10^{-11} coulomb) are presented in Figures 4 and 5. Data for the longer exposures was similar and therefore not presented. Figures 4 and 5 show a tendency for the γ-corrected relative areas of the higher abundance ions to be low—i.e., negative residuals—compared with their "actual " electrical scan data. The drop-off in relative areas was particularly evident for *m/e* 119 and 131 (both 90% relative intensity), and is due to saturation of the photographic plate. Therefore the 95% error factors for the ratio of 2 abundances were recalculated for *m/e* 132–281, and the results are presented in Table V. The γ-corrected data under these conditions exhibit error factors similar to the error factors from the HCP internal calibrant corrected data.

In high resolution mass spectrometry, accurate mass measurements are of extreme importance and accurate ion abundance determinations are of rather secondary importance. However, as shown by the data in Table IV some type of correction to photoplate relative ion abundances should be employed. The use of an internal calibrant such as HCP has been shown to be slightly better than the incorporation of a γ function correction, especially for the more intense ions. A further decrease of up to 30% in the variability of results can be expected in the HCP interval calibrant technique by 4-point smoothing of the intensity data for the HCP. However, with the internal calibrant method one has the inconvenience of introducing carefully controlled amounts of calibrant with each run. The peak heights of the largest peaks in the unknown and calibrant must be approximately equal to allow for interpolation of these unknown ion abundances over the same intensity range on the photoplate. For laboratory operations where maximum ion abundance accuracy from a photoplate is not needed, the γ function correction method should be both useful and convenient.

Table V. Estimated 95% Level Error Factors for the Ratio of Two Abundances (*m/e* 132–281)

Exposure	HCP corrected untransformed data	No HCP correction γ transformed data
4×10^{-11} exposure	2.0	2.2
2×10^{-11} exposure	1.9	2.0

CONCLUSION

The procedures outlined here and the presented data illustrate the accuracy obtained by direct on-line communication between a microdensitometer-comparator system measuring photoplates and a remote digital computer which is involved in decision making during the data acquisition step. The transmitted parallel input data is over 500-foot cables. The rate of data transmission for time-shared operation is variable up to approximately 30 mm/min and a scanning time of 8–10 minutes.

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Photometric Determination of Substances in Presence of Strongly Interfering Unknown Media

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The conventional methods for photometric determination of substances are shown to lead to errors in the presence of strongly interfering unknown media. A method is suggested which may allow an accurate photometric determination of a substance in spite of the interferences. The theoretical considerations are illustrated by experiments on a solution of calcium $10^{-4}M$ in the presence of very large excess of $LaCl_3$ and HCl. Under these conditions, the use of working curves can introduce an error of 100% while the use of the method of standard addition or of successive dilutions introduces an error of about 30% even with an absolute precision of the measurements. The use of the method of changing parameter, introduced in this paper, allows the determination of a substance despite the interference with an accuracy limited only by the precision of the measuring equipment.

APPLICATION of spectrometry to analytical chemistry is based on the fact that a reading of a spectrometer corresponds to some definite concentration of a substance investigated. If the concentration of the substance in some solution X is denoted by C_X, and if the reading obtained is R_X, the above statement can be expressed as

$$R_X = F(C_X, P_{X1}, \ldots, P_{Xi}, \ldots, P_{Xn}) \quad (1)$$

where P_{Xi} is the i'th of n parameters affecting the reading of the spectrometer. Some of the P's refer to the instrument (e.g., the intensity of the flame, the composition of the burning mixture, the wavelength used, etc.); other P's can refer to the nature of the solution X (its viscosity, its surface tension, the effect of the interfering substances dissolved, etc.). Thus the value of n in Equation 1 may be very large, as can be seen from the extensive treatises of Mavrodineanu and Boiteux (*1*) or of Pungor (*2*). In fact, it is doubtful whether a fully explicit form of Equation 1 could be written, and were it possible, its use would not commend itself to an analytical chemist.

A small change in the instrument reading would be expressed, according to Equation 1 as

$$dR_X = \frac{\partial F}{\partial C_X} dC_X + \Sigma_i \frac{\partial F}{\partial P_{Xi}} dP_{Xi} \quad (2)$$

Thus, if the P's due to the instrument and the P's due to the nature of the solution X remain constant, Equation 2 becomes a function of only the concentration of the substance investigated:

$$dR_X = \frac{\partial F}{\partial C_X} dC_X \quad (3)$$

In practice, Equation 1 may take a simple form. If an addition of the small amount of dm_X moles of the substance to a constant volume V_X of the solution X increases the reading always by the same increment dR_X, it is possible to write:

$$\frac{dR_X}{dm_X} = k_X \quad (4)$$

and on integration of Equation 4 we get for Equation 1:

$$R_X = k_X m_X + R_{mX=0} \quad (5)$$

This form of Equation 1 is very convenient, and theoretical considerations indicate that it might be applicable (*3*, *4*), but whether it really is or not has to be determined experimentally. Fortunately, Equation 5 generally is applicable to dilute solutions, when the introduction of dm_X does not change the properties of the solution such as viscosity, flame temperature caused by the solution, etc. It is possible to utilize Equation 3 even when it deviates from the linearity of Equation 5 (*4*, *5*), but we shall deal here only with systems behaving according to the simple Equation 5.

The methods used in practice for the spectrometric determination of a given substance have been presented in recent reviews (*3*, *6*, *7*), and we shall summarize here only the arguments showing why these methods can give erroneous results in the presence of interfering media. For convenience we shall assume, anticipating the experimental part and without loss of generality, that the substance to be determined is calcium, that the "unknown" solution X is an aqueous solution of $CaCl_2$ approximately $10^{-4}M$ in the presence of $LaCl_3$ approximately $10^{-1}M$ and HCl approximately $4 \times 10^{-1}M$, and that the photometric determination is made with the aid of an atomic absorption flame photometer (*8*).

The choice of La and HCl has been made as the use of La and HCl is recommended in the determination of Ca (*8*), so that their effect on Ca is of practical interest [see also (*9*)]. However, it should be remembered that usually La and HCl are introduced as suppressing agents, while here they are discussed as the interfering agents themselves.

Working Curves and Simulation Method. The simplest spectrophotometric method is that of constructing a working curve for some solution Y (e.g., $CaCl_2$ in pure water). A reading R_Y on such a curve indicates a concentration C_Y of calcium. The unknown solution giving a reading R_Y is assumed also to have a concentration C_Y. This assumption is not generally justified. The method can be improved by making the solution Y as similar to solution X as possible.

(1) R. Mavrodineanu and H. Boiteux, "Flame Spectrometry," Wiley, New York, 1965.
(2) E. Pungor, "Flame Photometry Theory," Van Nostrand, Princeton, N. J., 1967.
(3) A. Walsh, in "Advances in Spectrometry," H. W. Thompson, Ed., Interscience, New York, 1961, Vol. II, p 1.
(4) T. E. Beukelman and S. S. Lord, Jr., *Appl. Spectrometry*, **14**, 12 (1960).
(5) W. Lang and R. Herrmann, *Z. Anal. Chem.*, **199**, 161 (1964).
(6) J. A. Dean, in "Developments in Applied Spectroscopy," E. N. Davis, Ed., Vol. 4, Plenum Press, New York, 1965.
(7) R. Herrmann and C. T. J. Alkemade, "Chemical Analysis by Flame Photometry," 2nd rev. ed., Interscience, New York, 1963.
(8) "Calcium in Standard Conditions," in Perkin-Elmer's "Analytical Methods for A.A.S." Norwalk, Conn., Nov. 1966.
(9) C. Monder and N. Sells, *Anal. Biochem.*, **20**, 215 (1967).

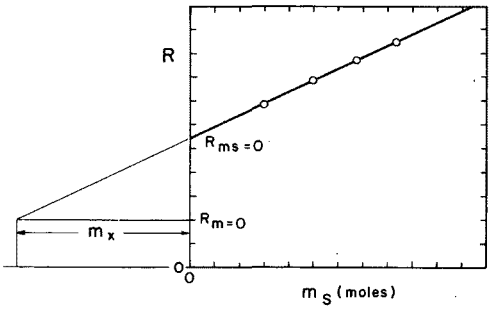


Figure 1. Schematic representation of the method of addition of standards

This includes the introduction of substances tending to suppress the "interfering" factors (*10*), lanthanum and HCl being such interfering factors in our example. The difficulties encountered are evident when solution X is a biological fluid, or even a reasonably complicated mixture. The above shortcomings of the Simulation Method have been already discussed in detail in the excellent book of Herrmann and Alkemade (*7*). It will be shown, however, that in addition to the above objections, the working curve method may yield satisfactory results at some concentration, while giving apparently nonsystematic errors at other concentrations. This point will be elaborated when dealing with the experimental results.

The Standard Addition Method. To avoid the use of working curves, Chow and Thompson (*11*) suggested a method which they called "internal standards technique." To avoid confusion with the "internal standardization–double beam method" (e.g., ref. 7, p 160), it is better to refer to the method as the Standard Addition method. Only one pertinent point of this method will be discussed here: to the best of my knowledge the error introduced by interfering substances when using the above method has not been analyzed up to now. We proceed to do it briefly.

The essence of the Standard Addition method is that to a series of constant volumes V_X of the solution X (each containing the unknown quantity m_X of calcium) we add constant volumes V_S of standards made with pure solvent. Each V_S contains a different quantity m_S of calcium. The solution obtained by the mixture of V_X and V_S will be called solution M, to distinguish it from the original solution X. As V_X and V_S are constant, the properties of the solution M (such as viscosity, surface tension, etc.) will remain constant, and the only parameter that changes in the series of solutions obtained is the concentration of calcium. It should be emphasized that the properties of M have changed as compared with solution X, because the concentrations of the interfering agents (e.g., $LaCl_3$ and HCl) have changed significantly. However, for the new solution M, the linearity of Equation 4 can well be maintained, so that

$$R_M = k_M C_M + R_{C_M=0}$$

$$= k_M \frac{m_X + m_S}{V_X + V_S} + R_{m=0} \qquad (6)$$

In Equation 6 $R_{C_M=0}$ and $R_{m=0}$ represent the reading of the spectrophotometer when no calcium is present in the solution M. Theoretically, $R_{m=0}$ might be obtained by extrapolating the straight line which should be obtained by plotting R_M *vs.* the known increments of m_S to the point where $m_X + m_S = 0$. This is shown in Figure 1.

Practically, since m_X is unknown, it is possible to obtain experimentally only $R_{m_s=0}$ — i.e., the reading where $m_S = 0$ but where there remains still the original amount m_X of calcium. Considering Figure 1 and Equation 6, it is evident that

$$R_{m_S=0} = R_{m=0} + \frac{k_M}{V_X + V_S} m_X \qquad (7)$$

It is possible to evaluate readily k_M from V_X, V_S, and the slope of the straight line in Figure 1. Analytically k_M is obtained from Equation 6:

$$k_M = (V_X + V_S)\left(\frac{\partial R_M}{\partial m_S}\right)_{V_X, V_S, m_X} \qquad (8)$$

Considering Equation 7, it is evident that the experimentally obtainable data, such as k_M and $R_{m_S=0}$, are insufficient to evaluate m_X.

A tacit assumption is made by Chow and Thompson that $R_{m=0} = 0$ — i.e., that whenever there is no calcium at all in any solution the reading of the spectrometer is the same and may thus be set arbitrarily to zero in pure water. Using this assumption, Equation 7 can yield the value of m_X.

An elaboration of the method suggested above has been introduced by Beukelman and Lord (*4*), for a case where the instrument reading is not a linear function of the concentration of the unknown substance. However, the important point is that even in the ideal case, where the function is linear, the neglect of $R_{m=0}$ can be unjustified. In fact, it will be shown in the corresponding part of the section "Results and Discussion" that the neglect of $R_{m=0}$ is sufficient to introduce an error of over 30%.

Successive Dilutions. Another interesting attempt to avoid the use of working curves is illustrated by the method of successive dilutions, as employed by Gilbert (*12*).

In the simple form of this method, the unknown sample is diluted a number of times, and the apparent concentrations obtained for each dilution (by comparison with calcium in pure water) are converted into calculated concentrations. These calculated concentrations are extrapolated to infinite dilution, where the solution is supposed to behave as the pure solvent, with no interfering effects. It is suggested, on the strength of experimental results, that the plot of the calculated concentration against the dilution yields a straight line, easily extrapolated to zero dilution. By dilution, Gilbert means the volume of the sample (V_X) divided by the final volume (V_{total}). The quotient V_X/V_{total} might perhaps be better called "relative concentration," as it is unity for the undiluted sample and tends to zero on increased addition of solvent — i.e., when dilution *increases*.

The literature (*7*) notes two obvious limitations to the method of successive dilutions: first, the method requires considerable dilution in order to obtain enough data for an extrapolation. Next, the error in the reading of the scale at any relative concentration is magnified by the factor of the reciprocal of the relative concentration on obtaining the calculated concentrations.

We suggest, however, that there are more fundamental limitations to the method of successive dilutions. It was

(10) J. Yofé and R. Finkelstein, *Anal. Chim. Acta.*, **19**, 166 (1958).
(11) T. J. Chow and T. G. Thompson, ANAL. CHEM., **27**, 910 (1955).
(12) P. T. Gilbert, Jr., *ibid.*, **31**, 110 (1959).

said that the instrument is calibrated by setting zero for pure water. We have also stated that one cannot assume that $R_{m=0} = 0$, thus the unknown solution could possibly have a reading even if all the calcium were extracted from it. In such a case, the apparent concentration of Ca would be related to the true concentration in a manner illustrated in Figure 2.

As the reading $R_{m=0}$ can be ascribed to some interference, we shall use for it the notation R_I. The dilution is effected by the addition of the volume V_S of pure solvent to the volume V_X of the unknown solution, so that:

$$C_{\text{relative}} = \frac{V_X}{V_{\text{total}}} = \frac{V_X}{V_S + V_X} \tag{9}$$

and the real concentration is

$$C_{\text{real}} = \frac{(R_M - R_I)(V_S + V_X)}{k_M \quad V_X} \tag{10}$$

When the unknown solution is diluted to infinity, R_I tends to 0, and the two straight lines in Figure 2 will coincide. The coefficient k of the unknown solution will then be equal to the slope of Ca in pure solvent. We shall denote it by k^∞. The calculated concentration can be expressed as:

$$C_{\text{calcd}} = C_{\text{apparent}}/C_{\text{relative}}$$

$$= \frac{R_M(V_S + V_X)}{k^\infty \quad V_X} \tag{11}$$

From Equations 10 and 11, it is evident that $C_{\text{calcd}} = C_{\text{real}}$ when

$$\frac{R_M}{k^\infty} = \frac{R_M - R_I}{k_M} \tag{12}$$

When $R_I = 0$, the equality in Equation 12 will be approached as $k_M \to k^\infty$ — i.e., on dilution to infinity. When $R_I \neq 0$, there is a value of V_S for which the equality holds. On one side of this V_S, the calculated concentration will be higher than the real one; on the other side the opposite is true.

The slope of $C_{\text{calcd}}/C_{\text{rel}}$ was taken by Gilbert to be a straight line, "under the reasonable hypothesis that all interferences . . . exert a quenching . . . effect . . . which is . . . independent of the cadmium concentration and proportional to the concentration of interferents" (*12*). Our treatment makes it possible to a get a better insight into the behavior of C_{calcd} *vs.* C_{rel}. It can be seen that the slope is:

$$\frac{dC_{\text{calcd}}}{dC_{\text{rel}}} = -\frac{1}{V_X{}^2 k^\infty} \times \left[(V_X + V_S)^2 R_I + (V_X + V_S)^2 C_{\text{real}} V_X \frac{dk_M}{dV_S} + (V_X + V_S)^3 \frac{dR_I}{dV_S}\right] \tag{13}$$

It follows from Equation 13 that for an ideal system, in which $R_I = 0$ and $dk_M/dV_S = 0$, the slope is 0, as expected.

When $R_I = 0$ but $dk_M/dV_S \neq 0$, as assumed by the dilution method, Equation 13 yields:

$$\frac{dC_{\text{calcd}}}{dC_{\text{rel}}} = -\frac{(V_X + V_S)^2 C_{\text{real}}}{V_X k^\infty} \frac{dk_M}{dV_S} \tag{14}$$

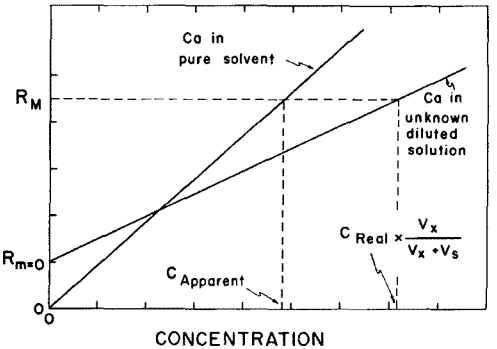


Figure 2. Schematic representation of the method of successive dilutions

It will be shown in the discussion of the experimental results that k_M is, to a good approximation, a hyperbolic function of V_S, so that we can write

$$k_M \simeq k^\infty - \frac{(k^\infty - k_M{}^\circ)A_k}{V_S + A_k} \tag{15}$$

In Equation 15 $k_M{}^\circ$ is the k_M in the undiluted solution ($V_S = 0$), and A_k is some constant. As another approximation we can write:

$$A_k + V_S \simeq V_X + V_S \tag{16}$$

Equation 16 would become exact for an infinite dilution for any value of A_k, but it is a good approximation even at small values of V_S; this can be seen on considering Equation 15: A_k can be considered as the volume from which V_S has to be subtracted in order to send k_M to infinity. From physical considerations it appears, therefore, that $A_k \simeq V_X$. Applying Equations 15 and 16 to Equation 14, we obtain:

$$\frac{dC_{\text{calcd}}}{dC_{\text{rel}}} = -\frac{C_{\text{real}} A_k (k^\infty - k_M{}^\circ)}{k^\infty V_X} = \text{constant} \tag{17}$$

Thus, when $R_I = 0$, we obtain a sloping straight line intercepting the ordinate at C_{real}. However when $R_I \neq 0$, Equation 13 has to be considered in full. In the discussion of the experimental results, it will be shown that R_I is also to a good approximation a hyperbolic function of V_S, so that

$$R_I = \frac{R_I{}^\circ A_I}{V_S + A_I} \tag{18}$$

where $R_I{}^\circ$ is the R_I of the undiluted solution, and A_I is a constant, also approximately equal to V_X. Thus employing Equations 15, 16, and 18 in Equation 13, we obtain again Equation 17. Now, however, the sloping straight line does not intercept the ordinate at C_{real}, as shown in the discussion of Equation 12.

A certain improvement in the method of successive dilutions can be introduced by using for the working curve not the pure solvent, but some mixture somewhat approximating the unknown solution—i.e., combining the successive dilutions method with the simulation method. For each dilution of the unknown solution, the standard solutions are diluted correspondingly, and the apparent concentration is read off the working curve yielded by the diluted standards. Such a combined method was used successfully by Gilbert.

The improvement combines obviously all the advantages and disadvantages of the two original methods. Further examination of the simple and the improved method of successive dilutions will be made in the discussion of our experimental results, where we shall show how the method fails in the presence of strong interfering agents.

Changing Parameter. The errors introduced through the neglect of R_I could be eliminated were it possible to determine experimentally the R_I of the unknown solution. Thus, the introduction of R_I into Equation 6 would enable us to obtain m_X from the knowledge of V_X, m_S, V_S, and the corresponding k_M and R_M. Unfortunately R_I is also a function of V_S, and so cannot be obtained directly. This difficulty could be overcome by knowing the exact form of the function R_I (V_S). As R_I decreases on dilution asymptotically to 0, the following two functions suggest themselves:

$$R_I = \frac{R_I^\circ A_I}{A_I + V_S} \tag{19}$$

or

$$R_I = R_I^\circ e^{-A_I V_S} \tag{20}$$

where A_I is some constant and R_I° is the value of R_I when $V_S = 0$.

It will be shown later that Equation 19 approximates closely the experimental results, while Equation 20 gives a much poorer approximation.

Introduction of Equation 19 or 20 into Equation 6 would allow us, in principle, to evaluate R_I° (and consequently any R_I) from any three experimental values of R_M and the corresponding values of k_M, V_S, and m_S. Simultaneously the values of A_I and of m_X would be obtained.

In practice the above method fails, as will be shown in the discussion of our experimental results. However, a similar approach suggests itself to arrive at R_I through a controlled change of one of the parameters P_{Xi} of Equation 1. If the change of this parameter affects differently the substance investigated than the interfering substance, then the photometric behavior at different values of P_{Xi} may allow the evaluation of R_I. Thus differentiating Equation 6 with respect to the chosen parameter (denoted P for brevity) yields:

$$\frac{dR_M}{dP} = \frac{dR_I}{dP} + \frac{dk}{dP} C_M$$

$$= \frac{dR_I}{dP} + \frac{dk}{dP} \frac{R_M - R_I}{k} \tag{21}$$

It has been said above that the change in the parameter P must affect differently the substance investigated than the interfering substance. This statement is implicit also in Equation 21: if R_I can be expressed as some constant C_I (concentration of the interfering substance) multiplied by the same k as that appearing before C_M in Equation 6, then Equation 21 would yield

$$\frac{dR_M}{dP} = \frac{dk}{dP}(C_M + C_I) \tag{22}$$

and the change of R_M and of k with P would not allow us to separate C_M from C_I. This crucial point is discussed again in the final paragraphs of this section.

Using the notation for the experimentally obtainable quantities:

$$F \equiv \frac{dR_M}{dP} - \frac{R_M}{k}\frac{dk}{dP} \tag{23}$$

and

$$f \equiv \frac{dk}{kdP} \tag{24}$$

Equation 21 can be written as

$$\frac{dR_I}{dP} - F - R_I f = 0 \tag{25}$$

The solution of Equation 25 is:

$$R_I e^{-\int_{P^0}^{P} f dP} - R_I^\circ - \int_{P^0}^{P} F e^{-\int_{P^0}^{P} f dP} = 0 \tag{26}$$

The superscript 0 indicates, as in our previous notation, the state of the original unknown solution before any change in the parameter P.

Equation 26 can be useful if the experimental results are such that the first member of it can be allowed for; otherwise R_I remains in the equation, and the integral form is no more useful than the differential form of Equation 25. In such a case R_I can still be expressed as a convenient function of R_I° and P (as in Equations 19 or 20), and so allow the evaluation of R_I°, and consequently of m_X.

A case of special interest is when the parameter P is the concentration itself. This is a parameter which can be easily and accurately adjusted — in fact it is the only parameter which can be so used in the case of our atomic absorption flame photometer. When an unknown solution containing m_X moles of the unknown substance is diluted (i.e., $m_S = 0$ and V_S increases), it is possible to obtain again Equations 25 and 26, but now f and F have to be redefined as:

$$F \equiv \frac{dR_M}{dV_S} - \frac{R_M}{k}\left(\frac{dk}{dV_S} - \frac{k}{V_S + V_X}\right) \tag{27}$$

and

$$f \equiv \frac{1}{k}\left(\frac{dk}{dV_S} - \frac{k}{V_S + V_X}\right) \tag{28}$$

When a search for the best values of R_I° and A_I has to be made, it is convenient to use Equation 29, which follows from Equations 19, 25, 27, and 28.

$$F + \frac{R_I^\circ A_I}{(A_I + V_S)^2} + f\frac{R_I^\circ A_I}{A_I + V_S} = 0 \tag{29}$$

On introduction of the experimental values of F, f, and V_S into Equation 29, with some assumed values for the constants R_I° and A_I, the result in general will not be zero, unless R_I° and A_I correspond to the true values of a hyperbolic R_I. When many experimental values of F, f, and V_S are available, any values of R_I° and A_I can be tried, till the sum of all the sets of Equation 29 is minimized. Such a minimum will coincide with the true value of R_I°. However, one can expect not one but two values of R_I° to which Equation 29 applies. This becomes evident on considering the basic Equation 6; if R_M itself approximates closely a hyperbolic function of V_S, then decrease in the tacitly assumed value of m_X decreases the effect of the first term on the right hand side in Equation 6, and an R_I is obtained tending to R_M for $m_X \to 0$, with $R_I^\circ \to R_M^\circ$ and $A_I \to A_M$. Obviously in such a case the experimentally obtained function of k with respect to V_S becomes redundant, and this vital information is not utilized. In other words, on assuming that there is no calcium at all in the solution, and that all the absorption is due only to the interference, a mathematically correct answer can be obtained, although it is an improbable one. The practical effect of this difficulty is that the two

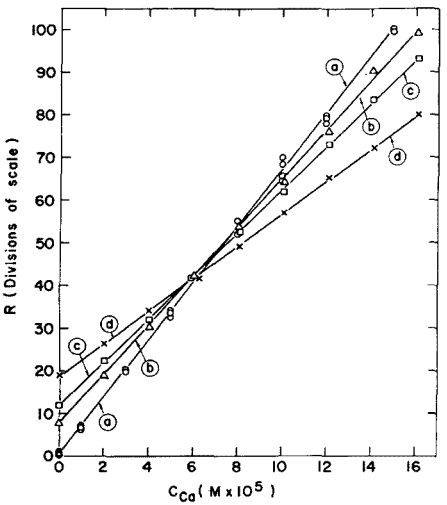


Figure 3. Working curves

a. **Standards based on pure water**
b. **Standards based on La + HCl 0.5%**
c. **Standards based on La + HCl 1.0%**
d. **Standards based on La + HCl 2.0%**

Points: Experimental
Straight lines: Calculated by least squares

minima corresponding to the two alternative R_I° will be separated by a relatively low maximum, which can be easily masked by small experimental errors.

The method of the Changing Parameter has been suggested in order to determine R_I—the absorption caused by the interfering agent when the medium contains no calcium at all. When $R_I = 0$ the photometric behavior obeys the comparatively simple equation (cf. Equation 6):

$$R_M = k\frac{m_X + m_S}{V_X + V_S} \tag{30}$$

and, even when k is not constant on dilution, m_X can be accurately determined either by the Standard Addition method or by the Successive Dilutions method, as shown above. It is, therefore, of interest to be able to deduce from the photometric behavior of the sample whether $R_I = 0$ or not. We suggest that this can be achieved by considering the behavior of k on dilution:

Assuming temporarily that R_I is zero, and determining k° experimentally, it is possible to evaluate m_X on this assumption. Inserting this value in Equation 30, it is possible to calculate k for any V_S, as R_M for any V_S is also experimentally available. Such calculated k (k_{calcd}) can be compared with the k's obtained experimentally, as in Equation 8 (k_{exp}).

It remains to estimate quantitatively the deviation of k_{calcd} from k_{exp}. Using Equation 7 we obtain:

$$\frac{k_{\text{calcd}}}{k_{\text{exp}}} = \frac{(R_M^\circ - R_I^\circ)R_M}{(R_M - R_I)R_M^\circ} \tag{31}$$

This expression reduces to unity when $R_I = 0$. When $R_I \neq 0$ the ratio of $k_{\text{calcd}}/k_{\text{exp}}$ will depend on the values which the various R's assume. If both R_M and R_I are hyperbolic functions of V_S (cf. Equation 19), then Equation 31 yields:

$$\frac{k_{\text{exp}}}{k_{\text{calcd}}} = \frac{R_M^\circ}{R_M^\circ - R_i^\circ}\left[1 - \frac{R_I^\circ A_I(V_S + A_M)}{R_M^\circ A_M(V_S + A_I)}\right] \tag{32}$$

Note that Equation 32 again reduces to unity when $V_S = 0$, even when $R_I \neq 0$.

It can be seen that the greatest difference between k_{exp} and k_{calcd} can be obtained on infinite dilution, where Equation 32 reduces to:

$$\frac{k^\infty_{\text{exp}}}{k^\infty_{\text{calcd}}} = \frac{R_M^\circ - R_I^\circ(A_I/A_M)}{R_M^\circ - R_I^\circ} \tag{33}$$

so that the maximum ratio beteeen the two k's is determined by the ratio A_I/A_M. This statement is of fundamental importance. It means that when $A_I = A_M$ then the photometric behavior of the interfering substance is exactly equal to that of calcium itself, and obviously no information obtained photometrically can be utilized to resolve the contribution of the interference and that of calcium. When $A_M \neq A_I$ such a resolution is possible — but the practical utilization of the difference in photometric behavior will depend on the precision of the measurements. The bigger the difference between A_I and A_M, the easier it will be to resolve R_M into the true absorption of calcium and the R_I of the interfering substance.

The above considerations will be illustrated in the discussion of our experimental results.

EXPERIMENTAL

Materials. All the materials employed were analytical grade. The water was triply distilled. Standard solutions of calcium were prepared from calcium carbonate and dissolved by the addition of HCl. As a control we have prepared solutions from solid $CaCl_2$ and determined the concentration of Ca in the stock solutions gravimetrically and volumetrically with EDTA.

The stock solution of lanthanum in HCl was prepared according to the instructions of Perkin-Elmer (*8*): 29.3 grams of La_2O_3 (Fluka puriss, 99.99%) were dissolved in 125 cc of HCl (Frutarom, analytical, 35.4%) and diluted to 500 cc with triply distilled water. The solution obtained is 0.360*M* in $LaCl_3$ and 1.78*M* in HCl; it corresponds to the 5% stock solution of Perkin-Elmer. This concentrated solution was usually diluted by five to yield a solution of $LaCl_3$ $7.2 \times 10^{-2}M$ in HCl $3.6 \times 10^{-1}M$. Such a dilute solution will be referred to (following Perkin-Elmer) as 1% La + HCl solution.

Our unknown sample consisted of 8 cc of the 1% La + HCl solution, containing 6.40×10^{-7} mole of calcium chloride (i.e., $8.00 \times 10^{-5}M$).

Equipment and Procedure. All the volumetric equipment employed (burets and flasks) was calibrated by us. The volumes and concentrations quoted may be taken as accurate within ±0.5%.

The spectrophotometric measurements were made with a commercial Perkin-Elmer 290 Atomic Absorption Spectrophotometer. Hollow cathode lamp was used, with the wavelength of 4227 Å. The slit was 20 Å. The Boling burner head was used. Settings were as advised by the manufacturers (*8*). The scale was divided into 100 equal divisions. Zero was set for the triply distilled water, and 100 was set with $1.50 \times 10^{-4}M$ solution of $CaCl_2$ in water, without La. As an independent check, 74 was read when $1.22 \times 10^{-4}M$ solution of $CaCl_2$ in 1% La + HCl was tested. The zero point was adjusted before every reading, and the sensitivity (100 scale divisions and 74 scale divisions) was checked after every 5 readings, and adjusted if necessary. Every sample was tested twice at intervals of about 30 minutes, and the difference in readings did not exceed ±1 scale division.

It should perhaps be emphasized that while the details of

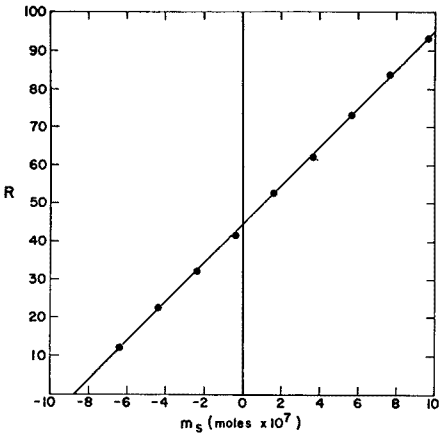


Figure 4. Addition of standards to unknown solution

Points: Experimental
Straight line: Calculated by least squares

the scale are given above, so as to allow the reproduction of the results cited below, the scale itself has no importance in our discussion, as long as Equation 5 is satisfied.

The value of k for each V_S was determined using 9 samples of the unknown solution to which $CaCl_2$ was added in varying amounts. To obtain dk/dV_S, some 60 series of such measurements were carried out, each series in a different concentration of the La + HCl mixture (i.e., at different V_S), corresponding to a single k.

As the stock solution of La + HCl was 5%, while the unknown solution was 1% La + HCl, it was possible to obtain values of k and of R_M also for some negative values of V_S.

RESULTS AND DISCUSSION

Use of Working Curves and Simulation Method. A working curve was constructed using eight solutions of $CaCl_2$ in pure water (curve a in Figure 3).

Each experimental point on this curve represents average of about three independent measurements for the same solution on the same day. The scattering is due to the fact that the various concentrations were produced repeatedly, sometimes from different stock solutions, and the measurements were taken at intervals of some days. A measurement of a series of solutions during a continuous single experiment yields results with less scattering, as shown in the other curves of Figure 3. Despite the scattering, the experimental points of curve a lie fairly close to a straight line, with a slope of $(6.6 \pm 0.1) \times 10^5$ divisions of scale per molar concentration. All the slopes were calculated by linear least squares from the experimental results. The unknown solution ($CaCl_2$ $8.00 \times 10^5 M$ in a 1% solution of La + HCl) yields a reading of 52.5 scale divisions. Thus, a direct comparison of the unknown solution against the working curve suggests that the unknown concentration is $7.96 \times 10^{-5} M$. This discrepancy of 0.5% is within our experimental error, and the result appears to be satisfactory, especially on considering that the working curve is constructed for a solution very dissimilar from the unknown solution. Thus the use of pure water for the working curve may appear to be justified. This conclusion, however, is wrong, as will be shown immediately.

A similar experiment was conducted using for the standards a 0.5% solution of La + HCl instead of pure water. This time the working curve obtained (curve b in Figure 3) is a straight line with a slope of 5.73×10^5 divisions per molar concentration. It should be noted that as the settings of the photometer were constant during all the experiments (and 0 was set on pure water), the intercept of curve b is determined experimentally; in our case it is 7.5 divisions. The unknown concentration obtained by using curve b is now $7.80 \times 10^{-5} M$—i.e., an underestimate by 2.5%. Next, a working curve was constructed using for the standards a 1% solution of La + HCl — i.e., the standards were identical with the unknown solution. The working curve obtained (c in Figure 3) is a straight line with a slope of 4.95×10^5 scale divisions per molar concentration, and an intercept of 12.5 divisions. The unknown concentration obtained by using curve c is $8.05 \times 10^{-5} M$ — i.e., the error is less than 1%. Finally, a working curve was obtained using for the standards a 2% solution of La + HCl. The curve obtained (d in Figure 3) is again straight line, with a slope of 3.75×10^5 divisions/molar, and an intercept of 19 divisions. The concentration of the unknown sample derived from this curve is $8.9 \times 10^{-5} M$ — i.e., an overestimate by about 11%.

Considering Figure 3, it can be seen that there is a range of concentrations (at about $6 \times 10^{-5} M$) where the choice of any of the above standards is not very relevant. At such a concentration the reading obtained from our unknown solution could be read off the pure-water working curve (or any other La + HCl working curve) and the results would correspond closely to the true concentration of calcium as checked, for instance, by gravimetric or complexometric analysis. A spurious conclusion might be drawn that such a working curve allows the accurate evaluation of Ca at any concentration within the photometer setting—say from $10^{-5} M$ to $1.6 \times 10^{-4} M$ in our case. Obviously using such a conclusion for samples deviating from $6 \times 10^{-5} M$, wrong results would be obtained. Against a pure water standard, an unknown solution of $1.00 \times 10^{-5} M$ in 1% La + HCl would appear to be $2.4 \times 10^{-5} M$ (an overestimate of more than 100%), while an unknown solution of $1.6 \times 10^{-4} M$ would appear to be $1.38 \times 10^{-4} M$ (underestimate of about 14%). Thus, the experiments showing that a working curve obtained for a mixture containing suppressing agents yields a value for an unknown concentration which is confirmed independently, do not ensure that such a working curve may be used for other unknown concentrations. It appears that only if consistent results are obtained over a considerable range of concentrations can the working curve be accepted as reliable.

Standard Addition Method. In the next series of experiments it was attempted to evaluate m_X by the use of "Standard Addition," as described in the theoretical section. To 8 cc of the unknown solution were added 2 cc of $CaCl_2$ in pure water, at varying concentrations (in our notation $V_X = 8$ cc, $V_S = 2$ cc, m_X unknown but constant, m_S varies). The results obtained are plotted in the righthand part of Figure 4 ($m_S > 0$).

A straight line is obtained, yielding $(\partial m_S/\partial R_M)_{V_X,V_S,m_X} = 1.985 \times 10^{-8}$ mole/division of scale, and an intercept of 44.3 divisions. Introducing these values into Equation 7 and assuming that $R_I = 0$, we obtain $m_X = 8.79 \times 10^{-7}$ mole—i.e., $1.10 \times 10^{-4} M$, an overestimate of 37%.

The great discrepancy between the expected and the calculated value suggests the possibility of contamination by Ca either of the La_2O_3 used, or of the HCl, or of the final 5% solution of La + HCl used in the preparation of the unknown solution. Such a contamination could account also for the

intercepts obtained in the experiments with the working curves described in the last section. Indeed, a solution of 0.8% of La + HCl—i.e., our unknown solution not containing any added $CaCl_2$—gives a reading of 12 scale divisions. To account for the error, the La_2O_3 should contain 0.02% of a Ca salt as impurity. This means that the La_2O_3 should contain twice the maximum impurity allowed by the manufacturers, and that all of it should consist of a calcium salt; this could not be tested with the analytical equipment at our disposal, but it appears improbable. The HCl should contain 6×10^{-2} gram of $CaCl_2$ per liter ($5.4 \times 10^{-4}M$) to yield the observed effect, which also appears improbable in an analytical reagent.

To test experimentally the possibility of contamination by calcium, we have prepared a solution of HCl without lanthanum, in which the concentration of Cl corresponded to the 1% La + HCl solution. Such a solution yielded a reading of 0.05 scale division, confirming that it was practically calcium free.

A solution of La without HCl was prepared by dissolving the La_2O_3 in a slight excess ($\approx 5\%$) of HNO_3. Such a solution yielded a reading of 7.5 scale divisions. It appears, therefore, that HCl neither contains Ca nor contributes by itself to the reading. La_2O_3 apparently does not contain the amount of Ca necessary to give the reading of 7.5 divisions—this reading is due to La, and not to Ca in La_2O_3. Finally, the mixture of La and HCl gives a considerably higher reading than the sum of the readings which these components give separately. We conclude, therefore, that the presence of HCl enhances the absorption by La. Such an effect of acid is not unexpected (*1*, *7*), and the interaction of La_2O_3 and HCl was not investigated any further. A paper by Monder and Sells has been published recently (*9*), in which the effect of La and HCl on the absorption of Ca is discussed. The results support the conclusions stated above.

It is of interest to note that if the reading of 12 scale divisions is considered as the interference R_I, and introduced so into Equation 7, the experimental results obtained yield for m_X the value of 6.41×10^{-7} mole ($8.02 \times 10^{-5}M$)—i.e. almost exactly the true value of the unknown concentration.

Method of Successive Dilutions. It was attempted to evaluate m_X also by the method of successive dilutions, as presented in the theoretical section. The simplest approach is that of applying the instrument reading at any dilution to the working curve of $CaCl_2$ in pure water, as presented in curve *a* of Figure 3. The results of the calculations are given in Figure 5 (closed circles). Use of the 5% La + HCl solution allowed us to obtain points also at relative concentrations greater than unity.

It can be seen that an approximately straight line is obtained, intersecting C_{calcd} at about $11 \times 10^{-5}M$—i.e., 30% higher than the true concentration.

The true concentration of $8.00 \times 10^{-5}M$ corresponds, on the curve obtained, to the relative concentration of 0.95. Independent experiments carried out at this relative concentration yield the values of $R_M = 50$ divisions, $R_I = 13$ divisions, and $k_M = 5.00 \times 10^5$ divisions/M. k^∞ has already been stated to be $\simeq 6.7 \times 10^5$ divisions/M. Introducing these values into Equation 12, we obtain for the left hand part the value of 7.46×10^{-5} and for the right hand part the value of 7.40×10^{-5}. Thus the two sides of the equation are equal within the limit of our experimental error.

The slope dC_{calcd}/dC_{rel} is roughly $-2 \times 10^{-5}M$/relative concentration. However, it can be seen in Figure 5 that the slope is greater in the dilute solutions and smaller (about $-1.5 \times$

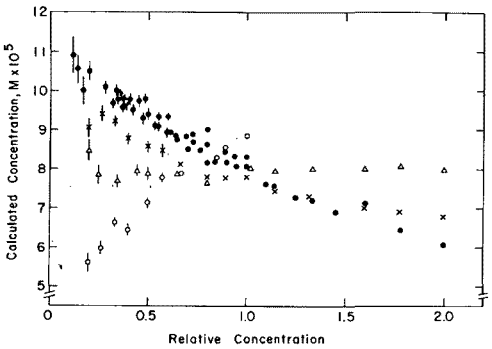


Figure 5. Method of successive dilutions

- ○ Against standards of pure water
- × Against standards of La + HCl 0.5%
- △ Against standards of La + HCl 1.0%
- ○ Against standards of La + HCl 2.0%

$10^{-5}M$/rel concn.) in the concentrated solutions. Equation 13 was used to calculate the slope from experimental values. For $C_{rel} = 0.5$, the following results were obtained: $V_X = 8$ cc, $V_S = 8$ cc, $R_I = 8.5$ divisions, $dk_M/dV_S = 5.00 \times 10^6$ divisions/mole, $dR_I/dV_S = -0.385$ division/cc. The calculated dC_{calcd}/dC_{rel} is $-3.31 \times 10^{-5}M$/rel concn. For $C_{rel} = 1.33$, the following results were obtained: $V_X = 8$ cc, $V_S = -2$ cc, $R_I = 15.5$ divisions, $dk_M/dV_S = 3.35 \times 10^7$ div/mole, $dR_I/dV_S = -1.23$ div/cc. The calculated dC_{calcd}/dC_{rel} is $-0.9 \times 10^{-5}M$/relative concn.

As will be shown in the section dealing with the "changing parameter" method, k_M can be represented quite accurately by Equation 15, where $k^\infty = 6.52 \times 10^5$ div/M, $k_M{}^\circ = 4.94 \times 10^5$ div/M, and $A_k = 9.19$ cc. Introducing these values into the approximate Equation 17, we obtain for dC_{calcd}/dC_{rel} the constant value of $-2.2 \times 10^{-5}M$/rel concn, which agrees fairly well with the experimental results.

In the next series of experiments instead of the standards based on pure water, we employed standards based on 0.5% La + HCl. A working curve was constructed of R_M *vs.* C_{Ca}, and the reading of the undiluted unknown solution was checked against this curve, yielding the apparent concentration of the unknown solution (which in the case of the undiluted solution is also the calculated concentration). For each dilution of the unknown solution, the standards were diluted correspondingly, and a new working curve was constructed. For each such working curve, the 0 had to be shifted, so that the standard without any added calcium read 0. The reading of the diluted unknown solution was checked against the new working curve, and the obtained apparent concentration was divided by the relative concentration to obtain the calculated concentration. This somewhat laborious procedure was carried out for a number of dilutions. The results are summarized by crosses in Figure 5. The intercept is now about $1.0 \times 10^{-4}M$, so that the overestimate is now only 25%.

When the standards are based on a solution of La + HCl of 2%, the results denoted by open circles in Figure 5 are obtained. Here the intercept indicates a concentration of about $5 \times 10^{-5}M$—i.e., an underestimate of about 37%.

As a final check, the standards were based on a 1% solution of La + HCl—i.e., identical with the unknown solution. The results are presented as triangles in Figure 5. They yield, as

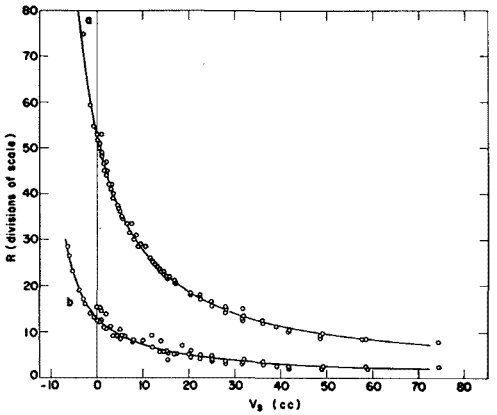


Figure 6.

a. R_M of 8 cc of unknown sample, on addition of V_S cc of water. Points, experimental. Curve, Equation 19 with R_M° = 52.5 div, and A_M = 11.1 cc
b. R_I of 8 cc of La + HCl 1% on addition of V_S cc of water. Points, experimental. Curve, Equation 19 with R_I° = 13 div, and A_I = 12.5 cc

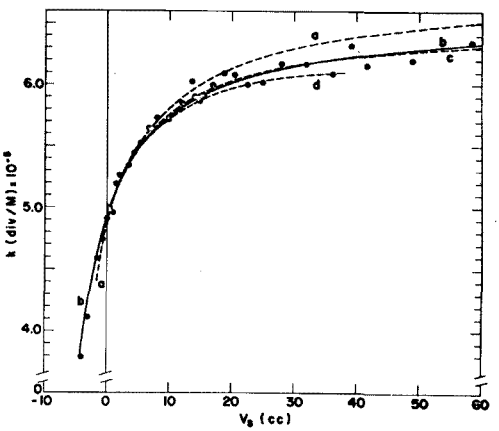


Figure 7. k of Equation 6 as function of V_S. Points, experimental
Curves: *a.* Calculated assuming $R_I = 0$
b. Calculated assuming hyperbolic R_M and R_I
c. Calculated from Equation 15, with $k^\infty = 6.52 \times 10^5$ div/M, $k^\circ = 4.94 \times 10^5$ div/M, and A_k = 9.19 cc
d. Extreme experimental results

expected, a horizontal line at practically the correct value of $8 \times 10^{-5}M$.

The above experiments seem to support the following conclusions: The theoretical treatment given to the method of successive dilutions in the first part of this paper appears to be valid. The method of successive dilutions appears to be unsuitable for the determination of substances in the presence of strong interference, unless the standards used approximate very closely the unknown solution—but in such a case the simulation method will also yield good results.

Determination of R_I Using the Changing Parameter Method. In the Standard Addition method discussed above, k_M and R_M were obtained for V_S = 2cc. The same procedure was carried out for other values of V_S. The results obtained are summarized in Figures 6 and 7.

The measurements of R_M appear to be well reproducible, while those of k exhibit considerable scatter. Part of this impression is due to the difference in scale: R_M is measured from practically zero to about 80 divisions, while k is measured only in the interval of 4–7 ($\times 10^5$ div/M). Nevertheless it has to be admitted that the accuracy of k is only within $\pm 2\%$ of the value of k. Efforts to obtain more reproducible results were unsuccessful. It is hoped, however, that a better experimental technique can increase the reproducibility so that the error becomes less than $\pm 1\%$.

Plots of log R_M *vs.* V_S and of $1/R_M$ *vs.* V_S show that R_M can be better approximated by a hyperbolic function of V_S (such as Equation 19) than by an exponential function (such as Equation 20). Using least squares for a hyperbolic function, we obtain for the 87 experimental points of Figure 6, part *a*, the values R_M° = 52.5 and A_M = 11.1. It can be seen that the curve obtained by using the above constants in a hyperbolic function of the form of Equation 19 (but with R_M instead of R_I) fits well the experimental data.

In the discussion of the Standard Addition method, we have used the experimentally obtained R_M and k for the case when V_S = 2 cc, assuming that R_I = 0. When V_S = 0, Figures 6 and 7 yield the corresponding experimental values of R_M° = 52.5 and $k^\circ = 4.91 \times 10^5$ divisions/M. Introduction of these values into Equation 7 (again assuming that R_I = 0) yields for m_X the value of 8.56×10^{-7} mole, and for C the value of $1.07 \times 10^{-4}M$ — i.e., an overestimate of about 34%. It is now possible, however, to compare the consistency of this result with the behavior of R_M and of k on dilution, as discussed in the theoretical section. If the assumption that R_I = 0 is correct, k for any V_S can be calculated using Equation 7, with $m_X = 8.56 \times 10^{-7}$ mole and the corresponding R_M obtained from Figure 6. The values of k's thus obtained are presented as curve *a* in Figure 7.

It can be seen that the assumption of R_I = 0 leads to values of k which deviate significantly from the experimental results; this deviation becomes noticeable already when $V_S \simeq 20$ cc, and approaches 3% of the value of k at $V_S > 50$ cc.

The expected ratio between k_{exp} and k_{calcd} has been given in Equations 31–33. Using the values of R_M° and A_M obtained above, and assuming R_I° = 13 divisions and A_I = 12.5 cc (in anticipation of the following discussion of R_I), we obtain for the ratio k_{exp}/k_{calcd} = 0.98—i.e., k_{exp} should be about 2% less than k_{calcd} — agreeing well with our results.

The maximal discrepancy between the two k's is to be expected at infinite dilution. In our case, Equation 33 yields the value of 0.97, so that the largest expected experimental deviation from the value of k calculated on the assumption that R_I = 0 is only 3%. However, as k can be determined within $\pm 2\%$, such a deviation can be detected, as shown in Figure 7.

While the experimental results support the conclusion that in our system $R_I \neq 0$, it still remains to determine the value of R_I°, and consequently the value of m_X.

An attempt to evaluate the constants R_I°, A_I, and m_X using Equations 6 and 19 yields widely scattered results, as the equations are quadratic, and include division of differences between large numbers by small numbers. A search for the best values of the above three parameters to fit the ex-

perimental values of R_M and k listed in Figures 6 and 7 is very cumbersome, and again yields inconclusive results.

Better results can be obtained through the use of Equation 29, with F and f defined by Equations 27 and 28, and calculated employing the values of R_M, k, dR_M/dV_S, and dk/dV_S from Figures 6 and 7.

It will be noted in Figure 7 that the behavior of k appears to be consistent with Equation 15. Indeed, search for the three constants best fitting the experimental results yields the values of $k^\infty = 6.52 \times 10^5$ div/M, $k^\circ = 4.94 \times 10^5$ div/M, and $A_k = 9.19$ cc, which have been used in the discussion of the method of Successive Dilutions. The k's obtained from Equation 15 using the above constants are represented by curve c in Figure 7, and agree well with the experimental results. This might suggest the use of Equation 15 with the constants obtained above to calculate k and dk/dV_S as functions of V_S, in order to utilize these values for easy calculation of the functions f and F. Unfortunately on inspecting Equations 7, 19, and 15, it can be seen that they are incompatible; if both R_I and R_M are exact hyperbolic functions of V_S, then k cannot possibly be an exact hyperbolic function of V_S, for it is determined already by R_I and R_M, as stated in Equation 7. Use of Equation 15 to obtain f and F introduces thus an error which affects significantly Equation 29, expecially as f and F are very sensitive to changes in the parameters k^∞, k°, and A_k. Thus, while algebraic calculation of R_M and dR_M/dV_S using $R_M{}^\circ$ and A_M appears justified by the results presented in part a of Figure 6, such a procedure is unjustified for k, and the values of k and of dk/dV_S have to be obtained graphically from the experimental points presented in Figure 7.

This has been attempted, and the values of R_M, dR_M/dV_S, k, and dk/dV_S have been obtained for the 31 integral values of V_S, from $V_S = 0$ to $V_S = 30$. Search was then made for the values of $R_I{}^\circ$ and A_I which would best fit Equation 29.

A search for the best two parameters can be conveniently made (*13*), unlike the search for three parameters attempted above. We were interested, however, not only in the best value of $R_I{}^\circ$, but also in the behavior of σ as function of $R_I{}^\circ$ and of A_I. Therefore we preferred the more laborious method of mapping the function σ against a grid of A_I and $R_I{}^\circ$, where σ utilizes Equation 29, and is defined as:

$$\sigma \equiv \frac{31}{\Sigma_i F}\sqrt{\Sigma_i\left(F + \frac{R_I{}^\circ A_I}{(A_I + V_S)^2} + f\frac{R_I{}^\circ A_I}{A_I + V_S}\right)^2} \qquad (34)$$

i applying to the 31 values of the experimentally determined variables f, F, and V_S. σ is thus the mean square deviation relative to the average value of F, and when R_M and R_I behave like perfect hyperboles and σ has been determined without any error at all, σ should be zero. A simpler utilization of Equation 29 would also be sufficient to search for $R_I{}^\circ$ and A_I — e.g., the sum appearing under the root sign of Equation 34 without the root and the coefficient—but Equation 34 allows the direct comparison of results obtained for any value of i and for different experimental conditions. As explained in the theoretical section, σ should be zero not only when the true $R_I{}^\circ$ is introduced, but also for $R_I{}^\circ = R_M{}^\circ$.

To illustrate the behavior of σ in ideal conditions, R_I was determined experimentally as function of V_S, by measuring the absorption on dilution of pure 5% La + HCl. The

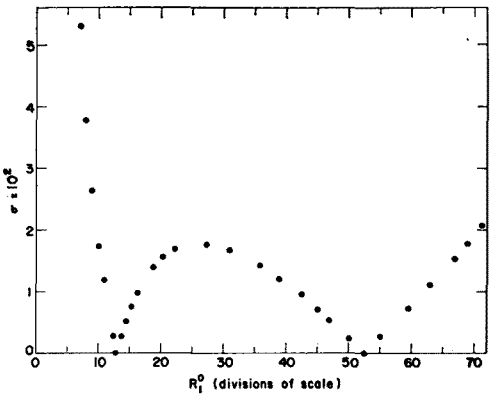


Figure 8. Points, minimum σ calculated with Equation 34 for hyperbolic R_M and R_I

results are summarized in part b of Figure 6. Search for the best $R_I{}^\circ$ and A_I yields the values $R_I{}^\circ = 13$ and $A_I = 12.5$. The curve b in Figure 6 represents Equation 19 when these values are introduced into it. The experimental R_I can be represented very closely by such a hyperbolic function.

Having m_X, R_M, and R_I, the values of k and of dk/dV_S can be calculated accurately using Equation 7. The k's so obtained are plotted as curve b in Figure 7. They correspond very well with the experimental data. It will be noted that curve b does not coincide with curve c—the hyperbolic function which attempts to represent k. The difference between b and c may appear slight, but it is significant, in particular as regards slopes, which affect strongly the values of f and F.

Utilizing the values of R_M, dR_M/dV_S, k, and dk/dV_S obtained above, the form of σ as function of $R_I{}^\circ$ can be determined. The final results are plotted in Figure 8.

A minimum appears at $R_I{}^\circ = 13$, and another at $R_I{}^\circ = R_M = 52.5$, as explained in the theoretical section.

In order to illustrate the effect of inaccuracy in the determination of k, a curve was drawn in Figure 7 assuming the lowest possible values of k (curve d). Values of k and dk/dV_S were obtained graphically, and σ was again calculated for $V_S = 0$ to $V_S = 30$. Again two minima were obtained: the irrelevant one at $R_I{}^\circ = R_M{}^\circ = 52.5$, and the experimental at $R_I{}^\circ = 2$. The values of σ were, as expected, much higher than those for an ideal case; even σ_{min} at $R_I{}^\circ = 2$ was 0.3—i.e., out of scale of Figure 8. Introduction of the above $R_I{}^\circ$ into Equation 7 yields for the unknown concentration the value of $1.02 \times 10^{-4}M$—i.e., reduces the error from about 35% of the Standard Addition method to about 28%—not a great gain in accuracy, as might be expected when taking an extreme experimental result.

The following conclusions can be reached on the basis of the above considerations. It appears that the different forms of the working curves methods, the standard addition method, and the method of successive dilutions are unsuitable for determination of substances in the presence of strong interference. The inaccuracy of these methods is due to the neglect of R_I, so that despite high precision in instrumentation and technique, serious errors may result. The method suggested by us is laborious, but the results may be obtained with high accuracy, when the precision is increased. With the rapid advance in photometric technique, such method may have some value.

(13) E. A. Unwin, R. G. Beimer, and Q. Fernando, *Anal. Chim. Acta.*, **39**, 95 (1967).

It would be of interest to extend the present investigation in three directions: First, a system of practical interest, such as some biological fluid, could be investigated by the above method, and the results compared with those obtained by other analytical methods. Next a more sensitive (though perhaps less convenient) parameter than V_S could be employed —e.g., the frequency of the absorbed light. Finally, the treatment described in the theoretical section could be applied to some other analytical methods, in which the instrument reading is a linear function of concentration—e.g., polarography.

ACKNOWLEDGMENT

We are indebted to Prof. M. Anbar of the Isotope Dept. of the Weizmann Institute of Science, under whose direction this investigation was carried out, for his interest and advice. We are grateful to Dr. S. Szapiro of the Weizmann Institute of Science for his many helpful suggestions.

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Time Resolution in Spark Source Mass Spectrometry

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The application of time resolution to rf spark source mass spectrometry has been studied and has shown variation on a time scale previously unpredicted. Ion yield variations were found over a 100-μsec pulse length and were dependent on the element and matrix under consideration. A comparison was made of a metallic iron sample and a biological ash-graphite matrix. The electronics necessary for pulse synchronization, instrumental requirements, and a method of data reduction are described. In addition to providing information on the spark source excitation, the use of time resolution to improve the analytical method is illustrated.

THE SPARK SOURCE MASS SPECTROGRAPH utilizes a pulsed oscillatory excitation causing the resultant ion beam to vary with time. Essentially each rise in the radio-frequency voltage causes a spark breakdown across the electrode gap followed by a period of low-voltage, high-current excitation (*1*). This process, requiring about 0.1 μsec, is repeated throughout the duration of the rf pulse. Thus the ion beam consists of ion bursts, and the ion intensity is time dependent. An analogous situation exists in emission spectrometry.

In many of the spectrometric light sources, important parameters, such as current, voltage, and temperature, vary with time. As a consequence, it is often useful to time-resolve the radiation to better understand or explain the excitation as well as improve the analytical method. With time resolution, workers have investigated such parameters as the order of appearance of various spectral lines (*2, 3*), the temperature of the discharge (*4*), and line shifts (*5*). One of the most important benefits of time resolution is the improvement of detection limits in spectrochemical analysis (*6–9*).

The success of time resolution when applied to the emission spectrograph suggests that information on excitation and an improved analytical method may result from study of the time-dependence of the spark source ion beam. In spite of the attractiveness of this method, Franzen and Schuy (*10, 11*) are the only workers to have time resolved the ion beam from a solid source mass spectrometer. The ions they studied were not produced by the radio-frequency spark but by the condensed vacuum discharge (also called a pulsed dc source).

Because time resolution has shown a utility in emission spectrometric analysis and with the pulsed dc source, a method was developed which allows the study of the time variance of the ion beam emanating from an rf spark source. The electronics necessary for pulse synchronization, instrumental requirements, a method of data reduction, and preliminary results will be discussed.

During the analysis of biological materials, the biological ash–graphite electrodes exhibited quite an unusual behavior (*12*). There were a large number of inorganic molecular ions produced, the sensitivity of the rare earths was depressed, and multiply-charged ion production was suppressed. Because of these unusual characteristics, the time behavior of these samples will be compared to that of a "normal" metallic matrix, iron.

EXPERIMENTAL

Mass Spectrograph. The Nuclide Analysis Associates GRAF 2.1 mass spectrograph previously described (*12*) was used in this study.

Figure 1 details the modifications to the instrument necessary to achieve time resolution. A trigger pulse of +10 V, 1 μsec length generated by the E-H Model 131 pulse generator determines time zero. This pulse is shaped and amplified by a Stromberg-Carlson Model AR-410 amplifier and then used to trip the monostable multivibrator in the rf pulse generator of the mass spectrograph. The pulse duration is determined by the settings on the control panel of the rf pulse

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(1) R. E. Honig in "Mass Spectrometric Analysis of Solids," A. J. Ahearn, Ed., Elsevier, New York, 1966, p 16.
(2) A. Schuster and G. Hemsalech, *Trans. Roy. Soc. (London)*, **193**, 189 (1900).
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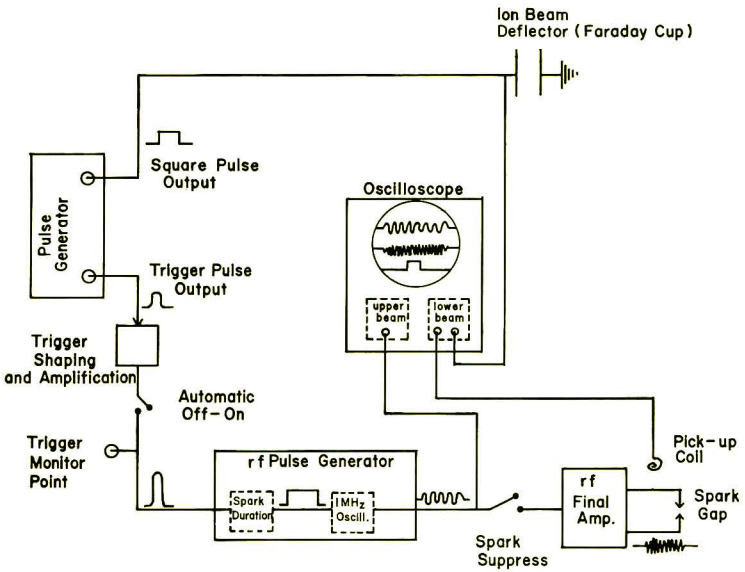


Figure 1. Electronics for time resolution

generator and used to drive the internal 1 MHz oscillator. This output of the multivibrator (called the driving pulse) is amplified to about 6 kV and stepped-up to 60 kV by the Tesla coil. The rf spark pulse from the Tesla coil then causes the electrode breakdown to occur. The repetition rate of the trigger pulse from the E-H pulse generator is continuously variable allowing selection of any desired spark pulse repetition frequency.

To time resolve the ion beam a square pulse of variable width and delay after $t = 0$ is generated by the E-H pulse generator. This time resolving pulse is imposed on a retractable Faraday cup located just after the beam monitor (The Faraday cup has a length of 1.4 cm parallel to the ion path). The ion beam is deflected while this voltage pulse is on the Faraday cup and travels a slightly different path through the magnetic sector. Both ion beams (time selected and normal) are resolved according to their mass-to-charge ratio, striking the photoplate slightly separated. The time resolved ions can be made to fall at either higher or lower apparent mass and at a variable distance in relation to the undisturbed ions by chosing the appropriate square pulse polarity and amplitude, respectively. In this study a +48 V square pulse was used for time selection of the ions.

Several time resolving pulse lengths were used for study of the two matrices. The resolving pulse was set at a given time after time-zero and 2 to 4 photoplate exposures were made at predetermined beam monitor values to allow the detection of elements at various concentration. The resolving pulse was then advanced to another time period and the same exposures were made. This process was repeated until the desired time period was covered. Although data was taken for some 15 different species, only a few examples will be given for any one type of behavior.

Unless otherwise stated, a 10-μsec square pulse was used for the time resolution of the 60-μsec radio-frequency pulses.

A constant electrode separation was maintained by the use of the oscilloscope as presented under the section on Results and Discussion.

RG-58A/U, 50-ohm impedance shielded cable was used where necessary to maintain pulse rise times. A Narda 22625, 50-ohm terminator was used to match the impedance of the external circuit to the output impedance of the E-H pulse generator.

Oscilloscope. A Tektronics Model 551 dual-beam oscilloscope with Type K Fast Rise Time and Type 1A2 Dual Trace Preamplifiers were used. A Beattie-Coleman Oscillotron MII oscilloscope camera and Polaroid Type 47 film were used to record any desired oscilloscopic traces.

Direct electrical connections were used for observation of the square pulse and the output of the rf Pulse Generator. A five-turn coil of wire placed near the Tesla coil was used to pick up the spark signal, since the very high voltages involved precluded a direct connection.

Samples. As an iron sample, National Bureau of Standards Standard Iron No. 464 was cut and machined to serve as self-electrodes. Ten different elements (Eu, Tm, Y, Cd, Cu, Co, Cr, Mn, S, and Fe) were doped into spectrographic grade graphite (National Carbon SP-1C) at about 5000 ppm (weight) by the addition of high purity oxides (Mn and S were added as MnS). For the studies of the 50:50, biological ash:graphite matrix, the necessary amounts of air-ashed sugar beet leaves, the 5000-ppm graphite mix, and spectrographic grade graphite were blended to yield a 1000-ppm doped mix.

All blending was accomplished by using a tungsten carbide capsule and shaking in the Spex Industries No. 8000 mixer/mill.

Data Reduction. The elemental ion yield for a given time period was calculated by ratioing the intensity of the photographic line produced during that period to the intensity of the ions produced during the entire discharge. The % transmission readings were converted to intensity using the Seidel function and background corrected. The total ion intensity was calculated by adding the intensity of the time-resolved and the undeflected ions. The ratio of the time-resolved image to the total ion image intensity was then used as a measure of the relative ion yield. When possible, the two intensities were taken from the same photoplate exposure in order to minimize the effects of sample inhomogeneity. If the two intensities were taken from different exposures, the appropriate correction was made for exposure

values but no correction could be made for any scatter caused by the inhomogeneity of the electrode.

For presentation and ease of examination and discussion the calculated ratios have been multiplied by 10^3 and labeled "Relative Ion Yields."

RESULTS AND DISCUSSION

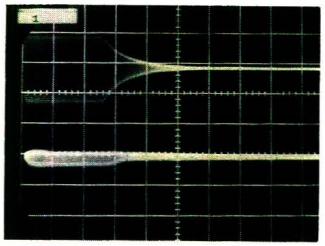
Oscilloscope. In addition to allowing time and voltage measurements pertinent to the time resolution study, the oscilloscope provided other valuable information. Several workers in the field (*13*, *14*) have mentioned the advantage of using an oscilloscope in conjunction with the spark source mass spectrograph to monitor the electrode gap and for tuning the rf circuitry (*15*). The peak to peak voltage of the rf signal during sparking is dependent on the electrode separation. Figure 2 shows the spark signal and its relation to the driving pulse for shorted electrodes (*a*) and sparking electrodes (*b*) and 2(*c*) compares the spark signal for a wide and a narrow electrode gap. Figure 2(*d*) is the oscilloscope pattern observed while sparking iron electrodes with a 340-μsec rf pulse.

The oscilloscopic traces were quite different when the biological ash–graphite electrodes were sparked. Figure 3(*a*) is the pattern seen for a single rf pulse. The normal rf signal from the Tesla coil is seen for the first 20 μsec and then a trace is seen which is similar to the shorted electrode type signal [Figure 2(*a*)]. The relative amounts of rf and shorted electrode type signal in a given pulse varied from very little rf to complete rf type breakdown. Figure 3(*b*) presents the integrated oscilloscope trace for 10 rf pulses. Also shown is the square pulse used for time resolution. If enough pulses were observed, as in Figure 3(*c*), there would be rf signal throughout the full pulse duration, but the occurrence of the rf during a single packet was quite unpredictable. This is in direct contrast to the oscilloscope pattern of the iron electrodes with spark breakdown occurring during the entire 60-μsec rf pulse. The rf discharge and/or the shorted electrode type signal observed with the ash–graphite electrodes lasted past the "cut-off" time of the iron electrodes.

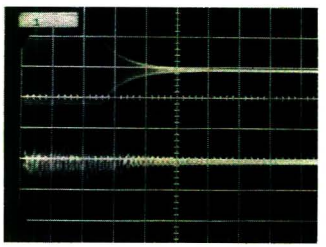
As is seen in Figure 3(*b*), the third channel of the oscilloscope displays the time resolving pulse with its relation to time-zero and the rf pulse. As mentioned above, the delay from $t = 0$ and the width of the square pulse (100 and 10 μsec, respectively, in Figure 3(b)) are both variable to allow selection of the desired time segment.

Iron Electrodes. The iron sample was chosen to test the time resolution method and as a "normal" matrix for comparison to the ash–graphite electrode. The iron sparks similar to most metallic electrodes, generally yields sensitivity factors within a factor of three of unity (as noted in the authors' laboratory) and presents a reasonably uncomplicated rf signal on the oscilloscope.

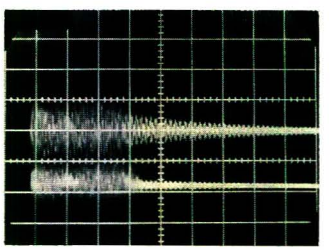
Figures 4, 5, and 6 present the relative ion yield *vs.* time for representative elements in the iron electrodes using resolving pulses of 2, 5, and 10-μsec duration, respectively. All three figures present the time behavior of the 60-μsec rf pulse shown in Figure 2. The 2-μsec and 5-μsec resolution studies were conducted in an attempt to localize in time the initial ion yield maximum noted when using the 10-μsec pulse. As is seen in Figures 4 and 6, a shift in the maximum from 6 μsec to 10 μsec is caused by the increased resolving pulse length. This expected shift and a slight decrease in the height of the maximum are the only differences noted for resolving pulses of 2 and 10 μsec. The initial maximum in the ion yield *vs.* time distributions indicates that a greater number of ions are produced by the first spark discharge (or discharges) than by any others during the rf pulse. The maximum occurs at 6 to 8 μsec after



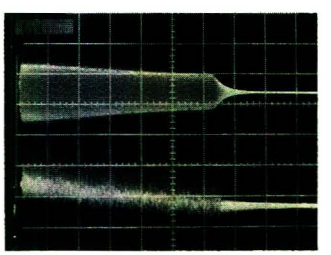
(a) Electrodes shorted. (20 μsec/div)



(b) Electrodes sparking. (20 μsec/div)



(c). Electrodes sparking. (20 μsec/div)



(d). Electrodes sparking, 340 μsec pulse.

Figure 2. Oscilloscope traces for iron electrodes

(*a*) electrodes shorted (20 μsec/div), (*b*) electrodes sparking (20 μsec/div), (*c*) electrodes sparking (20 μsec/div), (*d*) electrodes sparking (340 μsec pulse)

(13) W. L. Harrington and J. R. Woolston, private communication, David Sarnoff Research Center, Princeton, N.J. 08540. November, 1967.
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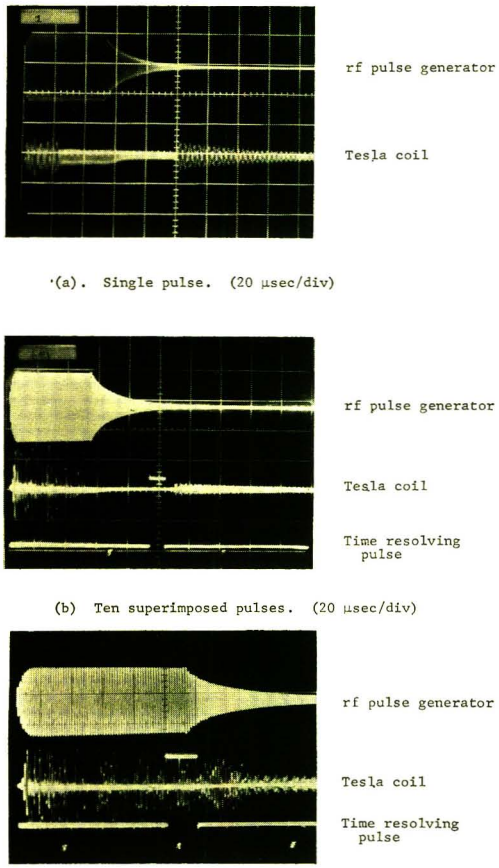


Figure 3. Oscilloscope traces for biological ash–graphite electrodes

(*a*) single pulse (20 μsec/div), (*b*) ten superimposed pulses (20 μsec/div), (*c*) multiple superimposed pulses (10 μsec/div)

time-zero which is approximately the time after time-zero that the first ions would be passing the deflector plates. (The oscilloscope shows the first discharge occurring at 3 to 4 μsec and 2 to 3 μsec are required for time-of-flight to the Faraday cup.) The ion production is reasonably constant during the majority of remaining pulse and dies out as the driving pulse "rings-out" (see Figure 2).

Except for a slightly more intense initial maximum for Fe^+, no definite correlation between ion yield *vs.* time and element or classes of elements was observed. In addition, the +2 ion yields for the metallic elements (Fe, Cu, Mn, etc.) closely parallel that of the singly-charged species. Figures 4, 5, and 6 show +1 to +2 ratios which are essentially constant. The minor variations seen are much less than the variations from unity found in other matrices.

As discussed by Honig and Woolston (*16*), the radio-frequency spark source produces ions with a large range of initial energies. After acceleration and passage through the electrostatic sector, the ions are distributed into an energy spectrum formed at the beam monitor as shown in Figure 7. These data are obtained by varying the accelerating potential while the electrostatic field is maintained constant, thereby shifting the energy spectrum across the energy slit. This energy slit is set to admit approximately 600-V portions of the energy spectrum to the magnetic sector. Constant value exposures, as measured by the ion beam monitor, are taken over the range of accelerating potentials, the plate is developed, and the % transmission data are converted to intensity via the Seidel function. Because the iron comprises the vast majority of the

(16) J. R. Woolston and R. E. Honig, Twelfth Annual Conference on Mass Spectrometry and Allied Topics, Montreal, Canada, 1964, p 377.

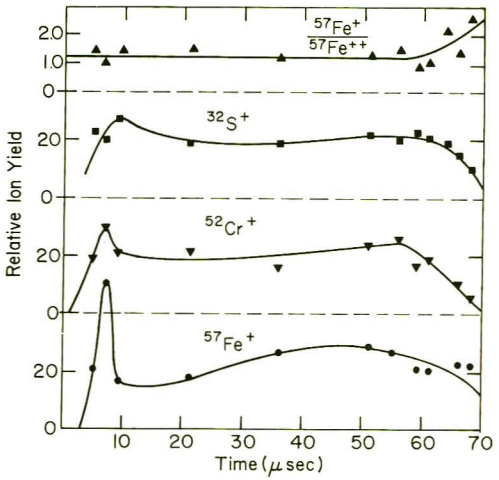


Figure 4. Ion yield *vs.* time for iron matrix (2 μsec resolving pulse)

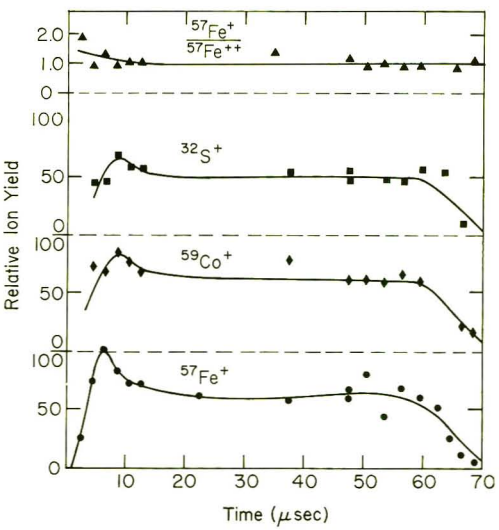


Figure 5. Ion yield *vs.* time for iron matrix (5 μsec resolving pulse)

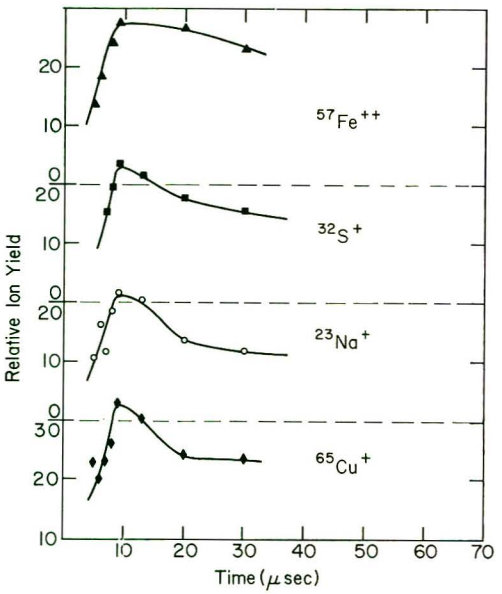


Figure 6. Ion yield *vs.* time for normal energy ions (iron matrix)

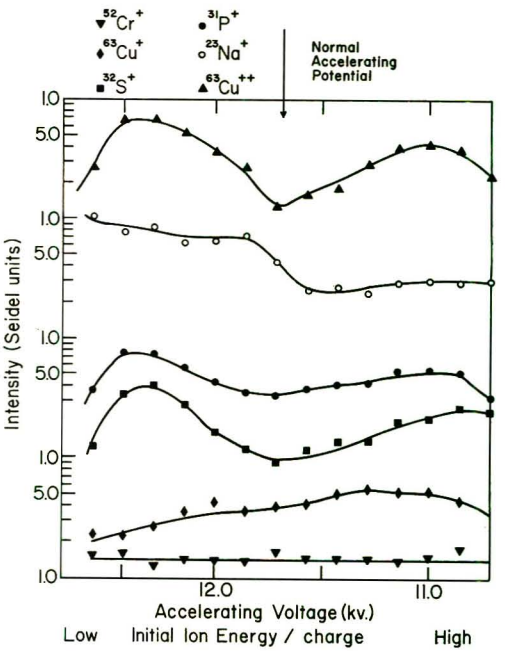


Figure 7. Ion intensity *vs.* accelerating voltage for iron matrix

ion beam, the use of constant ion beam exposures results in data which are normalized to iron.

The flat distribution shown for Cr^+ and Cu^+ was characteristic for the normal metallic ions (Fe^+, Mn^+, V^+, Co^+, etc.). The singly-charged ions of S, P, As, and Sn gave the double peaked distribution characterized by the curves for S^+ and P^+ in Figure 7. The distribution for K^+ was very similar to that shown for Na^+. The plateau at the high accelerating voltages (denoting low primary energy) continued to rise for Na^+ and K^+, as opposed to the break noted for the non-metals, S and P. The doubly-charged metal ions all showed a two-peaked ion yield *vs.* energy distribution with the valley falling at the accelerating potential normally used in an analysis. The energy distributions for the non-metals, S and P, and the doubly-charged species are quite similar to those found by Woolston and Honig for their MS-7 (*16*). As is shown on the abscissa of Figure 7, the ions can be thought of as having a low, medium, or high primary energy depending on whether a high, normal, or low accelerating potential is necessary to bring them into focus on the energy pass window. Those ions which exist at a final energy less than that of the accelerating potential are thought to be produced from neutrals which drifted into the accelerating region and were created by secondary electron collision (*17*). Because the ions were formed in the accelerating region, they did not experience the full effect of that voltage and had a final energy less than the accelerating potential.

As the previous time resolution data were taken at the normal accelerating voltage, it was decided to examine the initial maximum in the ion yield *vs.* time curves as a function of ion energy. The ion beam was time resolved at three accelerating potentials (12.5 kV, 11.7 kV, and 11.1 kV) giving time dependency data for ions with low, medium, and high primary energy, respectively. Figures 6, 8, and 9 present the variations in ion yield *vs.* time distribution for the early part of the rf pulse for low, medium, and high primary energy, respectively. For all three cases, a 10-μsec time resolving pulse was used so that the intensity ratio for the resolved and unresolved ions could be calculated for data from the same exposure. This prevented distortions caused by electrode inhomogeneities. Only the first 30 to 40 μsec were covered in Figures 6 and 8 allowing the use of the entire photographic plate to better define this time region. Since there was little initial peaking for the high primary energy ions, Figure 9 presents the data for the entire rf pulse. As mentioned earlier, the instrumental conditions for the data presented in Figure 6 are the same as in Figures 4 and 5, except for the use of a 10-μsec time resolving pulse.

The ion yield *vs.* time maximum shows a definite energy dependence. For species with a high primary energy, the ion production is fairly constant throughout the radiofrequency pulse, whereas at a low primary energy the yield *vs.* time maximum is sharper than under normal experimental conditions. As with the ions of medium primary energy, there seems to be no variation of yield *vs.* time with element or element class for the low and high primary energy ions.

In general, each electrode discharge is composed of a spark break-down (high voltage, low current) and an arc discharge (low voltage, high current). The presence and length of the arc period is very dependent on the amount of energy in the rf power circuit. This whole discharge cycle lasts only 0.1 μsec and is repeated throughout the rf pulse as dictated by the circuit design. The design of the spark source does not dictate that the initial discharges be any different than the

(17) J. Franzen, K. D. Schuy, and H. Hintenberger, Twelfth Annual Conference on Mass Spectrometry and Allied Topics, Montreal, Canada, 1964, p 251.

following ones, yet the time resolution data indicate an initial burst of ions. Possibly there is more energy available from the inactive circuit for the first discharge(s) than from an active circuit for the later closely spaced sparks. Two possible explanations for the energy dependence of the ion yield *vs.* time maximum depend on the premise that all or a major part of the low primary energy ions are neutrals ionized by collisions (with electrons, ions, or neutrals) in the accelerating region.

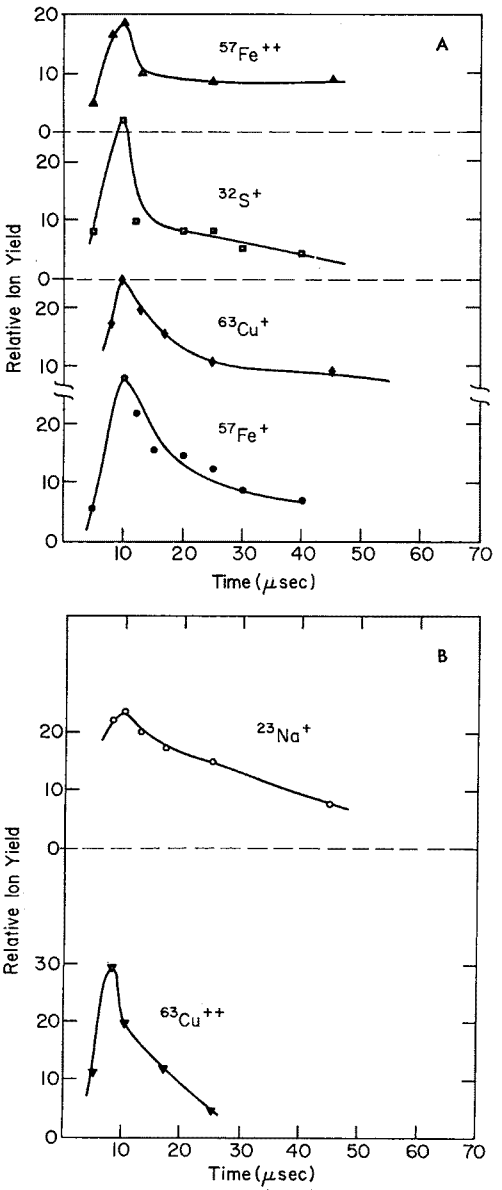


Figure 8. (*a*) **Ion yield** *vs.* **time for low primary energy ions (iron matrix), (*b*) Ion yield** *vs.* **time for low primary energy ions (iron matrix)**

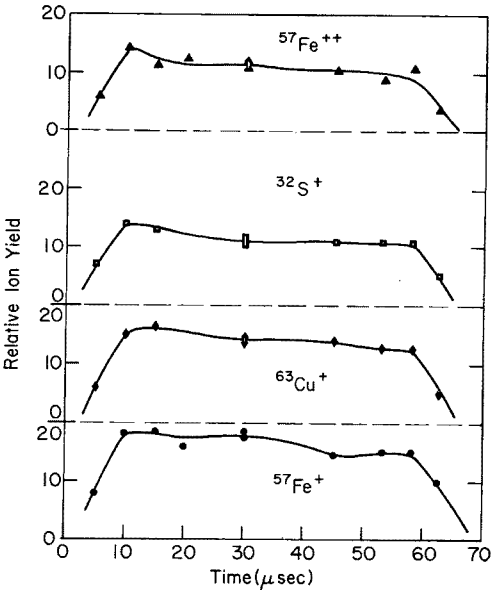


Figure 9. Ion yield *vs.* **time for high primary energy ions (iron matrix)**

It may be that there are more neutrals ejected by sputtering, etc. near time-zero, and consequently more neutrals available for collision excitation. Alternately, the production of neutrals is constant with time and there is an initial burst of particles, causing more collisions, and, consequently, more neutrals are ionized in the accelerating region.

This energy dependence of the ion yield *vs.* time could also be attributed to limitations of the accelerating potential power supply. After the first few microseconds, the ion current could be sufficiently high enough to load the high voltage power supply causing the accelerating potential to decrease with a consequent shift in the ion energy spectrum at the beam monitor energy slit. If the ion yield *vs.* energy distribution were as in Figure 10 as discussed by Franzen and Hintenberger (*18*), the observed ion yield *vs.* time distributions could be explained by a shifting of the energy distribution across the energy window.

The apparent time differences in the rf discharge could be observed if at the lower accelerating voltages, the energy window were passing ions from the flat portion of the ion intensity *vs.* voltage distribution. Thus a change in accelerating potential would not cause a change in the ion intensity. Whereas, at higher accelerating voltages a change in the accelerating potential power supply would cause a significant change in the ion intensity because the intensity *vs.* voltage curve is peaked at these higher potentials.

Biological Ash–Graphite Electrodes. Possibly because of the complexity of the matrix, a variety of yield *vs.* time behaviors were found in the ash–graphite samples. Figures 11–15 give representative curves for the elemental ions and Figures 16 and 17 illustrate the behavior of several molecular ion species. The curves of Co^{+}, Co^{2+}, and Fe^{+} in Figures 11

(18) J. Franzen and H. Hintenberger, *Z. Naturforsch.*, **18a**, 397–409 (1963).

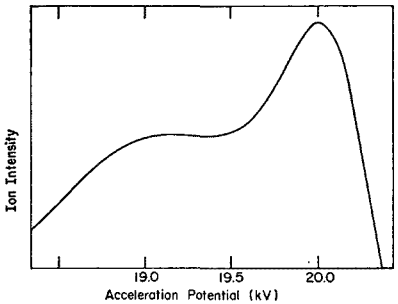


Figure 10. Ion intensity *vs.* accelerating potential found by Franzen and Hintenberger (Ref. 18)

and 12 are quite representative of the behavior of the metallic elements, and Figure 13 presents the typical time dependence of the rare earth ion yield.

The singly-charged metallic ions exhibit a behavior different from that in the iron matrix. A broad maximum was always noted around 20 μsec with a second peak sometimes occurring between 40 and 60 μsec. Also, the 20-μsec maximum was always more intense than the one occasionally found later in the pulse.

Although the singly-charged ions demonstrated a different behavior in the iron and biological-ash matrices, the 2+ ions maintained essentially the same time behavior. Except for being much sharper in the ash-graphite matrix, the same 10-μsec maximum for the 2+ ion yield is observed in Figure 11 as in Figures 4, 5, and 6.

The shape of the ion yield curve for the singly-charged rare earths was found to be different from that of the metallic elements. A broad maximum in the yield curve appeared around 40–50 μsec with no early maximum as noted with Fe^+ and Co^+. As is shown in Figure 13, the doubly-charged rare earth ions have a maximum near 10 μsec just as the 2+ metallic elements did in the iron matrix.

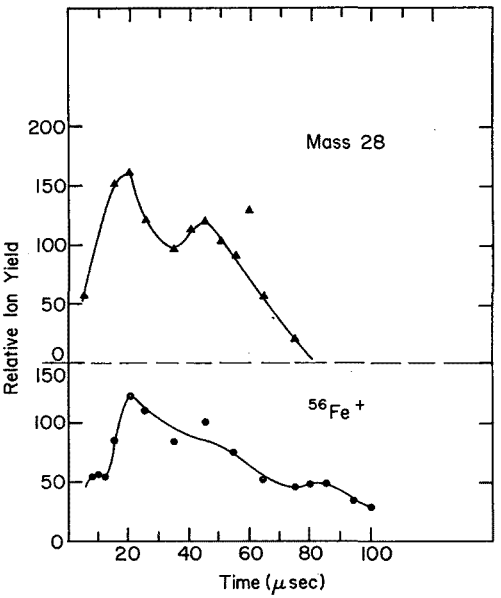


Figure 12. Ion yield *vs.* time for biological ash–graphite electrodes

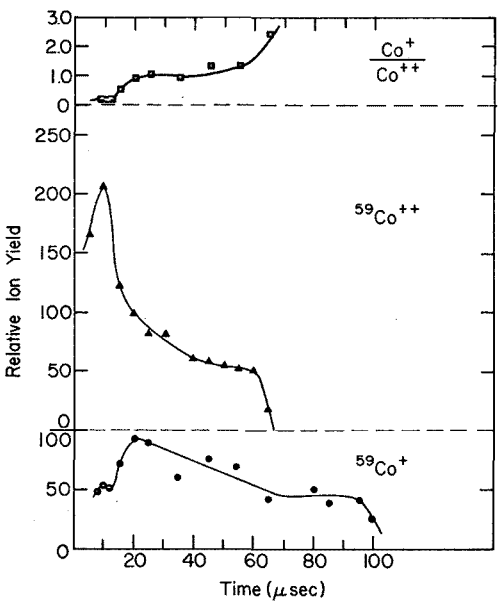


Figure 11. Ion yield *vs.* time for biological ash–graphite electrodes

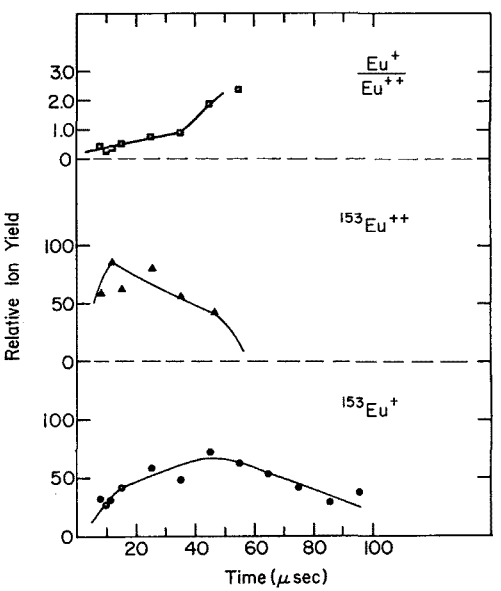


Figure 13. Ion yield *vs.* time for biological ash–graphite electrodes

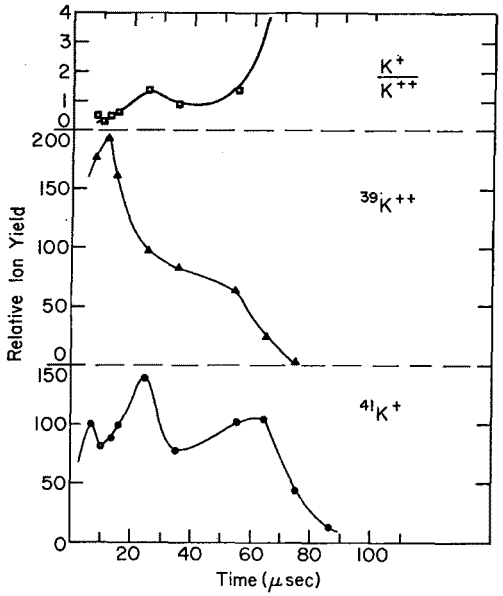


Figure 14. Ion yield *vs.* time for biological ash–graphite electrodes

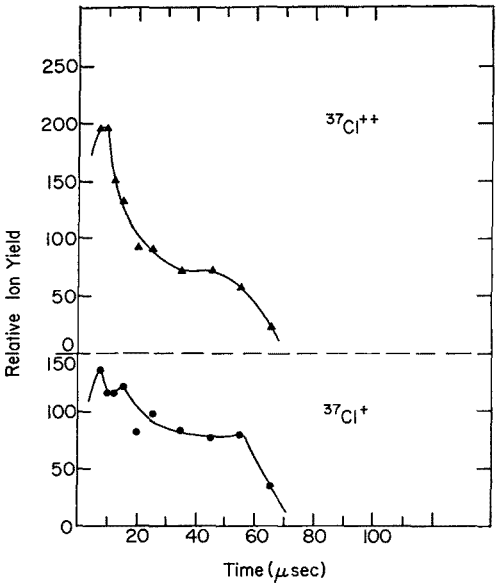


Figure 15. Ion yield *vs.* time for biological ash–graphite electrodes

Figures 14 and 15 show the yield *vs.* time curves for two of the ionic species of K and Cl. These elements were not at a concentration suitable for study in the iron matrix and therefore there is no situation for comparison. The 2+ ions both show a behavior similar to that seen for the 2+ metallic elements and the 1+ ions show no behavior more unusual than the other 1+ species in the ash-graphite matrix.

Figures 16 and 17 present the yield-time data for several molecular species. The molecular species of Figure 17 are several of the interferences encountered in the analysis of biological materials as discussed by Evans and Morrison (*12*).

The most striking aspect of these time-resolution curves was that ions were produced from the ash-graphite electrodes after the normal "cut-off" time seen in the iron electrodes. In many instances, singly-charged ions were detected at 105 μsec (No ions were observed in the Fe electrodes after 70 μsec) and with an unusually wide electrode gap, ions were produced at 120 μsec after time-zero. However, the 2+ ions generally were not produced after 70 μsec. This increased relative production of 1+ ions at later times is illustrated by the variation from unity seen in the 1+/2+ *vs.* time curves of Figures 11 and 13.

When the ion yield curves are compared with the oscilloscopic traces, some of the various phenomena can be correlated. For instance, the initial maximum in the 2+ ion production observed for the ash-graphite electrodes can be related to the oscilloscopic traces noted for that matrix (Figure 3). As seen in Figure 3(*b*), the spark-type discharge was generally observed early in the rf pulse and the shorted electrode type signal became more apparent at the later times. At 60–70 μsec, the spark "hash" signal decreases in amplitude just as the 2+ ion yield becomes undetectable. Even though the low-voltage (shorted electrode type) signal sometimes alternated during an rf pulse with the high-voltage signal (the rf or spark signal), it seemed a spark discharge always preceded the low-voltage signal. It is possible the occurrence of the initial high voltage discharge induces a very large number of ionic species from the easily volatilized and ionized oxide matrix into the electrode gap. The high current plasma causes additional sputtering of neutrals and their ionization which contribute to the maintenance of a low voltage, high-current discharge, as if the electrodes were shorted. The similarity between this portion of the discharge and the shorted electrode type signal of Figure 2(*a*) would suggest the presence of a low resistance gap caused by a large number of charge carriers. The volatility and ease of ionization of the matrix allow this process to occur over a longer time for the available energy in the circuit. When the energy in the tank circuit is depleted or the number of charge carriers drops below a critical value, the discharge stops and the circuit recovers to the energy required for another spark discharge.

On a time average, more spark breakdowns occur in the beginning of the rf pulse and their number decreases with an increase in time from time-zero. This would mean there is a greater percentage of spark-like excitation near the beginning of the pulse and more low-voltage type of excitation as the pulse progresses. If this is true, correlation with the ion yield curves of Figure 11 would indicate the enhanced production of 2+ ions by the high-voltage spark discharge while singly-charged ion production is favored during the low-voltage discharge. Honig's postulate (*19*) of the predominance of multiply-charged ions during the arc portion of a single rf discharge suggests an unusual type of excitation of the biological ash–graphite electrodes. This reversal of expected behavior when exciting this easily volatilized and ionized matrix has been observed with another type of discharge. The pulsed dc source of Franzen and Schuy (*10*, *11*) generally produces a large

(19) R. E. Honig, Twelfth Annual Conference on Mass Spectrometry and Allied Topics, Montreal, Canada, 1964, p 233.

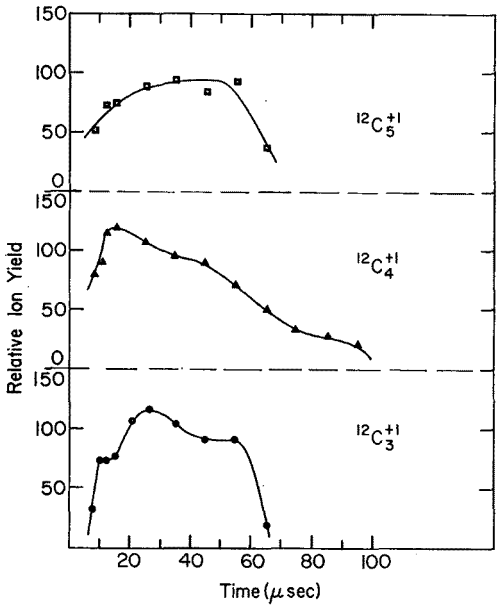


Figure 16. Ion yield *vs.* time for biological ash–graphite electrodes

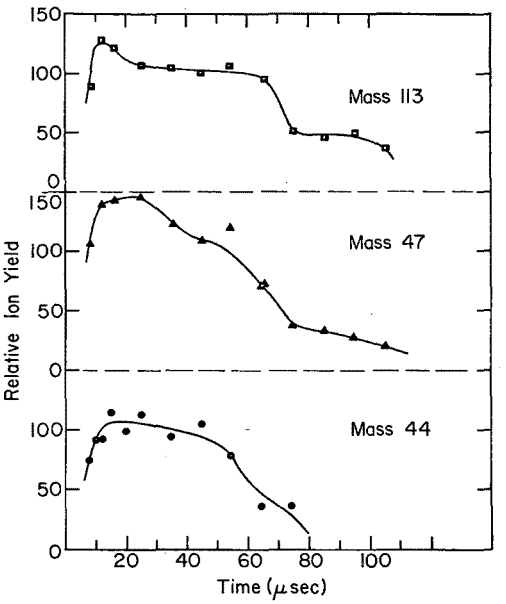


Figure 17. Ion yield *vs.* time for biological ash–graphite electrodes

amount of multiply-charged ions during the arc or low-voltage portion. But Franzen (*20*) found the production of multiply-charged species during the arc cycle was drastically reduced when a potassium halide–graphite sample was sparked with the pulsed dc source.

Both studies using time resolution (this work and that of Franzen and Schuy) suggest a different excitation when sparking an easily volatilized and ionized matrix than when a metallic matrix is under study. This difference can probably be attributed to the increased number of charge carriers in the electrode gap (low gap resistance) which drastically alter the gap parameters.

Analytical Applications. In addition to providing information on the spark source excitation, time resolution can be used to improve the analytical method. Jackson, Whitehead, and Vossen (*21*) have shown that nonsynchronous beam chopping can be used to improve the analytical precision of the spark source. Because their method consumed more sample, the scatter due to sample inhomogeneities was reduced.

Synchronous chopping or time resolution can also improve the accuracy of a qualitative or quantitative determination. As an illustrative example, Figure 12 presents the ion yield *vs.* time for $^{56}Fe^+$ and mass 28 which may be $^{56}Fe^{2+}$ or a singly charged ion of mass 28 [e.g., $^{28}Si^+$ or $(^{12}C^{16}O)^+$]. By comparison to the previously established behavior of a 2+ metallic ion (Figure 11), it can be seen that the intensity of mass 28 has very little relation to the yield *vs.* time of a 2^+ metallic ion. In addition, the time behavior of mass 28 has greater similarity to the 1^+ metallic ions of Figures 11 and 12 than the 1+ molecular species shown in Figure 17. This would infer that the major contribution to the intensity of mass 28 was from $^{28}Si^+$. So using time resolution data and similar reasoning, added confidence can be placed in a questionable spectral assignment.

In addition to providing qualitative evidence, time resolution can be used to improve the spectral purity of an analytical line. If the production of an interfering specie and the ion line of interest are different in time, selection of the proper time segment would give an improved line-to-interference ratio. As seen from the yields presented in Figure 11 and 13, the influence of a 2+ metallic ion at a given mass could be greatly reduced by the use of the latter portion of the rf pulse.

The yield *vs.* time curves were dependent on many parameters such as tuning and pulse length. Almost certainly the shape of these curves will differ from one instrument to another. Any or all of these parameters could be varied to optimize the line-to-interference ratio to improve the analytical uses of the instrument.

SUMMARY

The application of time resolution to the rf spark source has shown variations on a time scale previously unpredicted. Honig (*19*) and Franzen, Schuy, and Hintenberger (*14*, *17*) have predicted the variable production of ion species within a single rf discharge which is of the order of 0.1 μsec in duration and is repeated throughout the length of the rf pulse. This study has shown variations in ion yield existing on a much larger time scale and depending on the element and matrix under consideration.

An oscilloscope was an important part of the study. The oscilloscope provided a method for the maintenance of a constant electrode gap and the desired time relationships. In addition, major differences were found in oscilloscopic traces for various matrices. A correlation between time-yields of the

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ash-graphite matrix and the oscilloscopic traces was postulated. The unusual placement of the deflector plates used for time resolution allowed a method of data reduction which minimized variations caused by sample inhomogeneity.

In addition to presenting time resolution as a possible means of studying the excitation of the rf spark source, two uses were postulated which could improve the analytical uses of the technique.

ACKNOWLEDGMENT

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Studies on the Anion Exchange Behavior of Carboxylic Acids and Phenols

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The uptake of carboxylic acids and phenols by an anion exchange resin is studied from aqueous solutions containing acetone or methanol. Distribution coefficients are higher in basic solutions where the acid anion predominates, but a significant uptake also occurs from acidic solution. A higher proportion of organic solvent in the solution lowers the distribution coefficients. Several practical separations are demonstrated on short columns. Distribution coefficients and capacity measurements are reported for organic acids on a nonionic polystyrene resin and compared with those for the polystyrene anion exchange resin. Also, uptake of organic acids by a quaternary ammonium salt dissolved in cyclohexane is determined and compared with the two resins studied.

ALTHOUGH anions of carboxylic acids (*1–4*) and phenols (*5, 6*) may be taken up and separated by an anion exchange column, a complicating factor is the uptake of some types of nonionic organic compounds by ion exchange columns. Salting-out chromatography and solubilization chromatography are separation techniques based on selective sorption of organic molecules by ion exchange columns. Thus, cation exchange resins have been used for the separation of the lower aliphatic carboxylic acids (*7–11*), aromatic acids (*12*), and phenols (*13, 14*).

In the present work, the sorption of some aliphatic carboxylic acids, benzoic acid, *o*-nitrobenzoic acid, phenol, and *o*-nitrophenol by a macroreticular anion exchange resin, Amberlyst A-26, was studied over a wide range of pH in aqueous–organic solvent mixtures. From the data obtained, conditions were selected and successful separations of some of these acids were obtained on a short anion exchange column. Also the sorption behavior of some of these acids on A-26 resin was compared with the sorption on a porous polystyrene–divinylbenzene copolymer, XAD-2, and with extraction by a liquid anion exchanger, Aliquat 336. From these experiments, some conclusions are drawn regarding the ion exchange behavior of carboxylic acids and phenols.

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EXPERIMENTAL

Resins. Amberlyst A-26, macroreticular anion exchange resin was obtained from Rohm and Haas Co. The resin was ground and sieved to 150 $\sim$ 200 mesh for use in both the batch and column experiments. The resin was washed several times with hydrochloric acid–ammonium sulfate solution–sodium hydroxide solution cycles and, finally converted into chloride form and air dried. Amberlite XAD-2, a macroreticular resin obtained from Rohm and Haas Co., was treated the same as described above. Aliquat 336 liquid anion exchanger was obtained from General Mills. The concentration of this exchanger was determined by nonaqueous titration with perchloric acid in glacial acetic acid (*15*).

Distribution Coefficients. The distribution coefficients of organic acids on resins were measured by a batch method. Twenty milliliters of organic solvent–water mixture which contained about 0.4 milliequivalents of organic acid, inorganic salt and acid, or base to adjust the pH of the solution was added to 1.5 grams of resin in a 125-ml glass-stoppered flask, shaken mechanically for 1–2 hours and allowed to stand for several hours. After the liquid phase was filtered free from resin, an aliquot of the liquid was taken and analyzed for the organic acid present. The distribution coefficient was calculated from the difference in the concentration of organic acid before and after achievement of equilibrium.

Analysis of lower aliphatic acids employed titration with sodium hydroxide solution. In the experiment for alkaline pH solution, the carboxylic acid in resin phase was determined as follows: The resin which filtered free from the liquid was washed into a small column with 85% acetone–0.01*M* HCl solution, and the same solution was passed through the

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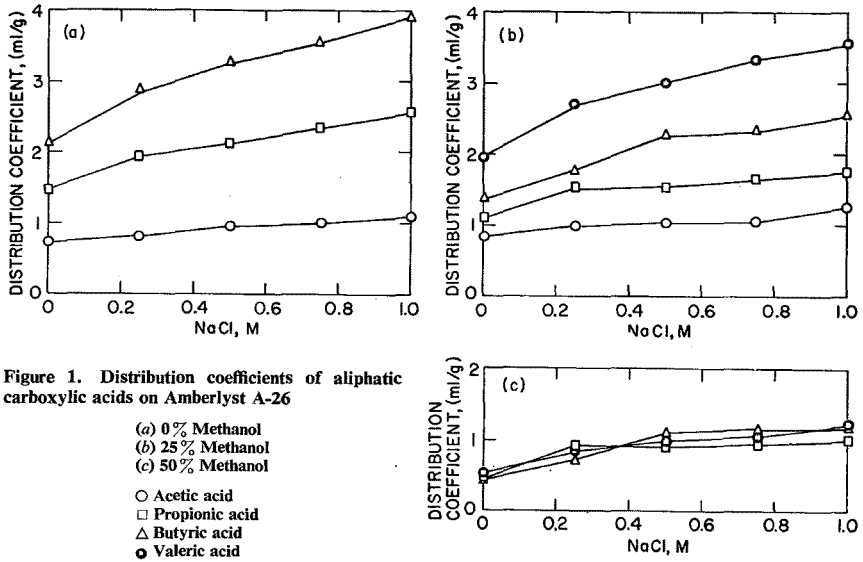


Figure 1. Distribution coefficients of aliphatic carboxylic acids on Amberlyst A-26

(*a*) 0% Methanol
(*b*) 25% Methanol
(*c*) 50% Methanol

○ Acetic acid
□ Propionic acid
△ Butyric acid
● Valeric acid

column to elute the carboxylic acid. The effluent was titrated potentiometrically with 0.05*M* to 0.001*M* sodium hydroxide solution; the second potentiometric break was used to determine the concentration of carboxylic acid.

The concentration of other acids was determined spectrophotometrically by reading the absorbance of the organic acids at the peak wavelength of the absorption curve in acidic solution with a Spectronic 600 spectrophotometer. Because acetone interfered, solutions containing phenol, benzoic acid, or *o*-nitrobenzoic acid, were diluted to be below 5% acetone. Sodium hydroxide was added and acetone was removed completely by heating at 65 ~ 75 °C on a water bath for 1.5 hours.

Column Separation Procedure. For column experiments, the air dried resin was soaked in the eluent, added to the column, and washed with the eluting solution. The volume of sample added to the column was 0.5 ~ 1.0 ml. A flow rate of approximately 0.5 ml per minute was employed to adsorb the sample onto column and also for the elution.

Extraction Procedure. Ten milliliters of acetone–water mixture, which contained a known quantity of organic acid and was adjusted to the desired pH, was added to a 60-ml separatory funnel. Ten milliliters of 20% solution of Aliquat 336 in cyclohexane was added also, and the mixture was shaken for 2 to 3 minutes and the phases allowed to separate. An aliquot of the acetone–water phase was taken and analyzed. To prevent volume changes, each phase was preequilibrated with the other before use.

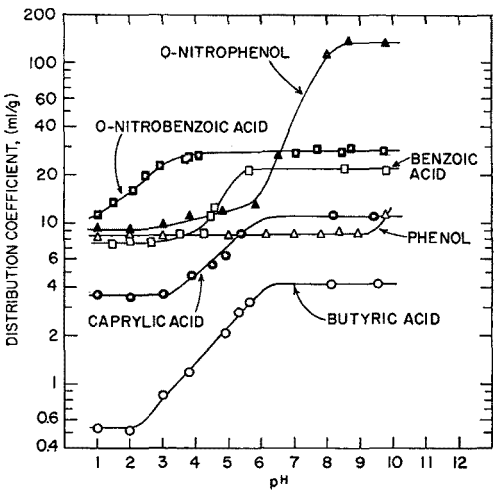


Figure 2. Effect of pH on distribution coefficients of organic acids on A-26 from 25% acetone solution

RESULTS AND DISCUSSION

Distribution Coefficients of Organic Acids on Amberlyst A-26. The distribution coefficients of acetic, propionic, butyric, and valeric acids on Amberlyst A-26 were measured as a function of the content of methanol and the concentration of sodium chloride. The results are shown in Figure 1. The sorption of these lower carboxylic acids increases with increased concentration of sodium chloride and decreases with a higher proportion of methanol in the solution. The acids are probably in their molecular form, and the increased sorption caused by sodium chloride might be a salting-out effect. Carroll (*2*) showed that an organic acid can be eluted faster from an anion exchange resin with a methanol–water mixture than with water alone.

Distribution coefficients of organic acids on Amberlyst A-26 from acetone– or methanol–water mixtures were studied as a function of pH of the solution. The solution contained 0.1*M* ammonium chloride and the pH was adjusted with hydrochloric acid or ammonia. The pH was apparent pH value of methanol or acetone solution measured with pH meter. In methanol solution experiments in the acidic pH range were not completed because the organic acids are partially converted into their esters. Results are shown in Figures 2–5.

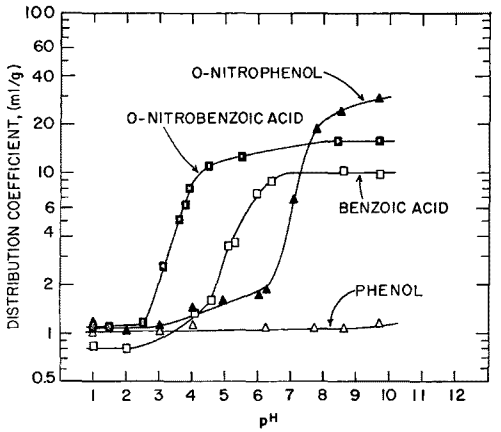


Figure 3. Effect of pH on distribution coefficients of organic acids on A-26 from 50% acetone solution

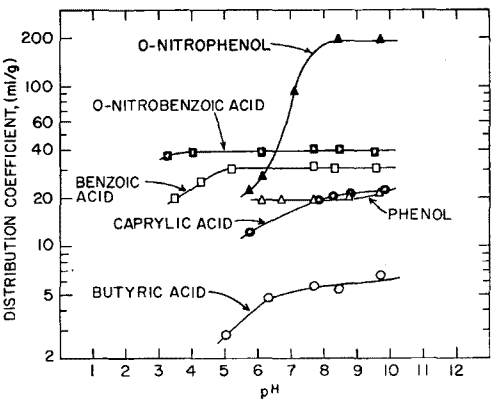


Figure 4. Effect of pH on distribution coefficients of organic acids on A-26 from 25% methanol solution

Distribution coefficients of organic acids in alkaline solution are generally larger than those in acidic solution. The pH at which the uptake of an organic acid increases seems to correspond to the pK value of that acid. For example, in Figure 2 the sorption of *o*-nitrobenzoic acid (pK = 2.2) increases at pH 1–3, butyric acid (pK = 4.8), caprylic acid (pK = 4.85), and benzoic acid (pK = 4.2) increase at pH 3–6, *o*-nitrophenol (pK = 7.2) increases at pH 6–8, and phenol is constant over the pH range studied but begins to increase from pH 9.8. The distribution coefficients of organic acids from methanol solution are higher than from acetone solution but show a similar behavior pattern. Therefore, the sorption behavior of organic acids on A-26 may be considered as anion exchange in alkaline solution and as molecular sorption of the free acid in acidic solution.

Several possibilities for the separation of mixtures of carboxylic acids and phenols are apparent from Figures 2–5. One technique for separation of binary mixtures is to choose a pH where one compound is largely present as the anion while the other is present as the molecular acid. Elution of a

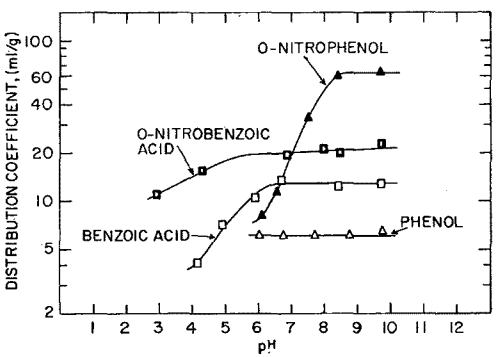


Figure 5. Effect of pH on distribution coefficients of organic acids on A-26 from 50% methanol solution

Table I. Separation of Organic Acid Mixtures

Resin: Amberlyst A-26, 150 ~ 200 mesh, Cl^- form
Flow rate: 0.5 ml/min

Compounds separated	Column size	Eluent		Recovery of compound		
		Vol, ml	Composition	Taken, mg	Found, mg	Recovery, %
Butyric acid	1.01 × 14.1 cm	20	25% Acetone, pH 5.1	1.708	1.696	99.3
Caprylic acid		35	25% Acetone, pH 5.1	2.081	2.097	100.7
Phenol	0.80 × 7.4 cm	20	50% Methanol, pH 8.6	0.983	0.994	101.2
o-Nitrophenol		120	50% Methanol, pH 8.6	1.433	1.475	102.9
o-Nitrophenol	0.80 × 17.0 cm	20	50% Acetone, pH 6.3	0.295	0.295	100.0
Benzoic acid		50	50% Acetone, pH 6.3	3.791	3.855	101.7
Benzoic acid	0.80 × 17.0 cm	25	50% Acetone, pH 4.1	3.627	3.407	93.9
o-Nitrobenzoic acid		65	50% Acetone, pH 4.1	0.715	0.702	98.2
Phenol	1.01 × 16.9 cm	60	50% Methanol, pH 8.6	0.274	0.273	99.6
Benzoic acid		120	50% Methanol, pH 8.6	0.873	0.860	98.5
o-Nitrobenzoic acid		170	50% Methanol, pH 8.6	0.179	0.172	96.1
o-Nitrophenol		205	50% Acetone, pH 2.7	0.080	0.084	105.4
Phenol	1.01 × 17.9 cm	25	50% Acetone, pH 7.5	4.300	4.300	100.0
o-Nitrophenol		50	50% Acetone, pH 6.3	0.997	0.993	99.6
Benzoic acid		75	50% Acetone, pH 4.15	3.126	3.100	99.2
o-Nitrobenzoic acid		105	50% Acetone, pH 4.15	0.647	0.638	98.7

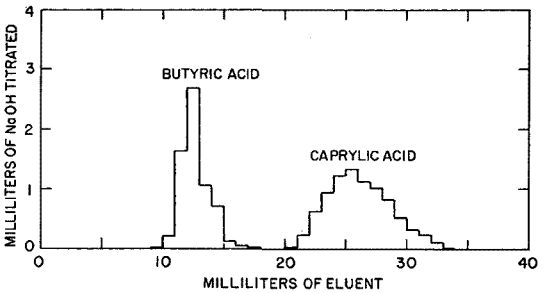


Figure 6. Separation of butyric acid and caprylic acid

Eluent: 25% acetone, pH 5.1
Column size: 1.01 × 14.1 cm

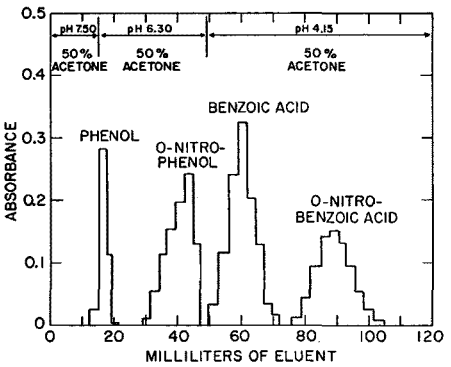


Figure 7. Separation of phenol, *o*-nitrophenol, benzoic acid, and *o*-nitrobenzoic acid

Column size: 1.01 × 17.9 cm

Table II. Comparison of Distribution Coefficients on Amberlyst A-26 and Amberlite XAD-2 from 25% Acetone

One gram of resin was added to 20 ml of solution

Compound	Resin	D [ml/g] Acidic soln[a]	Alkaline soln[b]
Benzoic acid	A-26	9.12	22.8
	XAD-2	15.2	~0
Phenol	A-26	8.65	8.66
	XAD-2	13.9	13.3
o-Nitrophenol	A-26	10.7	143
	XAD-2	72.1	6.85

[a] pH of the solution are 2.7 for benzoic acid, 2.9 for phenol, and 2.5 for *o*-nitrophenol.
[b] pH of the solution are 8.3 for benzoic acid, 8.6 for phenol, and *o*-nitrophenol.

sorbed acid is facilitated by using a more acidic eluent containing 50% acetone.

Data for quantitative separations on A-26 columns are given in Table I; typical elution curves are shown in Figures 6 and 7.

Sorption Behavior of Organic Acids. Diamond, Chu, and Whitney (*16*) emphasized the importance of solvation in determining the selectivity of anion exchange resins for carboxylic acid anions. Our studies on the effect of pH on distribution coefficients on A-26 anion exchange resin (Figures 2–5) suggest that organic acids are sorbed by an anion exchange mechanism from basic solution and by molecular sorption of the free acid from more acidic solution. To obtain further evidence regarding the sorption mechanism, several acids were studied using Amberlyst XAD-2 resin. This is a highly porous polystyrene–divinylbenzene resin that is physically similar to A-26, but it has no quaternary ammonium or other functional group necessary to make it an anion exchange resin like A-26.

Distribution coefficients of benzoic acid, phenol, and *o*-nitrophenol from acidic and basic solutions with XAD-2 resin are given in Table II and are compared with distribution coefficients using A-26 resin. The distribution coefficients with XAD-2 are much larger from acidic solution than from basic solution for benzoic acid and *o*-nitrophenol. Because anion exchange is impossible with this resin, the uptake must be explained by some form of chemical interaction between the acid and the polystyrene matrix. The anionic forms of the acids are more strongly solvated by the aqueous–acetone solution and thus have much lower distribution coefficients than do the acidic forms. Phenol is largely in its acidic form at both pH values studied.

To obtain more information about the sorption on XAD-2 resin, the capacities of benzoic acid and *o*-nitrophenol on XAD-2 and A-26 from both acidic and basic solutions were measured by column experiments and compared. One gram of the resin was packed into a small column and washed with 25% acetone of the desired pH. Benzoic acid or *o*-nitrophenol (0.005 *M*–0.1 *M*), dissolved in 25% acetone of the desired pH, was passed through the column containing one gram of resins with a very slow flow rate until the concentrations of organic acid entering and leaving the column were equal. The organic acid on the resin was desorbed with 50% acetone containing 0.2*M* hydrochloric acid, and the acid content of the column was determined. The volume of free, interstitial liquid in the column was determined and a correction was applied to take into account the acid in this liquid. The corrected capacities of A-26 and XAD-2 resins are shown in Table III.

In alkaline solution, where benzoic acid and *o*-nitrophenol dissociate completely to their ions, the quantity of each acid sorbed onto Amberlyst A-26 is slightly larger but nearly the same as the exchange capacity of the resin measured for the chloride form. In acidic solution, where each acid exists as the undissociated molecule, the quantities of benzoic acid and *o*-nitrophenol on Amberlyst A-26 are significantly smaller, 0.56 and 0.55 milliequivalent, respectively. For the sorption on XAD-2 higher capacities are obtained from acidic solution, the opposite from the A-26 capacities. If the basic solution capacity of XAD-2 is subtracted from the basic solution capacity of A-26, the difference is 3.51 milliequivalents/gram for benzoic acid and 3.55 milliequivalents/gram for *o*-nitrophenol. These values are in rather good agreement with the capacity for chloride ion which is 3.52 milliequivalents/gram. Thus it appears that the uptake of these acid anions by A-26 resin is primarily an anion exchange mechanism, but there is a small amount of another type of sorption which contributes to the resin capacity.

Davies and Owen (*1*) noted the excess or nonionic sorption of aliphatic carboxylic acids and phenylacetic acid on resins.

(16) R. M. Diamond, B. Chu, and D. C. Whitney, *J. Inorg. Nucl. Chem.*, **24**, 1405 (1962).

Table III. Capacity of Benzoic Acid and *o*-Nitrophenol on Amberlyst A-26 and Amberlite XAD-2 from 25% Acetone

		Amberlyst A-26		Amberlite XAD-2	
Benzoic acid	pH of solution	2.25	10.40	2.25	11.50
	capacity, meq.	0.561	3.634	0.951	0.126
o-Nitrophenol	pH of solution	2.60	11.0	2.60	12.0
	capacity, meq.	0.548	3.642	1.995	0.093

Table IV. Comparison of Distribution Coefficients of Organic Acids on Amberlyst A-26 and Aliquat 336–Cyclohexane from 25% Acetone

The concentration of Aliquat 336 in cyclohexane was 0.365*M*. The condition of Amberlyst A-26 is same as Table II.

		Acidic solution[a]			Alkaline solution[b]		
		D_0[c]	D[d]	D[d] [ml/meq]	D_0[c]	D[d]	D[d][ml/meq]
Benzoic acid	Aliquat 336	0.56	10.0	27.5	0.02	18.3	50.0
	A-26			2.50			6.13
Phenol	Aliquat 336	0.79	14.4	39.4	0.80	14.6	40.1
	A-26			2.36			2.36
o-Nitrophenol	Aliquat 336	12.7	2.82	7.72	1.08	183.7	56.4
	A-26			2.93			39.1

[a] pH of the solution are 2.3 for benzoic acid and phenol, and 2.5 for *o*-nitrophenol.
[b] pH of the solution are 8.3 for benzoic acid and phenol, and 8.5 for *o*-nitrophenol.
[c] D_0 is the distribution coefficient with cyclohexane alone represented ml/ml as dimension.
[d] D is the distribution coefficient with Aliquat 336–cyclohexane calculated by subtracting the quantities of organic acid extracted by cyclohexane alone from the total quantities in organic phase extracted.

Anderson and Hansen (*17*) also investigated the excess sorption of phenols on resin, and showed that the uptake of phenols is by the functional group of the resin.

It was felt that studies with a high molecular weight, liquid quaternary ammonium chloride might be interesting. Such a compound has the same functional group as an anion exchange resin like A-26, but it lacks the polystyrene matrix and any special effects due to the physical characteristics of a solid polymer would be missing. Accordingly, the extraction of benzoic acid, phenol, and *o*-nitrophenol from 25% acetone solution was studied with a solution of Aliquat 336 in cyclohexane. Because the organic acids are somewhat extracted by cyclohexane alone, the distribution coefficients for the extraction with Aliquat 336–cyclohexane are calculated by subtracting the concentration of organic acid extracted by cyclohexane alone from the concentration extracted by Aliquat 336 in cyclohexane. To compare the distribution coefficients on Amberlyst A-26, the distribution coefficients are calculated in terms of uptake per milliequivalent of ion exchange capacity instead of uptake per gram of ion exchange resin.

The results in Table IV show that although the acid anions are more strongly extracted by Aliquat 336 than are the free acids, extraction of the free acids also occurs to a considerable extent. Addition of the more polar Aliquat 336 to cyclohexane increases the extraction of the free acid in every case studied, but the increase in much less for *o*-nitrophenol.

The constants in the last column of Table IV indicate that Aliquat 336 in cyclohexane appears to be a more efficient extractant for acid anions than A-26 resin, at least when the two are compared on the basis of an equivalent amount of quaternary ammonium functional group.

CONCLUSIONS

Our experiments show that uptake of organic acids may occur by anion exchange of the acid anion, and chemical interaction (possibly solvation) of the acid or acid anion by the resin matrix (polystyrene), liquid solvent (cyclohexane), and/or the quaternary ammonium functional group.

Opposing these forces are: (1) Solvation of the acid or acid anion by the solution outside the resin. For organic acids a higher proportion of acetone or methanol in the outside, aqueous solution increases this solvation and lowers the distribution coefficient. (2) Other anions (such as chloride) in the outside solution will compete with the organic anions for the cation sites of the resin or liquid ion exchanger and thus reduce their distribution coefficients. However, inorganic ions may increase the distribution coefficients for free acids by a salting out effect.

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Copper(II) Oxidation of Thioureas in Acetonitrile

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The oxidation of a series of thioureas by copper(II) in acetonitrile has been investigated. In most cases, a 1:1 stoichiometry is observed. The reaction proceeds with formation of a red complex which was found by electron spin resonance to be a paramagnetic copper (II)–thiourea complex which shows no evidence for copper–nitrogen in-plane bonding.

THIOUREAS ARE OXIDIZED in aqueous solution by several common oxidants, including dichromate, cerium(IV), permanganate, hydrogen peroxide, and bromine. A variety of products are formed, depending on the oxidant and the reaction conditions (*1*, *2*). Except for a few isolated cases, the effect of solvent on the course of these oxidations has not been investigated, although solvent properties are recognized to be important in determining the direction and extent of organic oxidation processes. Thus, when bromine is added to thiourea in carbon tetrachloride, bromine addition products are produced (*3*), but in glacial acetic acid either disulfides or benzothiazoles are formed depending on the substituent groups present on the thiourea nitrogens (*4*). By considering solvent effects, it is possible to obtain data about mechanisms of homogeneous electron transfer processes which are useful in predicting the products of functional group oxidations, in aiding selection of solvent–oxidant combinations which yield desired reaction products in syntheses, and in providing reactions suitable for analytical applications.

Copper(II) perchlorate in acetonitrile has been shown to be an effective oxidant for a variety of compounds, including thiourea (*5*, *6*). This paper reports the oxidation of a series of thioureas by copper(II) in acetonitrile, and considers the nature of the intermediates formed in the oxidation process.

EXPERIMENTAL

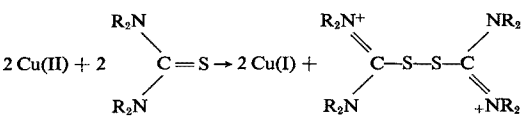
Acetonitrile was purified by the method described previously (*5*). The water content, determined by Karl Fischer titration, was in the range of 1 to 5 $\times 10^{-4}M$. Several experiments were done using anhydrous solutions and conditions. Generally water in moderate concentration had no effect, however, so most of the work could be carried out without special precautions. When needed, anhydrous copper(II) perchlorate solutions were prepared by dissolving tetrakis(acetonitrile) copper(II) perchlorate, prepared from nitrosyl perchlorate and copper metal (*5*), in anhydrous acetonitrile. These solutions were dispensed from automatic burets and protected from the atmosphere by drying tubes containing magnesium perchlorate. Where exclusion of water was not required, solutions were prepared by dissolving hexaquocopper(II) perchlorate in acetonitrile, filtering the solution to remove a small amount of white precipitate that formed, and storing in a glass stoppered bottle. Thiobenzanilide, thiourea, *N,N'*-diphenylthiourea, and tetramethylthiourea were obtained from Eastman Organic Chemicals, Rochester, N. Y., and the other thioureas from Aldrich Chemical Co., Milwaukee, Wis. Recrystallization of several of the thioureas from various solvents produced little change in either the melting points or in the oxidation equivalent weights, so they were used as received.

Potentiometric titrations were performed in a 75-ml weighing bottle with a machined Teflon lid containing openings for a platinum foil indicating electrode, a silver–0.01*M* silver nitrate in acetonitrile reference electrode which made contact with the cell solution through a 0.1*M* lithium perchlorate in acetonitrile salt bridge via ultrafine glass frits, a buret tip, and a nitrogen inlet. Magnetic stirring was used. For titrations at −40 °C the cell was immersed in a 25% ethanol–75% acetonitrile slurry cooled with liquid nitrogen. ESR spectra were recorded with a Varian Model V-4502-13 spectrometer equipped with 100 kc modulation. Measurements of the g factors were made using 2,2-diphenyl-1-picrylhydrazyl (DPPH), obtained from Eastman, as reference. The acid–base titrations were done in a cell similar to the one described above but with a Beckman 40471 glass electrode in place of the platinum indicating electrode. A Leeds and Northrup Model 7401 pH meter was used for both potential and pH measurements.

Visible spectra of the copper(II)–thiourea intermediates were recorded at −40 °C with a Cary Model 14 recording spectrophotometer equipped with cell holders designed to allow circulation of an acetonitrile–liquid nitrogen slush coolant around the cells. The cell compartment was flushed with dry nitrogen during runs to prevent moisture condensation on the cell surfaces.

RESULTS

Potentiometric Titrations. Most of the substituted thioureas studied showed one oxidation equivalent per mole when titrated with copper(II) in acetonitrile. The reaction products were considered to be the disulfides on the basis of the oxidation stoichiometry.



For thiourea, the oxidation product was isolated from the titration solution as the hydrochloride salt. Differential thermal analysis showed an exotherm at 76–77 °C and an endotherm associated with melting at 172–173 °C. A sample of diformamidine disulfide·2HCl prepared by the method of Preisler and Berger (*7*) gave a corresponding exotherm and

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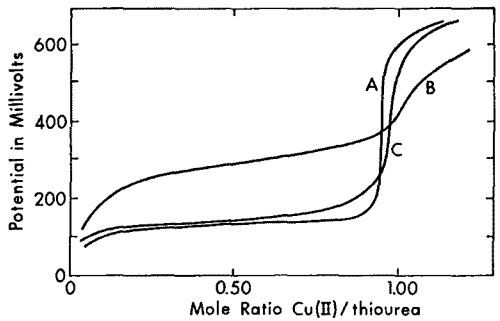


Figure 1. Potentiometric titration of representative thioureas with 0.1*M* hydrated copper(II) in acetonitrile

A. N,N'-di-*n*-butylthiourea; *B. N,N'*-diphenylthiourea; *C. N,N'*-dimethyl-*N'*-*m*-tolylthiourea. All potentials refer to silver–0.01*M* silver nitrate in acetonitrile as reference

endotherm at 75–77 and 173–176 °C. The melting point of diformamidine disulfide·2HCl is reported to be 173–175 °C (*8, 9*). Also, for thiourea and the *N,N'*-tetramethyl derivative, the expected imine salt bands of the oxidation products were observed in infrared spectra of acetonitrile solutions of thiourea–copper(II) reaction mixtures and in fluorolube mulls of 1:1 thiourea–copper(II) mixtures which had been evaporated to dryness. Solution spectra were run in cells with silver chloride windows because alkali halides are attacked rapidly by copper(I) in acetonitrile. (Even silver chloride cells are fogged to some extent by the reaction mixtures.)

A list of the derivatives titrated and the observed equivalence point ratios is given in Table I, and the shapes of some representative titration plots are shown in Figure 1. Considerable sulfur precipitated during the oxidation of several of the aryl-substituted compounds, but the stoichiometry remained near unity. At room temperature *N,N'*-di-*tert*-butylthiourea is oxidized further to a mixture of reaction products, but when the titration is carried out at −40 °C a single one-electron oxidation is observed. The presence of small amounts of water had no observable effect on the reactions other than to decrease the size of the potential break in an amount comparable to that found for the parent thiourea (*5*).

The addition of perchloric acid to solutions of thioureas prior to titration with copper(II) gave titration curves in which the end points were observed much earlier than 1:1, and which became more drawn out with increasing acid concentrations. Also, potentials reached equilibrium much more slowly when acid was present.

The pK_b of thiourea in acetonitrile was determined by titration with perchloric acid in order to evaluate the extent of thiourea protonation in the acid system. A glass electrode calibrated with a buffer mixture of picric acid–tetraethylammonium picrate was used; this mixture has been shown to be a useful reference buffer in acetonitrile (*10, 11*). A slope of 0.056 V was obtained for a plot of the glass electrode

Table I. Oxidation of Thioureas with Copper(II) Perchlorate in Acetonitrile

Thioureas	Reaction stoichiometry [Cu(II)/thiourea]	Solution color	Behavior of potentials[a]
Thiourea	1.000	None	Stable
N-methylthiourea	1.002	None	Stable
N,N-dimethylthiourea	0.962	None	Stable
N,N'-diethylthiourea	0.989	None	Stable
N,N'-diisopropylthiourea	0.995	None	Stable
N,N-di-*n*-butylthiourea	0.929	None	Stable
N,N'-di-*n*-octylthiourea	0.974	None	Stable
Tetramethylthiourea	0.977	Red[b]	Stable
N,N-diphenylthiourea	0.933	Red-brown[c]	Unstable[d]
N,N-di-*o*-tolylthiourea	1.022	Red-brown[c]	Unstable
N,N-di-*tert*-butylthiourea	...	Red-brown[c]	Unstable[d]
N,N-dimethyl-*N'*-*o*-tolylthiourea	0.853	Red-violet[b]	Unstable
N,N-dimethyl-*N'*-*m*-tolylthiourea	0.928	Red-violet[b]	Unstable[d]
N,N-dimethyl-*N'*-*p*-tolylthiourea	0.872	Violet[b]	Unstable[d]

[a] Potentials are listed as stable if system reached equilibrium within 30 seconds after each addition of copper(II). Equilibration time for systems listed as unstable were on the order of 4–5 minutes. [b] Color persisted through approximately the first half of titration. [c] Color observed only immediately after addition of titrant increments. [d] Sulfur produced in reaction.

potential *vs.* log of the ratio of protonated to nonprotonated thiourea, so the system is nearly reversible. The pK_b of thiourea determined in this way was 23.15, or, using a value of 6.3×10^{-33} for the autoprotolysis constant of acetonitrile (*12*), $pK_a = 9.0$ for protonated thiourea.

Nature of the Red Species. During titrations of the thioureas, a momentary red color appeared after each addition of copper(II) in the region before the equivalence point. The stabilities of these species were assessed qualitatively by carrying out titrations of thioureas with copper(II) at temperatures just above the freezing point of acetonitrile, −45.7 °C. The intensity of the color increased with copper(II) addition up to a copper(II)–thiourea ratio of approximately one to two, then decreased. Some of the red species were found to be stable for hours if kept below −40 °C; at −196 °C (liquid nitrogen b.p.) several appeared stable for days. The order of stability was tetramethyl>*N,N*-dimethyl-*N'*-*o*-tolyl>*m*- and *p*-tolyl derivatives >*N,N'*-di-*o*-tolyl >*N,N'*-diphenyl>*N,N*-di-*tert*-butyl>mono- and di-substituted alkyl derivatives.

ESR measurements were made on a number of the thiourea–copper mixtures. Colored reaction products of the alkyl derivatives were too unstable to be investigated by the techniques employed in this work; they could be prepared only by reaction at the interface of cold solutions of copper(II) perchlorate and the corresponding thiourea, and in these cases the large excess of unreacted copper(II) present swamped out the ESR spectrum of the colored species. Because solutions in pure acetonitrile tended to become polycrystalline upon freezing, producing broadening of the spectra and loss of hyperfine splitting, ethanol–acetonitrile solvent mixtures were used for most of the ESR work. No difference was observed between spectra recorded in predominately ethanol or in pure

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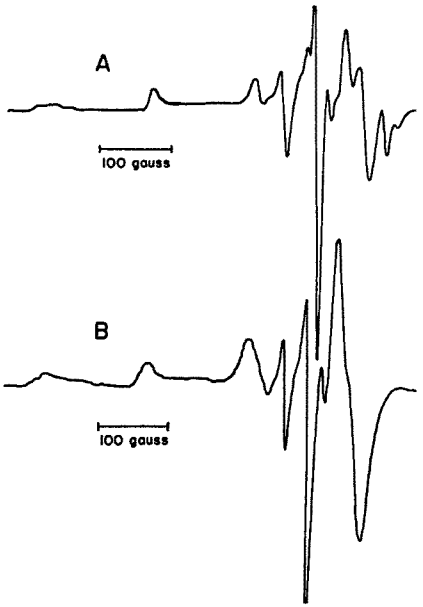


Figure 2. First derivative ESR spectra of copper (II) derivatives in ethanol at 77 °K

A. *N,N′*-di-*tert*-butylthiourea; *B.* *N,N′*-di-*o*-tolylthiourea

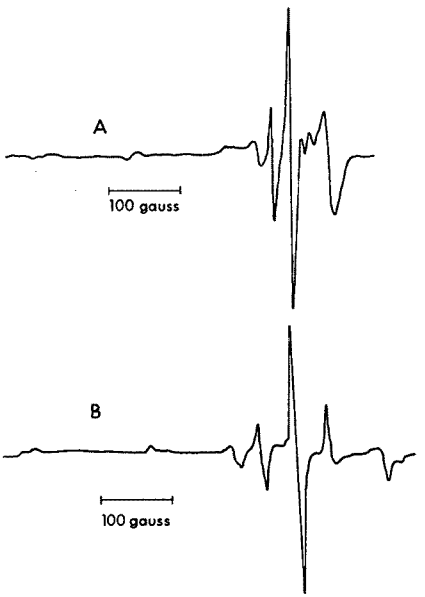


Figure 3. First derivative ESR spectra of copper (II) derivatives in ethanol at 77 °K

A. *N,N*-dimethyl-*N′*-*o*-tolylthiourea; *B.* diethyldithiocarbamate

Table II. Magnetic Parameters for Cu(II) Complexes of Substituted Thioureas in Ethanol at 77 °K

Substituted thiourea	$g_{\parallel}$ [a]	$A_{\parallel}$ [a] (gauss)	$g_{\perp}$	$A_{\perp}$ (gauss)
Tetramethyl[b]	2.117	128	2.031	30
	2.117	138		
sym-di-*o*-tolyl-	2.118	140	2.033	32
	2.117	150		
sym-diphenyl-	2.116	138	2.032	33
	2.115	150		
sym-di-*tert*-butyl-	2.118	142	2.025	35
	2.117	153		
N,N′-dimethyl-*N′*-*o*-tolyl-	2.128	122	2.032	24
	2.127	132		
N,N-dimethyl-*N′*-*m*-tolyl-	2.123	125	2.030	25
	2.122	133		
N,N-dimethyl-*N′*-*p*-tolyl	2.126	122	2.031	25
	2.125	131		
Copper(II)–bis(diethyldithiocarbamate)	2.090[c]	162	2.028	47
		174		
	2.098[d]	162	2.035	43
		177		
	2.121[e]	144	2.040	27
		157		
	2.108$_5$[f]	152	2.023	24
		162		

[a] Values for ^{63}Cu and ^{65}Cu, respectively.
[b] In acetonitrile.
[c] In 60% toluene-40% chloroform and in ethanol.
[d] Reference *13*, 60% toluene–40% chloroform.
[e] Reference *13*, 40% pyridine–60% chloroform.
[f] Reference *14*, single crystal.

acetonitrile glasses, though the latter were much more difficult to obtain. First derivative spectra of representative substituted copper(II)–thiourea complexes are shown in Figures 2 and 3. A spectrum of the complex formed between copper (II) and diethyldithiocarbamate is included in Figure 3 for comparison, since the magnetic and spectral properties of the copper(II)–thiourea derivatives are very similar to each other and to copper(II)–bis(diethyldithiocarbamate) (see Tables II and III). Molar absorptivities in the visible spectra could not be determined because of partial decomposition of the intermediates during their preparation.

DISCUSSION

It has been shown by proton magnetic resonance studies that thioureas are protonated in strongly acidic solvents on the sulfur rather than one of the nitrogen atoms. If a sufficiently acidic solvent, such as concentrated sulfuric acid, is used, one of the nitrogen atoms appears to protonate also (*15*). Titrations of thiourea with perchloric acid in glacial acetic acid indicate a slight inflection at two equivalents of acid per equivalent of thiourea, but the size of the break is not adequate for calculation of a second acid dissociation constant. A Lewis acid such as copper(II) would be expected also to coordinate preferentially to the more basic sulfur site, as indicated by the greater resistance of thiourea to copper(II)

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oxidation when the sulfur atom is protonated by the addition of perchloric acid.

The similarity of the magnetic properties of the red copper(II)–thiourea species and copper(II)–bis-(diethyldithiocarbamate) suggest the structures may be related. In both cases well defined isotopic splitting by the copper-63 and copper-65 isotopes is observed in the ESR spectra; this is not generally seen if copper(II)–nitrogen bonding is present. Also, no nitrogen hyperfine splitting was detected in any of the copper–thiourea spectra. This fact does not by itself indicate that copper–nitrogen bonding is absent. However, the lack of line broadening, as shown by the appearance of well defined isotopic splitting on the weak downfield peak of $g_{\|}$ suggests that nitrogen interaction with the copper equatorial sites is absent. Axial copper(II)–nitrogen interaction could of course be occurring, since this weaker interaction would not be expected to affect the shape of the $g_{\|}$ absorption lines and so could not be detected from the ESR spectra. In fact, the magnetic parameters of the copper(II)–thiourea complexes most closely resemble those of copper(II)–diethyldithiocarbamate in pyridine–chloroform solvent, where pyridine nitrogen axial interaction with the copper seems quite probable. Further, from the visible spectra, the same electronic transitions appear to be occurring in each. On the basis of these observations we conclude that the red species produced by the action of copper(II) on thiourea and its derivatives are probably complexes between copper and thiourea involving primarily copper(II)–sulfur bonding. This appears to be the first report of copper(II)–thiourea complex formation. The complexes are very likely intermediates in the overall oxidation process, although this has not been proven.

Table III. Visible Spectra Maxima for Selected Copper(II)–Thiourea Complexes

Thioureas	Maxima (cm^{-1})
Tetramethylthiourea	19,600, 25,000
N,N-dimethyl-*N'-o*-tolylthiourea	19,200, 23,800
N,N-dimethyl-*N'm*-tolylthiourea	19,100, 23,400[a]
N,N-dimethyl-*N'-p*-tolylthiourea	19,800, 24,200[a]
N,N'-di-*o*-tolylthiourea	21,400, 24,500
Copper(II)–bis(diethyldithiocarbamate)	19,200, 23,100[b]
	20,000, 23,800[c]

[a] Very weak.
[b] Reference *13*, 60% chloroform-40% toluene solvent.
[c] Reference *13*, 60% pyridine-40% chloroform solvent.

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Mixed-Metal Hydroxycarboxylic Acid Complexes

The Chromium(III) Inhibition of the Solvent Extraction of Indium(III)

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The solvent extraction of indium(III) by thenoyltrifluoroacetone is inhibited by chromium(III) if certain hydroxycarboxylic acids are also present. The experimental results are explicable only on the basis of the formation of a mixed complex containing indium, chromium, and the hydroxyacid. The inhibitory effect was observed only if the acids had the functional group arrangement of malic acid. Such mixed complex formation exists for many different metals and can cause serious interference with separation processes. Spectrophotometric measurements on the chromium, indium, citrate system indicate a complex of stoichiometry 1:1:2. Structural arrangements for the mixed complexes are postulated and discussed.

SEVERAL EXAMPLES of complexes of hydroxycarboxylic acids containing two different metal ions have been reported in the recent literature (*1–6*). The formation of a mixed complex of cerium(III), chromium(III), and citrate has been shown to repress strongly the solvent extraction of cerium (*3*). If such behavior is general, it would be of fundamental importance to solvent extraction and ion exchange separations, inasmuch as citric, tartaric, and other hydroxycarboxylic acids are widely used as auxiliary complexing and buffering agents. For this reason, a search was made for other examples of this behavior. It was found that the extraction of indium(III) from citrate media of pH 4 was significantly decreased in the presence of iron(III), aluminum(III), and chromium(III). Similar experiments using thallium(I), cadmium(II), and lead(II) showed no appreciable effect. Chromium(III) gave the most pronounced effect, and the chromium (III)–indium(III) interaction in the presence of various hydroxy acids was accordingly chosen for further study.

EXPERIMENTAL

Apparatus. Continuous spectra were recorded with a Cary Model 14 spectrophotometer, and absorption measurements at single wavelengths with a Beckman Model DU

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spectrophotometer. Radioactivity measurements on the separated organic and aqueous phases were made by γ-counting in a "well-type" scintillation counter.

Reagents. Thenoyltrifluoroacetone (TTA). The source and purification of TTA has been previously described (*7*). It was dissolved in benzene to make 0.15*M* solutions.

ACETATE BUFFER. A concentrated solution which on five-fold dilution gave a pH of about 4.0 was prepared by adding 120 ml of glacial acetic acid to 54 grams of $NaC_2H_3O_2 \cdot 3\ H_2O$ and diluting to 1 liter. The total concentration of acetate was 2.5*M*.

HYDROXYCARBOXYLIC ACID SOLUTIONS. Citric and D-tartaric acids (J. T. Baker); DL-malic and tartronic acids (Aldrich); glutaric and tricarballylic acids (Eastman White Label). Stock solutions of these acids were prepared by direct weighing of the materials as received. They were all adjusted to pH 4.00 with sodium hydroxide using a pH meter, and then diluted to a concentration of 0.25*M*. β-Methyl-β-hydroxyglutaric acid (dicrotalic acid, K and K Labs) was visibly impure as received and it was recrystallized from ether–petroleum ether (*8*). A 0.25*M* solution was prepared as described above. DL-Isocitric acid (Aldrich) was supplied in the lactone form and was weighed as such. The aqueous solution was treated with excess NaOH and was stored overnight at 45 °C to assure saponification (*9*). After cooling, it was brought to pH 4.00 with $HClO_4$ and was diluted to 0.25*M*. DL-α-hydroxyglutaric acid (K and K Labs) was supplied as its zinc salt and was weighed as such. It was dissolved in water by the gradual addition of HCl and the pH was set at 3.0. The zinc was precipitated by saturating the solution with H_2S and then readjusting the pH to 3.0 with NaOH. Zinc sulfide was removed by filtration through a Millipore membrane filter. The filtrate was concentrated by evaporation at room temperature by a stream of dry filtered air for a period of 3 days. No odor of H_2S was detectable after this time, so the solution was adjusted to pH 4.00 and diluted to 0.20*M*. Itamalic acid was synthesized starting from triethyl-1,1,2-ethanetricarboxylate (Aldrich Chemical Co.) using the method of Piskov (*10*). The procedure yields the lactone of itamalic acid, paraconic acid, which was converted to the free acid by base hydrolysis (*11*). After adjustment to pH 4.00, the solution was diluted to 0.20*M*.

INDIUM STOCK SOLUTION. Indium metal (Fisher, 99.99%) was dissolved in excess 1:1 HCl. The resulting solution was evaporated to dryness on a steam bath and the residue was dissolved in water. The solution was 0.01993*M* based on the weight of metal taken, and had a pH of 3.1.

CHROMIUM STOCK SOLUTION. $Cr(ClO_4)_3 \cdot 6\ H_2O$ (46 grams, G. F. Smith) and 1 ml of 1*M* $HClO_4$ were dissolved to make 1 liter of solution which had a pH of 2.4. The chromium content was determined iodometrically (*12*) and was found to be 0.0886*M*.

TRACER INDIUM-114 SOLUTION. Indium-114 chloride in HCl solution (Oak Ridge National Laboratory) was diluted to give a stock solution of 8×10^{-6}*M*. The original solution and the aqueous phase after extraction of the indium with TTA were examined by γ-spectrometry over the energy range of 0.002 to 2.46 MeV and found to be free of γ-emitting contaminants.

TRACER CHROMIUM-51 SOLUTION. Rachromate-51 (Abbott Laboratories), an aqueous chromium-51 solution as sodium chromate, was treated with sulfurous acid to reduce the chromate to chromium(III). Excess sulfurous acid was removed by heating and purging with nitrogen; the final pH was 2.5.

Procedure. All extractions, unless otherwise noted, were carried out at pH 3.90 ± 0.04 in 0.5*M* acetate buffer. Concentrated buffer solution, stock solutions of indium and chromium, the tracer solution, and the solution of the acid under study were pipetted into 40-ml glass vials sealed with polyethylene. The volume was made up to 15 ml with water making the concentrations of chromium, when present, and indium each equal to 0.00267*M*. The vials were sealed and placed in a water bath at 45 °C for 24 hours. Then the solutions were extracted with 15 ml of 0.15*M* TTA in benzene on a mechanical shaker for about 24 hours. Although the phase separation was usually excellent, the vials were centrifuged before sampling the phases. Aliquot portions of 2 ml of each phase were transferred to 10-cm test tubes for γ-counting in the well of a scintillation crystal. The sum of the counts recorded in both phases was generally around 100,000 cpm. Values of the distribution ratio, *D*, of indium where,

$$D = \frac{\text{Total concentration of In in the organic phase}}{\text{Total concentration of In in the aqueous phase}}$$

were calculated from the ratio of the counting rates of the organic and aqueous phases. Each counting rate was corrected for background which typically was 140 to 155 cpm.

RESULTS AND DISCUSSION

Kinetic Factors. It is well known that substitution reactions on the aquo chromium(III) ion proceed slowly. Spectrophotometric measurements on mixtures of chromium(III) perchlorate, citric acid, and acetate buffer at pH 4 required 2–3 days standing at room temperature before constant absorbances were obtained. Consequently, all experiments at room temperature were allowed to equilibrate 10 days before measurements were made. By increasing the temperature to 45 °C it was found that constant absorbances were obtained after about 10 hours standing. An equilibration time of about 24 hours at 45 °C was therefore arbitrarily chosen as a standard procedure prior to contact with the TTA–benzene extraction solvent.

Extractions with TTA are, in general, slower than most other types of solvent extractions and mechanical shaking for 30 minutes is usually required for most metals (*13*). Some data showing the effect of prolonged mechanical shaking on the distribution of indium were obtained. The aqueous phases containing indium, chromium, citrate, and acetate buffer were held at 45 °C for 116 hours followed by 20 hours at room temperature before they were extracted with 0.15*M* TTA in benzene. The phases were shaken for 2 and for 33 hours. No significant changes occurred in the distribution of indium with prolonged shaking, indicating that the TTA extraction equilibrium is readily achieved.

Similar experiments established the following facts about this system:

(1) The equilibrium between indium, citrate, and TTA in benzene at pH 4 is reached in about 10 minutes of mechanical shaking.

(2) Indium which has been extracted from citrate–acetate buffer with TTA will re-establish the same distribution ratio if the TTA–benzene phase is contacted with fresh citrate–acetate solution which contains no indium. In other words,

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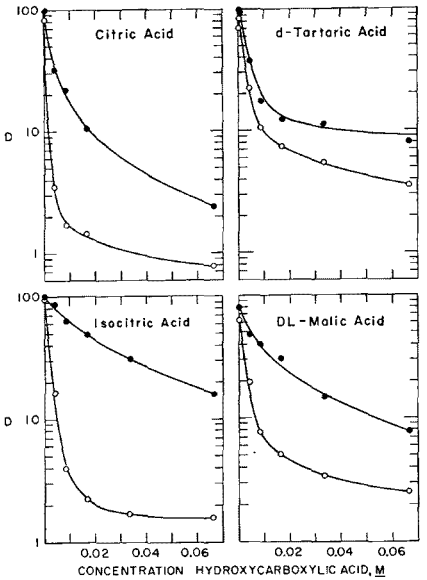


Figure 1. Hydroxycarboxylic acids which show the inhibitory effect of chromium on the extraction of indium

o Indium only, 2.67×10^{-3} M
○ Indium plus chromium, each 2.67×10^{-3}M
For this and all succeeding figures the aqueous phase: 0.5M acetate buffer at pH 3.9; and when applicable the organic phase: 0.15M TTA in benzene.

the once-formed indium–TTA species can be reversibly stripped back into the aqueous phase.

(3) The equilibrium between indium, chromium, citrate, and TTA in benzene is reached in about 10 minutes of shaking provided that the chromium and citrate has been pre-equilibrated for a day at 45 °C or for several days at room temperature.

(4) If the chromium and citrate have not been allowed to react and the extraction of indium is carried out, the indium will readily extract, but on prolonged shaking it is pulled back into the aqueous phase as the chromium reacts with the citrate.

(5) The indium–TTA species in the benzene phase reacts rapidly with chromium in the aqueous phase if the chromium is pre-equilibrated with citrate. The chromium greatly lowers the distribution ratio of indium with only 10 minutes of shaking.

From these observations we conclude that the indium–chromium–citrate system behaves as a simple equilibrium with TTA where all of the steps are moderately fast with the single exception of the complexation of chromium by citrate. This behavior should be contrasted to the chromium–cerium–citrate system investigated by Schulz *et al.* (*3*). Here it was found that the extracting agent, bis(2-ethylhexyl)phosphoric acid, completely decomposed the mixed complex of chromium–cerium–citrate when it was contacted with the aqueous phase for 24 hours. Consequently, all of their studies were carried out under nonequilibrium conditions.

Different Carboxylic Acids. A series of experiments was carried out with various hydroxycarboxylic acids to discover what structural requirements must be met to observe the inhibitory effect of chromium on the extraction of indium Figure 1 shows some of the distribution ratios of indium in the presence and absence of chromium as a function of the concentration of hydroxycarboxylic acid. The decrease of D in all cases with increasing hydroxy acid concentration indicates increasing complexation of the indium in the aqueous phase. For citric, isocitric, malic, and tartaric acids the presence of chromium is seen to depress strongly the distribution ratio of indium. On the other hand, with tricarballylic, dicrotalic, α-hydroxyglutaric, and itamalic acids (Figure 2) this inhibitory effect of chromium is not observed to a significant extent. Glutaric and tartronic acids (data not shown) also behaved similarly. In these cases it is likewise seen that D decreases with increasing carboxylic acid concentration. This was especially true for tartronic acid studied over the same concentration range. The value of D decreased by three orders of magnitude thereby indicating very strong complexation of tartronic acid with indium.

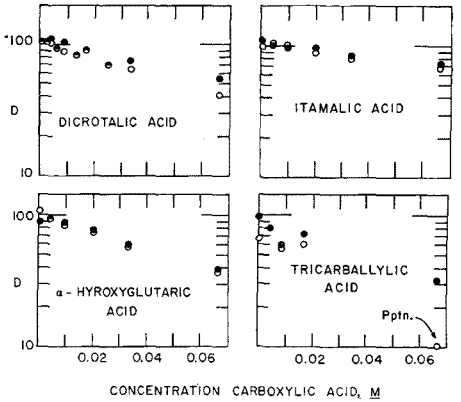


Figure 2. Carboxylic acids for which the inhibitory effect of chromium on the extraction of indium is not observed

Concentrations and media used are the same as cited for Figure 1

Table I. Acids Showing the Inhibitory Effect of Chromium on the Extraction of Indium

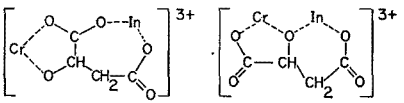
Name	Formula	Acidic dissociation constants
Citric acid	CH_2—COOH HO—C—COOH CH_2—COOH	$pK_1 = 3.13$ $pK_2 = 4.76$ $pK_3 = 6.40$
Isocitric acid	HO—CH—COOH CH—COOH CH_2—COOH	$pK_1 = 3.29$ $pK_2 = 4.71$ $pK_3 = 6.40$
Tartaric acid	HO—CH—COOH HO—CH—COOH	$pK_1 = 3.04$ $pK_2 = 4.37$
Malic acid	HO—CH—COOH CH_2—COOH	$pK_1 = 3.46$ $pK_2 = 5.10$

Table II. Acids Not Showing the Inhibitory Effect of Chromium on the Extraction of Indium

Name	Formula	Acidic dissociation constants
Tricarballylic acid	$CH_2(COOH)-CH(COOH)-CH_2(COOH)$	$pK_1 = 3.50$, $pK_2 = 4.63$, $pK_3 = 5.95$
Dicrotalic acid	$CH_2(COOH)-C(OH)(CH_3)-CH_2(COOH)$	unknown
α-Hydroxyglutaric acid	$HO-CH(COOH)-CH_2-CH_2(COOH)$	unknown
Itamalic acid	$HO-CH_2-CH(COOH)-CH_2(COOH)$	unknown
Tartronic acid	$HO-CH(COOH)-COOH$	$pK_1 = 2.02$, $pK_2 = 4.24$
Glutaric acid	$CH_2(COOH)-CH_2-CH_2(COOH)$	$pK_1 = 4.14$, $pK_2 = 5.01$

From the data collected, the acids tested can be easily classified into two groups: those which show the inhibitory effect of chromium (Table I), and those which do not (Table II). Because the TTA extraction of indium is strongly pH dependent, it was necessary in all of these experiments to keep pH constant with 0.5*M* acetate buffer so that comparative data could be obtained. The acidic dissociation constants, if known, are shown in Tables I and II and only rather small variations are seen within these groups of compounds. Consequently, although the fractions of each acid present as univalent and divalent anions may be slightly different at pH 4, the effects observed are certainly more than can be explained by the different acidic strengths of the complexing agents.

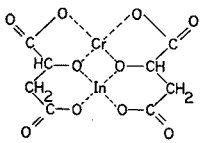
Consideration of the formulas in Tables I and II leads to the conclusion that the simplest acid which will form mixed complexes of this type is malic acid. At least two carboxyl and one hydroxyl group seem to be required; furthermore, the carboxyl groups must be bonded to adjacent carbons, one of which must also be bonded to a hydroxyl group. Any compound not containing this arrangement does not show the inhibitory effect of chromium. That this effect is due to the chelation of chromium is quite evident because it disappears when methylene groups are inserted or removed from the molecule while the same functional groups are maintained. For example, the insertion of a methylene to make the carboxyl groups nonadjacent (as in α-hydroxyglutaric acid), or the removal of a methylene to put the carboxyl groups on the same carbon (as in the tartronic acid), destroys the effect. If chromium were held in the mixed complex by bonding to a single group, these changes would be expected to be without effect. The hydroxyl group is also required for the effect. Tricarballylic acid and glutaric acid show no evidence of mixed-metal formation. Neither does itamalic acid where the hydroxyl groups is bonded to a carbon not also bonded to a carboxyl. It is evident, therefore, that a chelate structure is involved and that the ring size is critical. The conclusion drawn is, that a 5-membered ring chelate structure must be set up involving the hydroxyl and carboxyl on one carbon atom, and then a second ring involving the other metal must be formed. For the simplest of these acids, malic acid, two bonding arrangements suggest themselves for a 1:1:1 complex:



I II

Structure I utilized the carboxyl group to join the two metals together. A 7-membered ring containing the indium is also formed. Although 7-membered rings are generally regarded as having low stability, in these cases it is thought that they might be stabilized by the prior formation of a 5-membered ring in the same molecule. There is some precedence for this view when the stabilities of the complexes of chromium with succinic, fumaric, and maleic acids are considered. The reaction of succinic and fumaric acids with chromium(III) results in the formation of insoluble chromium polymers. On the other hand, with maleic acid where the carboxyls are held in adjacent positions by the double bond, soluble chromium complexes containing 7-membered rings are formed (*14*). Similar stabilization may be occurring in this system.

In structure II the hydroxyl oxygen is simultaneously bonded to the two metals to form one 5- and one 6-membered ring. This arrangement puts the metal atoms much closer together and it has been suggested for the structure of the dinuclear uranyl tartrate and malate complexes (*15*, *16*) and also for the dinuclear copper malate, citrate, and tartrate (*17*). By analogy to these structures and on the basis of spectrophotometric evidence (vide infra), we suggest the following arrangement for the structure of the mixed-metal malate complex:



III

The question of the number of polydentate ligand groups in the mixed-metal complex has not been definitely established for the acetate medium. The spectral evidence of Figure 8 suggests that two citrates are most likely. In the absence of acetate, the presence of more than one citrate in the mixed-metal complex is indicated by ion exchange. When a solution at pH 4 containing chromium, indium, and citrate in the ratio of 1:1:2 is passed over Dowex-1 resin in the chloride form, nearly all of the chromium is observed to be retained by the column even after extensive washing with water. Under the same conditions, 86% of the indium was

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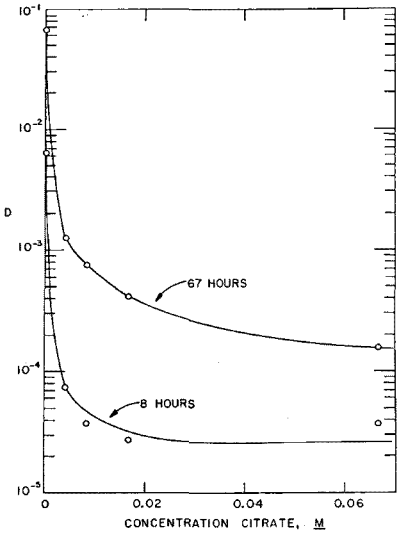


Figure 3. Extraction of chromium by TTA from acetate medium after various shaking times ($4 \times 10^{-3} M$ Cr)

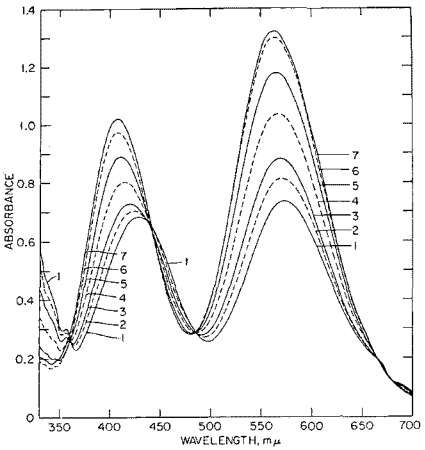


Figure 4. Absorption spectra of chromium (III) in the presence of increasing citrate concentrations ($2 \times 10^{-3} M$ Cr)

10-cm cells. Curve number, citrate concentration; 1, 0.0M; 2, 1×10^{-4}; 3, 2×10^{-4}; 4, 4×10^{-4}; 5, 6×10^{-4}; 6, 8×10^{-4}; 7, 1×10^{-3}

also found to be retained as was determined using ^{114}In tracer. One concludes, therefore, that the mixed complex must be negatively charged because it is known to be present in the solution in major proportion. If it were a 1:1:1 complex, the lowest charge possible would be 2+, and no retention would be expected. This assumes the absence of hydrolysis which at pH 4 should not be extensive. For these reasons, the 1:1:2 composition is the most likely, and the structures analogous to III are assumed for all the mixed-metal complexes. Unfortunately, all attempts to elute the complex from the resin for direct analysis have failed because the retention is so strong that the conditions required result in decomposition.

Molecular models reveal that structure III needs to be modified only slightly to accommodate the additional —CH_2-COOH group of citric acid. This group may be considered to replace the hydrogen on the carbon with the hydroxyl group, and in III it may be visualized as forming an additional 6-membered ring to the indium ion. The number of different reasonable structures, however, is large, and at present no one structure can be strongly favored. Attempts to resolve this question by preparation of a solid compound suitable for X-ray analysis have all failed because the complexes are extremely soluble and crystallize poorly.

Extraction of Cr(III) by TTA. Chromium(III) is known to be extracted at pH 4 by TTA in benzene with a distribution ratio of about 0.3. Acetate, however, inhibits the extraction. Consequently, to achieve complete recoveries of chromium it is necessary to extract quickly after the addition of acetate buffer in order to avoid complexation of the chromium (*18*). It was of interest, therefore, to see the degree to which chromium is extracted after long standing in the presence of acetate and citrate. A series of solutions containing $4 \times 10^{-3} M$ Cr(III), some ^{51}Cr tracer, 0.5M acetate buffer of pH 4, and various concentrations of citrate were kept 20 hours at 45 °C. They were then extracted with 0.15M TTA in benzene. After 30 minutes of shaking there was no detectable ^{51}Cr activity in any of the organic phases. After 8 and 67 hours of shaking there was some distribution of the chromium; the data are shown in Figure 3. It is evident that under the experimental conditions used in this work the extraction of chromium by TTA is completely negligible.

Reaction of Chromium with Citrate. Very little information on the complexation of chromium(III) with citrate exists. A recent pH study of the reaction assumes that Cr(III) and citrate combine in the ratio of 1:1 but no direct evidence for this is cited. All of the experimental data were taken with citrate in large excess (*19*). In a kinetic study of the reaction of chromium with various organic acids the 1:1 complex with citrate was assumed to be the only important species present. This conclusion was based on a continuous variations experiment but no data or experimental conditions were given (*20*). A 1:1 complex has also been reported as being formed at pH 3.2. The method of continuous variations was also used in this work in the region of 235 to 255 mμ. The 1:1 combining ratio was unambiguous and there was no evidence whatever of the formation of other complexes (*21*). These studies, of course, only indicate the simple proportion of chromium to citrate in the complex, and do not preclude the possibility of the formation of a binuclear complex of chromium and citrate as has been demonstrated to exist in the copper–citrate system (*17*).

Since the experimental conditions of this study were significantly different from those above in that most of the solutions were strongly buffered with acetate, an experiment was done

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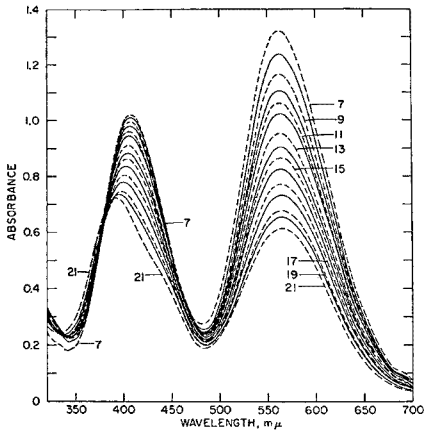


Figure 5. Absorption spectra of chromium(III) in the presence of increasing citrate concentrations (2 × 10^{-3} *M* Cr)

10-cm cells. Curve number, citrate concentration; 7, 1 × 10^{-3}*M*; 9, 1.4 × 10^{-3}; 11, 1.8 × 10^{-3}; 13, 2.5 × 10^{-3}; 15, 3.5 × 10^{-3}; 17, 5.0 × 10^{-3}; 19, 8.0 × 10^{-3}; 21, 2.0 × 10^{-2}

to check the combining ratio of chromium to citrate. The absorption spectra of chromium (III) solutions in 0.5*M* acetate buffer at pH 4 in the presence of increasing amounts of citrate are shown in Figures 4 and 5. In all solutions the concentration of chromium was 0.002*M*. After preparation, the solutions were allowed to equilibrate 10 days at room temperature before making measurements. The addition of citrate up to a concentration of 0.001*M* results in a series of spectral curves showing three well-defined isosbestic points at 361, 440, and 486 mμ (Figure 4). On further addition of citrate above 0.001*M* the absorption in the visible region decreases and a new isosbestic point is established at 378 mμ (Figure 5). All curves pass through this point until a ratio of chromium to citrate of 1:5 is reached. These data and the plots of absorbance *vs.* citrate concentration (Figure 6) clearly point to the formation of a complex where the chromium to citrate ratio is 2:1. The straightness of the region where small amounts of citrate are added to excess chromium indicates a complex of high stability.

This latter contention is also borne out by the fact that solutions containing chromium to citrate in the ratio of 2:1 in 0.5*M* acetate buffer of pH 4 follow Beer's law at 564 mμ within experimental error over the concentration range of 3 × 10^{-2}*M* to 3 × 10^{-4}*M* (1- to 10-cm cells were used). This evidence also suggests the absence of polymerization or dissociation reactions in this medium.

Because the 2:1 ratio of chromium to citrate has not been previously reported, an experiment in acetate medium was done using the method of continuous variations and the same ratio was again obtained. To test whether the acetate was playing an important role in this reaction, the experiment of Figures 4, 5, and 6, was repeated without any acetate buffer. Control of the pH in this case was very difficult; the pH was adjusted with sodium hydroxide three times after heating periods at 45 °C for 24 hours or longer. After the final adjustment and heating period of more than 2 days, the pH's were measured and found to lie in the range of 3.4 to 3.8. The spectra were then recorded. Although the data were

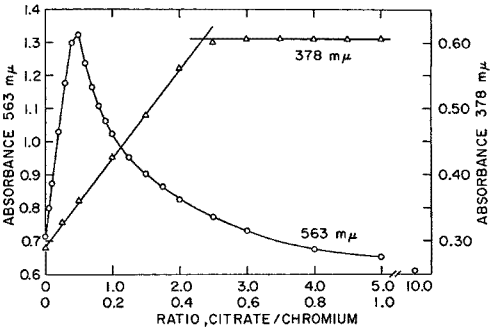


Figure 6. Absorbance as a function of the ratio of citrate to chromium

Conditions same as Figures 4 and 5. Upper abscissa, 563 mμ. Lower abscissa, 378 mμ. 10-cm cells.

somewhat more erratic than those of Figure 7, there was no evidence of a break in the absorbance at the 2:1 ratio; the absorbance continued to rise to a maximum value at the 1:1 point, and then to diminish gradually as the citrate concentration increased. When the experiment was done in 2*M* lithium chloride medium with no acetate present, the data showed less scatter and again indicated the 1:1 composition. Thus these results confirm those of other workers that a 1:1 chromium–citrate complex is formed, and establish that acetate is necessary for the stabilization of the 2:1 chromium–citrate complex.

Reaction of Chromium with Malic Acid. Experiments analogous to those described above with citric acid were also done with malic acid. The results obtained were similar.

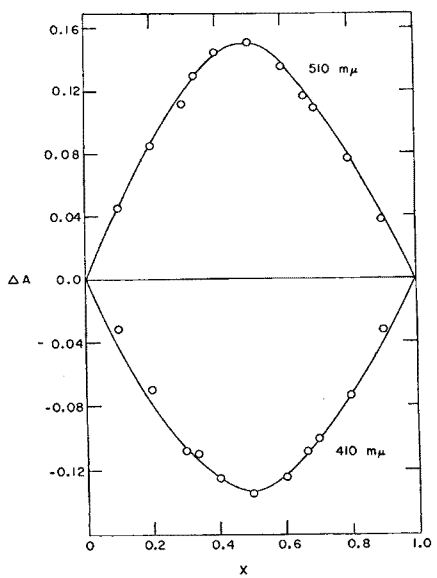


Figure 7. Continuous variations curve

Absorbance difference *vs.* mole fraction chromium (2 × 10^{-3}*M* total metal)

The gradual addition of malate to chromium in 0.5M acetate buffer at pH 4 resulted in increased absorption at 564 mμ as was observed with citric acid. However, a sharp break in the absorbance at the ratio of chromium to malate of 2:1 was not observed. Instead, the absorbance continued to increase, though less rapidly, until the 1:1 ratio was reached. Beyond this point, it decreased gradually with increased malate. The curve was quite rounded and the presence of more than one complex was indicated. The same conclusion was reached from a continuous variations experiment. The maximum of the curve appeared at $X = 0.67$ corresponding to a chromium to malate ratio of 2:1. The curve was distorted, however, and the absorbance at $X = 0.5$ was only 7% less than at $X = 0.67$. Consequently, it is evident that both the 2:1 and 1:1 complexes are capable of simultaneous existence over a wide range of metal to ligand ratios, and that in the acetate medium the malate complexes are much weaker than the corresponding citrates.

Ratio of Chromium in Indium in the Mixed Complex. Because the presence of indium was observed to change the color of the chromium citrate mixtures from bluish purple to pinkish purple, an attempt was made to determine the combining ratio of chromium to indium in the mixed complex by direct spectrophotometry. When spectra of chromium citrate solutions with and without the presence of indium are compared, the most significant differences in absorption occur at 510 and 410 mμ. An experiment using the method of continuous variations was carried out at these wavelengths in 10-cm cells. The set of solutions were 0.0020M in total metal (the sum of the concentrations of indium and chromium), 0.0022M in citrate, 0.5M in acetate, and were at pH 4.0. If X is defined as the mole fraction of chromium (moles Cr/total moles of metal) and $\Delta A = A - XA_1$, where A_1 is the absorbance of the solution containing all chromium and no indium, then a plot of ΔA *vs.* X gives the typical continuous variations curve. The data are shown in Figure 7 and unambiguously show the combining ratio of indium to chromium to be 1:1. The values of ΔA at 410 mμ are negative because the addition of indium to chromium citrate results in a decrease in absorbance at this wavelength.

Addition of Citrate to Chromium–Indium Mixtures. The absorption spectra of a series of solutions containing 0.002M chromium perchlorate, 0.002M indium perchlorate, 0.5M acetate buffer at pH 4, and various concentrations of citrate were measured. Some of these are shown in Figure 8. It should be noted that, over the wavelength region used, all of the indium species not containing chromium are completely transparent. At the 1:1:1 ratio of chromium to indium to citrate the spectrum is seen to be very similar in both the positions and intensities of the absorption maxima to that for chromium and citrate at the ratio of 2:1 (Curve 7, Figure 4). It is therefore probable that the solution at this composition contains mainly the 2:1 chromium–citrate complex and some indium–citrate species. However, as further citrate is added to reach the ratio of 1:1:2, the absorption maximum shifts to 548 mμ and decreases slightly in intensity. Further addition of citrate to the ratio of 1:1:6, shifts the band to 544 mμ and its intensity is changed hardly at all. This behavior is markedly different from that observed with chromium alone. In Figure 5 the absorbance is seen to decrease greatly in the presence of excess citrate and the wavelength of the absorption maximum remains unchanged at about 564 mμ. It follows, then, that the indium has a profound effect on the absorption spectrum of chromium citrate and that this effect cannot simply be a competition between the metals present. For if this were the case, when the indium became coordinatively saturated in the presence of excess citrate, the same large decrease in absorbance would then be expected. Because this does not occur, a reasonable postulate for the formation of a mixed-metal complex when citrate is gradually added to a 1:1 chromium-indium mixture in acetate medium is:

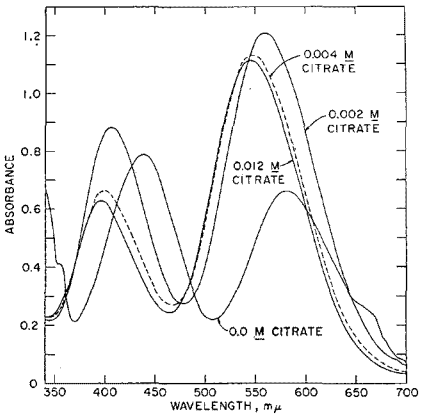


Figure 8. Absorption spectra of chromium with indium in the presence of various amounts of citrate (Cr = In = $2 \times 10^{-3}M$) (10-cm cells)

(1) $2\,Cr + cit \rightleftarrows Cr_2cit$

(2) $In + x\,cit \rightleftarrows In(cit)_x$

(3) $Cr_2cit + 2\,In(cit)_x \rightleftarrows (2x - 1)\,cit + CrIn(cit)_2$.

Steps (1) and (2) probably occur simultaneously and are followed by step (3). No acetate is shown in any of the above formulas although it was shown previously to be

Table III. The Effect of Acetate on the Formation of the Mixed Complex

pH 4.0; organic phase, 0.15M TTA in benzene

No.	Concentration, M In	Cr	Citrate	Acetate	Distribution ratio, In	
1	0.00267	0.0	0.0167	0.5	13.2	$D_1/D_2 = 9.0$
2	0.00267	0.00267	0.0167	0.5	1.47	
3	0.00267	0.0	0.0167	0.0	36.5	$D_3/D_4 = 7.6$
4	0.00267	0.00267	0.0167	0.0	4.80	

involved in the Cr_2cit species. The state of the reacting indium is unknown also since nothing is known of its relative affinity for citrate and acetate under these conditions. One might also speculate that acetate is involved in the mixed-metal complex, but this is shown to be unnecessary from solvent extraction data (Table III). The ratio of distribution ratios of indium in the presence and absence of chromium were compared with and without the presence of acetate and were found to be similar.

CONCLUSIONS

The foregoing study shows that complexes of numerous hydroxycarboxylic acids with more than one kind of metal can have high stability. Quite clearly in a great deal of practical work where these acids are used as buffering or complexing agents their presence must be taken into account. Calculations of separability, for example, which are based on formation constants for the individual metals will be significantly in error. As of yet, no formation constants of mixed-metal complexes of this type have been measured. Until this is done, corrections for mixed-metal complex formation cannot be applied to these calculations. Several systems are currently under study in this laboratory with this objective; in particular, a mixed complex of uranyl ion, indium(III), and citrate of very high stability is under detailed investigation.

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New Extraction Chromatographic Method for Rapid Separation of Americium from Other Transuranium Elements

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A simple, rapid method is described for the separation of americium from curium and other actinide elements. The method exploits a new oxidation technique for the preparation of americium(V) in dilute nitric acid solution with ammonium persulfate. Isolation of the americium is achieved by extraction chromatography with small Teflon columns containing di(2-ethylhexyl)-phosphoric acid as the stationary phase. The method considerably simplifies the purification and determination of ^{243}Am in the presence of high levels of ^{244}Cm. Several useful applications for both analytical and purification purposes are discussed.

IN HIS SEARCH for more highly selective methods for the isolation and determination of the transplutonium elements, the radiochemist in recent years has turned to an intriguing area—exploitation of their unusual oxidation states. Pressing demands for a faster, simpler method for ^{243}Am in transplutonium process streams containing high levels of ^{244}Cm led the author to explore this concept.

Current radiochemical methods for ^{243}Am are based on the high solubility of Am(VI) in lanthanum fluoride (*1*, *2*) or calcium fluoride systems (*3*), sorption of Am(VI) on extraction chromatographic columns (*4*) containing di(2-ethylhexyl)phosphoric acid(HDEHP), ^{239}Np daughter ingrowth on a purified sample (*5*), and the inextractability of Am(V) with 0.5*M* thenoyltrifluoroacetone–xylene (*6*). These methods are either time consuming, require too many manipulations, or provide inadequate decontamination from ^{244}Cm for many process applications. For instance, our present method based on solvent extraction with thenoyl trifluoroacetone requires 4 to 6 hours, because recycling is mandatory to remove the bulk of the ^{244}Cm interference. Similarly, the method based on ^{239}Np daughter ingrowth requires 24 to 72 hours.

The classical separation of americium from curium is based on the oxidation of Am(III) to Am(V) in potassium carbonate or potassium bicarbonate solution (*1*). Am(V) precipitates as a double carbonate, $K_3AmO_2(CO_3)_2$; curium (III) remains in solution as a carbonate complex. Successful industrial processes (*7*, *8*) are based on this principle. Inasmuch as micro levels of Am(V) do not precipitate in this alkaline system (*1*, *9*), attempts were made to utilize the Teflon–HDEHP system (*10*) for the separation of Am(V) from Cm (III). Such a system is most effective for the strong sorption of Cm(III); one would expect Am(V) to show very low sorption in this method. This approach proved impractical because of the very low yields and difficulties associated with the alkaline precipitation of various metal ions; moreover, excess solids in the eluates precluded direct measurements of alpha particles.

A particularly attractive alternative is to utilize an acidic solution for both the preparation of Am(V) and its subsequent separation from Cm(III). Until recently such an approach remained unexplored, because chemists regarded the AmO_2^+ ion too intractable to exploit for separations in acid systems. Early work in this area is described in one recent paper (*6*) relating to the inextractability of Am(V) with thenoyltrifluoroacetone–xylene at pH ~5. Attempts to adapt the aqueous conditions cited therein to extraction chromatography (*10*) were unsuccessful.

Further studies by the author led to the discovery of a simple technique for the preparation of Am(V) with high yield in nitric acid solution. Most importantly, the conditions used are optimum for exploiting the chemical behavior of Am(V) in an extraction chromatographic system based on Teflon–HDEHP–HNO_3. For analytical applications, the

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(2) F. L. Moore, ANAL. CHEM., **35**, 715 (1963).
(3) H. P. Holcomb, *ibid.*, **36**, 2329 (1964).
(4) E. K. Hulet, *J. Inorg. Nucl. Chem.*, **26**, 1721 (1964).
(5) C. J. Banick, ANAL. CHEM., **37**, 434 (1965).
(6) J. R. Stokely, Jr., and F. L. Moore, *ibid.*, **39**, 994 (1967).
(7) W. D. Burch, Oak Ridge National Laboratory Unclassified Report, **ORNL-3880**, p 28 (1966).
(8) G. A. Burney, *Nucl. Appl.*, **4**, 217 (1968).
(9) H. P. Holcomb, 155th National Meeting, ACS, Div. of Nuclear Chemistry and Technology, Paper 16, San Francisco, Calif., (Mar. 31–Apr. 5, 1968).
(10) F. L. Moore and A. Jurriaanse, ANAL. CHEM., **39**, 733 (1967).

Table I. Effect of Variables on Oxidation and Recovery of Americium by Extraction Chromatography

HNO_3, *M*	$(NH_4)_2S_2O_8$, *M*	$AgNO_3$, *M*	Temp., °C	Time, min.	^{241}Am tracer recovered, %
0.03	0.10		23	10	<0.01
0.01	0.10		85	10	80.1
0.03	0.03		85	5	39.0
0.03	0.03		85	10	61.3
0.03	0.06		85	5	70.0
0.03	0.06		85	10	81.5
0.03	0.10		85	5	81.7
0.03	0.10		85	10	92.6
0.03	0.25		85	10	90.2
0.03	0.40		85	10	87.6
0.05	0.10		85	10	89.7
0.03	0.10	0.01	85	10	38.2
0.03	0.10	0.04	85	10	19.1

isotope dilution technique in conjunction with alpha spectrometry is used for an accurate determination of ^{243}Am.

Principle of Separation. Am(III) is oxidized to Am(VI) in dilute nitric acid solution in the absence of silver ion (ordinarily used as a catalyst). In the absence of a stabilizing anion the Am(VI) reduces to Am(V). Extraction chromatography with Teflon–HDEHP allows the nonsorbable Am(V) to elute rapidly while Cm(III), other actinide(III,IV,VI) ions, lanthanide(III,IV) ions, and many other metal ions sorb tightly on the column.

EXPERIMENTAL

Apparatus. An internal sample methane proportional counter was used for fission, alpha, and beta counting at voltage settings of 2100, 2900, and 4300, respectively.

A NaI well-type scintillation counter, $1\frac{3}{4} \times 2$ inches, was used for gamma counting.

A silicon diode detector (3 cm^2) coupled to a 256-channel analyzer was used for alpha spectometry.

A glass tube, 5-mm i.d. and 150 mm in length was drawn to a tip at one end. A small glass wool plug was inserted in the tube to retain the support. To prevent disruption of the column, a small glass wool plug was placed on top of the column.

Reagents. Di(2-ethylhexyl)orthophosphoric acid, 1*M*.

Purify di(2-ethylhexyl)orthophosphoric acid (HDEHP, available from Union Carbide Chemicals Co., New York, N. Y.) by mixing gently for 3 minutes with an equal volume portion of ethylene glycol. If mixed too vigorously, the phase separation is poor. Repeat the treatment of the HDEHP twice with fresh portions of ethylene glycol. Separate the phases by centrifugation. The final purity of the HDEHP was 99.7%. Weight 32.2 grams and dilute to 100 ml with *n*-heptane.

Inert Support. Teflon-6, polytetrafluoroethylene powder, is available in specially pre-sieved form (60–70 mesh) from Analytical Engineering Laboratories, Hamden, Conn.

Column Preparation. Add 10 ml of 1*M* HDEHP–heptane to 8 grams of Teflon-6 powder in a 1-oz glass bottle. Cap the bottle and shake vigorously for 1–2 minutes. Prepare columns from this mixture by the following procedure:

By use of a medicine dropper, add to the glass tube the solvent-treated Teflon powder, 3–4 drops at a time. Tamp firmly after each addition with a glass rod, being careful to eliminate air bubbles. When the column is packed to a height of 70 mm, allow the excess solvent to drain off. Condition the column by passing 5 ml of 0.01*M* nitric acid through it. A flow rate of 5–6 drops per minute is attained.

Procedure. Adjust the sample solution to 0.1*M* nitric acid. Pipet an aliquot, 25–100 μl, into a 10 × 75 mm test tube. Wash the pipet with 0.01*M* nitric acid, transferring the wash solution to the tube. Add an aliquot, 25–100 μl, of a standardized solution of ^{241}Am (5.48 mev) contained in 0.1*M* nitric acid. Wash the pipet with 0.01*M* nitric acid, transferring the wash solution to the tube. The alpha radioactivity of the ^{241}Am added should be about one half the estimated ^{243}Am alpha radioactivity (5.27 mev) in the sample aliquot. Add 100 μl of freshly prepared 0.5*M* ammonium persulfate and gently swirl the tube to mix.

Oxidize the americium by heating the tube in a water bath at 80–90 °C for 10 minutes. Remove the tube and cool in a ice bath for 5 minutes.

Place a 5-ml volumetric flask under the column to collect the americium fraction. Carefully pipet the solution onto the center of the column using about 200-μl additions for each transfer. Wash the tube with 1–2 ml portions of 0.01*M* nitric acid and transfer these washes to the column. Continue to elute at 5–6 drops per minute with 0.01*M* nitric acid until 5 ml are collected. Mix well. Prepare suitable aliquots (preferably 100 μl or less) on tantalum plates for alpha measurements.

If the ^{244}Cm and ^{252}Cf isolations are desired, proceed as follows: Elute the ^{244}Cm from the column with 10 ml of 0.3*M* nitric acid. Mix well and prepare suitable aliquots on stainless steel plates for alpha measurements.

Elute the ^{252}Cf from the column with 10 ml of 4*M* nitric acid. Mix well. Prepare suitable aliquots on stainless steel plates for fission and/or alpha measurements. Alternatively, one may count the prompt gamma rays from ^{252}Cf (*11*) or the fission neutrons.

RESULTS AND DISCUSSION

Principle of Separation. Am(III) is oxidized to Am(VI) in dilute nitric acid solution in the absence of silver ion (ordinarily used as a catalyst). In the absence of a stabilizing anion, the Am(VI) reduces to Am(V). Extraction chromatography with Teflon–HDEHP allows the nonsorbable Am(V) to elute rapidly while Cm(III), other actinide(III, IV, VI) ions, lanthanide(III, IV) ions, and many other metal ions sorb tightly on the column.

OXIDATION OF AMERICIUM TRACER

Experiments were performed to define the optimum conditions for the oxidation–reduction sequence, Am(III)→Am(VI)→Am(V), and subsequent purification based on the Am (V) oxidation state.

Pertinent variables were evaluated by the procedure described above. For exploratory studies, ^{241}Am tracer contained in 0.1*M* nitric acid was used. Counting rates were

(11) F. L. Moore and J. S. Eldridge, ANAL. CHEM., **36**, 808 (1964)

1.2×10^7 alpha counts per minute per milliliter and 5.3×10^6 gamma counts per minute per milliliter. Typical data are shown in Table I. On the basis of these studies, the following conditions were selected for the preparation of Am(V): 0.01–0.05*M* nitric acid, 0.05–0.4*M* ammonium persulfate, 10-minute oxidation at 80–90 °C followed by a 5-minute cooling period in an ice bath.

In previous methods (*2–4*) for the oxidation of Am(III) to Am(VI), silver catalyzed persulfate oxidation has been shown to be clearly superior to persulfate oxidation alone. We found early in this study that silver ion was detrimental to the production of the desired Am(V) oxidation state. Presumably Am(VI) is maintained as long as the high oxidation states of silver are present. Am(VI), like Am(III), sorbs very efficiently on the column, thereby lowering the yield drastically.

Nitric acid concentrations greater than about 0.2*M* reduce yields by inhibiting the oxidation of Am(III) (*2*). Moreover, under such conditions premature elution of Cm-(III) and other elements occurs. Although Am can be recovered in high yields at nitric acid concentrations <0.01*M*, it is often impractical; hydrolysis and precipitation of other metal ions introduce mechanical problems, such as clogging of columns and coprecipitation losses.

Ammonium persulfate does not oxidize Am(III) at room temperature. A 10-minute oxidation period at 80-90 °C is satisfactory. Following oxidation the solution is cooled for 5 minutes in an ice bath. Actually, experiments indicated little difference in americium recoveries at cooling periods of 1 to 20 minutes. In addition, high yields were demonstrated when the hot oxidized solution was transferred to the column with no cooling period. However, direct sorption from hot solution is not recommended because of possible damage to the column.

Interchange between ^{243}Am and ^{241}Am is readily achieved in the oxidation step.

EXTRACTION CHROMATOGRAPHY OF AM(V)

Following the preparation of Am(V), extraction chromatography is used as a highly effective method for the isolation of Am(V) from Cm(III) and many other elements.

Teflon powder was selected as the inert support, because it is exceptionally stable to chemical reagents and solvents and requires no special treatment to render it hydrophobic. The advantages of Teflon over various other supports in extraction chromatography have been reviewed (*10, 12*). Highly efficient applications (*10*) based on Teflon–HDEHP–HNO_3 systems have been demonstrated recently for the separation of californium from curium and berkelium from cerium. However, no separation of americium from curium is effected in those systems.

Exploratory experiments indicated that Am(V) exhibited negligible sorption in the system, Teflon — 1*M* HDEHP–heptane — 0.01–0.05*M* HNO_3. Under such conditions Cm (III), other actinide(III,IV,VI) ions, lanthanide(III,IV) ions, and various other metal ions were strongly sorbed — a fact which provides an excellent separation of americium from many other elements.

Eluents containing nitric acid in the range, $1 \times 10^{-2} - 1 \times 10^{-6}$*M*, appeared equally satisfactory for the recovery of americium from the column. For a standard procedure, 0.01*M* nitric acid was selected as an eluent in order to circumvent hydrolytic problems with other elements at higher pH's. Ammonium persulfate is not required in the eluent. Pretreatment of the eluent with HDEHP–heptane was found unnecessary. Elutions at elevated temperatures were not studied because of the excellent room temperature separations obtained. Most of the studies were performed at flow rates of 4 to 6 drops per minute; however, results were essentially the same at flow rates of 10 drops per minute.

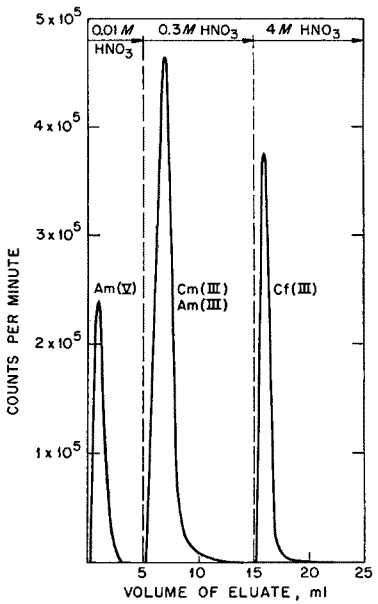


Figure 1. Separation of Am, Cm, and Cf by extraction chromatography

Column: 5 × 70 mm, 1 *M* HDEHP–heptane on Teflon-6 powder (60–70 mesh), 23 °C, flow rate = 5–6 drops per minute

Inasmuch as decontamination factors from ^{244}Cm of $>10^5$ were effected on the 5 × 70 mm columns, larger columns were not evaluated.

On the basis of our studies, the following conditions were selected for the extraction chromatographic isolation of americium, curium, and californium: 5 × 70 mm column of Teflon-6 powder (60–70 mesh) containing 1*M* HDEHP–heptane as the stationary phase, room temperature operation at a flow rate of 5 to 6 drops per minute; eluents, 5 ml of 0.01*M* HNO_3 for Am, 10 ml of 0.3*M* HNO_3 for Cm, 10 ml of 4*M* HNO_3 for Cf and heavier elements.

Typical elution curves are shown in Figure 1. The pH range of the americium product is 1.9–2.1.

The recovery of americium and its decontamination from ^{244}Cm is excellent. Yields average 85–95% with a relative standard deviation of 3.6% (n = 12). ^{244}Cm decontamination factors average 2.8×10^5. The method may be performed in about 1½ hours.

The elution data for Cm(III) and Cf(III) are presented to demonstrate their sequential behavior in this system. It is similar to our current method (*10*) for the separation of Cf(III) from Cm(III), Am(III) except that 1*M* HDEHP–heptane (instead of 0.5*M*) is used as the stationary phase.

(12) K. Preobrazhenskii and G. S. Katykhin, *Radiokhimiya*, **4**, 536 (1962).

To minimize tailing of the curium at the higher solvent concentration, the nitric acid concentration in the eluent has been increased from 0.2 to 0.3*M*. Recoveries of the ^{244}Cm and ^{252}Cf under the conditions described are typically >99%. Any Am(III) present in the oxidized solution elutes with the Cm(III).

Persulfate ion in the americium fraction corrodes stainless steel plates, thereby decreasing the resolution of alpha particle measurements. To avoid this problem, one may use tantalum or platinum plates, because they provide excellent sources for ordinary process control measurements. Also the need for an additional electrodeposition step is eliminated, but for more elegant studies, electrodeposition is still recommended.

A plausible explanation for the experimental results is the following: persulfate oxidizes Am(III) to Am(VI). In the absence of a holding oxidant, like silver ion, or a strong complexing anion, like fluoride ion (*2*), Am(VI) readily reduces to Am(V). Further reduction is more difficult because of the necessity to break oxygen bonds. Am(V) disproportionates to form Am(III,VI) slowly—an observation which is successfully exploited in this new method. Inasmuch as the large AmO_2^+ ion exhibits negligible tendency to complex with HDEHP and sorb on the column, it elutes rapidly.

Under the conditions used, the AmO_2^+ ion is relatively stable for some time, even in the presence of a large excess of hydrogen peroxide. For instance, in the first exploratory experiments, it was thought that a mild reductant, like hydrogen peroxide would be required to provide high yields of Am(V) by reduction of Am(VI). Interestingly, the yields of Am(V) were essentially equal, whether excess hydrogen peroxide (as high as 5*M*) was present or not. In a brief study, after the persulfate oxidation in the standard method, the solution was adjusted to 1.8*M* hydrogen peroxide and allowed to sit for various periods of time at room temperature (~23 °C) prior to sorption on the column. Recoveries of Am(V) were 87% after 5 minutes, 74% after 1 hour, and <5% after 16 hours. As expected, the Am(V) reduced to Am(III) easily if the solution was heated at 85 °C for 5 minutes.

These experiments clearly showed that the addition of hydrogen peroxide as a reductant was unnecessary. However, it should not be construed that some hydrogen peroxide is not present. The acid-catalyzed thermal decomposition of persulfate is known to produce hydrogen peroxide.

APPLICATIONS

The method is regarded as invaluable for glove box or hot cell work because of its simplicity, speed, and minimum number of manipulations required. Although the main objective in this study was the development of a simple method for the isolation of ^{243}Am, highly decontaminated from ^{244}Cm, valuable additional decontamination is effected from many other elements. We have found the method to be an excellent preparative tool for the purification and isolation of americium in solutions containing other actinide (III, IV, VI) ions, lanthanide(III,IV) ions, and various other ion

The most common interferences encountered in process work are α-hydroxyisobutyric acid and chloride ion. Evaporations with concentrated nitric acid readily destroy these interferences. For analytical purposes involving high dilutions of sample solutions with nitric acid, chloride ion may often be reduced to an innocuous level (<0.001*M*).

Ferric iron seriously interferes in the method. Less than 3% plutonium follows through the procedure. This value may be compared with 43% plutonium which accompanies americium in the thenoyltrifluoroacetone method (*6*).

ACKNOWLEDGMENT

The author gratefully acknowledges the capable assistance of G. I. Gault in the experimental work and E. C. Lynn for some of the analyses.

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Corrections

Reaction Rate Measurements with Fluoride Ion-Selective Membrane Electrode

Formation Kinetics of Ferrous Fluoride and Aluminum Fluoride Complexes

In this article by K. Srinivasan and G. A. Rechnitz [ANAL. CHEM., **40**, 1818 (1968)] an error appears in the subtitle. In the editorial process of spelling out chemical formulas the words "ferrous fluoride" were erroneously used instead of "ferric fluoride."

Short-Time Electrode Processes and Spectra in a High-Voltage Spark Discharge

In this article by J. P. Walters [ANAL. CHEM., **40**, 1540 (1968)] an error appears on page 1541, Figure 2. Identification of the axes was inadvertently omitted, and they should read as follows:

Vertical axis–200 amp/cm
Horizontal axis–5 μseconds/cm

Spectrophotometric Determination of Cysteine

In this article by T. J. Bydalek and J. E. Poldoski [ANAL. CHEM., **40**, 1878 (1968)] an error involving the preparation of the nitrilotriacetate solution appears on page 1878 in the Experimental Section. Line 12 should read:

"200 ml of distilled water containing 1.20 grams of NaOH."

Vapor-Programmed Thin-Layer Chromatography, A New Technique for Improved Separations

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To obtain full benefit of the influence of vapor in TLC a new development chamber has been designed. This chamber provides full vapor control over the entire plate. Optimum conditions can be established by vapor programming and the migration rate of each individual spot can be guided. Thus, more efficient separations are obtained, particularly of chemically related substances which are inadequately separated with the classical TLC techniques. The properties of the vapor-programming chamber are discussed and results are shown in separations of dyes and sulfonamides.

RECENT work (*1*, *2*) on the influence of solvent vapor in thin layer chromatography has shown that if development of the plate is done in unsaturated chambers then separations with multicomponent solvents are more efficient than in saturated chambers. The improvements are caused by a concentration gradient of adsorbed vapor on the dry part of the plate, with the gradient mainly dependent on the rate of evaporation of the solvent components and on their affinity for the adsorbent used.

It will be clear that little or no control can be exercised on the extent to which the gradient develops on the plate after development is started. With highly polar solvent components the gradient may become too steep on the lower parts of the plate, with the upper parts showing no gradient at all because maximum vapor adsorption will take place here. With less polar solvent components the gradient may be too flat or will not reach its maximum because of fast development. Furthermore, differences in evaporation velocity between the solvent components may cause failures in the desired gradient. Thus, although unsaturated chambers may well yield improved separations the conditions are not necessarily optimum for every case.

Therefore, we have searched for development techniques providing a more efficient control of the vapor processes during development. This has led to the apparatus described below, which allows full vapor programming over the entire plate, thus making it possible to affect the migration of each individual spot.

APPARATUS

Description. The vapor-programming chamber (Figure 1), VP-chamber (patents applied for, soon obtainable from C. Desaga, Heidelberg), consists of three parts, all of chromium plated brass. The solvent reservoir, *A*, is a rectangular tank 20 × 1 × 2 cm. The ground plate, *B*, 20 × 20 × 1 cm, is fitted with a solvent reservoir holder and a tube to pass warm water, *D*, insulated from the ground plate by 2 mm of asbestos and 4 fixation clamps, *E*. The inner part of the ground plate contains a tube system for water-thermostating, with the inlet and outlet visible at *F*. The trough chamber, *C*, contains 21 troughs, i.d. 6 mm and depth 12 mm. The partition walls have a thickness of 2 mm, the side walls are 5 mm. The chamber has been made of welded flat oval tubes, with the tops sawed off.

A space of about 1 mm is needed between the trough chamber and the solvent reservoir to prevent disappearance of solvent by capillary action between the walls.

Working Procedure. The samples are spotted on normal 20- × 20-cm TLC plates, 2–2.5 cm from the bottom edge of the plate and at least 1 cm apart. The side edges and the bottom edge are stripped 0.5 cm wide. The troughs are filled with a series of liquids of appropriate compositions to give suitable vapors. Most often the liquids show increasing polarity from bottom to top. This can be done, for example, by using mixtures of two or more solvent components of different polarities, with the mixtures having an increased proportion of the more polar components. The empty solvent reservoir is placed in the holder and fitted with a folded strip of filter paper, 18.5 × 2 cm, with 1 cm folded over the inner wall. The side walls of the chamber are fitted with small strips, about 0.5 mm thick. The TLC plate is then placed on the chamber, the adsorbent downward, facing the troughs, the stripped side edges resting on the side strips, and the bottom edge just covering the solvent reservoir. The side strips should prevent the adsorbent layer from touching the walls and the thickness should be adapted to that of the layer. The solvent reservoir is then filled with about 25 ml of the appropriate solvent, which is subsequently sucked up by the filter paper strip and thus brought in contact with the plate. The solvent reservoir and the filter paper are pressed smoothly to the plate by means of two springy metal strips underneath the reservoir. This ensures good contact between the plate and the paper strip. Figure 2 shows the VP-chamber at work, with development in process horizontally.

The use of the VP-chamber permits vapor adsorption by the adsorbent from the underlying troughs. Thus, by filling the troughs with suitable liquid mixtures the vapor conditions can be programmed over the entire plate and optimal vapor gradients can be obtained because every desired polarity can be applied to the various parts of the plate via the vapor phase.

Materials. All parts of the VP-chamber are of chromium plated brass to ensure sufficient thermoconductivity. The troughs are made of flat-oval tubes, ranging from 6 mm to 17 mm in diameter with walls 1 mm thick. The tops are sawed off and a trough has a depth of about 12 mm. The troughs are kept together by side walls of 5 mm and by welds along the partition walls.

The thickness of the TLC glass plates may vary between 1 and 4 mm. Sagging plates or sheets or insufficiently flat plates can not be used.

Teflon (DuPont) or gasket plate are suitable materials for the side strips. Teflon is inert to most organic solvents but is somewhat slippery to use. Both are obtainable in several thicknesses and have good flexibility.

Thickness of the Side Strips. The thickness of the side strips plays an important role in the applicability of a certain

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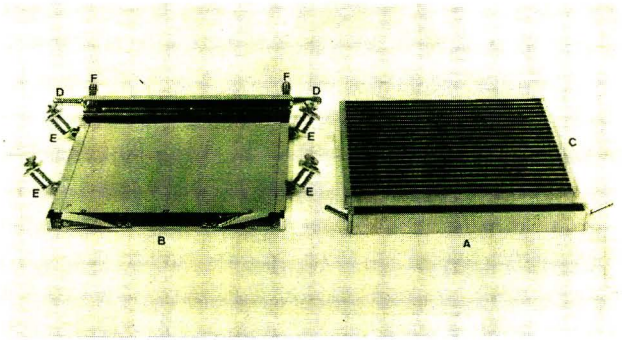


Figure 1. The vapor-programming chamber in parts

A, solvent reservoir; *B*, ground plate; *C*, trough chamber. The ground plate is equipped with a warm water tube (*D*), fixation clamps (*E*), and an internal tube system for water-thermostating, with the inlet and outlet visible at *F*

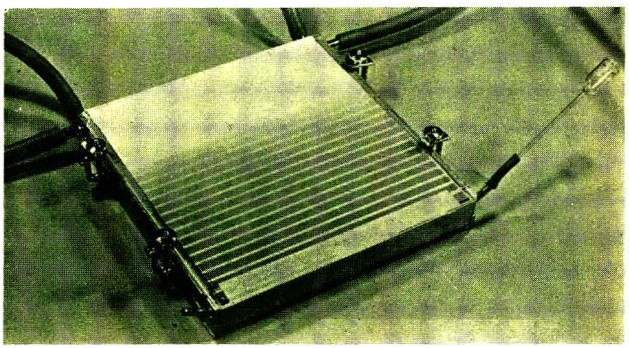


Figure 2. The vapor-programming chamber at work

The solvent makes the adsorbent transparent in relation to the underlying troughs and the filter paper strip becomes visible

gradient. It will be clear that because of the differences in liquid compositions in the troughs, strong vapor diffusion will occur if the space between the trough walls and the adsorbent is too large. These diffusions may well cause anomalies in the direction of solvent flow making the separation worthless. On the other hand the strips can not be too thin because the adsorbent must not touch the walls. If so, development stops immediately and the spots readily diffuse along the walls. It should be noted that most adsorbents swell more or less when wetted by the solvent. The rate of swelling is dependent on the polarity of the solvent and the thickness of the strips should be adapted to this phenomenon. In our experiments with layers of 0.25 mm good results were obtained with strips of 0.3–0.5 mm for solvents like hexane, benzene, chloroform, and ether, 0.5–0.8 mm for acetone, ethylacetate, and lower alcohols, whereas ammonia-containing solvents needed strips of 1 mm.

Saturation. To be sure that reproducible quantities of vapor are available for adsorption, it proved to be necessary to equilibrate the plate over the filled troughs for 10 minutes after it was fixed in position. During this period the small volumes over the troughs become almost saturated, resulting in a fixed amount of vapor available for adsorption. Not until after this saturation period is the solvent reservoir filled and development started.

The duration of the saturation period was experimentally established by comparing the reproducibility of the separations. If highly volatile components are used, the saturation period can be reduced to 5 minutes.

Temperature. It will be clear that constancy of room temperature, within ±1 °C, is required to obtain reproducible separations. However, in vapor-programmed TLC it was found that with higher room temperatures—over 22 °C—poorer separations were obtained in comparison with results at lower temperatures because the migration rates of the spots decreased markedly at higher temperatures. Presumably this is caused by too much adsorption of vapor which is then followed by condensation on the plate. Thus, solvent transport from the solvent reservoir will be diminished and, consequently, the migration rate of the spots will decrease.

Hence, cooling of the VP-chamber is necessary in those cases and we therefore have equipped the ground plate with an internal tube system to be linked with a water bath thermostat having a lower temperature than the ambient room temperature. The temperature of the cooling system, if kept constant, thus enables good control of the vapor adsorption rate. In our investigations at average room temperatures of 21 ± 1 °C optimal separations wereo btained with cooling temperatures between 18–20 °C.

Continuous Development. Very careful development is needed to separate closely related substances of almost identical polarity. In those cases a solvent with low polarity and a flat vapor gradient, especially on the lower parts of the plate, should be used. However, this implies a slow migration of the substances, with the spots still migrating at the lower parts of the plate when the solvent front has already reached the top of the plate. To overcome this difficulty the VP-chamber can be used for continuous development. The top end of the plate (1 cm) is not accompanied by an underlying trough, but lies 0.5 cm over a warm water tube. The solvent reaching the top will evaporate, thus allowing continuous solvent transport over the plate. With solvents of low volatility the warm water tube should be kept at about 50 °C. With highly volatile solvents, warming is not necessary for evaporation is fast enough.

When publishing chromatographic data obtained with continuous development, the length of a run can no longer be stated. In our opinion the development time should be given or a colored reference substance should be used, stating the required distance to be moved by this reference. The optimal development time or the optimal distance to be migrated by the reference substance can be established when searching for optimal vapor gradients. Furthermore the term R_f value requires a special definition for continuous development. We prefer to define the R_f values for continuous development as the distance moved by the substance divided by the distance of the starting point to the top of the plate.

The Construction of the Vapor Gradients. In vapor-programmed TLC one should use a running solvent of rather low polarity, giving the substances under investigation a small migration rate. The solvent may be single or multicomponent. The troughs underneath the starting points—*i.e.* the first two troughs—are filled with liquids having the same composition as the running solvent. Trough 3 is then filled with a liquid having a slightly higher polarity than the running solvent, trough 4 is filled with again a slightly higher polar liquid than in trough 3, etc. This can be done for example by using mixtures of two solvents, one polar, one nonpolar, with the mixtures having an increased percentage of the polar component. Thus, a stepwise vapor gradient would be obtained which can be compared to the continuous gradient in the unsaturated N-chamber.

However, one severe difficulty arises. Migration of the upper parts of a solute spot will be accelerated sooner than the lower parts and tailing will consequently result. Fortunately, this can be avoided by interspersing troughs with liquids of low polarity between the troughs containing the more polar mixtures, thus having a decelerating effect on the migration of the spots, particularly on the upper parts. If, for example, separation is required of chemically related sulfonamides ether can be used as the running solvent. With ether the substances should have R_f values between 0.05 and 0.25. Troughs 1 and 2, the former underneath the starting points, are also filled with ether. Trough 3 is then filled with ether–methanol 80:20, the methanol having an accelerating effect, troughs 4 and 5 are filled with ether (deceleration), trough 6 with ether–methanol 50:50, troughs 7 and 8 with ether, trough 9 with ether–methanol 20:80, etc. It can be seen that the polarity difference between the accelerating and decelerating troughs increases when going upward but this must be done to avoid tailing. In some instances it may be necessary to use three or more deceleration troughs after one acceleration trough.

We do not know how the process of deceleration and acceleration works in actuality; however, with the process compact spots can be obtained, without decreasing the improved separation efficiency. We presume the improvements not only to be caused by the acceleration forces but also by a more or less selective deceleration, with the less polar substances decelerated to a higher extent than the more polar substances.

It should be observed that the accelerating–decelerating stepwise gradient obtained in the VP-chamber is basically different from what is called gradient elution. The latter has a pushing effect on the spots, suitable for separations of substances showing great polarity differences. In the VP-chamber a pulling gradient is obtained which is more suitable for separations of closely related substances with small polarity variations.

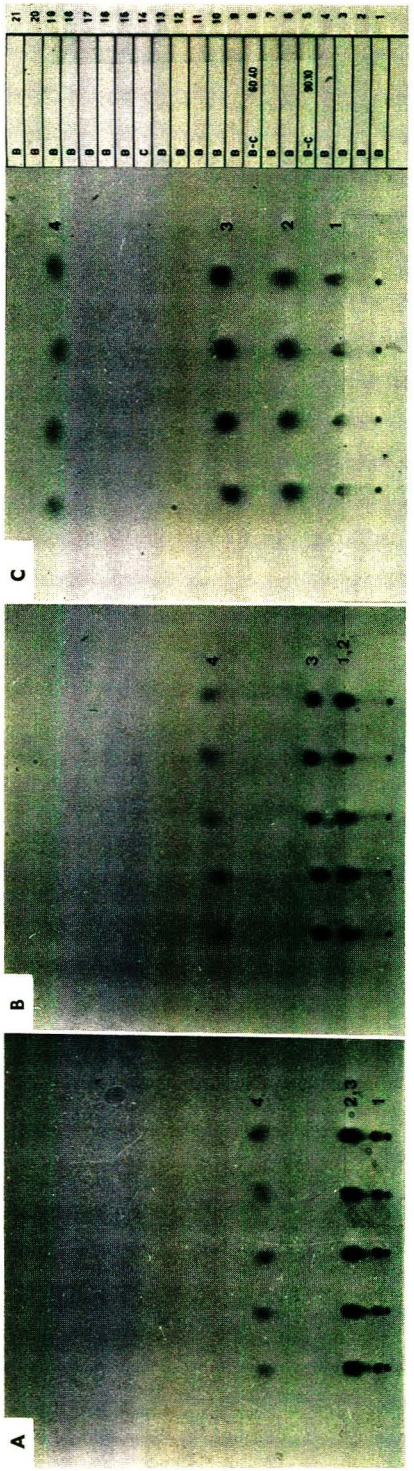


Figure 3. Improved separation of color dyes in the vapor-programming chamber as compared to classical development in saturated N-chambers

A: N-chamber, solvent benzene, temp 21.0 °C, rel. humidity 26%, development 36 min, saturation 45 min *B*: N-chamber, solvent benzene–chloroform 80:20, temp 22.0 °C, rel. humidity 30%, development 39 min, saturation 45 min *C*: VP-chamber, solvent benzene, temp 21.7 °C, rel. humidity 29%, development 110 min, saturation 10 min, strips 0.3 mm, cooling 19 °C; Code: *B* = benzene, *C* = chloroform. The position of the troughs and the liquid composition herein are given at the right
1 = indophenol, *2* = 4-nitroaniline, *3* = sudanred G, *4* = butter yellow. Plates: Silica gel GF 254, load: 20 μg

EXPERIMENTAL

Solvents and Standards. All solvent components were reagent grade (E. Merck). Solvent compositions are given by volume. Solutions of color dyes in benzene, 0.4% w/v and solutions of sulfonamides, 0.1% w/v in acetone, were used as test substances. All substances were 99.0% chromatographically pure. In case of sulfonamides, a reference substance (R), 4-nitroaniline, was run on each chromatogram.

TLC Apparatus and Procedures. Silica gel GF 254 (E. Merck) was used as adsorbent, 30 grams/60 ml distilled water to prepare 5 plates, 20 × 20 cm, for a layer thickness of 0.25 mm. After spreading (Desaga apparatus) the plates were air dried for 15 minutes, heated for 30 minutes at 110 °C in an oven with a fan, then cooled and stored in a desiccator. Samples, 0.003–0.005 ml, were applied with 0.01-ml micropipets (Desaga) with the aid of a hot air blazer, 2–2.5 cm from the bottom edge of the plate, and 1.5–2 cm apart. The side edges and the bottom edge were stripped 0.5 cm wide. After spotting, the plates were left in the ambient atmosphere for at least 15 minutes to ensure water adsorption in equilibrium with the ambient relative humidity.

The vapor-programming chamber was used for development, whereas normal tank chambers (N-chambers), 21 × 21 × 9 cm, were used as controls. In the latter the bottom edge of the plate was not stripped. The troughs of the VP-chamber were filled with about 5 ml each of the appropriate liquid mixture, then the plate was fixed in position. After a 10 minutes saturation period, the solvent reservoir was filled with 25 ml of solvent. N-chambers contained 100 ml of solvent and were saturated with solvent vapor by lining the inner walls with filter paper. After 45 minutes the plate was introduced and development started. The solvent was allowed to run 17 cm over the starting points. In the VP-chamber continuous development was applied, with the development time given in minutes. The composition of the liquids in the troughs is given in the photographic illustrations.

All experiments were made at 21 ± 1 °C and a relative humidity of 26–30% (color dyes) or 33–35% (sulfonamides). Within these ranges, reproducibility of the chromatograms was obtained.

Detection was carried out under UV light, 254 nm (Camag Universal lamp), followed by photography under two such lamps on Agfacolor CT 18 Diapositive film with an Asahi Pentax type SV camera with 49 mm UV ghostless filter, exposure 15 seconds, distance 70 cm, aperture 5.6.

RESULTS AND DISCUSSION

The separation of butter yellow, sudanred G, indophenol, and 4-nitroaniline in N-chambers with benzene as solvent is far from optimal as can be seen in Figure 3*A*. The spreading over the plate is poor and, furthermore, sudanred G and 4-nitroaniline do not separate. Changing the solvent to benzene–chloroform 80:20 does not improve the spreading or the separation significantly (Figure 3*B*). The spots run higher but the spreading remains almost the same. Sudanred G and 4-nitroaniline are separated but the latter now coincides with indophenol. The use of an unsaturated chamber would not provide better results, for the gradient is too flat for benzene–chloroform, and with more polar components the gradient becomes too steep.

With the aid of the vapor-programming chamber however, a much better separation is obtained (Figure 3*C*). Benzene is used as the solvent and decelerating liquid in combination with a simple benzene-chloroform vapor gradient. The four substances are clearly separated and the spots are not enlarged as compared to those obtained in the N-chambers. Furthermore, the entire plate is used to spread the spots. If necessary, the mutual distances between the spots can be

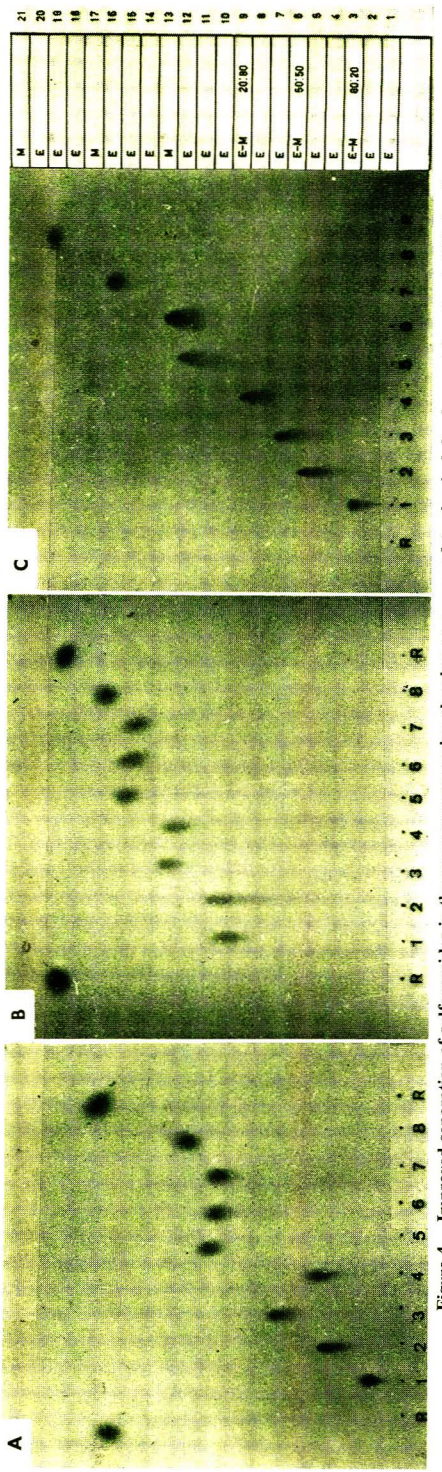


Figure 4. Improved separation of sulfonamides in the vapor-programming chamber as compared to classical development in saturated N-chambers

A: N-chamber, solvent ether–methanol 90:10, temp 21.5 °C, rel. humidity 35%, development 38 min, saturation 45 min *B*: N-chamber, solvent ether–methanol 80:20, temp 21.4 °C, rel. humidity 33%, development 39 min, saturation 45 min *C*: VP-chamber, solvent ether–methanol 95:5, temp 21.5 °C, rel. humidity 35%, development 63 min, saturation 10 min, strips 0.5 mm, cooling 19 °C, Code: *E* = ether, *M* = methanol. The position of the troughs and the liquid composition herein are shown at the right

1 = sulfaguanidine, *2* = sulfisomidine, *3* = sulfathiazole, *4* = sulfacetamide, *5* = sulfadimidine, *6* = sulfapyridine, *7* = sulfisoxazole, *8* = sulfanilamide. Plates: Silica gel GF 254, load 3 μg

changed by applying slightly different vapor gradients—*i.e.*, if a fifth component would be present between sudanred G and 4-nitroaniline, the migration rates of the three spots can be altered to obtain optimal separation and spreading. The time required for the separation in the VP-chamber is longer than in the N-chamber because of continuous development, but this is partially compensated for by the fact that less time is needed for the saturation of the VP-chamber.

Similar improvements could be obtained in the separation of a selection of sulfonamides: sulfaguanidine, sulfisomidine, sulfathiazole, sulfacetamide, sulfadimidine, sulfapyridine, sulfisoxazole, and sulfanilamide. These substances are poorly separated in N-chambers with ether–methanol 90:10 as solvent (Figure 4*A*). Changing the solvent ratio to ether–methanol 80:20 results in higher R_f values but the separation becomes worse (Figure 4*B*). With the VP-chamber all substances are clearly separated with the separation suitable for identification purposes. Ether–methanol 95:5 is used as solvent in combination with an ether–methanol vapor gradient and ether as decelerating liquid. The separation is shown in Figure 4*C*. It can be seen that now 70% of the plate is used to spread the spots. The over all time required for the separation in the VP-chamber is less than in the N-chamber because of the short saturation period.

The reproducibility of the separations in the VP-chamber is good. It will be obvious, however, that the factors involved in the reproducibility such as room temperature, cooling temperature, relative humidity, saturation, thickness of the strips and the layers, must be kept constant. Small variations in these parameters will have great influence on the vapor gradient and subsequently on the separation.

Thus, it becomes clear that vapor-programmed TLC offers new possibilities in the identification of closely related substances which are often inadequately separated by classical TLC techniques. Furthermore vapor-programmed development can also be valuable in preparative TLC, for the improved separations will allow more efficient isolations.

ACKNOWLEDGMENT

The author is grateful to J. Wijsbeek for skillful assistance, to J. S. Faber and D. A. Doornbos for discussions, and to A. Oosterhoff and G. P. Rijskamp for constructing the VP-chamber.

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2,6-Dichloroquinone 4-Chloroimide as a Reagent for Amines and Aromatic Hydrocarbons on Thin-Layer Chromatograms

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The range of utility of 2,6-dichloroquinone 4-chloroimide as a spray reagent for organic compounds on silica gel TLC plates was surveyed. A variety of intense colors was produced with primary, secondary, and tertiary aromatic amines, carbazoles, primary and secondary aliphatic amines, aromatic hydrocarbons, and an enol (2,4-pentanedione). Amides, amine oxides, and other oxidized nitrogen compounds gave weak or negative tests, as did aromatic compounds with electron attracting groups. The relationship of amine structure to color formation and the mechanism of reaction are discussed. The effects of some chromatographic variables on color formation with the reagent are reported. R_F values with neutral solvents are given.

2,6-DICHLOROQUINONE-4-chloroimide (*N*,2,6-trichloro-1,4-benzoquinone-4-imine) and 2,6-dibromoquinone-4-chloroimide, referred to as Gibbs (*1*) reagents, have been used as spot test and chromatographic spray reagents for phenols and certain other types of compounds. Dichloroquinone chloroimide has been recommended as a specific reagent for phenols (*2*, *3*), on the basis that the color reaction with phenols occurs after treatment of spot paper with ammonia, which is reported to cause the color produced by aromatic amines to disappear. The reagent has also been used for detection of antioxidants, including phenolic types and a few primary and secondary amines, on silica gel chromatographic plates (*4–6*). It was reported that the color produced with the amines persisted after spraying with borax solution, but that ammonia was not used because it darkened the silica gel background (*4*). 2,6-Dibromoquinone-4-chloroimide was investigated as a spray reagent for a variety of ring-substituted primary aromatic amines on silica gel (*7*); the colors changed, but did not disappear, upon treatment with ammonia. In a comparison of dichloroquinone and dibromoquinone chloroimides as reagents for substituted 3,4-methylenedioxybenzenes, the dichloro compound was reported to be superior (*8*). Some other types of compounds which have been detected by the quinone chloroimide reagents are pyridoxine (*9* and page 545 of ref. *3*), indole (*10*), hydrazones (*11*), and sulfur compounds (*12–14*).

Dichloroquinone chloroimide has now been found to give

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color reactions with an even wider range of organic compounds, including aliphatic amines and aromatic hydrocarbons, on silica gel plates. A survey of the range of utility of the chloroimide is reported here.

EXPERIMENTAL

Thin-layer chromatograms were made with Silica Gel G and Silica Gel $HF_{254+366}$, products of E. Merck. Except where stated otherwise, the aqueous silica gel slurry was spread by means of a straight-edge on frosted plates on decorative glass, in which the grooves, of rounded cross-section, were 12 mm wide and had a maximum depth of one mm. The coating was scraped from the ridges between the bands; a 15-mm strip along the starting edge of the plate was left unscraped so that the points for application of samples could be quickly located along the line at which scraping began. Plates were activated by heating for approximately one hour at 110 °C. Solutions containing 1–5 grams of the substance to be tested per 100 ml were spotted by means of 3 μl blood dilution pipets (Becton, Dickinson, and Co.), and developed for a distance of 10 cm in an ascending fashion, in a saturated chamber.

Dichloroquinone chloroimide (E. Merck) was sprayed as a 1% (w/v) solution in J. T. Baker reagent denatured alcohol, with an aerosol type sprayer (*15*). Solvents for development were reagent or spectro grade. Unless indicated, the compounds tested were standard grades from Aldrich Chemical Company, J. T. Baker, Eastman Kodak, Matheson Coleman and Bell, or Chem-Service, used without purification.

The following were furnished as samples by the companies listed. 4-Chloro-2-methylaniline, 2,4-dichloroaniline, and 2,6-dichloroaniline were obtained from American Hoechst Corp.; 2,6-dichloroaniline was recrystallized from methanol, mp 36.5–38 °C [reference (*16*) mp 39°]. *N,N*-Diethylaniline was obtained from Allied Chemical Corp. *N*-Cyclohexylaniline and *N*-cyclohexylpiperidine were obtained from Abbott Laboratories. *N,N*-Diethylhydroxylamine (85%) and diethylamine were supplied by Pennsalt Chemicals Corp. 6-Ethoxy-1,2-dihydro-2,2,4-trimethylquinoline (Santoquin) was furnished by Monsanto Co. *N,N*-Dimethylhexadecylamine *N*-oxide (40%) was obtained from Armour Industrial Chemicals Co.

N-Methylcarbazole was prepared from carbazole in 93% yield by reaction with sodium hydride in tetrahydrofuran, followed by methyl iodide. The product recrystallized from methanol melted at 90–92 °C [reference (*17*) mp 88°].

N-Methyldiphenylamine was prepared similarly from diphenylamine. The fraction boiling at 125.5–127.5 °C (4 mm) [reference (*18*), footnote 4 of page 458, bp 142° (11 mm)], n^{27} D 1.6167 [reference (*19*) $n^{24.6}$ D 1.6166], amounted to 82% of theory.

3-(*m*-Chlorobenzoyl)-*N*-methylcarbazole was prepared by a Friedel-Crafts type reaction, based on similar preparations by Buu-Hoï and Royer (*20*). To a solution of 3.6 grams (0.020 mole) of *N*-methylcarbazole and 4.0 grams (0.023 mole) of *m*-chlorobenzoyl chloride in 40 ml of benzene, stirred under nitrogen and cooled in an ice bath was added 3.4 grams (0.026 mole) of aluminum chloride in portions over a 15-minute period. The temperature remained around 5 °C and a red solid separated as the aluminum chloride was added. When the mixture (which had been let stand overnight) was decomposed with ice and dilute hydrochloric acid, 2.1 grams of white solid, mp 136–138 °C, separated. Another 1.4 grams, mp 130–136 °C, was obtained from the benzene solution and extracts; total yield 54%. Recrystallization from benzene and then from methanol (160 ml/gram; solution green when hot, pale yellow after cooling) gave colorless prisms, mp 139–141 °C. The infrared spectrum (Infracord Model 137, with Nujol and Halocarbon mulls and dioxane solution) in the carbonyl and aromatic C—H bending regions had peaks at 1620 (weak), 1600 (presumably C=O, but not strong), 755, 745, and 715 cm^{-1}.

Analytical Data. Calculated for $C_{20}H_{14}ClNO$: C, 75.12; H, 4.41; Cl, 11.09; N, 4.38; found by Spang Microanalytical Laboratory, Ann Arbor, Mich.: C, 75.04; H, 4.63; Cl, 11.11; N, 4.41.

The compound is very soluble in chloroform and 1,4-dioxane, soluble in benzene, acetone, and dimethylsulfoxide, but only slightly soluble in carbon tetrachloride, carbon disulfide, lower alcohols, glacial acetic acid, and acetonitrile when cold. Its solution in concentrated sulfuric acid is red, and addition of nitric acid changes the color to green (*21*). It appears on silica gel plates as a faint yellow spot with a yellow fluorescence under either 254 or 366 mμ illumination. The effects of other detection reagents on silica gel chromatograms of the compound were determined; Munier modification of the Dragendorff reagent (*22* and page 74 of ref. *9*), pale orange; sodium nitrite in 0.5*M* sulfuric acid (*23*), negative, but subsequent treatment with concentrated sulfuric acid gave a red-orange color; 3-methyl-2-benzothiazolinone hydrazone-ferric chloride (*24*), whitish on blue background; ferric chloride-ferricyanide (page 176 of ref. *9*), intense blue; 2,4-dinitrophenylhydrazine (page 87 of ref. *9*), faint pink. The location of the *m*-chlorobenzoyl group on the carbazole ring has been assigned on the basis of previous acylation studies of *N*-alkylcarbazoles (*20* and page 311 of ref. *21*).

N,N-Dimethylaniline-*N*-oxide and *N*-methyldiphenylamine-*N*-oxide were prepared by oxidation of the amines with peroxyacids; details will be reported along with a study of detection methods for *N*-oxides. Nitrosorbenzene was prepared from nitrobenzene by a commonly used procedure (*25*).

RESULTS

The colors produced by spraying the chromatograms of several classes of compounds with dichloroquinone chlorimide are listed in Table I, along with R_F values for compounds tested. A detailed description of the sometimes complex color changes was not attempted in the tables. In a number of cases a color which appeared immediately on spraying faded as the spray solution evaporated, but reappeared a few minutes later. In other cases no color was seen for several minutes; with dimethylaniline-*N*-oxide, the color appeared only after standing overnight.

Amines. All of the anilines with methyl and/or chlorine substituents gave positive tests. Not only primary (*7*) and secondary (*4–6*) amines, but also a variety of tertiary amines, including *N,N*-dimethylanilines with both *ortho*-, or the *para*- and one *ortho*-position blocked (see also julolidine) produced colors.

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Table I. Colors Produced with 2,6-

Compound	Color[a]	R_F Value: Cyclohexane	Benzene	Benzene–methanol (19:1)	Chloroform–methanol (6:1)
Substituted Anilines and Naphthylamines					
Aniline	V → Gr or Bl		0.14	0.3	0.6
o-Toluidine	R–V → B			0.45	
p-Toluidine	V → Br				0.65
2,4-Dimethylaniline	V → Br	0.01	0.07	0.3	0.7
2,6-Diethylaniline	V → B		0.2		
4-Chloro-2-methylaniline	V → Gr		0.2	0.4	
2-Chloro-6-methylaniline	V → B–V		0.4	0.65	
2-Chloro-4-methylaniline	V → R–Br		0.3	0.6	
2,6-Dichloroaniline	Gr–V	0.14	0.6	0.8	
2,4-Dichloroaniline	Gr–V		0.4	0.6	
2,4,6-Trichloroaniline	R–Br		0.6		
N,N-Dimethyl-*p*-phenylenediamine	Dark R–V			0.15	
Sulfanilamide	Pale V–Gr			0.	
N-Methylaniline	B–V → B		0.25	0.6	0.85
N-Ethylaniline	B–V → B			0.65	
N-Cyclohexylaniline	V → B		0.3		
Diphenylamine	V → B	0.04	0.6		
N-Methyl-*o*-toluidine	B			0.7	
N,N-Dimethylaniline	B		0.35	0.7	0.85
N,N-Diethylaniline	B		0.4	0.75	
N-Methyldiphenylamine	B	0.15	0.7		
Triphenylamine	B	0.2	0.75		
N,N-Dimethyl-*o*-toluidine	Pale G–B			0.7	
N,N-Dimethyl-*p*-toluidine	B[b]			0.7	
N,N,2,6-Tetramethylaniline	B–Gr	0.25	0.6	0.8	
N,N,2,4-Tetramethylaniline	Gr → Gr–G	0.03	0.18		
N,N-Diethyl-2,4-dimethylaniline	Gr[b]			0.75	
1-Naphthylamine	V → B				0.7
N,N-Dimethyl-1-naphthylamine	B			0.7	
4,4′-Bis(dimethylamino)benzophenone	Gr		0.02	0.35	0.7
N,N,N′,N′-Tetramethylbenzidine	G		0.04	0.45	0.85
Aromatic Nitrogen Heterocycles					
Pyridine	Gr (Very slowly)		0.04	0.2	0.7
2,4,6-Trimethylpyridine	Faint Gr				0.65
Quinoline	None			0.3	0.65
Isoquinoline	Faint Gr				0.6
Indole	R–V			0.6	
Carbazole	V	0.02	0.5	0.6	0.85
N-Methylcarbazole	V	0.1	0.7	0.8	0.95
N-Phenylcarbazole	V	0.06			
3-(*m*-Chlorobenzoyl)-*N*-methylcarbazole	None	0		0.6	0.85
2-Aminopyridine	Gr				0.45
2-Aminothiazole	R–Br				0.45
Partly Hydrogenated Nitrogen Heterocycles					
Indoline	B → V		0.08	0.4	
1,2,3,4-Tetrahydroquinoline	B → B–Gr, Y Cent		0.2	0.6	
6-Ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	B–Gr				0.8
Iminodibenzyl	B		0.6		
Julolidine	G		0.35		
Saturated Nitrogen Heterocycles					
2,6-Dimethylpiperidine	V–Gr				
2,2,6,6-Tetramethylpiperidine	V–Br				0.1[c]
N-Cyclohexylpiperidine	V–Br		0.04		0.2[c]
Piperazine	Dark Br				0.05
N-Ethylmorpholine	Faint Gr				

[a] Color abbreviations are B, blue; Bl, black; Br, brown; G, green; Gr, gray; O, orange; R, red; V, violet; Y, yellow.
[b] Two closely placed spots of different shade.
[c] Highly elongated spot.
[d] Average of four values.
[e] Average of five or more values.
[f] In Desaga dye mixture (E. Merck).
[g] CIBA dye (see pages 58, 114 of ref. *9*.)

Dichloroquinone 4-Chlorimide and R_F Values

Compound	Color[a]	R_F Value			
		Cyclohexane	Benzene	Benzene–methanol (19:1)	Chloroform–methanol (6:1)
Benzyl- and Cyclohexyl-amines					
Benzylamine	Br–V				
Dibenzylamine	Gr–V			0.25	0.5
Tribenzylamine	None				
Dicyclohexylamine	V–Gr				0.15[c]
Aliphatic Amines					
n-Octylamine	V → dark Br				0.1[c]
1-Methylheptylamine	Br				
2-Ethylhexylamine	R → Br–V				0.1[c]
t-Octylamine	V–Br				
Diethylamine	V–Br				0.05
Dibutylamine	R → Gr				0.15
Dimethyloctylamine	Faint			0.03	0.2[c]
Tributylamine	Pale P → Pale Gr				
Diethylenetriamine	Dark Br				0.04
Other Nitrogen Compounds					
Acetanilide	None			0.06	
N,N'-Diethyl-*N,N'*-diphenylurea	None				
N-Methyl-*N*-nitrosoaniline	Pale B–G			0.65	
Nitrosobenzene	None		0.45		
4-Nitrotoluene	None		0.55		
Azoxybenzene	Faint Y		0.5		
N,N-Diethylhydroxylamine	Olive G			0.2	0.55
Trimethylamine Oxide	None				0.03
N,N-Dimethylhexadecylamine Oxide	Faint Gr				0.16
N,N-Dimethylaniline Oxide	Faint Gr			0.01	0.11
N-Methyldiphenylamine Oxide	Faint B				0.35
Pyridine Oxide	Faint Gr			0.03	0.35
Trimethylanilinium Benzenesulfonate	Pale Br				0.02
10-Methylacridinium Chloride	Remained Y				
Oxygen Compounds					
Benzophenone	None		0.35		
Benzyl Alcohol	None		0.05		
Methyl *p*-Toluenesulfonate	None				
Sodium Benzenesulfonate	None				
Cholesterol	None				
Citral	None				
2,4-Pentanedione	Br		0.1	0.5	
Hydrocarbons					
Chrysene	Faint Br (slowly)	0.15			
Pyrene	Intense V	0.20[d]	0.75	0.75	
Anthracene	V → B	0.2			
Phenanthrene	O	0.25			
Naphthalene	Y → Y–O	0.3	0.75		
Fluoranthene	O	0.2	0.75		0.9
Fluorene	O				
p-Terphenyl	Faint	0.1			
Biphenyl	Y				
Bibenzyl	Faint Y	0.12			
Hexamethylbenzene	O → R–Br				
Mesitylene	Faint Y	0.35			
p-Cymene	Faint Y	0.45			
Diphenylfulvene	Pale O	0.12			
d-Limonene	None				
Reference Dyes					
Azobenzene	Slowly faded	0.07	0.66[e]		
4-Phenylazodimethylaniline (Butter Yellow)[f]			0.32[e]		
1-Phenylazo-2-naphthol (Sudan Yellow)			0.2	0.8	0.85
Sudan red[f]			0.11[e]		
Indophenol[f]			0.03	0.6[e]	0.85
Oracet orange 2R[g]			0.08	0.4[e]	0.69[e]
Oracet red 2G[g]				0.04	0.53[e]
Orasol scarlet 2B[g]				0.	0.17[e]
Rhodamine B				0.	0.07

Whereas indole and carbazole compounds were detected readily, except 3-(*m*-chlorobenzoyl)-*N*-methylcarbazole, tests with aromatic six-membered heterocycles were weak.

A variety of primary and secondary aliphatic amines and cyclic compounds without aryl groups attached to nitrogen gave good positive tests. Most of the tertiary amines of this type, however, gave faint colors.

Other Nitrogen and Oxygen Compounds. Most amine oxidation products, salts, and amides gave weak colors with dichloroquinone chloroimide. Several oxygen-containing aromatic compounds were included to evaluate the effect of electron attracting groups on an aromatic ring (for example, benzophenone in contrast to diphenylamine and the hydrocarbon bibenzyl); all gave negative results. 2,4-Pentanedione, an aliphatic compound which tends to exist largely as an enol (*26*) gave a distinct positive test.

Hydrocarbons. Condensed polynuclear hydrocarbons gave yellow, orange, or violet spots. Chrysene and *p*-terphenyl were tested as saturated benzene solutions. Their low solubilities may be at least partly responsible for the weak tests observed. The nonaromatic unsaturated cyclic hydrocarbon *d*-limonene gave a negative test.

R_F Values. The results represent a comparison of organic compounds of a wide range of structural types and polarity, developed with neutral solvents. Because of the range of polarity of the compounds, several solvents were used. Reference dyes were used on all plates, and their observed R_F values have been included after the other compounds. For compounds such as the dyes, which were examined on several different plates with different batches of solvent, average values are reported to two decimal places. In other cases R_F values above 0.2 have been rounded off to the nearest 0.05.

Whereas alkylamines, cyclohexylamines, and piperidines tended to give elongated spots which did not completely separate from the origin, anilines, aromatic heterocycles, dibenzylamine, and aromatic amine oxides gave well defined, somewhat elongated spots separate from the origin with neutral methanolic solvents. The amines and amine oxides which gave negative tests with the chloroimide were detected by means of the Munier modification of the Dragendorff reagent (*22*).

The sequence of R_F values was similar over a wide range of solvent polarity. The tertiary aromatic amines dimethylaniline, tetramethylbenzidine, and bis(dimethylamino)benzophenone, however, moved ahead with the hydrogen bonding solvents, whereas aniline, itself, assumed a lower relative position in the sequence.

Effect of Chromatographic Variables: Amount of Compound. A limited study of the effect of variables on the chromatographic results was made. The sensitivity of detection was evaluated by spotting solutions on 0.25-mm layers of Silica Gel G deposited on flat glass plates with a Desaga applicator, development, and spraying. Pyrene and trichloroaniline gave distinct spots at a concentration of 15 μg in 3 μl, the lowest concentration used, and *N,N*-dimethylaniline and octylamine gave distinct spots at 4 μg in 3 μl.

In the same experiments with 0.25-mm coatings, the effect of amount of dichloroquinone chloroimide spray reagent was investigated qualitatively. No significant difference was noted between a very light spray and a heavy spraying of pyrene, trichloroaniline, dimethylaniline, and octylamine spots.

Coating Materials. Aromatic amines and other aromatic compounds not showing strong fluorescence were examined on Silica Gel $HF_{254+366}$ so that the spots could be located by ultraviolet absorption. Fluorescent polynuclear hydrocarbons and aliphatic amines were examined chiefly on Silica Gel G. Dichloroquinone chloroimide spraying on the two coating materials produced the same or similar colors with aniline, *N,N*-dimethylaniline, *N,N*,2,4-tetramethylaniline, 2,6-dichloroaniline, diphenylamine, triphenylamine, dibenzylamine, pyrene, fluoranthene, and fluorene. In one experiment with Anasil B, a silica gel containing magnesium oxide, activated at 110 ° C for 1 hour, developed with chloroform–methanol (6:1), the R_F values of 2,4-dimethylaniline, dibenzylamine, and Oracet Red 2G were higher than on Silica Gel G, but the colors produced by spraying 2,4-dimethylaniline, dibutylamine, dibenzylamine, piperazine, and pyrene were essentially the same.

Effect of Base Treatment. The effect of weak bases was of particular interest because exposure of the sprayed plates to ammonia fumes has been used in detection of phenols, and solvents containing ammonia or volatile amines are commonly used in developing more basic amine spots. As noted by Seher (*4*), exposure to ammonia fumes was found to darken the background. The colors from triphenylamine and anthracene faded upon exposure to ammonia; those from 2,4-dimethylaniline, fluorene, and fluoranthene were intensified. The colors from aniline, diphenylamine, and piperazine were largely unchanged by ammonia treatment, whereas those from *N*-methylcarbazole, dibutylamine, dibenzylamine, and pyrene underwent changes, but did not disappear.

It was likewise found that developing solvents containing ammonia or diethylamine caused darkening of the background of sprayed plates when the plates were allowed to dry in the air for 15–30 min before spraying.

DISCUSSION

Because of the wide range of compounds detected by dichloroquinone chloroimide, considerable caution should be used in employing the reagent to confirm specific classes of compounds, such as phenols, in a mixture of uncertain composition.

With regard to the nature of the colors produced with quinone chloroimides, the wide range of compounds which develop colors suggests that more than one process may be responsible. In the earliest work with dibromoquinone chloroimide, the indophenol which results from its reaction with phenol was isolated (*27*), and later workers (*1–3*) have commonly interpreted color formation in terms of indophenol formation. In other studies the products of reaction of dichloroquinone chloromide with phenols have been isolated (*28*), and the kinetics of reaction of dibromoquinone chloroimide with phenol have been investigated (*29*). On the other hand, the colors produced with primary aromatic amines have been discussed in terms of dibromoquinone chlorimide acting as a pi-electron acceptor (*7*). The variety of compounds which give positive tests, including hexamethylbenzene, 2,4-disubstituted dimethylanilines, and aliphatic amines, indicate that charge-transfer complexes may well be formed, with the compound tested using either pi or unshared electrons. Some of the color changes which occur after spraying may result from successive reactions. A quinone chloro-

(26) G. W. Wheland, "Advanced Organic Chemistry," 3rd ed., John Wiley and Sons, New York, N. Y., 1960, p 685.

(27) R. Mohlau, *Ber.*, **16**, 2843 (1883).

(28) H. Inoue, Y. Kanaye, and Y. Murata, *Chem. Pharm. Bull.* (Tokyo), **7**, 573 (1959); *Chem. Abstr.*, **54**, 19559 (1960).

(29) H. D. Gibbs, *J. Phys. Chem.*, **31**, 1053 (1927).

imide could also act as an oxidizing agent, and perhaps as a chlorinating agent.

A wide range of aromatic amines reacts with quinone chloroimides; the reaction is affected little by methyl or chlorine substituents. A carbonyl group, in 4,4′-bis(dimethylamino)benzophenone, and a sulfonamido group, in sulfanilamide, did not prevent color formation. It was previously shown (*7*) that dibromoquinone chloroimide gave color reactions with a variety of primary arylamines having two bromines or two or three chlorines on the ring; nitroanilines gave weak colors which were intensified by ammonia treatment. It was stated that attempts to use dibromoquinone chloroimide for the differentiation of chloronitro-, dichloronitro-, and dinitro-anilines, as well as halo- and nitro-benzene derivatives were without success. In the present work nitrotoluene gave negative results. Thus, it appears that as long as an amino group is present on the ring, many compounds with halogens alone, or with one nitro group or similar electron attracting group, may be detected. On the other hand, *N*-acyl groups, in acetanilide and diethyldiphenylurea, and a *m*-chlorobenzoyl group on a carbazole ring, prevent color formation.

With regard to steric effects, methyl groups at both *ortho*-positions, which can reduce interaction of the electrons on nitrogen with the ring of dimethylanilines by decreasing coplanarity (*30*), do not greatly affect reaction. Although the results were mostly poor with aliphatic tertiary amines, reaction of primary amines was not affected by branching of the alkyl group. Likewise, the hindered 2,2,6,6-tetramethylpiperidine reacted well.

The poor results with *N*-oxides do not correlate in a simple way with basicity. Trimethylamine oxide and dimethylaniline oxide are bases (reacting at oxygen) of strength comparable with anilines (*31*). Because conversion of an aniline to an *N*-oxide makes the unshared electrons of nitrogen no longer available to the aromatic ring, it would be expected that both indophenol formation and pi-complexing would be diminished; such an effect may be responsible for the low reactivity of acetanilide. Pyridine oxide, however, which is more reactive than pyridine toward electrophilic reagents (*32*), produced a weak color reaction, as did pyridine.

Pyrene not only produced an intense color with dichloroquinone chloroimide, but had such a strong fluorescence that it could be seen against the fluorescing agents in the Silica Gel $HF_{254+366}$ coating. It was used, therefore, in the form of a solution containing 2 grams per 100 ml of benzene, as a reference compound in the development of weakly adsorbed aromatic amines with solvents of low polarity. The purest grade (No. 3627) from Eastman Kodak and a practical grade from Chem-Service gave the same results.

A recent communication (*33*) stated that dibromoquinone and dichloroquinone chloroimides decomposed exothermally on heating, and that the former exploded on a reagent shelf. It is recommended, therefore, that the compounds, which have been in use as analytical reagents for many years, be handled and stored with caution. In a personal communication, Mr. Taranto has suggested storage of small quantities in corked (not screw-capped) bottles in a steel safety jacket in a refrigerator. Dibromoquinone chloroimide has also been stated to be less stable on storage if moist (*1*).

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(31) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London, 1965.
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Resolution and Optimization in Gel Filtration and Permeation Chromatography

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Here we present a theoretical study of resolution in exclusion chromatography and the factors which influence it. Optimum parameters are suggested on the basis of general chromatographic theory and a recent entropy-based formulation for partition coefficients. It is concluded that highest resolution and speed will be associated with long, narrow columns with fine particles and high pressure drops. Temperature and solvent should be chosen to minimize viscosity. Pores should be relatively small, leading to early elution, and their total volume should be large. Grounds are presented for optimizing pore shape as well as size. Finally, these results are used to predict the size and molecular weight increments needed for satisfactory resolution in columns of different efficiencies.

GEL FILTRATION (*1*) and permeation (*2*) chromatography have established themselves as exceedingly useful techniques in separating macromolecules. Their relative usefulness derives more from the inherent difficulty of large-molecule chromatography (*3*) than it does from their basic separating efficacy, which is rather bad compared to other chromatographic methods. Here we examine the latter aspect, with the view that resolution must be improved and optimum conditions established if these methods are ever to make the highly refined separations which are so needed in the next stage of macromolecular studies. Since gel filtration and permeation chromatography depend on the same underlying phenomena, we group them both together for theoretical purposes, and lend them the common title, "exclusion" chromatography.

In an earlier paper (*4*), the total number of peaks resolvable by exclusion chromatography was deduced. By contrast to total peak capacity, we focus on the resolution of close-

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(2) J. C. Moore, *J. Polymer Sci., Part A*, **2**, 835 (1964); *Chem. Eng News*, **40**, 43 (Dec. 19, 1962).
(3) J. C. Giddings, *J. Gas Chromatogr.*, **5**, 413 (1967).
(4) J. C. Giddings, ANAL. CHEM., **39**, 1027 (1967).

lying pairs of peaks to arrive at criteria for their adequate and optimum separation. The present status of optimization studies has been well reviewed by Johnson *et al.* (*5*).

Partition coefficients in the exclusion methods are determined by the configurational entropy change which accompanies the transfer of solute into the porous particle (*6*). This entropy may be written

$$\Delta S^0 = \Re \ln \frac{\Omega}{\Omega_0} = \Re \ln \Omega_f \qquad (1)$$

where $\Re$ is the gas constant and $\Omega_f = \Omega/\Omega_0$ is the fraction of, for example, rotational and translational states remaining free in the pore network—*i.e.*, that fraction *not* lost because of interference at the pore walls. The partition coefficient, K, equals Ω_f. The latter was calculated as a function of pore and molecule size for several geometrical models of pores and molecules. As expected, K and Ω_f are determined by the relative size of molecule and pore.

The dominance of entropy effects in exclusion chromatography leads to certain unique characteristics not previously recognized. In particular, the role of solvent and temperature is unlike that applying to the usual enthalpy-dominated retention in chromatography, and leads to different (and simpler) criteria for optimization. The choice of pore size also presents rather special problems. These matters are explored below.

The resolution of close-lying peaks in chromatography is given rather generally by the approximation (*7*)

$$R_s = \frac{\sqrt{N}}{4} \frac{\alpha \Delta K}{1 + \alpha K} \qquad (2)$$

where $\alpha = V_s/V_m$

in which N is the number of theoretical plates, ΔK is the difference in partition coefficients, K_{II}–K_I, for the two species, and V_s/V_m is the ratio of mobile phase (interparticle) volume to stationary phase (intraparticle or pore) volume in an exclusion column. Quantities N and K represent average values for the two species.

If a certain degree of resolution, R_s, is required (usually $R_s \sim 1$), the increment in partition coefficients must be

$$\frac{\Delta K}{K} \geqq \frac{4R_s}{\sqrt{N}} \frac{1 + \alpha K}{\alpha K} \qquad (3)$$

as can be deduced from Equation 2. Because $(\Delta K/K) \sim (K_{II}/K_I) - 1$, and because $\Omega_f = K$, the fundamental requirement for resolution is that the ratio Ω_{fII}/Ω_{fI} must be a certain minimum in accord with

$$\frac{\Omega_{fII}}{\Omega_{fI}} \geqq 1 + \frac{4}{\sqrt{N}} \frac{R_s}{\alpha K} \frac{1 + \alpha K}{\alpha K} \qquad (4)$$

The significance of this expression in separating molecules depends on the basic relationship between Ω_f and molecular size and shape. This relationship, while differing somewhat between various pore models, can be approximated by the random-plane model (below) of a pore network which yields (*6*)

$$\Omega_f = K = e^{-cL} \qquad (5)$$

where L can be interpreted as a mean diameter or length for the molecule (as will be discussed), or as any arbitrary length parameter for geometrically similar molecules. Quantity c, inversely proportional to pore size, is constant for a given porous material. Substitution of Equation 5 into 4 leads to

$$\frac{\Delta L}{L} \geqq \frac{\ln \left(1 + \frac{4R_s}{\sqrt{N}} \frac{1 + \alpha K}{\alpha K}\right)}{\ln K} \qquad (6)$$

where $\Delta L = L_{II} - L_I$. (All incremental quantities will be expressed as that for trailing peak II minus that for leading peak I, even though some such quantities like ΔL are negative.) Equations 4, 6, and related expressions can be used to deduce minimum resolution requirements, as will be shown.

A numerical example will help illustrate the magnitude of terms in fundamental Equation 4. Not uncommonly we might find values in the vicinity of $N \sim 1000$, $\alpha \sim 1$, $K \sim 1/2$, and $R_s \sim 3/4$. In this case,

$$\frac{\Omega_{fII}}{\Omega_{fI}} = \frac{K_{II}}{K_I} \sim 1.3 \qquad (7)$$

This ratio is sufficiently large that some error in our results can be anticipated because we assume the peaks to be close-lying. One can avoid the latter assumption in a straightforward mathematical manner, but the gain in accuracy is not ordinarily worth the additional complexity of the results. The simpler and more direct approach used here is accurate enough to establish valid guidelines for most laboratory work, and is particularly applicable to well designed columns with large plate numbers.

NATURE OF OPTIMUM PARAMETERS

The resolution expression, Equation 2, can be broken into two parts: the part that depends on column efficiency, $N^{1/2}/4$, and the part that depends on equilibrium and retention, $\alpha\Delta K/(1 + \alpha K)$. Most column and operating parameters which influence column efficiency but not retention should be optimized by much the same criteria applicable to other forms of chromatography (*7*). Any parameter which strongly influences relative retention must be fixed by unique criteria because the retention mechanism is unique.

In the former category are such common parameters as column length, column diameter, flow velocity, pressure and pressure drop, particle size, and dead volume. As emphasized previously (*7*, *8*), optimum conditions are most likely to entail long, narrow columns packed with fine particles and an absolute minimum of dead pockets and free connections. Flow velocity and pressure drop should be fairly high. Presently the latter is often restricted by the softness and, thus, the variable compactness of ordinary gel beads. This poses a serious dilemma because the success of the long column–high velocity–fine particle combination hinges crucially upon high pressure drops. If "flexible" gel particles cannot be adapted to these conditions, it is probable that superior results will eventually be achieved with rigid porous particles, such as the porous glasses, which can be used in high-pressure columns.

ROLE OF SOLVENT AND TEMPERATURE

Solvent (mobile phase) properties, within limits, mainly influence efficiency too. (In this sense they are analogous to gas properties in GC, but are not comparable to any

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(6) J. C. Giddings, E. Kucera, C. P. Russell, and M. N. Myers, *J. Phys. Chem.*, in press.
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(8) J. C. Giddings and K. L. Mallik, ANAL. CHEM., **38**, 997 (1966).

conventional form of liquid chromatography.) The limits to this categorization are important and must be made clear: Changes in solvent properties must not cause precipitation, adsorption, or changes in molecular or pore dimensions. Within these limits, one may beneficially choose a solvent system with low viscosity and high diffusivity.

The role of temperature in the exclusion methods of chromatography is much like that of the solvent. Within the same limits outlined for solvent properties, temperature changes do not influence retention (*9*). This result is indeed unique, and is not characteristic of any other form of chromatography, gas or liquid. This is a consequence of the dominant role of entropy, as opposed to enthalpy, in partitioning equilibrium, as discussed. This can be best illustrated by substituting Ω_f for K in Equation 2:

$$R_s = \frac{\sqrt{N}}{4} \frac{\alpha\Delta\Omega_f}{1 + \alpha\Omega_f} \tag{8}$$

Because the fraction of free or allowed states, Ω_f, is a function only of molecular and pore dimensions, this is temperature independent as long as dimensions remain constant and sorption is absent.

The lack of temperature dependence means that a reduction in temperature has no beneficial effect on selectivity, contrary to most other forms of chromatography. The only role of temperature derives from its influence on the number of theoretical plates, N. If it is assumed once again that all dimensions remain constant, temperature affects only one basic parameter—diffusivity—out of all those which help determine plate height. Because mobile and stationary phases are composed of the same liquid, changes only in the diffusion coefficient, D_m, for solute in the mobile phase determine the temperature dependence of N.

PLATE HEIGHT AND OPTIMUM VELOCITY, TEMPERATURE, AND SOLVENT

A plot of reduced plate height, $h = H/d_p$, against reduced velocity, $\nu = d_p v/D_m$, yields curves roughly in superposition for all chromatographic systems (*7*, *10*). (By contrast, a plot of ordinary plate height, H, *vs.* linear velocity, v yields curves displaced from one another by factors of up to 10^6.) This correspondence principle, while mainly used to relate diverse chromatographic systems, can also predict the gradual change in optima caused by changes in, for example, temperature, and solvent.

The common curve alluded to above can be represented by (*7*)

$$h = \frac{2\gamma}{\nu}(1 + \beta_s) + \Omega'\nu + \Sigma \frac{1}{{}^1/_2\lambda_i + 1/\omega_i\nu} \tag{9}$$

where γ, ω_i, and λ_i are structure-retention parameters (related mainly to packing geometry) which can vary moderately from column to column. Quantity β_s is a term for longitudinal diffusion in the stationary phase; it depends upon R and the ratio of diffusion coefficients in the two phases, D_s/D_m, along with geometrical factors. Quantity Ω' accounts for stationary phase mass transfer and, in the partition forms of chromatography, is also a function of D_s/D_m and structural parameters. The "eddy" diffusion coefficient, λ_i, depends primarily on packing structure.

The "universal" curve concept is an approximation in most cases, if packing variations, structural differences in support particles, and the ratio D_s/D_m are ignored. (Neither does it allow for high-velocity turbulent flow.) If chromatographic experiments are conducted with the same column, and changes are allowed only in the temperature or solvent, all factors except D_s/D_m and retention will remain fixed and the h *vs.* ν curves will approach one another even more closely.

Exclusion chromatography is again unique because changes in temperature (or solvent) alter neither the D_s/D_m ratio nor retention. Therefore, h *vs.* ν curves obtained at different temperatures (or with different solvents) should coincide rather exactly.

This coincidence means that the same minimum value of h would be found at all temperatures. Because particle diameter d_p remains essentially constant, $H_{\min}$ would, therefore, be independent of temperature, and a velocity-optimized column would have the same number of plates at any temperature (or with any solvent).

While it is generally important to maximize resolution, as above, a more practical optimization in liqiud chromatography (which is inherently slow compared to GC) is that which minimizes the time required to achieve a given resolution. For this reason, laboratory velocities generally exceed those corresponding to $H_{\min}$, even though resolution is lost.

We may now assume that suitable conditions (which may be based on resolution, speed, or other criteria) for the operation of a column at a given temperature have been determined, and inquire about the possible role of temperature in speeding up the operation. Clearly a temperature increase will increase D_m. If flow velocity is increased by a corresponding amount, ν and resolution will remain unchanged (because ν is proportional to v/D_m), but there will be faster elution. In general, then, elution time is inversely proportional to D_m. If we consider liquid diffusion an activation process, we find the following relationship between elution time and temperature:

$$t = C' \exp(W_l/\mathcal{R}T) \tag{10}$$

where W_l, the activation energy, is 2.5 kcal/mole for many common liquid solvents (*11*). This corresponds to a 10 to 25% reduction in elution time for each 10 °C temperature rise.

The pressure drop in our variable-temperature column will be determined both by viscosity and flow velocity. In most liquid systems viscosity is inversely proportional to D_m. Consequently, viscosity would decrease as flow is made to increase (to keep pace with D_m); one effect would be exactly balanced by the other, making it possible to use a fixed pressure drop as temperature and speed increase.

The above principle is valid for changes in solvent as well as temperature if, as stressed before, adsorption and dimensional changes do not occur. Generally, we may state that speed increases in inverse proportion to viscosity, whether viscosity is manipulated thermally or chemically. Viscosity is the critical parameter and, within the stated limits, should be minimized.

An interesting prediction results from the above arguments. Chromatograms showing concentration *vs.* elution volume should be identical for a given pressure drop applied

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to a given column, even with arbitrary variations in solvent and temperature. The chromatograms showing concentration *vs.* time however, would stretch out in proportion to viscosity.

All the above arguments apply solely to entropy-controlled exclusion mechanisms. In some systems we may expect a mixture of entropy and enthalpy (adsorption, two-phase partitioning, etc.) effects. Enthalpy effects have been demonstrated in certain gel systems by the excessive retention of some components (*12*). In any such mixed case we must write the elution volume as a sum of terms corresponding to the different retention mechanisms (*13*):

$$V = V_m + KV_s + \Sigma K'V_s' \qquad (11)$$

The last (summation) term accounts for various enthalpic effects. Both kinds of effects are reasonably well understood, thus making it possible to synthesize an approximate description of mixed sorption-exclusion chromatography. The principal uncertainty revolves around the question of whether some molecules are kept away from "sorption" sites by the exclusion phenomenon; in this case, the extent of the sorptive phase or surface, V_s', is a function of molecular dimension—roughly, a function of K.

THEORY OF OPTIMUM PORE SIZE

Retention in the idealized exclusion column is a function only of the dimensions of the pores and of the molecules; temperature, solvent, sorption, and related effects are not directly involved. If the separation problem revolves around a certain group or pair of molecules of given size, the pore dimensions will be the only retention-controlling variables.

The specific effect of changes in pore size and shape hinges on the precise relationship between K and the dimensions of both molecules and pores. Generally we can assume that K is some function of a characterizing group of size and shape parameters: the L_j's for molecules and the d's for pores—*i.e.*,

$$K = K(L_1, L_2, \ldots L_m;\ d_1, d_2 \ldots d_n) \qquad (12)$$

The increment ΔK in the partition coefficient of close-lying molecules can be approximated by

$$\Delta K = \sum_{j=1}^{m} \frac{\partial K}{\partial L_j} \Delta L_j \qquad (13)$$

This can be substituted directly into the resolution expression, Equation 2. The latter can be optimized with respect to the pore dimensions by making $\partial R_s/\partial d_i = 0$ for all i. This gives n equations of the form

$$(1 + \alpha K) \sum_{j=1}^{m} \frac{\partial^2 K}{\partial d_i\, \partial L_j} \Delta L_j - \alpha \frac{\partial K}{\partial d_i} \sum_{j=1}^{m} \frac{\partial K}{\partial L_j} \Delta L_j = 0 \qquad (14)$$

whose solutions are the n optimum pore-size parameters, d_i.

The above treatment is not presently applicable in all its generality because the precise form of K has not been obtained for arbitrary systems. However, the exact theory which has been worked out for a number of models provides broad direction (*6*).

Model calculations indicate that a single length parameter will reasonably characterize a molecule's partitioning behavior irrespective of molecular shape. In earlier work, the radius of gyration (*14*) was suggested as a characteristic length; more recently, the hydrodynamic radius has been proposed (*15*). Our calculations for rigid macromolecules show that the former is the best of the two, particularly in providing a common denominator for comparing rod-shaped and spherical molecules. However, the best single parameter is apparently the mean external diameter, $\bar{L}$. Quantity $\bar{L}$ is obtained by noting the maximum length of the molecule projected along a given axis, then averaging this length over all possible molecular rotations. This is the only proposed length parameter which applies rigorously to all arbitrary molecular shapes within any chosen model of the pore network. In our case, the model network was created by intersecting random planes (the "random-plane" or "box-pile" model), but even in other networks $\bar{L}$ has been shown to characterize most reasonably diverse molecules (*6*).

The problem of characterizing "pore size" is perhaps even more difficult. For one thing molecules, even complex ones, are limited in extent, whereas a pore is part of a continuous, interconnected network which must be considered as a whole. There is no way known to characterize rigorously a pore network's partitioning behavior short of describing its detailed geometry. Experimental pore size distribution, while not uniquely specifying geometry, may approximately characterize exclusion partitioning (*16*) if some assumption is made about pore shape. Until better theoretical and experimental tools are available for studying the effects of pore geometry, pore size is perhaps best characterized by the simplest and most direct of experimental parameters, surface area per unit pore volume, s. Beyond the advantage of simplicity, s is a choice made more rational by the realization that exclusion stems from the restraints imposed by pore surfaces on molecular motion (*6*). Our previous work with various models confirms the broad correlating ability of quantity s.

If, then, we reduce the multiplicity of parameters in Equation 12 to just two, $\bar{L}$ and s, we can write $K = K(\bar{L}, s)$, and the optimum pore size, which is proportional to s^{-1}, is obtained from

$$(1 + K\alpha) \frac{\partial^2 K}{\partial s\, \partial \bar{L}} - \alpha \frac{\partial K}{\partial s} \frac{\partial K}{\partial \bar{L}} = 0 \qquad (15)$$

as opposed to the more involved group of expressions represented by Equation 14.

OPTIMUM PORE SIZE AND RETENTION BASED ON GEOMETRIC SIMILARITY

For the moment, our hypothetical problem will be the separation of two geometrically similar molecules—*e.g.*, spheres. We are to choose a pore network from a group having the same shape characteristics, but differing in pore size. Any geometric theory of partitioning (including the earlier mentioned entropic theory) in such geometrically similar systems will conclude that K is a function of only one dimensionless parameter, x, the ratio of molecular size to pore size. It does not matter which measure of size is taken so long as the measure is consistent in the series.

If we extend the theory, if only in approximation, to molecules and pore networks not exactly geometrically

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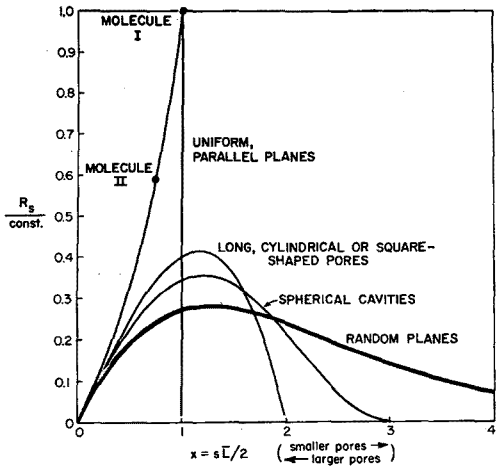


Figure 1. Relative resolution for two unequal spherical molecules in different kinds of pore networks and at various pore sizes (proportional to s^{-1})

similar, we should choose the most "universal" measures of size possible. In view of the earlier discussion, we will henceforth use $\bar{L}$ and s as parameters characterizing molecule and pore size, respectively, and therefore give x the meaning

$$x = {}^1/_2 s\,\bar{L} \tag{16}$$

Our theoretical development will not depend on these particular choices, but our calculated examples will. [Surface area, s, appears in the numerator because its reciprocal, s^{-1}, is directly proportional to pore size. The coefficient, $^1/_2$, is an arbitrary constant. We note that quantity $\bar{L}$ for spherical molecules is equal to the sphere diameter; for thin-rod molecules it is one-half the rod length, etc. (6).]

Once again we start with the basic resolution expression, Equation 2. We can write

$$\Delta K = \frac{dK}{dx}\frac{\partial x}{\partial \bar{L}}\Delta\bar{L} = x\frac{dK}{dx}\frac{\Delta\bar{L}}{\bar{L}} \tag{17}$$

The latter equality makes use of Equation 16.

With this expression, resolution becomes

$$R_s = \alpha\frac{\sqrt{N}}{4}\frac{\Delta\bar{L}}{\bar{L}}\frac{x\,dK/dx}{1+\alpha K} = \frac{\sqrt{N}}{4}\frac{\Delta\bar{L}}{\bar{L}}\frac{d\ln(1+\alpha K)}{d\ln x} \tag{18}$$

As an initial observation about the above expression, we note that resolution increases with α ($= V_s/V_m$)—*i.e.*, the optimum α is the largest possible value. Because the porosity of randomly packed spheres is about 0.40, α could be no larger than 0.6/0.4 = 1.5 in most present systems even if the pore walls were infinitely thin and the solid portion of the porous particle therefore vanishingly small. More typically, about one third of the particle may be assumed solid, leading to $\alpha \cong 1$.

There may be some virtue in partially compressing or fusing together such porous particles (carefully avoiding the destruction of pores) to increase α. This would aid total peak capacity as well as the resolution of individual pairs.

For the following examples we will assume α to be unity (slight variations from unity will have only a minor effect on our conclusions). We will compare hypothetical columns, all with the same efficiency, N, each attempting to separate a pair of molecules with constant $\Delta\bar{L}/\bar{L}$. Therefore, we will compare the magnitude of the function

$$\frac{R_s}{const.} = -\frac{x\,dK/dx}{1+K} \tag{19}$$

where

$$const. = -\sqrt{N}\,\Delta\bar{L}/4\bar{L} \tag{20}$$

at various values of x and for different models which have been theoretically evaluated. (Recall that, by convention, ΔL is negative. dK/dx is also negative, so that both R_s and *const.* are positive quantities.)

Figure 1 shows $R_s/const.$ *vs.* x for spherical molecules in various pore geometries. From these plots one can identify the optimum x for each pore type—*i.e.*, that value giving maximum resolution. From x_{opt} one can calculate the optimum pore size, s^{-1}, using Equation 16.

Besides optimizing pore size, these plots show how various pore types compare in their ability to separate spherical molecules. Uniformly spaced planes clearly offer the best resolution (by a factor of 2.3), but the resolution curve is more sharply peaked. This means that one must adjust the spacing or pore size more carefully than in the other cases so that it is neither too large nor too small. Because $R_s/const.$ falls to zero for $x > 1$, the largest of the two molecules, I, should lie at $x = 1$ (space between planes equals molecular diameter). The smaller molecule, II, would then lie on the downward sloping left branch of the curve (Figure 1) at $x = (\text{diameter})_{II}/(\text{diameter})_I$. This is preferable to straddling the peak—*i.e.*, making the peak correspond to the average of L_I and L_{II}—because absolutely no resolution is gained beyond $x > 1$. (The placement of two molecules individually on the curve recognizes that the separated peaks are not infinitesimally close-lying. Resolution is calculated as the mean of the two positions.)

While carefully spaced parallel planes offer the highest resolution, as we have seen, the narrowness of their resolution peak makes this model pore system inferior for separating a broad spectrum of molecular sizes—*i.e.*, a wide range of $\bar{L}$'s. As expected, the best capability for broad spectrum separation comes from the random-plane model. Clearly, any pore network having a strong element of randomness will have, among its diverse pores, a size highly selective for almost any pair of molecules. Thus, for the random-plane model the resolution, while not extremely high at any one point, stays within 50% of its maximum value over a 10-fold range of x values. This means that molecular size, $\bar{L}$, can range over a 10-fold scale without a severe loss of resolution for any of the pairs. By contrast, the x-ratio at half-height for uniform planes is only $(x_I/x_{II})^{1}/_2 = 1.5$, reflecting its narrow-spectrum characteristics. (For comparing with the 10-fold random-pore range, the x ratio 4.0 is more meaningful because over this range one has $R_s/const. > 0.14$, the half-height resolution for random pores.) The x ratio at half height for cylindrical or square-cross section pore is 4; for spherical cavities it is 5.

Resolution for all models peaks at nearly the same value of x (and, thus, surface area s). The variation is only 28% between extremes. Better still, all resolution is well within 90% of optimum at $x = 1$. This suggests that surface area alone can be adjusted to optimize the separation of known molecules irrespective of unknown pore-shape factors. Furthermore, we would hope that s could be generally

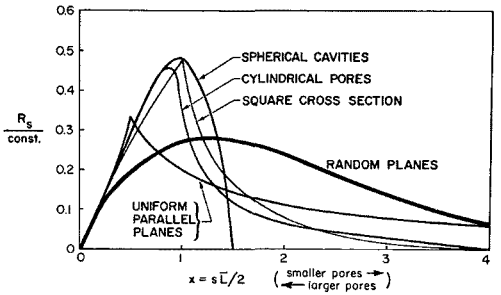


Figure 2. Relative resolution for two thin-rod molecules in different pore networks and pore sizes

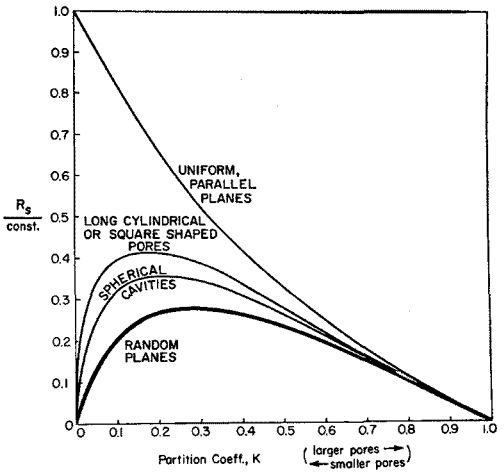


Figure 3. Relative resolution *vs.* K for two spheres

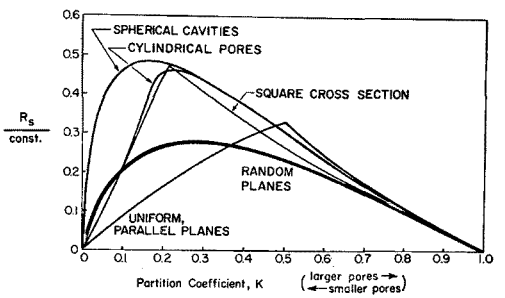


Figure 4. Relative resolution *vs.* K for two thin rods

chosen in advance, without trial and error methods, on the above theoretical grounds.

Figure 2 shows $R_s/const.$ for two thin-rod molecules, with the same group of pore models employed as above. The general results are similar, although the change from spherical to thin-rod molecules changes the relative advantages of the various pore types in making the separation. For example, the uniformly spaced planes now offer the poorest "peak" resolution of the uniform (nonrandom) pores, but the broadest spectrum. The optimum now lies at $x = 0.5$, for which the plane spacing equals the (average) rod length.

The random-plane model still offers the best broad-spectrum characteristics. In fact, its curve is identical in Figures 1 and 2, reflecting the universal nature of $\bar{L}$ as a measure of molecular "size" for this particular model (recall that $\bar{L}$ equals $^1/_2$ rod length for thin rods). The similarity of curves for the other models shows that $\bar{L}$ is a reasonable size measure for most porous networks. In most cases "peak" resolution lies near $x = 1$.

Because K is a unique function of x for each model, the data of Figures 1 and 2 can be alternatively presented as plots of relative resolution *vs.* K (Figures 3 and 4). This is more meaningful to the experimentalist because $K[=(1/\alpha)(V_e/V_m - 1)]$, limited to the range from zero to one, relates directly to elution volume, V_e. Maximum resolution is generally achieved toward the left side of these figures, in the K range 0 to 0.5. This means that the best resolution is with pores which are small enough to strongly exclude solute and force its early elution. Resolution falls off strongly for all models for $K > 0.5$, whether the molecules are spherical or rod shaped. The mutual agreement of these results would suggest that, in practice, pore size be chosen so that difficult pairs will elute early ($K \sim 0.25$), and that an attempt be made to avoid difficult separation work at $K > 0.5$ or 0.75.

While Figures 3 and 4 are for extreme molecular types—spheres and thin rods, respectively—the plots are roughly comparable. It is likely that similar results and conclusions would apply to other types.

Clearly Figures 1 through 4 could be used to tailor pore shape as well as size to fit specific separation problems. The

Table I. Optimum $x(= s\bar{L}/2)$ and K Values for Spherical Molecules in Different Types of Pores at $\alpha = V_s/V_m = 1$

Pore type	x_{opt} ($\alpha = 1$)	K_{opt} ($\alpha = 1$)	Eq for x_{opt}[a]	Gen. eq for K[a]
Random planes ("box pile")	1.28	0.28	$\alpha e^{-x} - x + 1 = 0$	e^{-x}
Parallel planes, uniform spacing	1.00	0.00	$x - 1 = 0$	$1 - x$
Long cylindrical pores	1.17	0.17	$x^2 - \frac{4}{\alpha}(\alpha + 1)(x - 1) = 0$	$\left(1 - \frac{x}{2}\right)^2$
Long square pores	1.17	0.17	$x^2 - \frac{4}{\alpha}(\alpha + 1)(x - 1) = 0$	$\left(1 - \frac{x}{2}\right)^2$
Spherical cavities	1.21	0.21	$\frac{1}{27}x^3 - \frac{1}{3}x^2 + \left(\frac{\alpha + 1}{\alpha}\right)(x - 1) = 0$	$\left(1 - \frac{x}{3}\right)^3$

[a] Equations can be used to obtain x_{opt} and K_{opt} for any α.

capability of uniform, parallel planes for spherical molecules and their unsuitability for rod-shaped molecules is but one example of many which could be suggested. Full implementation of this proposal depends on the development of better methodology for the control of pore shape.

The exact location of maximum resolution can be found, much as before, by using the condition $\partial R_s/\partial x = 0$ in combination with resolution Equation 19. Thus, the optimum pore size is that which yields an x satisfying the equation

$$(1 + K\alpha)\left(x\frac{d^2K}{dx^2} + \frac{dK}{dx}\right) - \alpha x\left(\frac{dK}{dx}\right)^2 = 0 \qquad (21)$$

This equation has been applied to the previously mentioned models. Calculated values of x and K optima are shown in Tables I and II, assuming $\alpha = 1$. These tables confirm our earlier conclusion that superior resolution is associated with low K values and, thus, early elution. Also shown in Table I are the equations for K for the various models as derived in the previous work (*6*). One can get K_{opt} for any α value by first solving for x in the equations for x_{opt} shown in the table. This solution, equal to x_{opt}, is then substituted into the K expression to yield K_{opt}. We have not presented the comparable thin-rod expressions because of their greater complexity (*6*).

The optimum K values obtained above emphasize high resolution as opposed to high speed. From theoretical and experimental work on other chromatographic systems, it can be concluded that speed-optimization will shift the K's to lower values (earlier elution). However, as our optimum K's are already low, speed-optimization would not be expected to alter the above conclusions to any significant degree.

EXAMPLES OF RESOLUTION AS RELATED TO MOLECULAR SIZE DIFFERENCES

We will use the random-plane model to estimate the increment in molecular size needed to achieve resolution at a given level. Using $K = \exp(-x)$, we obtain from Equation 18 the expression

$$\frac{\Delta\bar{L}}{\bar{L}} = \frac{4R_s}{\sqrt{N}}\frac{(1 + \alpha K)}{\alpha K \ln K} \qquad (22)$$

Here we have completed a full circle back to Equation 6, which is equivalent to the above for close-lying peaks—*e.g.*, large N, low R_s. The divergence in the two expressions for small N stems from the different use of the close-lying assumption in their respective formulations—*i.e.*, Equation 4 and 17. Setting $\alpha = 1$ and using the previously derived optimum, $K = 0.28$, we get

$$\Delta\bar{L}/\bar{L} = -14.3\ R_s/\sqrt{N} \qquad (23)$$

If we require unit resolution (we may often find it necessary to settle for less, perhaps using sharper methods of data interpretation, as the following calculations show), this becomes

$$\Delta\bar{L}/\bar{L} = -14.3/\sqrt{N} \qquad (24)$$

Table III shows the relative size difference, $-\Delta\bar{L}/\bar{L}$, which must exist between molecules for their separation at different column efficiencies. Also shown are the minimum molecular weight ratios of two barely separated species. The first of these, with subscript s, refers to geometrically similar space-filling molecules—*e.g.*, spheres—of constant density. The second, subscript p, refers to random-chain polymers.

Table II. Optimum $x(= s\ \bar{L}/2)$ and K Values for Thin-Rod Molecules in Different Types of Pores at $\alpha = V_s/V_m = 1$

Pore type	x_{opt} ($\alpha = 1$)	x_{opt} ($\alpha = 1$)
Random planes ("box pile")	1.28	0.28
Parallel planes, uniform spacing	0.50	0.50
Long cylindrical pores	0.71	0.33
Long square pores	0.90	0.27
Spherical cavities	0.97	0.17

Table III. Relative Sizes and Molecular Weight Ratios of Molecules Barely Separable ($R_s = 1$) on Columns of Different Numbers of Theoretical Plates, N

N	$-\Delta\bar{L}/\bar{L}$	$[(MW)_1/(MW)_1]_s$	$[(MW)_1/(MW)_1]_p$
100	~1.43	~200	~40
300	~0.83	~14	~6
1000	0.45	3.9	2.5
3000	0.26	2.2	1.7
10000	0.14	1.5	1.3
100000	0.05	1.15	1.10

For the latter, molecular weight is assumed to increase with the square, as opposed to the cube, of mean molecular length $\bar{L}$. The approximate signs (~) are used for the first two rows because the poor resolution severely stretches our assumption that the two peaks are close-lying. The $\Delta\bar{L}/\bar{L}$ figures are valid for molecules of any fixed shape, or even for two molecules of different shape, because of the generality of the random-plane model. However, any pore network would be expected to yield comparable results. Note that $\Delta\bar{L}/\bar{L}$, a dimensionless ratio, can be replaced by Δ(diameter)/diameter, Δ(length)/length, or any other related measure for geometrically similar molecules.

The message of Table III is clear. One must have a great number of theoretical plates to separate molecules which are at all comparable in size when using the exclusion methods of chromatography. At a typical 1000 plates, for instance, one could not separate spherical molecules whose diameters did not differ by almost 50% relative to the mean diameter and whose molecular weights were not almost fourfold different. Only at 10,000 plates do we get down to the separation of reasonably comparable molecules: They can differ by as little as 14% in diameter and 50% in molecular weight. We would need 10^4 to 10^5 and more plates to achieve the kind of fine separations normally expected with other chromatographic systems.

Much of the virtue of exclusion chromatography lies in its broad spectrum separations. Nonetheless, the method would be immensely more useful if macromolecules of comparable size could be resolved. It would certainly be worth seeking the high plate numbers suggested here, perhaps using long, high pressure columns as suggested earlier, to improve an already invaluable technique.

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Visual Titrimetric Determination of Total Reactivity and Differentiation of Trialkylaluminum and Dialkylaluminum Hydride in Mixtures

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A rapid, visual, titrimetric method to determine total reactivity, as well as to differentiate aluminum trialkyl (ATA) from aluminum dialkyl hydride (ADAH) moieties in mixed complex systems of aluminum alkyls, is desired. Phenazine used as the indicator forms red to brown complexes with ATA, and green to green-blue complexes with ADAH. The titration utilizes inexpensive, commonly available, laboratory apparatus, and is completed easily in 2 to 4 minutes after initial purging of the titration vessels. The method is applicable to alkyls ranging from C_2 to at least C_{30} separately or in mixtures. Precision is ±1% relative standard deviation for both low and high concentrations of ATA and/or ADAH, and accuracy, although unknown, should approach the precision.

A METHOD REQUIRING only commonly available, inexpensive laboratory apparatus to determine quantitatively the total reactivity, as well as to differentiate aluminum trialkyl (ATA) and aluminum dialkyl hydride (ADAH) in complex aluminum alkyl systems, would be most desirable. Visual end-point titration methods for ATA compounds, each with moderate speed, have been reported (*1*, *2*). In every case, except where ADAH was added to determine the ATA titration end point with isoquinoline (*1*), ADAH reacted with the titrant or indicator to liberate hydrogen which destroyed the indicating properties of the indicator (*4*). Spectrophotometry has been used to determine total reactivity (activity) and to differentiate ATA and ADAH (*2*, *3*, *5*). One method (*2*), which is an extension of another (*3*), has been operative in our laboratory for more than five years. Although it is an excellent method, it requires a minimum of 20 to 30 minutes after initial purging to complete an analysis, except with the most ideal samples. Further, moderately expensive equipment, cell modification, and multiple weighings are required to suitably carry out the determination. Gas volumetric (*6–8*) and thermometric (*9*, *10*) techniques have been used to differentiate ATA and ADAH in mixtures. Both, however, require elaborate and moderately expensive equipment. Gas volumetric methods are severely limited by the length of the hydrocarbon side chain, while thermometric methods are limited to known samples of ATA and ADAH with well-defined heats of reaction.

In the work described here, a rapid, visual, titration method is presented whereby ATA and ADAH, either separately or in wide molecular weight and concentration ranges of complex mixtures, are reversibly titrated with pyridine using phenazine as the indicator. After initial purging of the titration vessel, only 2 to 4 minutes are required to titrate a sample and only commonly available, inexpensive, laboratory equipment is required.

EXPERIMENTAL

Apparatus and Reagents. A nitrogen (air free) tank with appropriate pressure gauges was used. The 50-ml buret was equipped with an 18-gauge hypodermic needle delivery tip and was partially filled with 5A or 4A Linde Molecular Sieve. Rubber septums were selected to fit bottle caps and 2-oz narrow-necked bottles. A Kel F or Teflon-covered stirring bar (0.5 to 0.75- × 0.25-inch) was used. The smooth-bore, 1-ml Luer-Lok hypodermic syringes were equipped with Teflon plungers (Hamilton Syringe Co.).

The 1.5-inch hypodermic needles were 23 gauge, and the pressure release system was for a Nujol nitrogen gas scrubber. Silicon rubber plugs, $^5/_{16}$- × 0.5-inch, were obtained from the Kirkhill Rubber Co. Phenazine (J. T. Baker Co. 3T-178) was used to prepare a 0.5% w/v solution in redistilled dry xylene.

Xylene was distilled over calcium hydride from an all-glass still and only a heart cut was retained. The distilled xylene was stored over Linde Molecular Sieve 4A or 5A.

Reagent grade pyridine was 0.2*M* in dry xylene and was standardized against standard perchloric acid in glacial acetic acid solvent.

Procedure. A clean, dry, 2- or 4-oz bottle containing a magnetic stirring bar is rinsed with 5 ml of dry xylene. A second portion (10–20 ml) of dry xylene and 10 drops of phenazine indicator are added to the bottle. The bottle is closed with a septum-lined screw cap, and purged with stirring for 3 to 5 minutes with nitrogen, flowing 100–200 cc/minute. A 20-gauge needle connected to a pressure-release Nujol scrubber is inserted through the septum into the bottle atmosphere. Another 20-gauge needle connected to a nitrogen inlet is inserted through the septum into the bottle atmosphere and, while stirring, the bottle and contents are purged for 3 to 4 minutes with a nitrogen flow of 100 to 200 cc per minute.

The aluminum alkyl is sampled as described by Hagen and Leslie (*2*) and added to the dry xylene-indicator solution by carefully uncapping the needle, inserting it through the septum, and depressing the plunger. Then the needle is carefully withdrawn and capped. The buret is rinsed with standard pyridine, then filled to volume with more standard pyridine. Then the buret needle tip is inserted through the septum and the sample is titrated to the ATA end point (disappearance of brown or change to pure green] and the milliliters are recorded. The titration is continued for ADAH to colorless or until no further change occurs, and the total milliliters are recorded.

(1) E. Bonitz, *Chem. Ber.*, **88**, 742 (1955).
(2) D. F. Hagen and W. D. Leslie, ANAL. CHEM., **35**, 814 (1963).
(3) J. H. Mitchen, *ibid.*, **33**, 1331 (1961).
(4) G. A. Razuvaev and A. Graevskii, *Doklady Akad. Nauk. S.S.S.R.* **128**, 309 (1959).
(5) C. W. Wadelin, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1962.
(6) D. F. Hagen, J. L. Hoyt, and W. D. Leslie, ANAL. CHEM., **38**, 1691 (1966).
(7) W. P. Neumann, *Ann. Chem.*, **629**, 23 (1960).
(8) T. R. Crompton and V. W. Reid, *Analyst*, **88**, 713 (1963).
(9) W. L. Everson and E. M. Ramirez, ANAL. CHEM., **37**, 806 (1965).
(10) E. G. Hoffmann and W. Tornau, *Z. Anal. Chem.*, **188**, 321 (1962).

Aluminum Determination. Aluminum is determined by controlled deactivation hydrolysis (*11*) followed by chelometric titration with cyclohexane-diamine tetraacetate (CDTA) (*12, 13*).

Calculation.

$$\% \text{ Total reactivity} = \frac{\text{millimoles ATA + ADAH}}{\text{millimoles Al}} \times 100 \quad (1)$$

$$\% \text{ ADAH} = \frac{\text{millimoles ADAH}}{\text{millimoles Al}} \times 100 \quad (2)$$

$$\% \text{ ATA} = \% \text{ Total Reactivity} - \% \text{ ADAH} \quad (3)$$

or

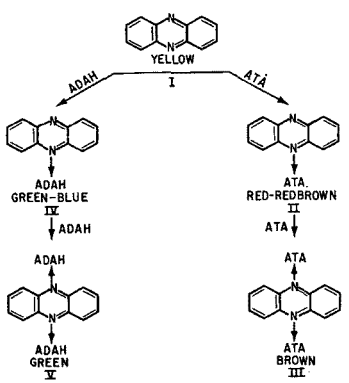
$$\% \text{ ATA} = \frac{\text{millimoles ATA}}{\text{millimoles Al}} \times 100 \quad (3A)$$

DISCUSSION

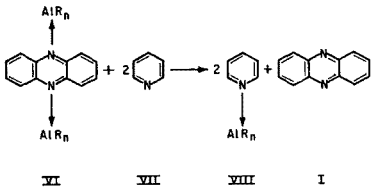
At the outset of this investigation the primary objective was to establish a simple, rapid method for total reactivity of aluminum alkyl mixtures to supplement the much slower spectrophotometric isoquinoline method (*2, 3*). In addition to the complexing indicators mentioned by Hagen and Leslie (*2*), at least a hundred others had been scanned for applicability to ADAH determination. Gas volumetric methods have been studied but were too limited for our system. Thermometric methods, such as described by Everson and Ramirez (*9*) and Hoffmann and Tornau (*10*), appear too limited for the complex mixtures to be analyzed because of overlapping heats of reaction in the wide molecular weight and concentration ranges, and offer no real advantage over the established method (*2*).

Hagen and Leslie (*2*) reported the use of phenazine (I) as an indicator suitable for ATA but not ADAH because of the possible formation of an Al—N bond with ADAH. Recently, we re-evaluated phenazine as an indicator for ADAH because structurally it appeared to fulfill model requirements to prevent alteration by ADAH and form reversible complexes with ADAH.

It was also observed that the 1:1 and 2:1 (II-III) red to red-brown complexes are due to ATA while the green complex reported earlier is due to ADAH which forms 1:1 green-blue (IV) and 2:1 green (V) complexes. In addition, at least currently, we have been unable to separate quantitatively and distinguish the red 2:1 and 1:1 complexes, but the green-blue 1:1 ADAH complex can be differentiated from the 2:1 green ADAH complex.

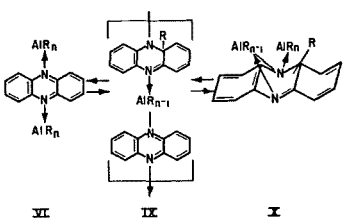


After establishing that phenazine formed reversible complexes with ATA and ADAH, it was necessary to determine not only the stoichiometry of the displacement of phenazine but to also determine if the ADAH could, in fact, be separated quantitatively from ATA. Of the several amines used in this study, pyridine was found most suitable. Pyridine (VII) quantitatively displaces phenazine (I) from both ATA and ADAH (VI) to form more stable 1:1 complexes (VIII).



WHERE R_n = TRIALKYL OR DIALKYL HYDRIDE

Phenazine forms very intensely-colored stable 1:1 and 2:1 complexes with both ATA and ADAH. In negligible concentrations, however, phenazine is suitable as an indicator, but it must also be remembered that the colors are actually due to stable complexes. A study of the displacement reaction kinetics showed that for up to 30 minutes phenazine could be quantitatively displaced with pyridine. After 30 minutes, the displacement reaction with pyridine was somewhat obscured, indicating the formation of a more stable complex or the possible formation of a true Al–N bond between ATA–ADAH and phenazine although the displacement of phenazine could be accomplished with other complex formers such as alcohols. Several possible phenazine complexes could exist that could explain the increased stability observed in a large excess of ATA and/or ADAH. For example, the nominal 2:1 complex (VI) could polymerize (IX) or interact



within the molecular complex (X). Many other possibilities exist, but it was beyond the scope of this work to attempt to elucidate them. Although phenazine is unconventionally used as an indicator, and the complex is affected by time, no errors in the determination will occur if the suggested method is followed, because once the pyridine complex is formed there is no tendency to disproportionate from pyridine to phenazine, even upon standing. Therefore, several sample additions could be made to the sample bottle and titrated for total (but not hydride) reactivity. Samples containing ADAH and titrated with pyridine are easily differentiated when one sample is added to the reaction chamber. However, if a second sample containing ADAH is added to the same reaction cham-

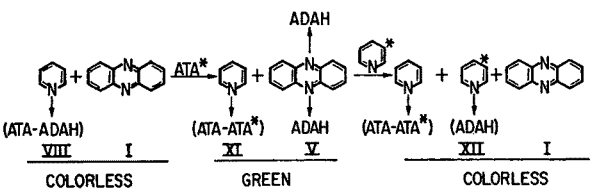
(11) D. F. Hagen, D. G. Biechler, W. D. Leslie, and D. E. Jordan, *Anal. Chim. Acta*, **41**, 557 (1968).
(12) E. Wannien and A. Ringbom, *ibid.*, **12**, 308 (1955).
(13) F. Nydahl, *Talanta*, **4**, 141 (1960).

Table I. Comparison of Results Obtained by the Described Phenazine Differential Titration and the Spectrophotometric Isoquinoline Procedures for ADAH and Total Reactivity

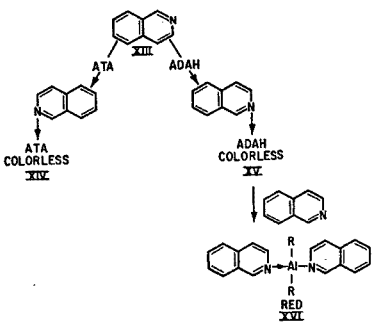
Sample	Mole % ADAH		Mole % ATA[b]		Mole % reactive	
	Phenazine	Isoquinoline	Phenazine	Isoquinoline	Phenazine	Isoquinoline
A	81.3[a] ± 0.85	80.8	10.5	11.1	91.8[a] ± 0.92	91.9
B	65.4	63.0	28.5	30.7	93.9	93.7
C	4.51[a] ± 0.05	4.55	...	...	...	...
D	58.8	58.9	23.8	24.1	82.6	83.0
E	16.1	17.4	40.7	37.8	56.8	55.2
F	<0.3	...	>96.6	96.8	96.9	96.8

[a] Five or more replicate analyses.
[b] ATA = Total Reactive − ADAH.

ber the hydride–pyridine complex is disproportionated to form ATA–pyridine and ADAH–phenazine by the mixed ATA–ADAH sample added because of the greater stability of ATA for pyridine and ADAH for phenazine. This then means that enough sample must be added to displace all the ADAH from the previous titration before a differentiation of the second sample can be accomplished. It is readily understood why such a system would soon become unwieldy. However, the same basic technique affords an excellent way to determine indirectly very low concentrations (<0.1%) of ADAH. That is simply to titrate the low ADAH to the end point (VIII). Then add additional hydride-free ATA until all the ADAH is displaced from pyridine (XI) to phenazine (V), as shown by the green color. Then add just enough more ATA to make the color an off-green or brindle. Now the sample is carefully titrated just to the pure green which eliminates the excess ATA, then to the colorless end point to accurately determine ADAH (XII).



Previous work in our laboratory, including reaction kinetics studies, showed that the 2:1 complex of each moiety was displaced preferentially before their 1:1 complexes by any applicable method. With phenazine (I), however, it was observed early that only a brown (II) to brown-red (III) color was formed with ATA, while with excess ADAH, the color was a pure green (V). Upon titration with pyridine the brown to brown-red color disappeared completely, leaving the green (V) to green-blue (IV) which indicated displacement of phenazine to form 1:1 ATA–pyridine complexes. To establish that ATA was completely displaced from phenazine before any ADAH was displaced, several samples of varying mole ratios were analyzed both by the described method (I-VIII) and the established isoquinoline spectrophotometric method described by Mitchen (*3*) and Hagen and Leslie (*2*) (XIII–XVI).



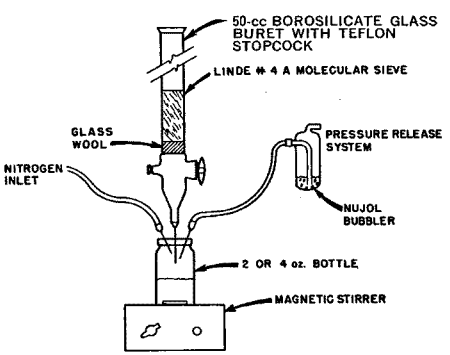


Figure 1. Reagent dispensing and titration apparatus

RESULTS

Figure 1 details the general component placement for the titration and purging used in this work. The total apparatus is essentially identical to that used previously (*2*) in this laboratory. In order to free adequately the titration bottle from all reactive impurities, a dry xylene rinse followed by purging for 3–5 minutes with predried and purified nitrogen gas is required. An alternate drying or "clean up" procedure is to add a few drops of ADAH-free ATA to the titration vessel, shake the bottle well to consume all impurities and reactants, then titrate with pyridine just to the phenazine end point before adding a weighed portion of the sample to be analyzed. Attention to precise details described is absolutely necessary to obtain accurate results using this procedure.

Table I compares the results obtained by the described procedure and the established isoquinoline spectrophotometric procedure (*2*). The results are generally in excellent agreement. The greatest differences are observed for the ATA values which are obtained, in each case, by difference. Of significance is the range of ADAH determined by the described method without alteration of the phenazine. The precision of the determination is slightly more than ±1% rela-

Table II. Results Obtained on Typical Samples by the Proposed Pyridine Titration of the Phenazine Complexes

Sample	Al, %	ADAH	ATA[a]	Total reactive
A8131	10.98	6.1	90.6	96.7
A8132	22.86	5.0	91.7	96.9
A8136	2.01	7.9	85.9	93.8
A8259	29.41	90.1	6.7	96.8
A8601	28.60	87.2	9.5	96.7
A81151	1.31	1.5	86.2	87.7
A1361	23.03	1.0	96.5	97.5
A1401	23.75	4.4	93.2	97.6
A2152-1[b]	26.95	79.8 ± 0.08	12.6	92.4 ± 0.8
A5152-1[b]	7.56	1.4 ± 0.01	68.0	69.4 ± 0.8
A2237	23.51	<0.1	98.3	98.3
A84373	29.42	91.9	<0.1	91.9
A84474	27.54	93.6	N.D.[c]	93.6
A84487	28.00	94.5	N.D	94.5

[a] ATA = Total Reactive − ADAH.
[b] Six or more determinations.
[c] None Detected.

tive throughout the range of ADAH values. Because standard samples are not available the accuracy is not known, but it should approach the precision.

Table II shows results obtained on typical day-to-day samples. These samples vary from "pure" to partially oxidized samples. The aluminum varies from 1.31% indicating extreme dilution to 29.41% indicating a completely solvent-stripped sample. The theoretical aluminum for aluminum triethyl is 23.63%, while for aluminum diethyl hydride it is 31.33%. The aluminum content of Samples A8259 and A8601 both indicate that considerable concentration of hydride must be present. Analysis shows this to be true. Additionally, Sample No. A2237 was a solvent-stripped "pure" aluminum alkyl. The aluminum concentration indicated it may or may not be ATE because various combinations of ADEH and ATE also yield aluminum values equal to the theoretical ATE value. A case in point is No. 81401 which was found to contain 4.4% ADEH. Thus, one can predict that if the aluminum content exceeds 23.63% then a molecule other than ATE (usually ADEH, but it could also be ATM) is present. If the aluminum is less than 23.63% ATE, as well as other ATA and some ADAH, can also be present. Again, the precision in all cases is essentially ± 1% relative.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the help of J. L. Hoyt and C. F. Maddox of the Inorganic Laboratory of the Chemical Analysis Group for their isoquinoline and aluminum analyses.

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Resolution of C_4 to C_{12} Petroleum Mixtures by Capillary Gas Chromatography

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A substrate for the resolution of many of the components which occur in the C_4 to C_{12} portion of nonolefinic petroleum has been developed. A capillary column coated with a mixture of squalane + Kel F_{40} has been used to obtain component breakdown by carbon number and/or type (*n*-paraffin, isoparaffin, cyclopentane, cyclohexane, or aromatic) of the components which occur in the C_4 to C_{12} portion of nonolefinic petroleum. Data are presented on the efficiency and selectivity of the column. A chromatogram of a 102 component (C_4 to C_{12}) synthetic hydrocarbon blend is presented which illustrates the resolution that can be obtained with a column coated with the substrate. The capabilities of the substrate are further illustrated by chromatograms which are presented by a long range naphtha, a raffinate, and a heavy isocrackate. By using a capillary column coated with this substrate, it is possible to obtain high resolution of C_4 to C_{12} nonolefinic petroleum samples by a single analysis.

SCHWARTZ and BRASSEAUX (*1*) reported that acapillary column coated with a mixture of a halogenated hydrocarbon, Kel-F_{10}, and hexadecane could be used for the separation of saturated and aromatic hydrocarbons which occur in the 28 to 114 °C portion of petroleum. In another paper (*2*), the resolution of certain isoparaffin–olefin alkylates was obtained by employing squalane as a capillary column substrate. Preliminary studies indicated that a mixture of squalane + Kel-F_{40} could be used as a substrate for the resolution of the hydrocarbons which occur in the C_4 to C_{12} portion of nonolefinic petroleum. The present study was undertaken to determine the resolution which could be obtained under such conditions.

EXPERIMENTAL

Equipment. A Varian Aerograph Model 1200 Hi-Fi III chromatograph with hydrogen flame detector, capillary splitter assembly, and isothermal- and program-temperature controls was employed in this study. The chromatograms were recorded on a 1-mV Leeds and Northrup recorder. Capillary columns were prepared from 0.02-inch i.d. 0.062-inch o.d. 316 stainless steel with a 20 microfinish (supplied by Handy and Harmon Tube Co., Norristown, Pa.)

Reagents. The hydrocarbons used in this study were obtained from Phillips Petroleum Co., Bartlesville, Okla., and Chemical Samples Co. of Columbus, Ohio. The halogenated hydrocarbon, Kel-F_{40}, was obtained from 3M Co. of St. Paul, Minn. The squalane was obtained from Eastman Organic Chemicals of Rochester, N. Y.

[1] Present address, Petro-Tex Chemical Corp., 8600 Park Place Boulevard, Houston, Texas

(1) R. D. Schwartz, and D. J. Brasseaux, ANAL. CHEM., 35, 1374 (1963).
(2) L. R. Durrett, L. M. Taylor, C. T. Wantland, and I. Dvoretzky, *ibid.*, 35, 637 (1963).

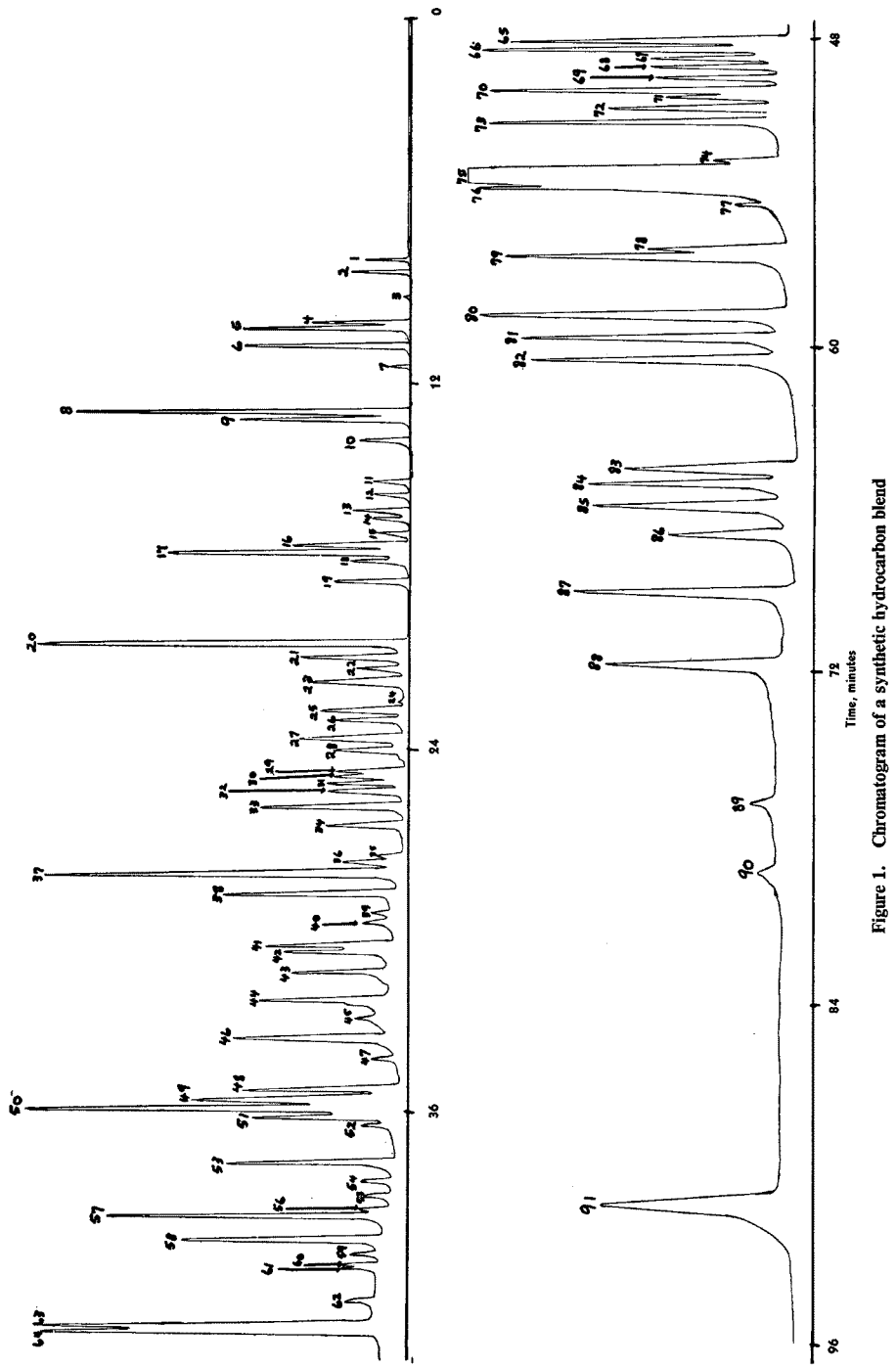


Figure 1. Chromatogram of a synthetic hydrocarbon blend

1. Isopentane
2. *n*-Pentane
3. 2,2-Dimethylbutane
4. Cyclopentane
5. 2,3-Dimethylbutane
2-Methylpentane
6. 3-Methylpentane
7. *n*-Hexane
8. Methylcyclopentane
9. 2,4-Dimethylpentane
10. Benzene
11. Cyclohexane
12. 1,1-Dimethylcyclopentane
13. 2-Methylhexane
14. 1-*cis*-3-Dimethylcyclopentane
15. 3-Methylhexane
16. 1-*trans*-3-Dimethylcyclopentane
1-*trans*-2-Dimethylcyclopentane
17. 3-Ethylpentane
18. 2,2,4-Trimethylpentane
19. *n*-Heptane
20. 1-*cis*-2-Dimethylcyclopentane
21. Methylcyclohexane
22. 1,1,3-Trimethylcyclopentane
23. Ethylcyclopentane
24. 2,5-Dimethylhexane
2,4-Dimethylhexane
25. 3,3-Dimethylhexane
26. 1-*trans*-2-*cis*-4-Trimethylcyclopentane
27. Toluene
28. 1,1,2-Trimethylcyclopentane
29. 2,3,4-Trimethylpentane
30. 2,3,3-Trimethylpentane
31. 2,3-Dimethylhexane
32. 2-Methylheptane
33. 3-Methylheptane
34. 1-*cis*-2-*trans*-3-Trimethylcyclopentane
35. 1,1-Dimethylcyclohexane
1-*trans*-4-Dimethylcyclohexane
36. 1-*cis*-3-Dimethylcyclohexane
1-Methyl-*trans*-3-Ethylcyclopentane
37. 2,2,4-Trimethylhexane
38. *n*-Octane
39. 1-*trans*-2-Dimethylcyclohexane
40. 1-*trans*-3-Dimethylcyclohexane
1-*cis*-4-Dimethylcyclohexane
41. 1-Methyl-*cis*-2-Ethylcyclopentane
42. Isopropylcyclopentane
43. 2,2-Dimethylheptane
44. *n*-Propylcyclopentane
1-*cis*-2-Dimethylcyclohexane
45. Ethylcyclohexane
46. Ethylbenzene
47. 1,1,3-Trimethylcyclohexane
48. *para*-Xylene
49. *meta*-Xylene
50. 2-Methyloctane
3-Ethylheptane
51. 3-Methyloctane
52. 1-*trans*-2-*trans*-4-Trimethylcyclohexane
1-*cis*-3-*trans*-5-Trimethylcyclohexane
53. *ortho*-Xylene
54. 1-*trans*-2-*cis*-3-Trimethylcyclohexane
55. 1,1,2-Trimethylcyclohexane
56. 1-Methyl-*cis*-3-Ethylcyclohexane
57. *n*-Nonane
58. Isopropylbenzene
59. 1-Methyl-*trans*-2-Ethylcyclohexane
60. 1-Methyl-*cis*-4-Ethylcyclohexane
61. 1-Methyl-*trans*-3-Ethylcyclohexane
62. Isopropylcyclohexane
63. *n*-Propylcyclohexane
64. *n*-Propylbenzene
65. 1-Methyl-3-Ethylbenzene
66. 1-Methyl-4-Ethylbenzene
67. 5-Methylnonane
68. 4-Methylnonane
69. 2-Methylnonane
70. 1-Methyl-2-Ethylbenzene
71. 3-Methylnonane
72. 1,3,5-Trimethylbenzene
73. *tert*-Butylbenzene
74. 3,3,4,4-Tetramethylhexane
75. *n*-Decane
76. *sec*-Butylbenzene
Isobutylbenzene
77. 1-Methyl-*trans*-2-*n*-Propylcyclohexane
78. 1,2,3-Trimethylbenzene
79. 1-Methyl-4-Isopropylbenzene
80. 1,3-Diethylbenzene
81. *n*-Butylbenzene
82. 1,4-Diethylbenzene
83. *n*-Butylcyclohexane
84. *trans*-Decahydronaphthalene
85. 1,3-Dimethyl-4-Ethylbenzene
86. 1,2-Dimethyl-4-Ethylbenzene
87. *n*-Undecane
88. *cis*-Decahydronaphthalene
89. Cyclopentylcyclopentane
90. Cyclopentacyclohexane
91. *n*-Dodecane

Table I. Substrate Evaluated as Coatings for Capillary Columns

Substrate	NC_6–NC_7 resolution	t_n/t_p	t_a/t_p
Squalane	48	1.26	1.02
Squalane + Kel F_{40}	42	1.23	1.09
Kel-F_{40}	36	1.06	1.28

Preparation of Capillary Columns. The 200-foot stainless steel capillary columns were each coated with one of the following substrates: 10% squalane, 10% Kel-F_{40}, or 7% squalane + 3% Kel-F_{40}, by weight dissolved in *n*-pentane. The columns were filled with the solution of one of the substrates under 10 psi helium pressure. After the liquid began to emerge from the columns, the columns were emptied, placed in the HiFi III chromatograph and purged with helium carrier gas at a flow rate of 2.5 ml per minute while the column temperature was maintained at 60 °C for 24 hours. Then the column temperature was programmed several times from 60 to 120 °C at a rate of 2 °C per minute.

Procedure. After installing a capillary column in the Hi-Fi III chromatograph, the helium flow rate at the column and splitter exits was adjusted to 2.5 ml per minute and 168 ml per minute, respectively. The temperature of the injector-splitter port and detector was adjusted to 350 °C. The column was heated for 20 minutes at 50 °C, then a 0.1- to 0.8-μl sample was injected (using a 1-μl Hamilton syringe) into the chromatograph. The temperature of the column was maintained at 50 °C for 10 minutes, then the column temperature was programmed at a rate of 2 °C per minute to 120 °C and then held isothermally until the analysis was complete.

RESULTS AND DISCUSSION

Several hydrocarbon blends were employed to determine the efficiency, resolving power, and column selectivity for capillary columns coated as described above. The degree of resolution between *n*-hexane and *n*-heptane as defined by Schwartz and Brasseaux (*1*), the naphthene–paraffin selectivity, t_n/t_p, and the aromatic–paraffin selectivity, t_a/t_p, (using the retention times of cyclohexane, t_n; 2,4 dimethylpentane, t_p; and benzene, t_a) were determined for the column substrates under identical conditions. The results are presented in Table I. Figure 1 is a chromatogram of a 102-component synthetic hydrocarbon blend which illustrates the resolution and range which can be obtained with a capillary column coated with squalane + Kel F_{40}; identification of the components and elution order are given in the legend. Although overlap occurs in some cases, the components which overlap are in a given carbon number and generally of the same type. The elution order of several other hydrocarbons which are not shown in Figure 1 has been determined: 2,2-dimethyl hexane elutes between components 19 and 20; 2,2-dimethylpentane elutes between components 8 and 9, 2,2,3-trimethylbutane and 3,3-dimethylpentane elute between components 10 and 11, indane elutes between components 89 and 90, and 2,3-dimethylpentane elutes between components 14 and 15. The mixtures methylcyclopentane–2,2-dimethylpentane, 1-*trans*-2-dimethylcyclopentane–3-ethylpentane, and methylcyclohexane–1,1,3-trimethylcyclopentane–2,2-dimethylhexane were unresolved when squalane was used as a capillary column substrate. By using Kel-F_{40} as a column substrate, the above-mentioned

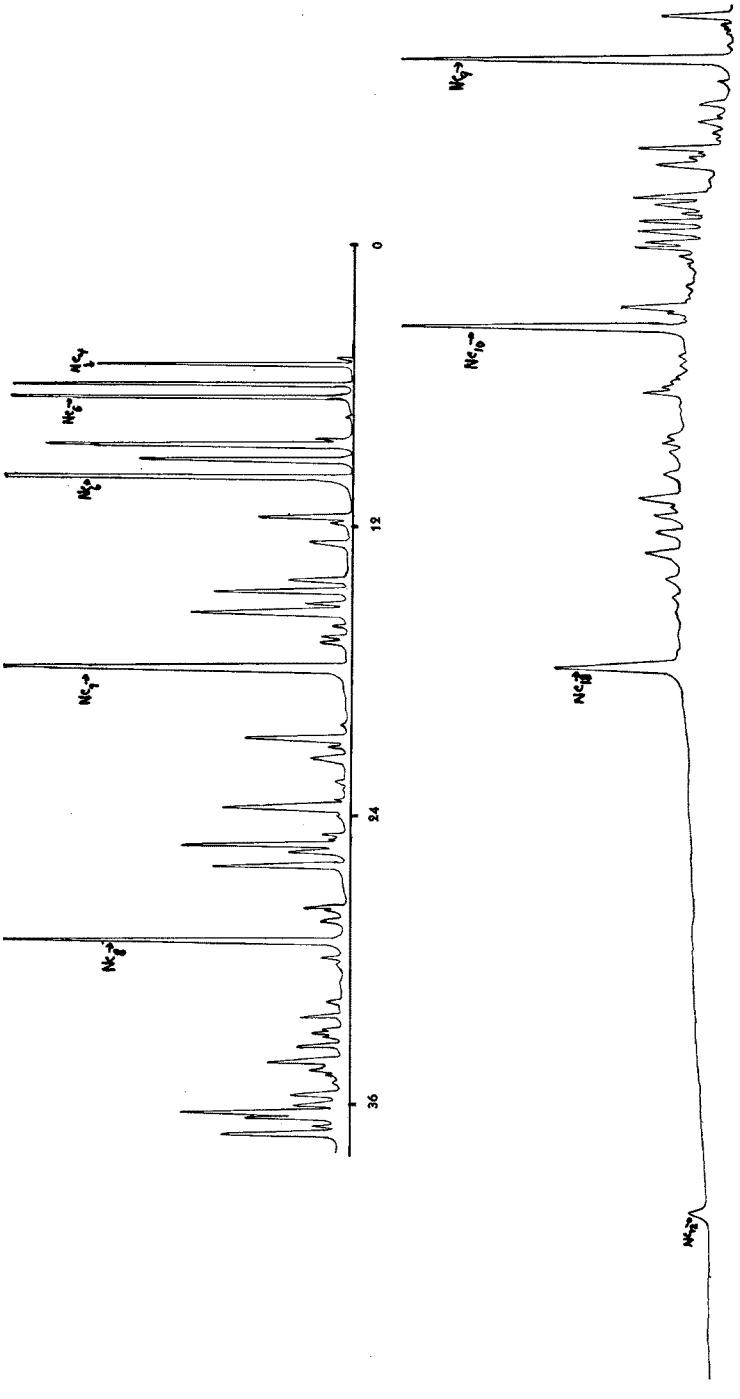


Figure 2. Chromatogram of a long range naphtha

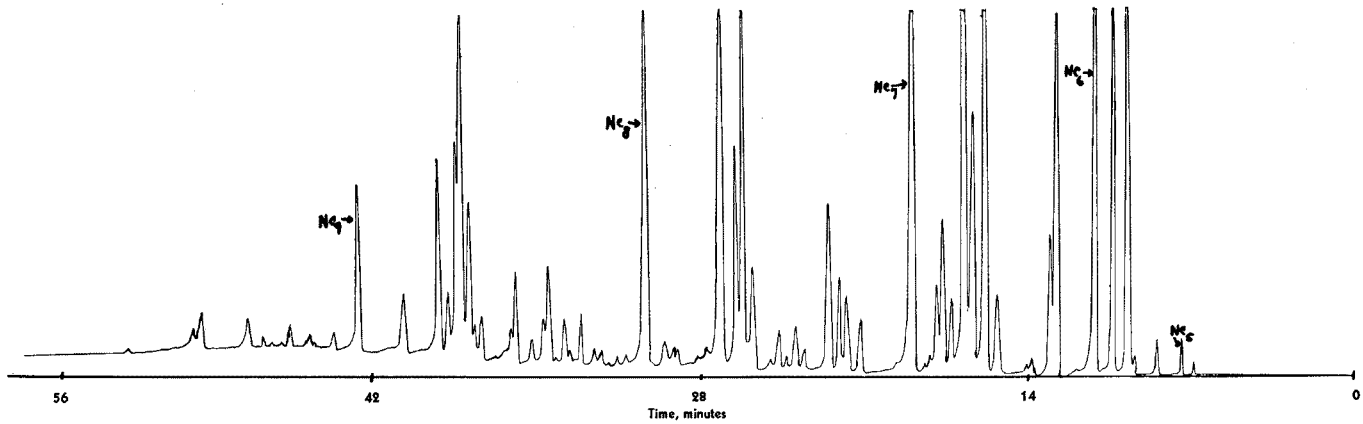


Figure 3. Chromatogram of a raffinate

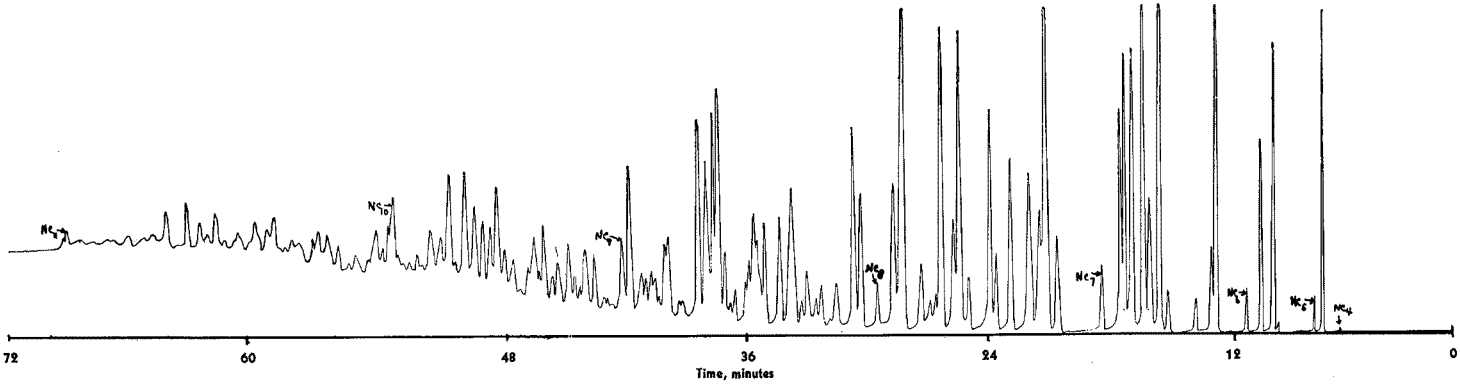


Figure 4. Chromatogram of a heavy isocrackate

mixtures were easily resolved; however, the mixtures benzene–1,1-dimethylcyclopentane, 3-methylpentane–1-*trans*-3-dimethylcyclopentane, and 2,3,3-trimethylpentane–1-*trans*-3-*cis*-3-trimethylcyclopentane were unresolved. All of the above-mentioned unresolved mixtures were easily resolved by using squalane + Kel-F_{40} as the substrate.

To illustrate further the capability of the substrate, Figures 2, 3, and 4 are chromatograms in which the *n*-paraffin peaks have been labeled in a long range naphtha, a raffinate and a heavy isocrackate. Gasolines isomaxates, and various distillates have also been analyzed by using squalane + Kel-F_{40} as substrate. Two squalane + Kel-F_{40} coated columns have been used to 120 °C for over six months and another to 140 °C for several months without any apparent loss of resolution.

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Rapid Separation by Carbon Number and Determination of Naphthene and Paraffin Content of Saturate Petroleum Distillates up to 185 °C

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A novel technique employing a high temperature gas-solid chromatographic process using Type 13X molecular sieve has been discovered which permits a quantitative separation of the saturate hydrocarbons of feedstocks boiling up to 185 °C by carbon number or by bulk hydrocarbon type within each carbon number. Factors influencing performance and the conditions necessary to achieve the separations have been assessed and the probable order of elution within the naphthene and paraffin types has been established with the use of auxiliary analytical procedures. In this way it is possible to obtain concentrates of particular series of isomers, for example 16 C_9 and 43 C_{10} bicyclo compounds have been successfully classified. Examples of capillary column chromatographic analyses of the segregated carbon number fractions and their individual naphthene and paraffin contents are also given. The apparatus is simple, easy to operate, and suitable for analytical determinations. The times for the analysis of distillates of 150 °C and 185° C end point can be reduced if required to 20 minutes and 40 minutes, respectively, without serious loss of resolution. This paper describes the technique and its application to the analysis of different naphthas.

THE CAPACITY TO RESOLVE saturate hydrocarbons into naphthenes and paraffins and to estimate the concentration of these types is of great practical importance within the petroleum industry. Previously some success has attended the use of liquid-modified Pelletex (*1*) to separate C_5–C_7 hydrocarbons by carbon number, but, until now there has been no practical means of quantitatively segregating naphthenes from paraffins. The relative concentration of naphthenes and paraffins however can be determined in a number of ways. In the lower boiling range, such estimations are obtained by capillary gas chromatography, but the accuracy of the determination deteriorates with the rise in the number of multicomponent peaks that occurs with increase in boiling range. Because of this, effective routine measurement is confined to distillates boiling up to about 130 °C. Hydrocarbon type analyses of higher boiling saturates consequently are usually performed by mass spectrometry or the results are derived by the use of correlations based upon physical property data. These methods all suffer from limitations consequent upon the use of average data. A new approach has now become available following the discovery of a novel property possessed by Type 13X molecular sieve (*2*) which can be adapted either to measure the naphthene and paraffin content of a saturate petroleum distillate at each carbon number, up to and including C_{10}, or to obtain fractions of segregated naphthenes and paraffins for further examination.

EXPERIMENTAL

Type 13X pelleted molecular sieves (Union Carbide and Carbon Corp.) were ground and screened to 40–60 mesh. The performance of this size of material was found to be superior to that of finer mesh; it also presents no difficulty in ensuring uniform packing of the relatively small bore columns employed.

For the analytical determination of the carbon number and naphthene/paraffin separations glass columns 12-inch × $^1/_8$-inch i.d. and 36-inch × $^1/_8$-inch i.d., respectively, were used. Both columns were packed with sieve in such a way that the sieve packing terminated $2^1/_2$ inches from the inlet and 1 inch from the outlet of the column. This arrangement tends to prevent any hold-up of high molecular weight material in the samples arising from cold spots at the end of the heater block. The inlet end was packed with $1^1/_2$ inches of 60–100 mesh Embacel (May and Baker Ltd) to assist in the even vaporization of the sample and to cut down dead space in the column; the exit end was left unpacked.

The analysis required the columns to be operated up to about 450 °C and a heater block (*3*) was used for this purpose. The columns were either maintained isothermally or temperature programmed from 180 °C at various rates up to about 450 °C with the flame ionization detector maintained at 200 °C. It is essential to eliminate all traces of oil from the

(1) F. T. Eggertsen and S. Groennings, ANAL. CHEM., **30**, 20 (1958).

(2) J. V. Brunnock and L. A. Luke, British Patent Application **08407/68**.

(3) J. V. Mortimer, and L. A. Luke, *Anal. Chim. Acta*, **38**, 119 (1967).

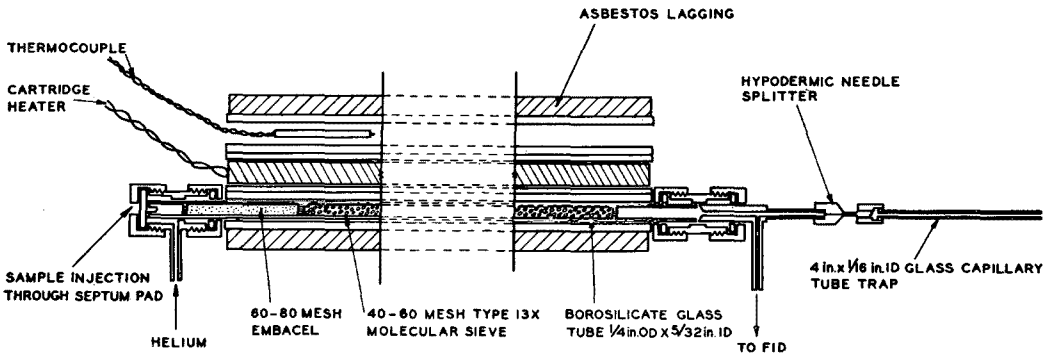


Figure 1. Schematic diagram of gas solid chromatographic apparatus

helium gas stream; otherwise, partial oxidation of the sample on the sieve will commence at temperatures in excess of 300 °C. Helium was used as the carrier gas at a constant mass flow of 80 ml/min. A schematic diagram of the apparatus is given in Figure 1.

For the carbon number analysis of a saturate petroleum distillate boiling up to 185 °C, the 12-inch × 1/8-inch i.d. column was maintained isothermally at 400 °C when at this temperature the C_{10} hydrocarbons were eluted within 20 minutes. The naphthene/paraffin analyses were obtained on the 36-inch × 1/8-inch i.d. column held at an initial temperature of 180 °C and temperature programmed at 2 °C per minute up to a final temperature of 400 °C. If the programming rate is increased up to about 20–25 °C per minute, more rapid analyses without too serious a loss of resolution may be obtained.

For separations where the fractions were required for further examination, glass columns 22-inch × 5/32-inch i.d. and 36-inch × 5/32-inch i.d. were used for the carbon number and naphthalene/paraffin separations, respectively. Both columns were packed with sieve in a similar manner to that employed for the analytical columns, and the fractions collected at the exit to the detector by means of capillary tubes chilled with cardice. The 22-inch × 5/32-inch i.d. column was found to be capable of handling sample sizes of up to 50 μl and when maintained isothermally at 400 °C and monitored with thermoconductivity detection, the individual carbon number eluates including C_{10} were collected easily in under 30 minutes.

For the naphthene/paraffin separations, the column employed was operated either isothermally or temperature programmed. The optimum sample sizes for the 36-inch × 6/32-inch i.d. column ranged from 8 μl at C_6 to <4 μl at C_{10}. These smaller sample sizes necessitated the use of a flame ionization detector with a 1:30 sample splitter. Temperature control and column loading are progressively more critical with each successive higher carbon number, so if a relatively large quantity of material of a particular carbon number is required, it is more convenient to use previously segregated carbon number fractions, an isothermally maintained column, and optimize the conditions accordingly. However, since the number of C_7 and C_8 isomers is small, their separation into naphthenes and paraffins is simple and they can be collected directly and consecutively from a feedstock using an initial column temperature of 200 °C and temperature programming at a rate of approximately 0.5 °C per minute. Any C_9 and C_{10} naphthenes and paraffins present can also be isolated in this manner. However, because of the low initial temperature required for the C_7 and C_8 separations, and the further reduction in programming rate needed above 300 °C their elution times are long.

In both the analytical and separation procedures, work with individual hydrocarbons showed that the residence time for the naphthene/paraffin separations at the high temperatures employed led to some irreversible adsorption of C_{10} isomers and that the hydrocarbon most affected was *n*-decane. This effect was due to the activity of the sieve which therefore has to be partially reduced by treatment with aqueous sodium hydroxide. The alkali treatment has to be controlled within narrow limits because the treatment alters the relative elution rates of the naphthenes and paraffins in such a way that the paraffins appear to elute more slowly than they do with untreated sieve.

This causes some of the C_9 paraffins to emerge concurrently with the more mobile of the C_{10} naphthenes. For analyses and separations of distillates boiling above 160 °C, therefore, the screened sieve prior to packing was treated by percolating 3% caustic soda solution through a 12-inch × 1/2-inch i.d. column of sieve at 4 ml/min for 25 minutes. The sieve was washed with water, then dried and heated to 450 °C for 3 hours. After treatment of the sieve in this manner, the reproducibility of retention volumes appears to be as good as that obtained with conventional liquid or support packed columns.

To demonstrate the separations achieved and to support investigations into the elution order, other auxiliary analytical procedures were employed. The separated fractions were examined by gas-liquid chromatography (GLC) using a Perkin Elmer 116 chromatograph fitted with a 300-foot × 0.010-inch i.d. glass capillary coated with silicone oil, and effluent from this column was also passed via a sample splitter to an AEI MS 12 mass spectrometer for hydrocarbon type classification. Meanwhile, in order to distinguish between the elution order of cyclopentanes and cyclohexanes, the cyclohexanes were dehydrogenated. This was accomplished using a microdehydrogenation apparatus consisting of a 6-inch × 5/32-inch i.d. glass column containing platinum on 40–60 mesh charcoal as catalyst (*4*). The dehydrogenations were carried out at 325 °C with hydrogen as the purge gas at a flow rate of 2 ml/min using a 100-μl sample.

RESULTS AND DISCUSSION

General Considerations. Carbon number separations on solid adsorbents have previously been reported (*1*). The separations are dependent upon specifically different energetically sorbing areas present on the surfaces of the sieve. The nature of the interplay between these active areas and the hydrocarbons absorbed is such that the differences that exist between the molecular characteristics of naphthenes and paraffins are sufficient to cause the residence time of most of

(4) H. C. Rampton, ANAL. CHEM., **21**, 1377 (1949).

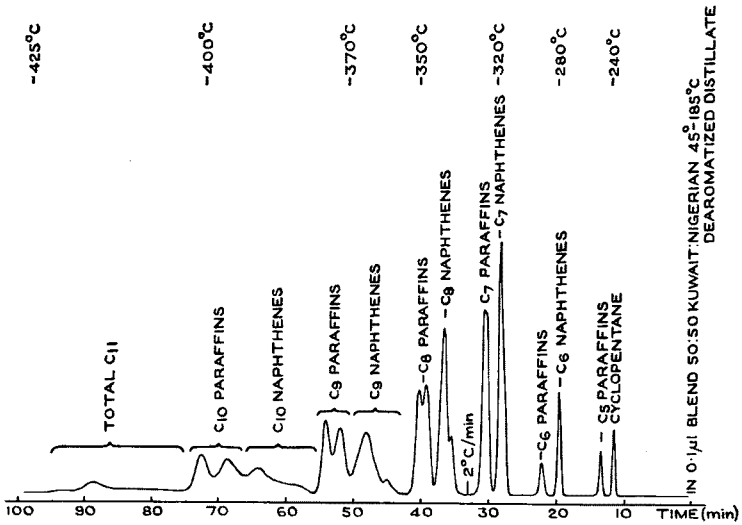


Figure 2. Typical GSC chromatogram obtained with Type 13X Sieve when used for quantitative analysis

Conditions	
Column:	3 ft × 1/8-inch i.d. Type 13X Sieve, 40–60 mesh. 3% NaOH treated
Temperature program:	175 °C + 5 °C/min + 2 °C/min
Flow rate:	80 ml/min He
Detector:	FID
Sample size:	0.1 μl
Chart speed:	15 inch/hour

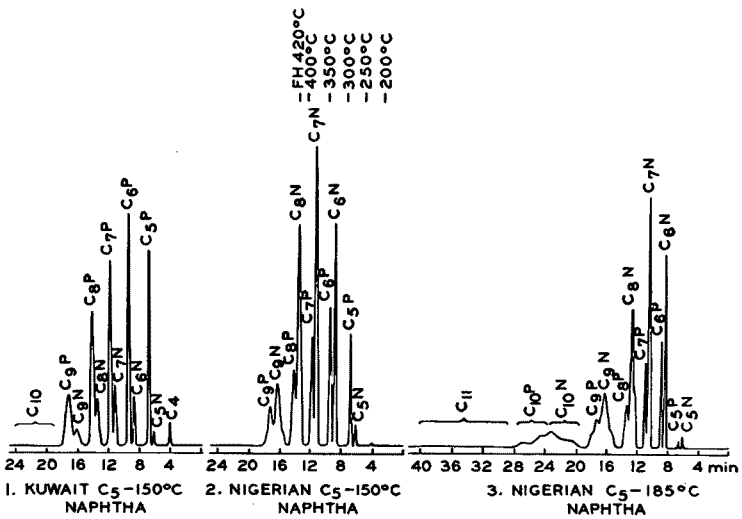


Figure 3. Rapid analyses of dearomatized naphthas

Conditions	
Column:	3 ft × 1/8-inch i.d. Type 13X Sieve, 40–60 Mesh. 3% NaOH treated
Program:	150 °C + 20 °C/min FH 420 °C
Flow rate:	80 ml/min He
Detector:	FID

Table I. Separation by Carbon Number Quantitative Results

Carbon number	Blend A			Blend B			Blend C		
	% Wt in blend	Found, %	Difference, %	% Wt in blend	Found, %	Difference, %	% Wt in blend	Found, %	Difference, %
C_7	25.42	25.32	−0.4	23.12	23.44	+1.3	24.31	24.30	0.0
C_8	27.16	27.41	+0.9	23.54	23.00	−2.3	24.57	24.73	+0.7
C_9	18.28	18.54	+1.4	28.50	28.22	−1.0	25.22	25.72	+2.0
C_{10}	29.13	29.00	−0.4	24.83	24.60	−1.0	25.90	25.95	+0.2

the paraffins on the surfaces of the sieve to be greater than that of most of the naphthenes (5). Therefore under suitable conditions, a naphthene/paraffin separation for each carbon number will occur. Too high a temperature will reduce the adsorption of the hydrocarbons below the level at which an effective separation of naphthenes and paraffins can occur. The result will be a carbon number separation only. A carbon number separation therefore, is achieved with the use of short columns maintained isothermally at temperatures high enough to ensure the elution of all the individual carbon number fractions. The temperatures are governed by the molecular weight range of the feedstock and need to be around 100–250 °C above the average boiling point for components of the highest carbon number. In the naphthene/paraffin separations, longer columns and lower average temperatures are required but in view of the separation factors between carbon numbers, it becomes necessary to program this temperature if a wide boiling feedstock is used. In order to avoid the interference that arises from the selective retention of aromatics on the surfaces of the sieve, dearomatized feedstocks have been used. The principal sources of this interference are benzene and toluene, for they elute concurrently with the C_9 and C_{10} saturated hydrocarbons, respectively. Higher aromatics were found to elute slowly, after the last of the saturates having a 185 °C end point. The naphthene and paraffin contents of a reasonably well fractionated distillate boiling up to 115–120 °C are capable of direct determination. Both benzene and toluene elute after the C_8 isomers, the highest boiling hydrocarbons present in this boiling range.

The type separation of straight run distillates boiling above 120 °C can also be determined, without prior dearomatization, if the total aromatic content of the distillate is known or if an internal standard, such as *n*-hexane, is incorporated before the determination. A limited amount of work on a number of distillates in the 185–250 °C boiling range, also showed that the limit of a carbon number separation appears to be between C_{11} and C_{12} when overlapping was found to occur. The existence of this overlap between components of different carbon number nullifies the effectiveness of the naphthene/paraffin separations, and the analytical determination of a carbon number or naphthene/paraffin separation is confined to distillates boiling up to about 200 °C. Even at this cut point, however, the C_{11} component may contain some C_{12} isomers.

Analysis. An analytical GSC chromatogram of a 45–186 °C saturate distillate obtained in a total time of 100 minutes is shown in Figure 2. Figure 3 shows the (GSC) gas solid chromatogram of distillates with 150 °C end points derived from naphthenic and paraffinic type crude oils when the programming rate is increased to 20 °C per minute. With distillates boiling above 150 °C, and a fast programming rate, the

(5) J. V. Brunnock and L. A. Luke, unpublished results.

Table II. Relative Recoveries of Naphthenes and Paraffins (C_7P = 1.00)

Carbon number	Untreated Type 13X molecular sieve, Blend A	Untreated Type 13X molecular sieve, Blend B	Untreated Type 13X molecular sieve, Blend C	3% NaOH modified Type 13X molecular sieve, Blend A	3% NaOH modified Type 13X molecular sieve, Blend B	3% NaOH modified Type 13X molecular sieve, Blend C
C_7N	1.02	1.04	1.01	1.02	1.02	1.00
C_7P	1.00	1.00	1.00	1.00	1.00	1.00
C_8N	1.02	0.99	1.04	1.03	1.02	1.01
C_8P	0.99	0.96	1.00	1.01	1.00	0.98
C_9N	1.04	1.00	0.99	1.04	1.04	1.02
C_9P	1.01	0.97	0.97	1.01	1.01	0.99
$C_{10}N$	0.95	0.94	0.93	1.02	1.05	1.05
$C_{10}P$	0.93	0.90	0.87	0.99	1.02	1.02

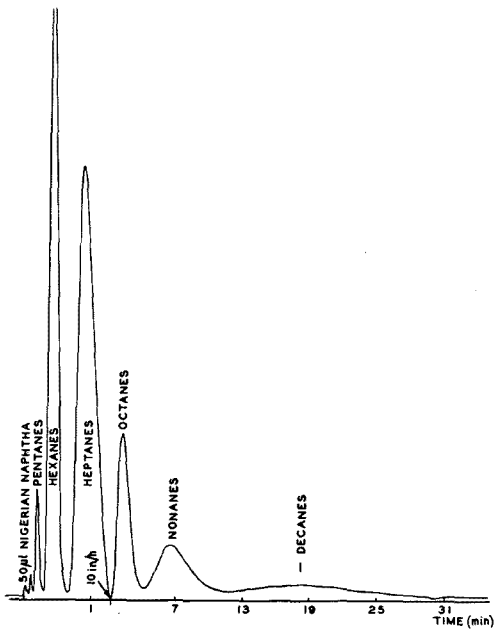


Figure 4. Carbon number separation with Type 13X Sieve

Conditions
Column: 22 inch × 5/32 inch i.d. type 13X Sieve, 40–60 mesh
Temperature: 400 °C
Flow rate: 80 ml/min He
Detector: TCD
Chart speed: 60 inch/hour and 10 inch/hour

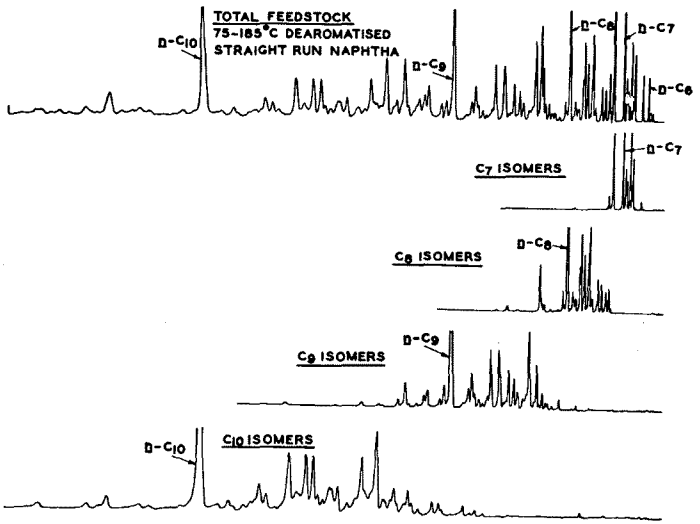


Figure 5. Chromatograms of feedstock and its components separated according to carbon number

Conditions	
Column:	300 ft × 0.010 inch i.d. silicone oil
Temperature:	70 °C
Carrier gas:	H_2
Inlet pressure:	2.0 kg/cm²
Detector:	FID

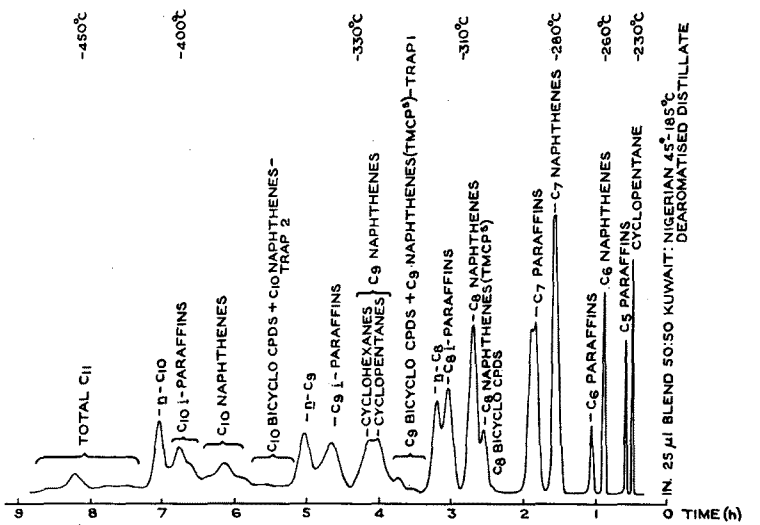


Figure 6. Typical GSC chromatogram obtained with Type 13X Sieve when used for collection and identification of fractions

Conditions			
Column:	3 ft × 5/32 inch i.d. type 13X mol sieve, 40–60 mesh. 3% HaOH treated		
Temperature:	Programmed	Splitter ratio:	30:1
Inlet pressure:	11 psig He	Sample size:	25 µl
Flow rate:	80 ml/min	Chart speed:	2½ inch/hour
Detector:	FID		

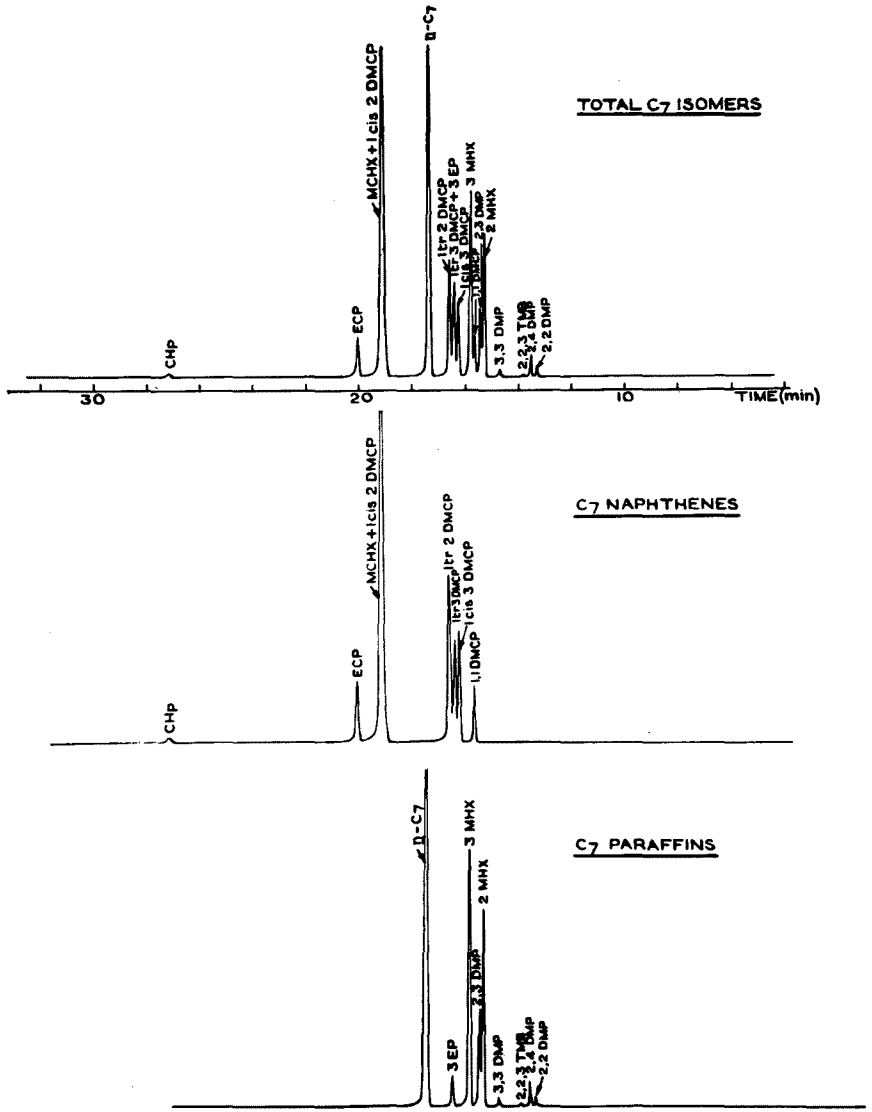


Figure 7. GLC chromatograms illustrating naphthene/paraffin separation of C_8 isomers ex 75–185 °C dearomatized feedstock

Conditions	
Column:	300 ft × 0.010 inch/i.d. silicone oil
Temperature:	50 °C
Inlet pressure:	1.25 kg/cm²H_2
Detector:	FID

separation deteriorates with the increase in the number of possible isomers, and the naphthene/paraffin ratio of the easily measurable total C_{10} content becomes more difficult to estimate; this is shown by the other chromatogram in Figure 3.

When the analyses were repeated in conjunction with a short precolumn of Type 5A molecular sieve, the individual *n*-paraffin content of the distillates may also be determined by difference.

The precision of the analyses was demonstrated by the agreement between the results of capillary GLC analyses of a number of light distillates and the totals obtained for C_7 naphthene and paraffin isomers. Three blends A, B, and C were prepared having a *n*-decane concentration of 5, 15, and

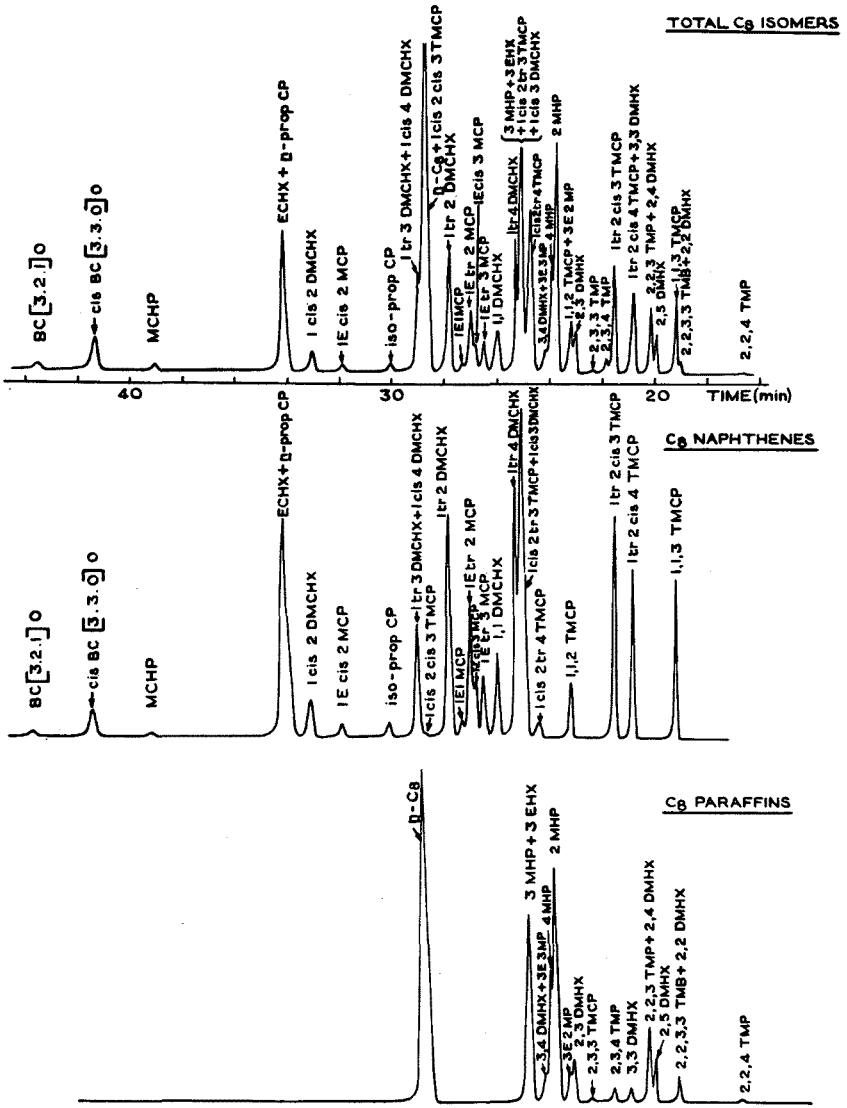


Figure 8. GLC chromatograms illustrating naphthene/paraffin separation of C_8 isomers ex 75–185 °C dearomatized feedstock

Conditions	
Column:	300 ft = 0.010 inch i.d. silicone oil
Temperature:	50 °C
Inlet pressure:	1.25 kg/cm^{2}H$_2$
Detector:	FID

50% of the total C_{10} paraffins, respectively. In each blend each bulk naphthene and paraffin had at least three components chosen in such a way that their boiling points covered the appropriate boiling range. The results demonstrating the quantitative basis of the carbon number separation obtained in a total analysis time of 20 minutes, are given in Table I. This ability to determine the carbon number concentration is useful for the rapid detection and estimation of the total concentration of any impurities of different carbon number present as saturates in petroleum gases and solvents; moreover because individual hydrocarbon impurities of the same carbon number elute together, there is a significant improvement in the lower limit of detection.

The naphthene and paraffin content of the blends were measured using both untreated and 3% NaOH treated sieve as the column packing. The recoveries expressed in terms of the

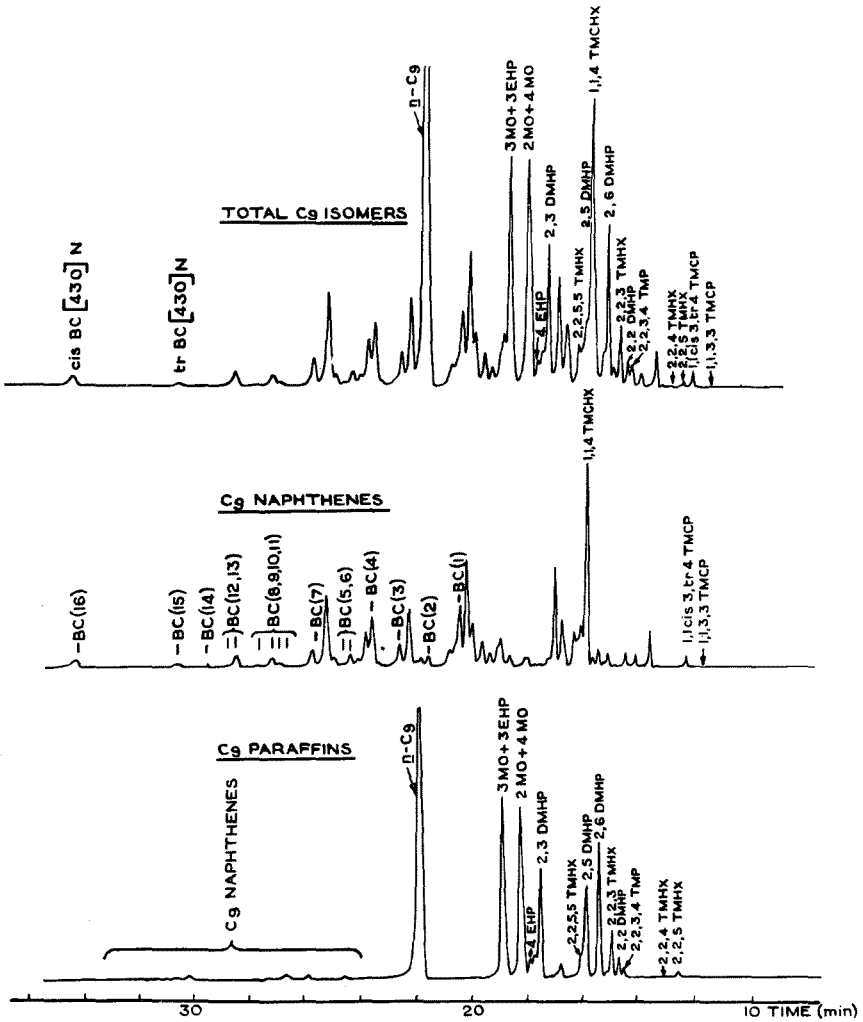


Figure 9. GLC chromatograms illustrating naphthene/paraffin separation of C_9 isomers ex 75–185 °C dearomatized feedstock

Conditions	
Column:	300 ft × 0.010 inch i.d. silicone oil
Temperature:	70 °C
Inlet pressure:	2.0 kg/cm²H_2
Detector:	FID

Relative Response Factors based on total C_7 paraffins = 1.00 are given in Table II. In the table the improvement brought about by the sodium hydroxide treatment is shown. It is also apparent that the response of the flame ionization detector for paraffins is slightly different than its response for naphthenes. This difference in response may be due to individual differences between components that constitute the blends, but it may also be influenced by the fact that the detector response is roughly proportional to the relative amount of carbon that the compounds contain. A study of the results indicates that a basis exists for the development of a successful method for the quantitative estimation of naphthenes and paraffins in distillates of this boiling range.

Carbon Number Separation. The separation by carbon number of a 45–185 °C dearomatized naphtha is illustrated in Figure 4 with a GSC chromatogram obtained using a thermal conductivity detector as monitor. The separated fractions after collection were examined by capillary column GLC and in Figure 5 chromatograms of the feedstock together with those of its separated components are shown. The silicone oil used

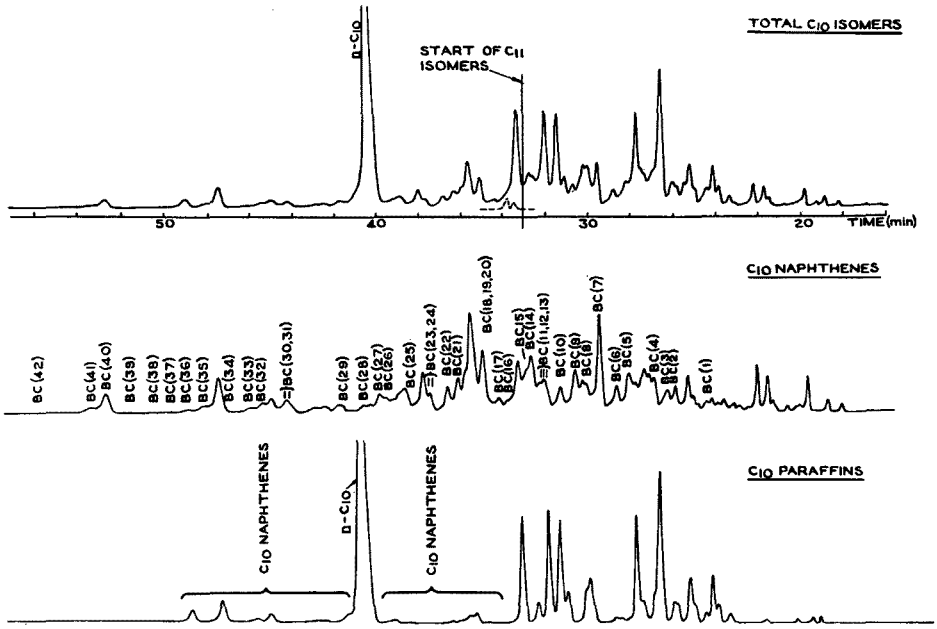


Figure 10. GLC chromatograms illustrating naphthene/paraffin separation of C_{10} isomers ex 75–185 °C dearomatized feedstock

Conditions			
Column:	300 ft × 0.010 inch i.d. silicone oil	Temperature:	70 °C
		Inlet pressure:	2.0 kg/cm²H_2
		Detector:	FID

as the stationary phase gives a boiling point separation, and the chromatograms are so arranged in the figure that the overlap that exists in the GLC chromatograms between hydrocarbons of similar volatility but different carbon number is demonstrated. While some loss of detail is inevitable in the method of presentation, the extent of the overlap and the number of multicomponent peaks that would exist in the overlap areas are strikingly illustrated.

Naphthene and Paraffin Separations. The naphthene and paraffin separations are illustrated in Figure 6 which shows a GSC chromatogram that is typical of a temperature programmed run on a wide boiling range feedstock, while capillary column GLC analyses of the carbon number and the naphthene/paraffin fractions isolated from a 75–185 °C dearomatized feedstock are shown in Figures 7, 8, 9, and 10. In Figures 7 and 8, the individual C_7 and C_8 hydrocarbons are identified from the retention volumes reported in (6). In Figure 9, the majority of the C_9 paraffins together with a few of the C_9 naphthenes have also been identified from the results of previous work done in these laboratories. The remainder of the C_9 and all of the C_{10} hydrocarbons except for relatively minor components were categorized by the use of GLC-mass spectrometry. The mass spectra obtained in this way confirmed the type separation of the C_9 and C_{10} naphthenes, and the peaks where the presence of bicyclo components were indicated, have been individually numbered. The mass spectra also showed that approximately 3% of naphthenes were present in the C_{10} paraffin portion. The C_{11} component (Figure 6) was shown to be mainly naphthenic in nature and as its concentration is small, only the commencement of the C_{10}/C_{11} overlap is indicated and has been included for convenience in Figure 10.

The unavoidable loss of detail in Figure 10 and the lack of identification of individual components prevents a proper appreciation of the simplification that results from the type separation of the C_{10} hydrocarbons. However a detailed study of the individual hydrocarbons, identified in Figures 7, 8, and 9 shows the excellence of the carbon number and naphthene/paraffin separations. In both the carbon number and naphthene/paraffin separations, reproducible capillary chromatograms were obtained and the comparisons made with the chromatogram of the original feedstock (Figure 5) indicate that the effect on the concentration of an individual component of any loss that may arise from either the method of trapping employed or the possibility of irreversible adsorption occurring, is insignificant.

Elution Order within a Carbon Number Separation. Examination of Figure 6 shows that in the higher molecular weight range the naphthenes and paraffins at any one carbon number are partially resolved into a number of peaks.

This partial resolution indicates that at relatively low temperatures either individual hydrocarbons or specific groups of hydrocarbons within the main hydrocarbon types are eluted in a certain order. The use of a small precolumn of 5A molecular sieve to remove *n*-paraffins confirmed that the second of the two peaks that constitute the total paraffin content at each of the higher carbon numbers is the *n*-alkane. The selective

(6) A. G. Pelgár, J. J. Holst, and S. Groennings, ANAL. CHEM., **34**, 1226 (1962).

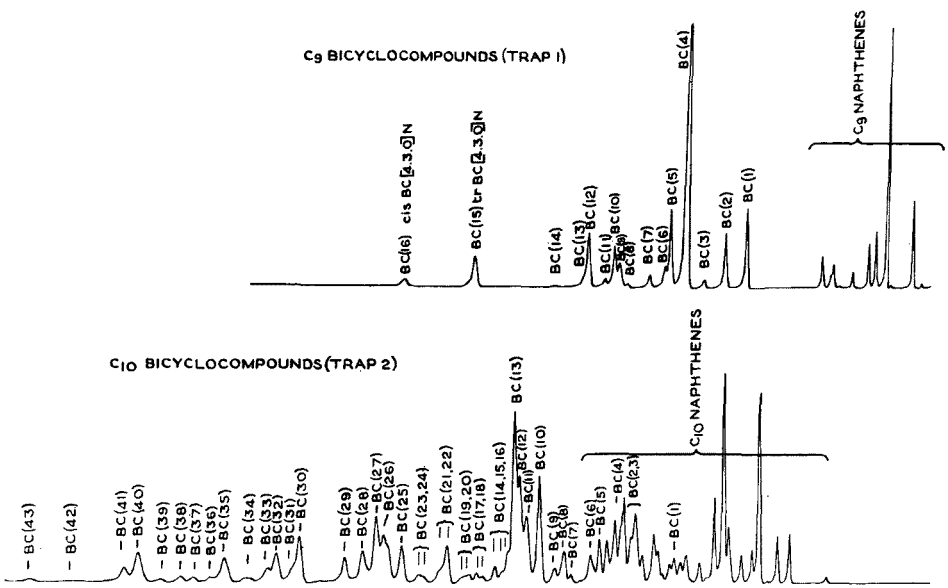


Figure 11. GLC chromatograms of C_9 and C_{10} bicycloparaffin concentrates

Conditions	
Column:	**300 ft × 0.010 inch i.d. silicone oil**
Temperature:	**70 °C**
Inlet pressure:	**2.0 kg/cm²H_2**
Detector:	**FID**

dehydrogenation of all except geminal substituted cyclohexanes, and the removal by sulfuric acid treatment of the aromatics that were formed, showed that the second peak occurring at the rear of the naphthene profile consists principally of cyclohexanes.

A series of trappings were then taken at the points indicated in Figure 6. The GLC/mass spectrometric analyses obtained on this C_9 and C_{10} trapped material, with the peaks numbered in the same sequence as they are in Figures 9 and 10 are shown in Figure 11. A comparison shows that the trapped material is a concentrate of bicyclo compounds and that these compounds are the first to elute in a naphthene separation. A total of 16 C_9 and 43 C_{10} bicyclo compounds are shown to have been concentrated.

The elution order of other hydrocarbon groups within the naphthene and paraffin types was also studied, mainly by an examination of the elution order of the C_8 isomers; these were chosen for the sake of simplicity and ease of identification.

A series of six consecutive trappings were taken over the C_8 elution band and analyzed by capillary chromatography. These analyses showed that the elution of the cyclopentanes was in the order tri, di, and monosubstituted cyclopentanes, the highest boiling disubstituted isomer 1 methyl-*cis*-2-ethylcyclopentane, bp 128.1 °C eluting before isopropylcyclopentane, bp 126.4 °C. The cyclohexanes behaved in a similar manner, the disubstituted isomers eluting as a class before the monosubstituted isomer. The elution of the paraffins was in the order tetra, tri, di, and monosubstituted alkanes with the *n*-alkane the last of the paraffins to elute.

A limited amount of further work suggested that a similar order of elution prevailed among the C_9 and C_{10} naphthenes and paraffins. The overlap between the different series of isomers is considerable but by the use of previously segregated material combined with careful control of temperature and trapping, it is possible to obtain concentrates of a particular group of isomers.

CONCLUSIONS

Saturate hydrocarbons in petroleum distillates boiling up to about 185 °C are quantitatively separated by carbon number or by bulk hydrocarbon type within each carbon number by the use, under certain conditions, of Type 13X molecular sieve. The influence of temperature and column length on performance has been examined and the conditions necessary for analysis or segregation and collection of the separated naphthene and paraffin components have been established, together with the probable order of elution within each bulk hydrocarbon type. The technique has been applied to different types of naphtha and numerous chromatograms illustrate the analyses and separations that are achieved.

It is envisaged that the technique in conjunction with other analytical procedures will enable a far more detailed and reliable individual component analysis of distillates in this boiling range to be obtained, while its simplicity and rapidity will also find many applications in refinery monitoring operations.

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Pyrolysis–Gas Chromatography of Hydrocarbons

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The pyrolysis gas chromatography of 83 C_6 to C_{10} compounds was studied. The pyrolysis product patterns for 24 alkanes, 49 straight chain, branched chain, and cyclic alkanes; and 10 alkynes are reported in terms of relative mole responses within specified retention index intervals. The patterns are repeatable and vary slightly within the temperature range 575° to 625 °C. A comparison of pyrograms with mass spectrograms for several C_6H_{12} isomers which are difficult to characterize mass spectrometrically is presented.

PYROLYSIS GAS CHROMATOGRAPHY (PGC) is a relatively new technique which has evolved in order to use the analytical capabilities of gas chromatography on nonvolatile solids. Levy (*1*) has carefully and in great detail reviewed the entire field of PGC. Materials such as high molecular weight polymers, drugs, and even bacteria have been thermally fragmented and the chromatogram of the pyrolyzate has been recorded. The method can also be applied to help solve one of the major problems remaining in gas chromatography today, namely, the qualitative identification of eluted compounds. Several investigators have recognized the potential of PGC in solving this problem and have reported on the vapor phase pyrolysis of organic compounds (*2–6*). Dhont (*2, 3*) and Weurman (*4*) utilized PGC by trapping the eluted vapors at the outlet of a conventional GC and pyrolyzing the trapped compounds. Levy and Paul (*7*) described a system which consists of a conventional GC, a flow delay-line trap pyrolyzer, and a second GC. A few selected compounds from an unknown mixture could be trapped in the delay-line and subsequently pyrolyzed. The chromatogram of the pyrolyzate (hereafter called pyrogram) was reproducible and could be used for identification. Sutton and Harris (*8*) connected the output from a conventional GC directly to the PGC system and studied the pyrolysis of several hydrocarbons. Goforth and Harris inserted a trapping column between a conventional GC and a rapid analysis PGC unit (*9*). Walker and Wolf (*10*) described a GC–pyrolysis–GC system for the complete analysis of chromatographic effluents. Here, the technique of interrupted elution chromatography was adapted to the separation chromatograph so that all the unknowns can be pyrolyzed and identified in a single GC analysis. Keulemans together with Perry (*5*) and Cramers (*6*) investigated the rates and mechanisms of gas phase thermal decomposition of hydrocarbons to determine the experimental parameters necessary to use PGC as an identification method. Wolf and Rosie (*11*) studied the effect of temperature on the vapor phase pyrolysis of 20 simple organic molecules.

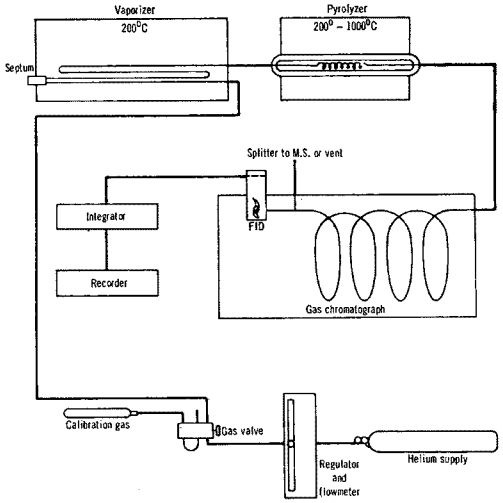


Figure 1. Block diagram of vapor phase pyrolysis gas chromatographic system

The pyrograms reported by the various investigators are not completely reproducible and at present they cannot be used for interlaboratory comparison. This paper is an attempt to form standard methods for the reporting of PGC data in a manner analogous to that used in reporting mass spectra. The results of the vapor phase pyrolysis of 83 different hydrocarbons plus several *cis–trans* isomers are reported. The hydrocarbons include straight and branched alkanes, alkenes, and alkynes and represent compounds which are similar, yet possess sufficient structural differences to determine the usefulness of PGC as a method of identification of chromatographic effluents. The pyrograms are significantly different so that, with the exception of *cis–trans* isomers, the compounds can be identified. In addition, it is shown that in several instances, compounds which are difficult to distinguish mass spectrometrically are readily identified by their pyrograms.

EXPERIMENTAL

Two separate pyrolysis systems were used for the work reported here. Two different systems were used to show that the thermal fragmentation pattern was repeatable, at least in our own laboratory, and to increase the rate at which compounds could be investigated. While identical in basic design, they contain different components obtained from different manufacturers. Both systems consist of a regulated helium supply, gas valve, injection system, vaporizer, variable temperature pyrolyzer, isothermal chromatographic column, splitter, flame ionization detector, recorder, and digital integrator. A block diagram of the system is shown in Figure 1. Liquid samples to be pyrolyzed were introduced through a silicone septum with a Hamilton Syringe (Model CR 700-20).

(1) R. L. Levy, *Chromatogr. Rev.*, **8**, 48 (1966).
(2) J. H. Dhont, *Nature*, **200**, 882 (1963).
(3) J. H. Dhont, *Analyst* (London), **89**, 71 (1964).
(4) C. Weurman, *Chem. Weekblad*, **59**, 489 (1963).
(5) A. I. M. Keulemans and S. G. Perry, "Gas Chromatography, 1962," M. Van Swaay, Ed., Butterworth, (Washington, D. C.), 1962, pp 356.
(6) C. A. M. G. Cramers and A. I. M. Keulemans, *J. Gas Chromatog.*, **5**, 58 (1967).
(7) E. J. Levy and D. G. Paul, *J. Gas Chromatogr.*, **5**, 136 (1967).
(8) R. Sutton and W. E. Harris, *Canadian J. Chem.*, **45**, 2913 (1967).
(9) R. R. Goforth and W. E. Harris, Preprints of papers "7th International Symposium on Gas Chromatography and Its Exploitation," C. L. A. Harbourn, Ed., paper 16.
(10) J. Q. Walker and C. J. Wolf, ANAL. CHEM., **40**, 711 (1968).
(11) T. Wolf and D. M. Rosie, *ibid.*, **39**, 725 (1967).

The gas valve was used to admit known calibration gases to the system. The vaporizer simulated a conventional GC column and was maintained at 200 °C. It was constructed of stainless steel tubing (3 ft by $\frac{1}{8}$ inch o.d.).

In both systems, the pyrolyzer consisted of a 20-inch long gold tube having a 0.040-inch i.d. and wound into a $\frac{1}{2}$-inch diameter helix. The pyrolyzer is similar to that described by Cramers and Keulemans (*6*). The gold helix was located inside a nickel cylinder of large thermal mass which was placed inside a combustion furnace controlled with a Wheelco 407 capacitrol coupled with a 610 Pilot Amplifier and a saturable core reactor. The temperature of the pyrolyzer was controlled to within ±5 °C. The systems could be operated and controlled at any temperature in the range 200 to 900 °C.

In one system the helium flow rate exiting the pyrolyzer was 50 ml/min. At the three temperatures used for pyrolysis 575, 600, and 625 °C, the corresponding residence times—*i.e.*, the time it takes the hydrocarbon to pass through the high temperature region of the furnace—were 1.9, 1.8, and 1.7 seconds, respectively. The analysis column was a 15-foot by $\frac{1}{8}$-inch o.d. stainless stee ltube packed with 25% DC 200 on 60/80 mesh Chromosorb P. The column was operated isothermally at 120 °C and was housed in an Aerograph Model 600-D gas chromatograph containing the flame detector (FID). The column conditions were chosen so that the pyrolysis products from C_8 compounds (including the unreacted parent) were separated in less than 8 minutes. The column separated on the basis of boiling point and did not always completely separate structural isomers.

In the second system, the helium flow rate leaving the pyrolyzer was 30 ml/min. The residence times in the furn ace were 3.2, 3.0, and 2.8 seconds for pyrolysis temperatures of 575, 600, and 625 °C, respectively. A 30-foot by $\frac{1}{8}$-inch o.d. DC-200 column on 60/80 Chromosorb P was used for the analysis. The column was operated isothermally at 170 °C in a Perkin-Elmer Model F-11 gas chromatograph equipped with a flame detector.

The splitter delivered 10% of the gas stream to the flame detector and 90% was either vented to the atmosphere

Table I. Thermal Fragmentation Patterns Observed from 600 °C Pyrolysis of Alkanes

		Normalized mole-area for a given retention index interval																		
Compound	C#	50/150 (C_1)	150/250 (C_2)	250/350 (C_3)	350/400 (C_4)	401/449	450/474	475/499	500/524	525/549	550/574	575/599	600/624	625/649	650/674	675/699	700/724	725/749	750/774	775/799	>800
n-Hexane	6	74	100	58	33																
2 Methylpentane	6	60	60	100	50				10												
3 Methylpentane	6	100	85	28	64				50												
Methylcyclopentane	6		57	100																	
2,2-Dimethylbutane	6	100	80		90																
n-Heptane	7	33	100	35	25				12				6								
n-Octane	8	32	100	35	20				13			12				5					
2,2,3 Trimethyl-pentane	8	100	19	50	87	17			15					7/2	12			19			
2,2,4 Trimethyl-pentane	8	50	2	30	100				3				8	11							
2,3,4 Trimethyl-pentane	8	95	12	100	49		9			63		3	4		4	25					
2,3,3 Trimethyl-pentane	8	100	64	75	53					52		4	9	27		3	10				
n-Nonane	9	34	100	35	16				10				7			9					
3,3 Diethylpentane	9	84	100	5	4				11				53		1	1	48			1	
2, 4 Dimethyl-3-ethylpentane	9	100	44	90	25		12		38		26		50	15				7		13	
2,2,5 Trimethyl-hexane	9	65	22	40	100		17		20								1		4		
2,2,4 Trimethyl-hexane	9	64	42	38	100		5		35				11				2/3		7		
4,4 Dimethyl-heptane	9	50	100	65	59				5				23				2			6	
3,3 Dimethyl-heptane	9	70	100	18	71				24				1	3		8					6
2,2 Dimethyl-heptane	9	82	89	51	100			31	19				2				6			13	
3 Ethylpentane	9	58	100	14	47				16				10		2	17				5	
2 Methyloctane	9	52	100	65	42		9		9		4		13		7				1		3
3 Methyloctane	9	48	100	44	25				32		4				3		5		1	6	
4 Methyloctane	9	51	100	62	23				11			17			4	9			2	2	
n-Decane	10	38	100	36	20				12				13			10				8	3

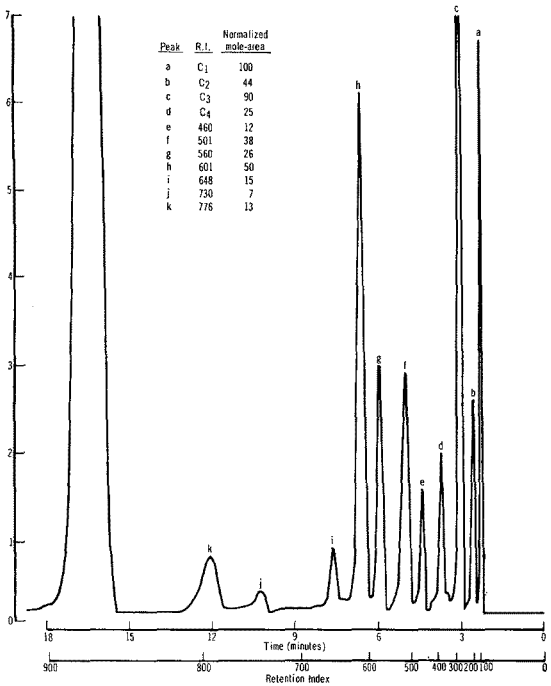


Figure 2. Pyrogram from the 600 °C thermal fragmentation of 2,4-dimethyl-3-ethylpentane

through a restrictor or delivered to the mass spectrometer through a molecular separator (*12*).

The compounds studied were obtained from either Chemical Samples Co., (Cleveland, Ohio) or from James Hinton Inc., (Valparaiso, Fla.). The purity of each sample was determined by decreasing the pyrolyzer temperature to 200 °C and injecting an aliquot of the material into the system. The purity of all compounds was equal to or greater than the manufacturers' stated value of 99%.

The sensitivity of the flame detectors was determined directly for most of the products reported. For those not directly determined the sensitivity was estimated from the response of similar compounds. The area and elution time of each peak in the program was measured and time recorded with the aid of an Infotronics digital integrator (Model CRS-100). The area of each peak was converted into moles. If a particular peak is actually a composite of two similar compounds, such as 1-pentene and 2-pentene, little error is introduced in the determination since the molar response in a flame detector is essentially identical for hydrocarbon isomers. The moles were normalized with respect to the most abundant compound in the pyrogram other than the parent. The normalization technique assures that the fragmentation pattern is preserved even though different amounts of sample may be decomposed.

Prior to the pyrolysis experiment, a mixture containing C_1 to C_{10} normal alkanes was introduced. The elution time of all 10 normal alkanes was determined. It was assumed that CH_4 was not retained by the column and that its elution time corresponded to the dead time of the system. The elution time of each peak in the pyrogram was converted to a retention index following the method of Kovats (*13*). The pyrograms

(12) M. A. Grayson and C. J. Wolf, ANAL. CHEM., **39**, 1438 (1967).
(13) E. sz. Kovats, "Advances in Chromatography," Vol. I, J. C. Giddings and R. Keller, Eds., Marcel Dekker, New York, 1965 pp 229.

Table II. Thermal Fragmentation Patterns Observed from 600 °C Pyrolysis of Straight Chain Alkenes

		Normalized mole-area for a given retention index interval																				
Compound	C#	50/150 (C_1)	150/250 (C_2)	250/350 (C_3)	350/400 (C_4)	401/449	450/474	475/499	500/524	525/549	550/574	575/599	600/624	625/649	650/674	675/699	700/724	725/749	750/774	775/799	800
1 – Hexene	6	38	100	89	68			23	4												
2 – Hexene	6	85	100	16	89		13		82			8									
3 – Hexene	6	88	17	2	12				100		3			3	3						
1 – Heptene	7	20	100	53	57				14		4		12								
Trans-2-heptene	7	41	100	38	45				4		22		1	2							
Trans-3-heptene	7	100	98	15	43				15	41		7	21	29							
1 – Octene	8	20	100	52	37				28				10	3							
Trans-2-octene	8	35	100	25	47				6		14		9	6			2			3	
Trans-3-octene	8	86	100	32	37				10	34				14	19		21	8	5		
Trans-4-octene	8	43	100	12	21				6	8			8	15	22			3	11		
1 – Nonene	9	39	100	66	44				22	5			36	8			6				
Trans-2-nonene	9	28	100	28	33				13	17			3				4				1
Trans-3-nonene	9	50	100	26	34				8	15			6	8	7						
Trans-4-nonene	9	46	100	30	23								6	7			7	6	15		
1 – Decene	10	39	100	63	50				19			4	23			33					
Trans-2-decene	10	39	100	47	37				9	19			19				4				
Trans-3-decene	10	44	100	33	28				14	16			4	6		9	3				
Trans-4-decene	10	33	100	20	26				4		5		5	5	6	4	6	6			
Trans-5-decene	10	86	100	45	45				26	14			12		22		27			10	21

Table III. Thermal Fragmentation Patterns Observed from 600 °C Pyrolysis of Branched and Cyclic Alkenes

Compound	C#	Normalized mole-area for a given retention index interval																			
		50/150 (C_1)	150/250 (C_2)	250/350 (C_3)	350/400 (C_4)	401/449	450/474	475/499	500/524	525/549	550/574	575/599	600/624	625/649	650/674	675/699	700/724	725/749	750/774	775/799	800
Cyclohexene	6		100	20	61					11		9			4						
3-Methyl-1-pentene	6	67	74	19	52		2	2	100			47									
4-Methyl-2-pentene	6	100	13	23	31		2		77					28							
4-Methyl-1-pentene	6	16	11	100	24			4	14					2							
3-Methyl-2-pentene	6	100						89				6									
2-Methyl-2-pentene	6	81	21	2	12			100						30							
3-Methyl-cyclopentene	6	21	27	33	30			30	37	60				100							
2-Ethyl-1-butene	6	100	24	12	16			89							43						
2,3-Dimethyl-1-butene	6	41	6	10	4				35				100	82							
3,3-Dimethyl-1-butene	6	67	11	9	26							8	100	10							
3,3,5 Trimethyl-1-hexene	9	77	33	45	100	9			54			11	11		6	5	8	11			
3,5 Dimethyl-3-heptene	9	100	85	27	10				18				9	23	25		7				
2,3 Dimethyl-2-heptene	9	94	100	65	11				14		14		49	18			13		19		11
2,6 Dimethyl-3-heptene	9	86	42	100	35				11	25		20		39	14				11		
2,2 Dimethyl-3-heptene	9	100	73	52	42				11	22				11/22	23			6	8		
2 Methyl-3-octene	9	88	100	46	17			9		18		8		24	3				6		
2 Methyl-2-octene	9	45	100	28	26		2		34					23			2				
2 Methyl-1-octene	9	31	100	40	55			46	17			11		1							

are, therefore, reported in tabular form, the normalized mole areas as a function of Kovats' Index (25 unit intervals). This procedure tends to minimize differences in analysis procedures by providing an index system which is essentially independent of column conditions.

With both systems usually 2–10% of the parent was thermally fragmented. The low decomposition rate minimized secondary reactions.

While the chromatograms of the pyrolytic products were not identical in both systems, the pyrogram spectra reported in terms of normalized concentration and retention index (Kovats index) are essentially identical.

The chromatogram of one of the more complex pyrolyzates, 2,4-dimethyl-3-ethylpentane, is shown in Figure 2. Both real times and the Kovats' retention index are shown along the abscissa. Eleven separate pyrolytic peaks are resolved together with the large parent peak at 870 R.I. Although peak *c* appears to be the largest peak, the sensitivity for CH_4, peak *a*, is much lower and on a mole basis CH_4 is the largest pyrolytic product. Peaks *e*, *f*, and *g* are C_5 compounds, *h* and *i* are C_6 compounds, while *j* and *k* are C_7 compounds.

After one of the gold reactors had been used for more than 1000 separate pyrolysis experiments, it was carefully slit lengthwise and opened. Surprisingly, there was no deposit of carbon. This is contrary to the results reported by Cramers and Keulemans (*6*) who stated that "cracking reactions are invariably accompanied by carbon formation; Au as reactor material has the advantage that carbon can easily be burnt off with air." It is possible that a carbon rich varnish is formed on the reactor walls, but there is definitely no carbon black formed.

RESULTS

The thermal fragmentation patterns observed from the 600 °C pyrolysis of 24 different saturated hydrocarbons are summarized in Table I. The name of the material pyrolyzed is given in the first column and the number of carbon atoms in the compound in the second column. The third column gives the normalized value for methane; the fourth column the value for ethylene and ethane; the fifth column the value for propylene; and the sixth column the value for 1-butene plus 2-butene plus butadiene. The rest of the columns show the normalized value for the product observed with retention index within the interval shown in the top row of the table. In a few cases two peaks are observed within the same interval. For example, in the pyrolysis of 2,2,3-trimethylpentane two products are observed whose retention index is greater than 625 but less than 649; this is indicated by the slanted line and shown as 7/2. The first elutant in the interval has a normalized value of 7, the second a value of 2. The only saturated products observed were methane and a small amount of ethane. However, the C_2 peak always contained much more ethylene than ethane.

Table IV. Thermal Fragmentation Patterns Observed from 600 °C Pyrolysis of Alkenes (Dienes)

		Normalized mole-area for a given retention index interval														
Compound	C#	50/150 (C_1)	150/250 (C_2)	250/350 (C_3)	350/400 (C_4)	400/450	450/475	475/500	500/525	525/550	550/575	575/600	600/625	625/650	650/675	675/700
1,3-Hexadiene	6	14	6	1	3			9	17				100			
1,4-Hexadiene	6	32	15	17	23				6	43			100	13	19	9
1,5-Hexadiene	6	8	21	100	25				1	10			3	7	23	30
2,4-Hexadiene	6	14	5	1	2				7	17			100			
1,3-Cyclohexadiene	6	54	20	7	14					72			9	100		
2-Methyl-1, 3-pentadiene	6	74	22	11	11				100			11				
3-Methyl-1, 3-pentadiene	6	64	21						100			9				
4-Methyl-1, 3-pentadiene	6	62							100							
2-Methyl-1, 4-pentadiene	6		3	5	30				6			100		77		
2,3-Dimethyl-1, 3-butadiene	6	100	76	50	15			28								
2-Ethyl-1, 3-butadiene	6	23	11	4	2			17						100		
2,7 Nonadiene	9	46	55	21	100				87				6/5			

Table V. Thermal Fragmentation Patterns Observed from 600 °C Pyrolysis of Alkynes

		Normalized mole-area for a given retention index interval																				
Compound	C#	50/150 (C_1)	150/250 (C_2)	250/350 (C_3)	350/400 (C_4)	401/449	450/499	500/524	525/549	550/574	575/599	600/624	625/649	650/674	675/699	700/724	725/749	750/779	775/799	800/849	850/899	>900
1-Hexyne	6	31	74	100/62	62			15					48	11	15							
2-Hexyne	6	97	100	6	6			13		81			3									
3-Hexyne	6	100	28	2	19		15		2													
4-Methyl-1-pentyne	6	28	6	100/10	10		8		23				23	4								
4-Methyl-2-pentyne	6	100	17	26	4		4	7		14			52		2							
1-Nonyne	9	40	100	53/32	38			14	9	6	47		6	15	9				10			
2-Nonyne	9	43	100	23	19	17		45		19				9				10	10	6	6	17
3-Nonyne	9	94	100	36	57			14	22				39					8	11	10	8	
4-Nonyne	9	44	100	65	24			16			6	6	6	8	8		19		8	23		
7-Methyl-3-octyne	9	100	50	91	88				31				62					13		18	18	

The fragmentation patterns from the 600 °C pyrolysis of 19 straight chain alkenes and 18 branched chain and cyclic alkenes are summarized in Tables II and III, respectively. The largest peak in the spectra of all straight chain alkenes except 3-hexene and 3-heptene is ethylene.

The thermal fragmentation pattern from 12 alkenes containing two double bonds (dienes) is shown in Table IV. In none of the examples cited is ethylene the largest peak. In only one case (2,3-dimethylbutadiene) is methane the largest and only with 1,5-hexadiene is C_3 the largest. The large peaks observed with retention indices of 500–650 indicate that considerable carbon skeleton rearrangement occurs without C–C bond cleavage.

The fragmentation patterns from 9 alkynes is shown in

Table VI. Repeatability of the Thermal Fragmentation Patterns from 600 °C Pyrolysis of 1-Hexene

Run No.	Normalized mole-area for a given retention index interval					
	50/ [a] 150	150/ [b] 250	250/ [c] 350	350/ [d] 400	475/ [e] 499	500/ [f] 524
1	38.2	100	90.6	67.9	23.4	3.4
2	38.0	100	83.7	67.5	23.9	4.1
3	38.2	100	98.2	68.0	23.8	3.8
4	38.2	100	90.1	68.1	23.3	3.5
5	38.0	100	89.5	68.2	23.8	3.9
6	37.9	100	90.4	68.4	24.2	4.4
7	37.8	100	88.6	67.8	23.8	4.4
8	40.0	100	86.5	65.6	21.0	5.4
Avg	38.2	100	88.8	67.6	23.3	4.1
σ	0.7	–	2.3	0.9	0.9	0.6

The products in the retention index intervals are: (a) CH_4, (b) C_2H_4, (c) C_3H_6, (d) 1- and 2-C_4H_8, (e) C_5H_{10}'s, and (f) C_5H_8

Table V. In the three 1-alkynes studied, a large amount of propyne was observed. With the chromatographic conditions used in our experiments, propyne is resolved from propylene and the ratio of these compounds is indicated in the C_3 column as propylene/propyne.

The fragmentation patterns observed from the pyrolysis of 1-hexene at 600 °C from 8 separate determinations is shown in Table VI. These data were obtained over a period of 2 weeks. The repeatability of the normalized molar areas is excellent; in fact, it is necessary to use 3 significant figures to show the deviation. The average value of the 8 determinations is shown in the second last row and the standard deviation (σ) is shown in the last row. The per cent deviation from the average value for C_1, C_3, C_4, 1-pentene (peak with retention index 480), and pentadiene (peak with retention index 520) is 1.8, 2.6, 1.3, 3.9, and 15%, respectively.

All of the 83 hydrocarbons shown in Tables I through V can be readily identified from their thermal fragmentation patterns. The only class of compounds which cannot be identified from their pyrograms are *cis–trans* isomers. This is indicated in Table VII where the fragmentation patterns from *cis*- and *trans*-2-hexene; *cis*- and *trans*-3-hexene; and *trans*-2-*trans*-4-, *cis*-2-*trans*-4-, and *cis*-2-*cis*-4-hexadiene are shown. The pyrograms from the *cis–trans* isomers are virtually identical and are not useful for qualitative identification. However, these results do give a good indication of the repeatability of the thermal fragmentation technique. There is, however, a small difference in the amount of parent which decomposes at a given set of experimental conditions. The *trans* isomer is usually slightly more thermally stable than its corresponding *cis* form.

The effect of pyrolysis temperature on the thermal fragmentation pattern of 4-methyl-2-pentene and 1-hexene is summarized in Table VIII. When the temperature in the pyrolytic reactor changes, the residence time of the hydrocarbon in the high temperature region also changes, so that two changes are produced simultaneously. Over the limited temperature range studied, the fragmentation pattern varies only slightly indicating that small variation in either the pyrolysis temperature or the residence time need not be considered. It is important to note that the per cent of parent converted into products increases with both temperature and residence time, but the normalized fragmentation pattern remains the same.

Sutton and Harris (*8*) reported that air had the effect of increasing the amount of hydrocarbon decomposition. When air was present, they observed that the amount of decomposition was equivalent to that observed at a temperature 10–20 °C greater than in the absence of air. In several experiments dry nitrogen was bubbled through liquid 1-hexene to remove all the dissolved air. A small sample (1 μl) was then carefully injected so that air was not present during the pyrolysis. The fragmentation pattern is identical in the presence and ab-

Table VII. Comparison of Thermal Fragmentation Patterns from 600 °C Pyrolysis of *cis* and *trans* Alkene Isomers

Compound	Normalized mole-area for a given retention index interval											
	50/150 (C_1)	150/250 (C_2)	150/350 (C_3)	350/400 (C_4)	400/450	450/475	475/500	500/525	525/550	550/575	575/600	600/625
Trans-2-Hexene	70	100	24	78		9		69		9		
Cis-2-Hexene	71	100	17	82		10		71		10		
Trans-3-Hexene	95	20	4	18				100		4		
Cis-3-Hexene	100	19	3	20				99		4		
Trans-2-trans-4 hexadiene	29	8	1	4				12		33		100
Cis-2-trans-4 hexadiene	31	10	3	7				13		36		100
Cis-2-Cis-4 hexadiene	31	10	1	4				14		39		100

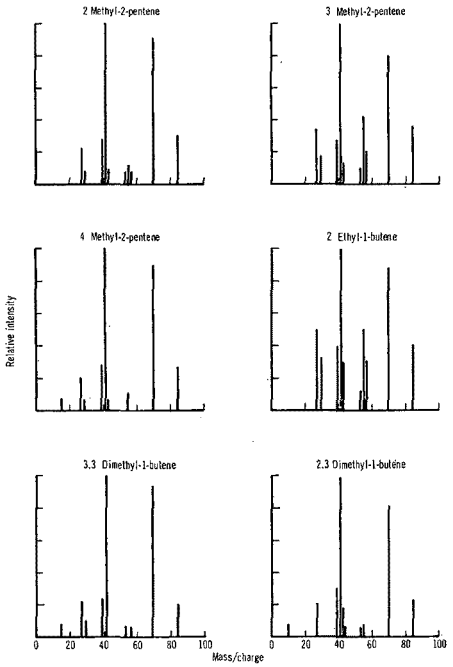


Figure 3. Mass spectra of six different C_6H_{12} isomers

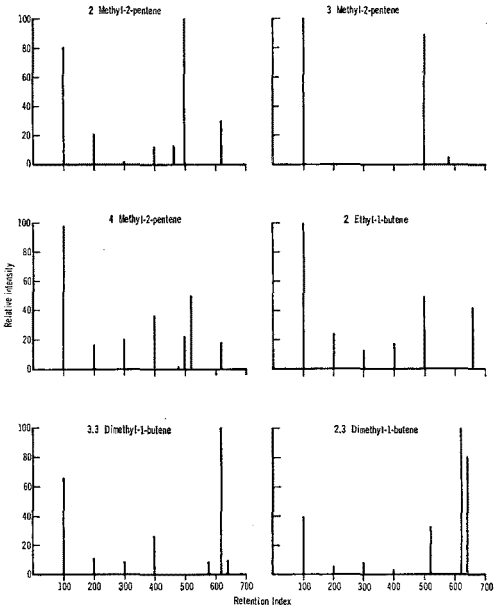


Figure 4. Pyrograms of six different C_6H_{12} isomers

sence of air and, contrary to the findings of Sutton and Harris (*8*), we find no enhancement of methane in the presence of air.

DISCUSSION

The spectra tabulated in Tables I through V are sufficiently different so that, with the exception of *cis–trans* isomers, the compounds are uniquely characterized. The identification technique is basically similar to that used in mass spectrometry although the physical processes in the two methods are entirely different. Hence, much of the terminology used in mass spectrometry to describe a spectrum can also be used to describe a thermal fragmentation spectrum. As in mass spectrometry where the peaks with large mass-to-charge ratios are of particular importance for identification, the peaks with large retention indices are also of interest. That is, in hydrocarbon analysis mass-to-charge peaks occurring at 15, 27, and 43 are of little use for identification because most hydrocarbon spectra show large values for these 3 peaks. Similarly, in hydrocarbon pyrolysis C_1, C_2, and C_3 are usually large. However, the absence (or small value) of any one of these three is important to note. The relative ratio of the C_1, C_2, C_3, and C_4 products can give a good indication of the degree of branching in the parent compound. For example, the pyrolysis of cyclohexene produces essentially no CH_4 (see

Table VIII. Effect of Pyrolysis Temperature on Thermal Fragmentation Pattern

		Normalized mole-area for a given retention index interval												
Compound	C#	Temp	50/150 (C_1)	150/250 (C_2)	250/350 (C_3)	350/400 (C_4)	401/449	450/499	500/524	525/549	550/574	575/599	600/624	625/649
4 Methyl-2-pentene	6	575	100	11	23	33		2	34	39			7	33
		600	100	13	23	31		2	37	40			7	28
		625	100	15	26	34		5	34	41			5	29
1-hexene	6	575	42	100	88	73		26		3				
		600	40	100	88	70		25		3				
		625	40	100	87	66		21		5				

Table IX. Comparison of Pyrograms from Three Independent Laboratories

	n-Hexane			Theo-	*cis*-2-Hexene		1-Heptene		1-Octene	
Product	This work[a]	Ref (6)[b]	Ref (7)[c]	retical[d]	This work[a]	Ref (6)[b]	This work[a]	Ref (7)[c]	This work[a]	Ref (7)[c]
$C_1 + C_2$	100	100	100	100	100	100	100	100	100	100
C_3	33	30	40	22	12	12	44	52	43	54
C_4	19	15	21	17	47	32	48	45	31	24
C_5	6	4	5	6	46	27	12	10	23	28
C_6							13	3	8	4
C_7									3	3

[a] Helium carrier gas, pyrolysis temperature 600 °C in Au tube, 4–5% decomposition.
[b] Nitrogen carrier gas, pyrolysis temperature 577 °C in Au tube, 30–60% decomposition.
[c] Helium carrier gas, pyrolysis temperature 650 °C in quartz tube, approximately 25% decomposition.
[d] Calculated from the Kossiakoff-Rice theory (*16*).

Table III) while the highly branched alkane 2,2-dimethylbutane forms only C_1, C_2, and C_4 products (see Table I).

In many cases, it is extremely difficult to differentiate between structural isomers with a mass spectrometer. The mass spectra of six C_6H_{12} isomers (2-, 3-, and 4-methyl-2-pentene; 2-ethyl-1-butene; 3,3-dimethyl-1-butene; and 2,3-dimethyl-1-butene) are shown in Figure 3 in bar graph form where the relative intensity (normalized with respect to the largest peak in the spectrum) is given on the ordinate and the mass-to-charge ratio (m/e) is plotted along the abscissa. The data for this figure were taken directly from Cornu and Massot (*14*). The spectra are all quite similar with large peaks occurring at m/e values of 41, 69, 84, 39, 27, and 42 and it would be difficult to positively identify which one of the compounds gave rise to an unknown spectrum. Although the large peaks at 53, 55, and 56 probably would distinguish 3-methyl-2-pentene and 2-ethyl-1-butene from the other compounds, these two compounds could not be distinguished from each other. The pyrograms can be compared in an analogous manner, that is, the relative peak intensity is plotted as a function of retention index. The bar graph pyrograms of the same six compounds are shown in Figure 4. The pyrograms of all six compounds are entirely different so that positive identification from the thermal fragmentation pattern is straightforward.

It is interesting to compare the results reported in this work with other similar studies. Cramers and Keulemans (*6*) and Levy and Paul (*7*) investigated the vapor phase pyrolysis of organic compounds while in a carrier gas and flowing through a reaction chamber. No attempt was made to obtain interlaboratory reproducibility and although the basic experiments are the same, many differences, such as reaction temperature, carrier gas, and total % decomposed, are to be noted.

A comparison of the 3 studies is shown in Table IX. The data reported by Levy and Paul are in terms of chromatographic peak areas. This data was recalculated in terms of a mole response using the sensitivity factors given by Dietz (*15*). The qualitative agreement among the three laboratories is quite good and suggests that when standard procedures are adopted, thermal fragmentation spectra between independent investigators may be as reproducible as are mass spectra. The theoretical product distribution calculated for the decomposition of *n*-hexane is shown in the fifth column. The technique developed by Kossiakoff and Rice (*16*) for thermal decomposition assumes that a chain reaction is initiated by the breaking of the parent molecule into two free radicals. The free radicals then abstract a hydrogen atom from another molecule of the parent forming a new large free radical. The large radical decomposes rapidly and unimolecularly in certain definite ways. Since C—C bonds are weaker than C—H bonds, the split occurs at a C—C bond and not at a C—H, C=C, or C≡C bond. The small free radical thus formed continues the chain; only the chain propagating steps need be considered in order to determine the product distribution. Three additional assumptions are made: the rate of decomposition of the large alkyl radical is faster than a bimolecular reaction with another radical, the exact nature of the radical initially formed by the abstraction reaction depends on the relative ease with which hydrogen can be removed from different sites in the parent molecule, and the free radicals formed by these processes undergo C—C bond rupture at the bond β to the carbon atom from which the hydrogen is missing. Further, they assume that the preexponential factor is the same for all hydrogen abstraction reactions and that the removal of a secondary hydrogen requires 2 Kcal less activation energy than a primary hydrogen while abstraction of a tertiary hydrogen requires 4 Kcal less energy. Thus, at 600 °C, the relative rates of hydrogen abstraction from a primary, secondary, and tertiary position are in the ratio of 1:3.2:10.1, respectively. Therefore, the initial rate of formation of each type of radical is taken to be proportional to this ratio times the number of C—H bonds of that type present in the parent molecule. The agreement between the three laboratories and with the Kossiakoff–Rice theory for *n*-hexane decomposition is good.

The interlaboratory reproducibility of the thermal fragmentation patterns and the agreement with the theoretical predictions of the Kossiakoff–Rice theory indicate that the vapor phase pyrolysis gas chromatography of hydrocarbons can be used for qualitative identification. The technique is of particular value when it is necessary to identify extremely small amounts (of the order of 10^{-8} g) of compounds which are difficult to identify by other sensitive methods, such as mass spectroscopy.

ACKNOWLEDGMENT

We greatly acknowledge the technical assistance of Thomas C. Harby, Jr. We are also indebted to Michael A. Grayson for his help with the mass spectrometer.

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(14) A. Cornu and R. Massot, "Compilation of Mass Spectral Data," Heyden and Son Ltd., London, 1966.
(15) W. H. Dietz, *J. Gas Chromatogr.*, **5**, 68 (1967).
(16) A. Kossiakoff and F. O. Rice, *J. Amer. Chem. Soc.*, **65**, 590 (1943).

Improved Techniques for Corrosive Fluoride Gas Chromatography

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Several new techniques are described which broaden the applicability of gas chromatography to corrosive fluoride gases. Columns prepared with Teflon-6 support have been applied. A new column utilizing fluorocarbon oil instead of the conventional chlorofluorocarbon oil as the liquid phase is described, with application to inorganic and organic fluoride compounds. The loss of small amounts of certain reactive fluoride gases is found to be caused principally by sorption on system surfaces, rather than on the column packing. Replacement of metal tubing with Teflon tubing reduces sorption losses, markedly improving detectability limits for these constituents. A two-step column technique speeds up analysis, without fraction storage, when late elutors are present.

APPLICATION of gas chromatography to reactive fluorine compounds is limited in the choice of suitably resistant column materials. Columns serviceable with such compounds have been restricted principally to chlorotrifluoroethylene (Kel-F, Halocarbon, MFL, Fluorothene, or Hostaflon) oils on Kel-F or Teflon supports in metal tubing (*1–6*). For some constituents, poor resolution, nonlinear response curves, and unexplained losses are observed.

This report describes several recent innovations made during application of corrosive gas chromatography to a wide range of problems. These include a new column based on fluorocarbon oil providing an alternate for the chlorofluorocarbon oil previously used, techniques for more sensitive analysis of reactive fluoride compounds, and a stepped-column arrangement which speeds up an analysis without storage of fractions.

Specially designed corrosive gas chromatographs (*4, 7*) constructed of fluoride-resistant materials and utilizing a brass gas-density detector were employed in the studies. All GLC columns were prepared with 40–60 mesh Teflon-6. The columns were prepared by the method recommended by Kirkland (*8*), except that the volatile solvent, F-113, was removed by vacuum distillation using a rotary evaporator.

FLUOROCARBON LIQUID PHASE

Columns prepared with perfluoroalkane oil (approximate formula, $C_{21}F_{44}$) (*9*) have been applied to inorganic and organic fluorine compounds. This provides a suitable alternative to the chlorofluorocarbon (Kel-F type) oils conventionally used for reactive fluorine compounds. Chemical structures of the two oils, the fluorocarbon ($C_{21}F_{44}$) and the Kel-F oils, are compared in Figure 1; the Kel-F monomer is characterized by the presence of a chlorine atom in place of a fluorine atom.

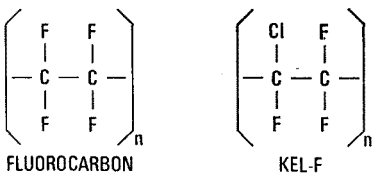


Figure 1. Structure of two oils

One necessary property of a satisfactory liquid phase is that it is essentially nonvolatile at the column operating temperature. The useful temperature range for fluorocarbon oil is comparable to that of the popular Kel-F No. 10 oil. Thermogravimetric scans, Figure 2, for the two oils indicate an upper temperature limit of about 100 °C for both oils before loss occurs. DTA scans, Figure 3, show approximately the same boiling point range for the fluorocarbon and Kel-F No. 10 oil, further demonstrating the similar thermal-volatility characteristics of the two oils.

Another requirement of a liquid phase is that it be inert toward the sample constituents. Experience indicates that columns prepared with the fluorocarbon liquid are stable to fluorine and reactive fluoride compounds, after pretreatment with chlorine trifluoride to remove moisture.

HALOCARBON COOLANT ANALYSIS

Halocarbon coolants are employed in heat exchangers to remove the heat of compression in the gaseous diffusion plants of the U. S. Atomic Energy Commission. Efficient operation of gaseous diffusion systems requires the inline measurement of halocarbon coolants that may leak into the uranium hexafluoride process gas stream. The coolants are C-114 (dichlorotetrafluoroethane), C-437 (trichloroheptafluorobutane), and C-816 (perfluorodimethyl cyclohexane).

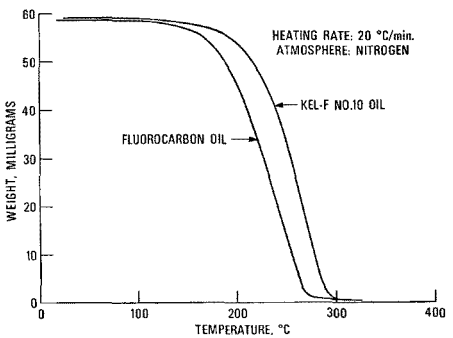


Figure 2. Thermogravimetric curves for liquid phases

(1) J. F. Ellis and G. Iveson, "Gas Chromatography 1958," D. H. Desty, Ed., Butterworths, London, 1958, pp 300–9.
(2) A. G. Hamlin, G. Iveson, and T. R. Phillips, ANAL. CHEM., **35**, 2037 (1963).
(3) I. Lysyj and P. R. Newton, *ibid.*, **35**, 90 (1963).
(4) J. G. Million, C. W. Weber, and P. R. Kuehn, *U. S. At. Energy Commission Rept.* **K-1639** (1966).
(5) E. L. Williamson, C. M. Johnson, T. J. Mayo, and W. R. Rossmassler, *ibid.*, **KY-485** (1965).
(6) V. H. Dayan and B. C. Neale, "Advanced Propellant Chemistry," R. F. Gould, Ed., ACS Publications, Washington, 1966, pp 223–30.
(7) J. G. Million, W. S. Pappas, and C. W. Weber, 155th National Meeting, ACS, San Francisco, April 1968.
(8) J. J. Kirkland, ANAL. CHEM., **35**, 2003 (1963).
(9) L. Spiegler, "Preparation, Properties, and Technology of Fluorine and Organic Fluorine Compounds," C. Slesser, Ed., NNES VII-I, McGraw-Hill, New York, 1951, p 492.

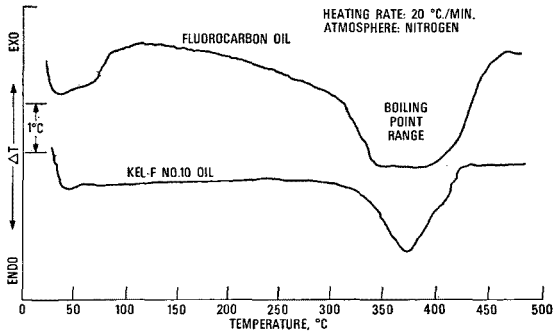


Figure 3. Differential thermograms for liquid phases

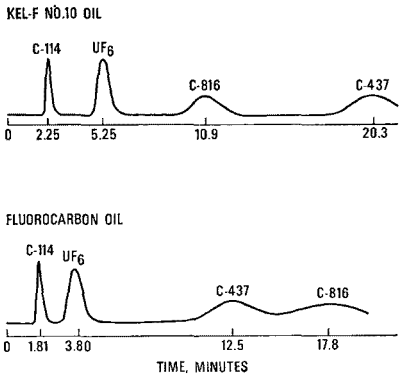


Figure 4. Separation of coolants and uranium hexafluoride

10-foot by 1/4-inch o.d. columns; 20% oil; 60 °C; Air carrier, 80 ml per minute

Figure 4 compares the separations provided by a Kel-F No. 10 oil column and a fluorocarbon oil column for the coolants and uranium hexafluoride. The significant finding here is the reversal of the order of elution of C-816 and C-437 from the two columns. The chlorofluoro-coolant has a higher affinity, Figure 5, for the chlorofluoro column while the fluoro-coolant shows more affinity for the fluorocarbon column. The two compounds are in a different chemical series; however, their boiling points are fairly close, 102 °C for C-816 (*10*) and 99 °C for C-437 (*11*).

FLUORINATING AGENTS FOR URANIUM FUEL RECOVERY

Several concepts to recover uranium from spent reactor fuels by fluoride volatility methods are under study (*12*). Some approaches involve fluorination to uranium hexafluoride with fluorine, directly or after conversion of oxidic fuels to lower fluorides with hydrogen fluoride. In one process the uranous oxide is converted to urano–uranic oxide (U_3O_8) prior to the fluoride volatility step.

Bromine pentafluoride and chlorine trifluoride are being studied for use as fluorinating agents in an effort to separate uranium from plutonium by selective fluorination of uranium with the interhalogen, plutonium being recovered as plutonium hexafluoride in a subsequent step by fluorination with fluorine (*12*).

Gas chromatographic techniques are being developed for volatility process analysis and control. Constituents of particular interest are bromine pentafluoride, chlorine trifluoride, fluorine, hydrogen fluoride, uranium hexafluoride, and reaction products.

The Analytical Loss Problem. In the chromatographic determination of certain reactive fluoride gases using halocarbon columns in nickel tubing, a loss of small amounts of the reactive gas is customarily observed. Calibration curves have been nonlinear, Figure 6, and detection limits relatively high. Peaks are characteristically skewed, and elution times are concentration-dependent. Prolonged and repeated treatment of the column with the pure constituent gives only a temporary improvement in detection limit. Different degrees of losses have been observed with columns seemingly consisting of the same materials and having the same history.

The peak magnitude for a given fluoride sample is a function of the column's immediate history of exposure to the fluoride gas. Point *A* (above the curve) of Figure 6 was obtained shortly after a larger sample, while point *B* (below the curve) was obtained after a lapse of several minutes in the sampling sequence. Point *C* corresponds to the value obtained after several repetitive determinations of the same sized sample.

Sample loss is also observed by peak area measurements. No signal is observed for samples containing less than 3 μmoles of chlorine trifluoride, 0.8 μmole of bromine pentafluoride, or 18 μmoles of hydrogen fluoride.

CHLORINE TRIFLUORIDE. For chlorine trifluoride the loss problem is virtually eliminated by simply replacing the nickel tubing with Teflon PTFE tubing. Figure 7 shows the marked improvement obtained. The new calibration curve (at 40 °C)

(10) *Ibid.*, p 484.
(11) W. T. Miller, Jr., *ibid.*, p 673.
(12) J. J. Barghusen and W. J. Mecham, *Reactor Fuel Processing*, **9**, 157–64, 168, Summer 1966.

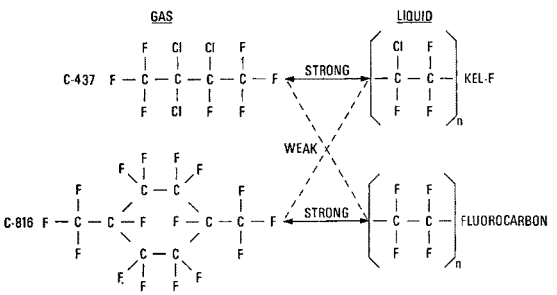


Figure 5. Gas–liquid affinities

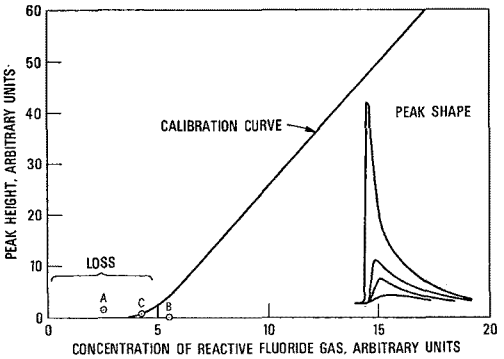


Figure 6. Halocarbon column in nickel tubing

is linear with a "zero" intercept; peaks are more symmetrical; elution time is fixed; and the lower detection limit is at least 10-fold better.

Apparently the problem was caused by chemisorption of small amounts of chlorine trifluoride by the nickel fluoride surfaces of the column tubing.

BROMINE PENTAFLUORIDE. Similar comparative results, Figure 8, were found with bromine pentafluoride; however, the loss was not as great as that found for chlorine trifluoride.

HYDROGEN FLUORIDE. The high affinity of hydrogen fluoride toward almost any surface is well known. Initial samples are often completely sorbed prior to reaching the detector. Pretreatment with large samples of pure hydrogen fluoride (*4*) or use of a carrier gas spiked with hydrogen fluoride (*5*) are previous methods used to attack this problem.

Figure 9 shows calibration curves obtained for hydrogen fluoride with halocarbon columns in nickel and Teflon tubing by the repetitive sampling technique. Detection limits are much better with the Teflon tubing. The loss still found with the Teflon-tubed column may be caused by sorption on metal fluoride surfaces of the sampling valve, the connecting nickel tubing, or the brass gas-density detector.

When conducting the tests, the nickel-tubed column was examined first, after which this column was quickly replaced with the Teflon-tubed column. Without any pretreatment, an initial 25-μmole sample of hydrogen fluoride, using the untreated Teflon column, gave the same response as 21

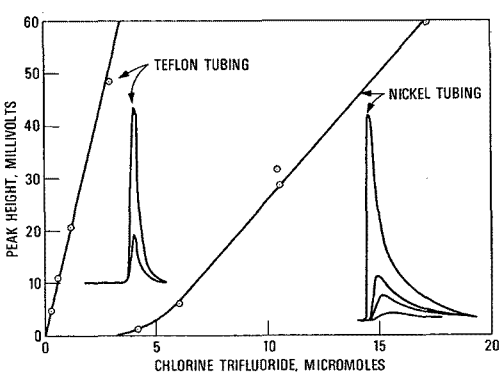


Figure 7. Comparison of halocarbon columns in Teflon and nickel tubing

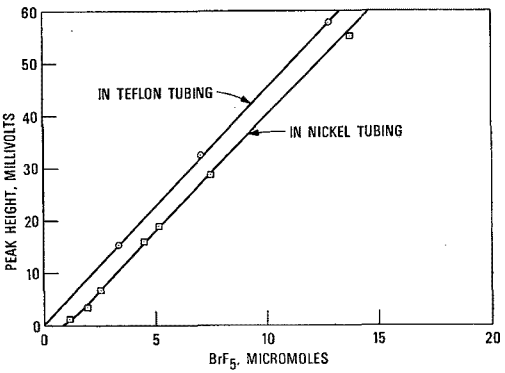


Figure 8. Calibration curves for bromine pentafluoride in halocarbon columns

μmoles gave after treatment with hydrogen fluoride, indicating a loss within the untreated Teflon-tubed column of only 4 μmoles.

Results of the following experiment, Figure 10, indicate that most of the loss of hydrogen fluoride occurred at surfaces separate from and downstream of the Teflon column. Samples of hydrogen fluoride run prior to the chlorine trifluoride drying treatment gave the normal negative peak, using dry air carrier with the gas-density detector; however, the first hydrogen fluoride sample injected after the chlorine trifluoride elution gave a positive peak at the hydrogen fluoride peak position. Chemisorbed chlorine trifluoride, downstream of the column, was apparently displaced by hydrogen fluoride which forms a stronger complex with the fluoride surface. If chlorine trifluoride had been displaced from within the column, it would have been retained longer by chromatographic action of the column. These experimental results suggest that a hydrogen fluoride-spiked carrier might minimize adsorption of other fluoride compounds in the fashion that water has been used to reduce adsorption of other polar compounds (*13*).

In an effort to eliminate completely the loss problem, an all-plastic system, principally of Teflon, is currently being designed, including the detector.

(13) H. S. Knight, ANAL. CHEM., **30**, 2030 (1958).

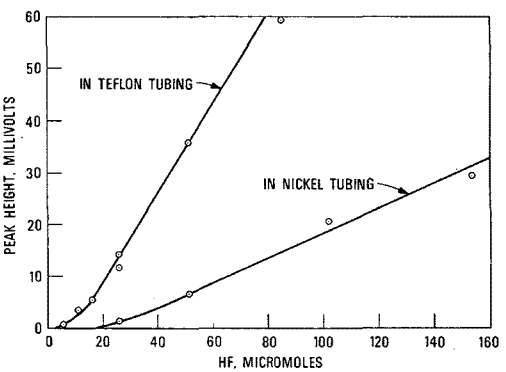


Figure 9. Calibration curves for hydrogen fluoride in halocarbon columns

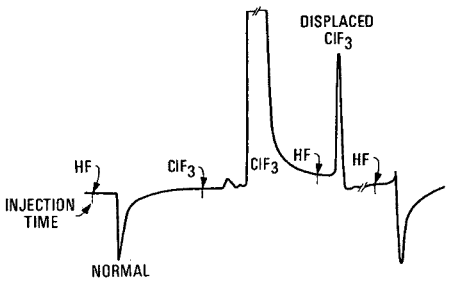


Figure 10. Sorption displacement

FLUORINE. The loss problem has not been observed with fluorine. For fluorine analysis in the presence of permanent gases, the salt converter technique (*14*, *15*) has proven satisfactory. In this method fluorine is converted to chlorine by a pre-column sodium chloride reactor; the chlorine is easily separated chromatographically from the permanent gases.

Bromine Pentafluoride System. In the evaluation of fluorinating agents for the uranium volatility process, bromine pentafluoride is reduced principally to bromine rather than to bromine trifluoride (*12*). Therefore, the major analytical emphasis in off-gases is in determining bromine, bromine pentafluoride, and uranium hexafluoride. Chromatographic separation provided by a fluorocarbon oil column is compared with that provided by Kel-F No. 10 oil in Figure 11. Fluorocarbon oil provides good resolution of all of the constituents in about 10 minutes, whereas no useful separation is effected with Kel-F oil in that period, in tests made at 50 °C. Furthermore, at 50 °C, Kel-F oil poorly resolves bromine from bromine pentafluoride even with a longer column in twice the time. At 40 °C, some separation was found, but it was still not analytically useful. Therefore, further studies were confined to the fluorocarbon column.

CALIBRATION. Figure 12 shows calibration curves for bromine, bromine pentafluoride, and uranium hexafluoride. With Teflon tubing, all are straight lines with "zero" intercepts.

Chlorine Fluorides System. The reaction of excess chlorine trifluoride at 40 °C with dehydrated U_3O_8 yields uranium hexafluoride, chlorine monofluoride, chloryl fluoride (ClO_2F), and to a smaller degree, chlorine. For a simulated off-gas

(14) C. W. Weber and O. H. Howard, ANAL CHEM., **35**, 1002 (1963).
(15) O. Rochefort, *Anal. Chim. Acta*, **29**, 350–7 (1963).

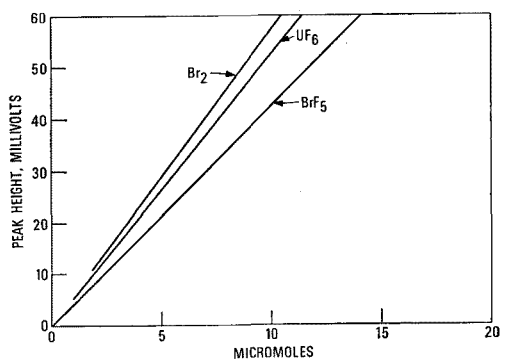


Figure 12. Calibration curves for bromine pentafluoride, bromine, and uranium hexafluoride

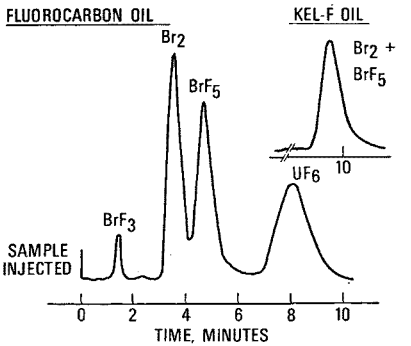


Figure 11. Separation of bromine fluorides and uranium hexafluoride

mixture, the separation provided by the fluorocarbon column is compared to that with a Kel-F oil column in Figure 13. Elution orders are generally the same; however, chloryl fluoride is not resolved from chlorine trifluoride by the fluorocarbon column. A range of conditions and longer times still did not provide useful separation on the fluorocarbon oil; therefore, the Kel-F oil column is the best choice here.

Of general interest in the volatility fuel recovery field is the relatively new compound, chlorine pentafluoride (*12*, *16*). In a single test, a separation factor of 1.14 was found for chlorine pentafluoride relative to chlorine trifluoride on a column of 20% Kel-F No. 10 oil on Teflon-6 at 40 °C.

TWO-STEP COLUMN. Uranium hexafluoride is eluted several minutes after chlorine trifluoride in the GC examination of these off-gases. A two-step column technique, Figure 14, has been devised which speeds the analysis for late elutors,

(16) D. F. Smith, *Science*, **141**, 1039 (1963).

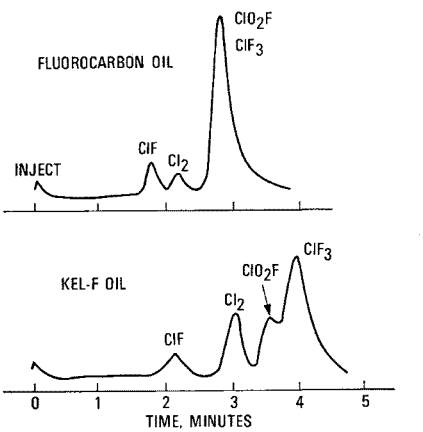


Figure 13. Separation of chlorine compounds

17-foot, 1/4-inch o.d. columns; 20% oil on Teflon-6; nickel tubing
Fluorocarbon oil column: 28° C; Air Carrier, 75 ml per minute
Kel-F No. 10 oil column: 32 °C; Air Carrier, 60 ml per minute

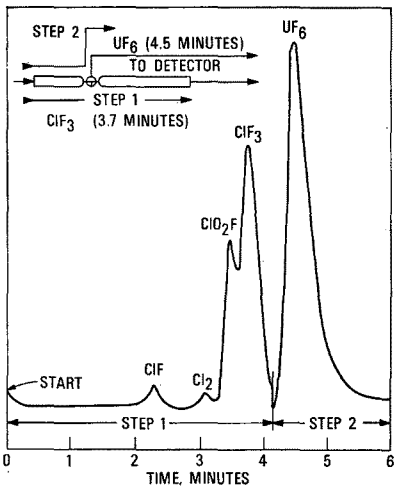


Figure 14. Chromatogram of a "two-step" column

20% Kel-F No. 10 oil on Teflon-6 at 40 °C with 85 ml per minute of air (initial); nickel tubing
Step 1 column: 27-foot by 1/4-inch o.d.
Step 2 column: 10-foot by 1/4-inch o.d.

without storing the marginally-resolved early fractions. Shortening of the column immediately after elution of chlorine trifluoride liberates the slower moving uranium hexafluoride, reducing the total analytical time to about one third. This method eliminates separation losses which occur in fraction storage associated with a similar technique reported previously (*2*).

The chromatogram of Figure 14 was obtained with nickel-tubed columns. On comparing later results obtained with Teflon-tubed columns, it was inferred that the nickel fluoride surface, while causing the loss of some chlorine trifluoride, contributed to the resolution of the two close peaks, chloryl fluoride and chlorine trifluoride. To obtain the equivalent separation with the Teflon-tubed column required about twice the elution time.

CHEMISORPTION COLUMN. Further studies of the chemisorption phenomenon indicated that a column using sodium fluoride as a solid phase might delay the chlorine trifluoride constituent in preference to the reaction products of the volatility process. Brief tests were conducted with a 10-foot by 1/4-inch o.d. column packed with Harshaw technical grade 1/8-× 1/8-inch pellets. Chlorine, chlorine monofluoride, and chloryl fluoride are eluted early, Figure 15, with other nonretained gases. Uranium hexafluoride and hydrogen fluoride off-gases are fixed as double salts and retained by the column. Chlorine trifluoride, therefore, is the only component transiently detailed by the column and it is resolved from the "composite impurities" peak in about 2 minutes.

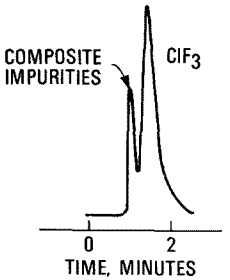


Figure 15. Chromatogram with sodium fluoride column

Although the sodium fluoride column shows promise in providing a more specific analysis for chlorine trifluoride without significant loss, further work is required. Divalent metal fluorides tested, such as magnesium and copper, indicate some loss of the chlorine trifluoride sample.

The authors are examining the possibility of spiking a halocarbon column with a metal fluoride (one which does not irreversibly complex any of the sample constituents) in an effort to improve the separation of chloryl fluoride from chlorine trifluoride.

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Electrochemical Reduction of Beta-Diketones in Dimethylsulfoxide

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Electrochemical studies of the reduction of 1,3-diphenyl-1,3-propanedione (DBMH) have been carried out in dimethylsulfoxide (DMSO) as solvent. Controlled potential coulometry at a potential on the first polarographic wave indicated an *n*-value of 0.55. The products were found to be the enolate of DBMH and the pinacol, 1,4-dibenzoyl-2,3-diphenyl-2,3-butanediol. A reaction scheme is proposed for this process. When electrolysis was continued after the $n = 0.5$ process, it was found that the current increased, passed through a maximum, then decreased to the residual value again. The *n*-value was 0.24 with respect to DBMH. This unusual behavior was caused by an electrolytic autocatalytic decomposition of the pinacol in a base-catalyzed reverse aldol condensation to benzil and acetophenone. The current was caused by the reduction of the benzil to its radical anion, the latter being the base which catalyzes the decomposition of the pinacol. The presence of benzil radical anion was confirmed by ESR spectrometry. A simplified theoretical expression for the controlled potential current–time curve with electrolytic autocatalysis was developed and it was found to agree satisfactorily with the experimental data. Other β-diketones were found to behave in an analogous fashion and ESR data for radicals produced by decomposition of the pinacols are given.

THE POLAROGRAPHIC characteristics of many β-diketones have been reported for protic solvents, usually ethanol–water. One of the few β-diketones whose electrochemistry has been studied more completely is 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, DBMH) (*1*). It was found that DBMH could be reduced in 50% ethanol–water to three products, depending upon the pH of the solution and the electrode potential. The one-electron reduction product at the first polarographic wave was the pinacol, 1,4-dibenzoyl-2,3-diphenyl-2,3-butanediol. This communication reports the results of studies of the electrochemical reduction of DBMH and other β-diketones in dimethylsulfoxide (DMSO) as solvent.

The enolate of DBMH has been reduced by chemical and electrochemical means and the visible and ESR spectra of the resulting dianion radical have been reported (*2, 3*). In the present study the neutral enol form was studied. The acidity of this species resulted in more complex electrochemical behavior involving the formation of radicals produced from the starting material through several reactions subsequent to the initial charge transfer.

EXPERIMENTAL

Reagents. The DMSO (J. T. Baker Reagent) was dried with calcium hydride and distilled at reduced pressure just before use. Tetrabutylammonium perchlorate (TBAP) (Matheson) was used as supporting electrolyte. A 0.1*M* solution of this material in the distilled DMSO produced a polarogram which was free of impurity waves at cathodic potentials up to about −2.7 volts *vs.* SCE (aq). Airco prepurified nitrogen was used for solution deaeration.

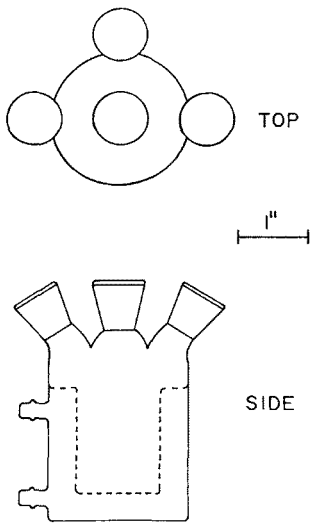


Figure 1. Polarographic cell

The various β-diketones and other materials studied were purified if required by recrystallization until constant melting points in agreement with literature values were obtained. These substances were obtained from Eastman (White Label) (1,3-diphenyl-1,3-propanedione, 1,3-bis(*p*-methoxyphenyl)-1,3-propanedione, 1,3-bis(*p*-fluorophenyl)-1,3-propanedione, 1-phenyl-1,3-butanedione, benzil, acetophenone) and Pfaltz and Bauer, Flushing, N. Y. (*p,p'*-dimethoxybenzil).

Apparatus and Procedure. The polarograph was a Sargent Model XV equipped with a Sargent IR Compensator. The polarographic cell is depicted in Figure 1. This jacketed cell is ideally suited for sample volumes of about 10 cc. The top of the cell allows for the introduction of the counter electrode, reference probe, nitrogen deaeration tube, and a DME, the latter being in the center.

The counter electrode was a spiral of platinum wire immersed in the test solution, hence it was not separated from the working electrode compartment. The amount of product formed at the counter electrode during a polarogram was so small that its presence did not affect the subsequent polarograms.

The reference electrode was a commercial SCE with either a sleeve or asbestos fiber junction. The SCE was immersed in a supporting electrolyte solution in the bridge tube which made contact with the test solution by means of a cracked-glass tip which was positioned within 1 cm of the DME. Both the DME and the reference electrode bridge tube were held in place by Teflon 14/20 ⅀ adapters with O-ring seals (Kontes Glass Co., #K-17980). These were particularly advantageous because they permitted vertical and angular adjustment of the electrodes to obtain the optimum configuration.

The potentiostat for controlled potential electrolysis was a Wenking Model 61RS. The cell was a 150-cc cylindrical glass cell with five glass joints in the top. A central 24/40 ⅀ joint

(1) D. H. Evans and E. C. Woodbury, *J. Org. Chem.*, **32**, 2158 (1967).
(2) N. L. Bauld, *J. Amer. Chem. Soc.*, **86**, 2305 (1964).
(3) N. L. Bauld and M. S. Brown, *ibid.*, **89**, 5413 (1967).

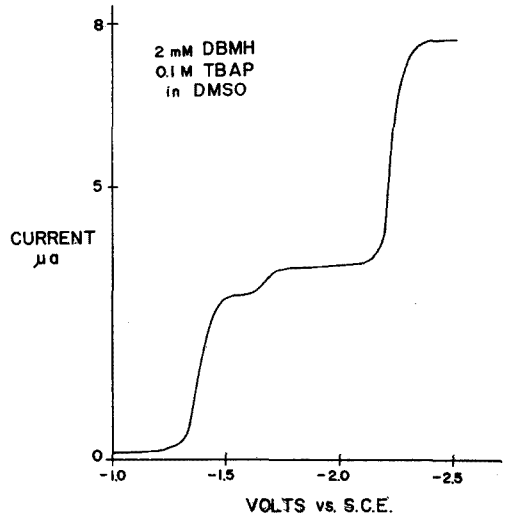


Figure 2. Polarogram of DBMH

received the counter electrode compartment which was a cylindrical 14-mm tube terminating in a 10-mm medium-porosity fritted-glass disk about 2 cm above the mercury pool working electrode. Three peripheral 14/20 ⅀ joints provided access for the nitrogen deaeration tube, the reference electrode bridge tube (similar to that used in the polarographic cell), and a DME (or thermometer). The latter two were also inserted through the Teflon adapters. The fifth joint (10/30 ⅀) was for nitrogen escape and sample introduction.

The counter electrode was a spiral of platinum wire. Both the test solution and the counter electrode compartment were continually deaerated during electrolysis. The solution was stirred with a magnetic stirrer. Electrical connection to the working electrode was made by means of a platinum wire sealed through the wall of the cell.

The electrolysis current was recorded on a Sargent Model SR recorder. Integrals were obtained with the aid of a planimeter (Gelman Model 39321).

The electron spin resonance (ESR) spectrometer was a Varian E-3. The Varian electrolytic cell was used for the internal generation of radicals. A Heath transistorized, variable dc power supply (EUW-17) and a microammeter were used with the electrolytic cell; a two-electrode system was employed because exact control of the reduction potential was not found necessary. To obtain samples of somewhat stable radicals produced during an electrolysis outside the ESR cavity—*i.e.*, by the external generation method—the electrolysis cell was placed in a glove bag filled with nitrogen, and capillary tubes filled by syringe were sealed in the glove bag to avoid oxygen attack.

The tetrabutylammonium enolate of DMBH was prepared by reacting in 95% ethanol stoichiometric amounts of the DBMH and tetrabutylammonium hydroxide. The resulting yellow solution was evaporated to dryness leaving a light yellow solid which was washed and recrystallized from diethyl ether. Anal. Calcd. for $C_{31}H_{47}NO_2$: C, 79.95; H, 10.17; N, 3.01. Found: C, 80.01; H, 10.24; N, 3.04. The pinacol of DBMH, 1,4-dibenzoyl-2,3-diphenyl-2,3-butanediol, was prepared as described previously (*1*).

Gas chromatography experiments were performed using an F & M Model 720 gas chromatograph incorporating a column of 10–15% silicone gum rubber on Analabs ABS.

Table I. Polarographic Data

Compound	$E_{1/2}$[a]
1,3-Diphenyl-1,3-propanedione (DBMH)	−1.38
	−1.69
	−2.25
1,4-Dibenzoyl-2,3-diphenyl-2,3-butanediol (DBMH pinacol)	−1.70
	−1.95
Enolate of DBMH	−2.25
Benzil	−1.04
	−1.76
Acetophenone	−1.94
1,3-Bis(*p*-methoxyphenyl)-1,3-propanedione	−1.56
	−1.87
	−2.5
p,p'-Dimethoxybenzil	−1.20
	−1.96
1,3-Bis(*p*-fluorophenyl)-1,3-propanedione	−1.41
	−1.73
	−2.3
1-Phenyl-1,3-butanedione	−1.54
	−2.41
	−2.7
1-Phenyl-1,2-propanedione	−1.10
	−2.16

[a] All potentials *vs.* aq. SCE, volts.

RESULTS AND DISCUSSION

Polarography. The polarography of the various substances was studied briefly in order to establish the appropriate potentials for controlled potential coulometry and to gain some insight into the probable course of the reactions. A polarogram for the reduction of $2 \times 10^{-3}M$ DBMH in $0.1M$ TBAP in DMSO is given in Figure 2. The current on the plateau of the first wave is not proportional to the concentration of DBMH, being relatively lower at high concentrations. The current is also not proportional to $h^{1/2}$, being relatively lower at low h (long drop times). These data are indicative of processes other than diffusion limiting the current and suggest that coupled chemical reactions are involved. The plot of log $[(i_d - i)/i]$ *vs.* E for the first wave had a slope of 70 mV.

The small wave at −1.69 volts *vs.* SCE appears at the same potential as the first wave for the reduction of DBMH pinacol and could be caused by its reduction or the reduction of a similar substance formed in the first step. This wave is relatively smaller at low concentrations of DBMH. The wave at −2.25 volts appears at the same potential as the wave for the enolate of DBMH. It is also relatively smaller at low concentrations of DBMH. These data suggest that DBMH is reduced at the potential of the first wave to a product which may give DBMH pinacol and enolate by further chemical reaction.

In Table I are summarized the polarographic data for the various starting materials and suspected products and intermediates.

Controlled Potential Coulometry. The current–time curve for the reduction of 50 mg of DBMH at −1.50 volts *vs.* SCE is shown in Figure 3. In the first part of the electrolysis the current decreases from its initial value to a minimum in about 40 minutes. Various shades of green color develop in solution though the final color is yellow. The integrals of the first part (to the minimum) of the current–time curves of a series of electrolyses like that of Figure 3 gave an average n-value of 0.55.

This nonintegral n-value may be explained most efficiently

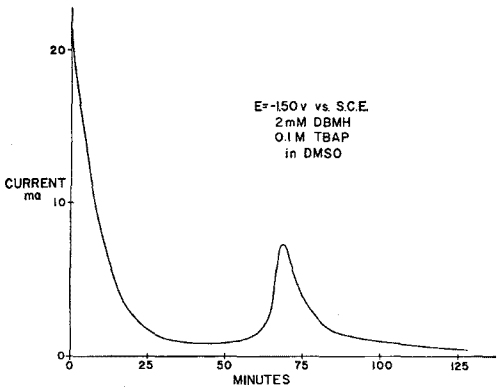
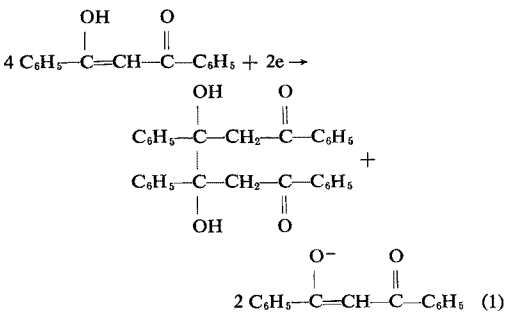


Figure 3. Controlled potential reduction of DBMH

by the following overall reaction scheme in which DBMH is written in the enol form which is the predominant form of β-diketones (*4*).



Though the mechanism for this process is not known, it would seem most probable that DBMH is first reduced to its radical anion which in turn is protonated by another molecule of DBMH leaving a neutral radical (which dimerizes to DBMH pinacol) and the enolate. Therefore, the final electrolytic products should be the pinacol and enolate.

A polarogram was obtained with the electrolysis solution. Waves were observed with half-wave potentials of -1.69, -1.95, and -2.25 volts. As may be seen in Table I, these are in excellent agreement with the half-wave potentials of DBMH pinacol and the enolate. Furthermore, the yellow color of the electrolysis solution (indicative of the enolate) was completely discharged by the addition of dilute perchloric acid which converted the enolate to DBMH. The resulting solution had a polarographic wave at -1.38 volts, indicating the presence of DBMH. The half-wave potential for hydrogen ion is -1.05 volts *vs.* SCE in DMSO.

Electrolytic Autocatalysis. The most striking characteristic of the electrolysis depicted in Figure 3 is the current–time maximum observed between 50 and 100 minutes. The solution develops a deep blue color during this period, and near the final tailing area it is deep green in color. The current–time integral corresponds to an average n-value of 0.24 with respect to the initial amount of DBMH.

The cause of this unusual current–time curve first became

(4) E. S. Gould, "Mechanisms and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N.Y., 1959, p 376.

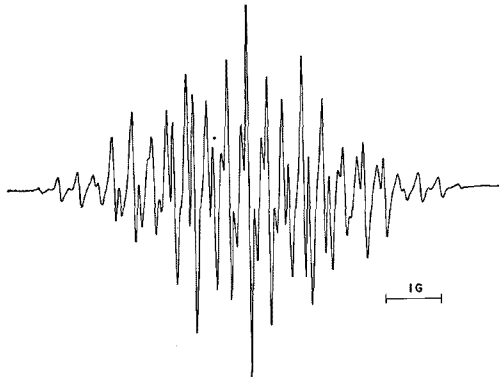
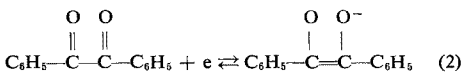


Figure 4. ESR spectrum of benzil radical anion obtained by electrolysis of DBMH

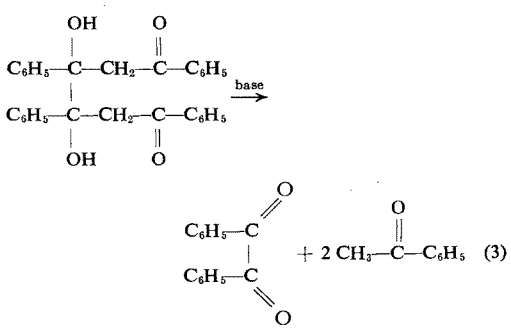
evident when it was discovered that the only paramagnetic material observed by ESR spectrometry with internal generation was the benzil radical anion.



The ESR spectrum of the benzil radical anion obtained by internal generation with a DMSO solution of DBMH is given in Figure 4. The ESR spectrum obtained by electrolysis of benzil or DBMH pinacol was identical to that in Figure 4. Furthermore, the same spectrum was obtained from samples taken from an electrolysis solution during the anomalous current increase (Figure 3). These ESR data strongly suggest that this increase in current is related to a reaction which produces benzil which in turn is reduced at the control potential to benzil radical anion, thus causing the observed current.

The observed splitting constants were 1.10 gauss for the *para* protons, 0.35 gauss for the *meta* protons, and 0.98 gauss for the *ortho* protons compared to 1.12, 0.36, and 0.99 gauss, respectively, which have been reported for benzil radical anion in dimethylformamide (*5*).

The reaction which most satisfactorily explains these observations is the decomposition of DBMH pinacol. Noting that DBMH pinacol is the formal aldol condensation product of benzil and two molecules of acetophenone, we write the decomposition reaction as the reverse aldol condensation.



(5) R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963).

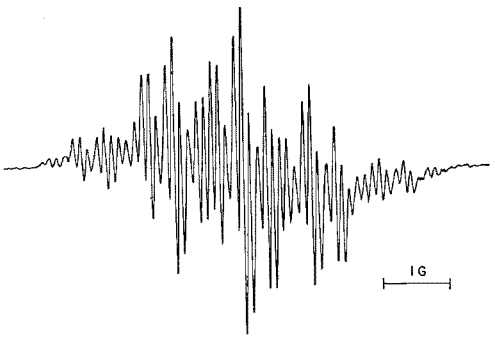


Figure 5. ESR spectrum of *p,p'*-dimethoxybenzil radical anion

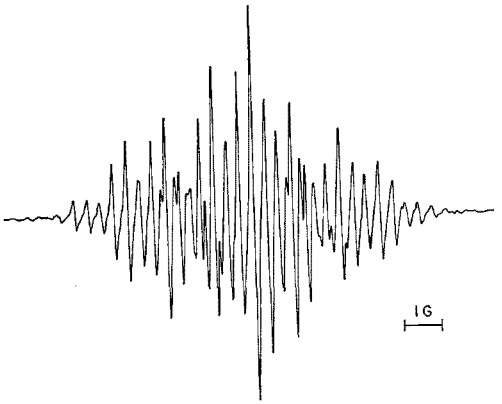


Figure 6. ESR spectrum of *p,p'*-difluorobenzil radical anion

The equilibrium for Reaction 3 is expected to favor the products benzil and acetophenone, and the process should be base-catalyzed. Once formed, benzil would be consumed by its reduction to benzil radical anion (cf. Table I). The one-electron reduction of benzil coupled with the stoichiometry of the dimerization and decomposition reactions results in an expected *n*-value of 0.25 with respect to DBMH for the current–time maximum.

The presence of benzil radical anion in the electrolysis mixture is indicated by the blue color and its ESR spectrum. The presence of acetophenone is more difficult to establish because its polarographic wave occurs at an $E_{1/2}$ near the second wave of benzil—*i.e.*, the reduction wave of benzil radical anion. Nevertheless, it was established that acetophenone is easily obtained by decomposition of DBMH pinacol. A solution of the pinacol in DMSO is stable. However, the addition of 2% sodium hydroxide at room temperature immediately produces the distinctive fragrance of acetophenone. In an attempt to demonstrate more convincingly the identity of acetophenone as a product, it was found that thermal decomposition of DBMH pinacol also produces acetophenone. Injection of a 9% DMSO solution of the pinacol in a gas chromatograph (injection temperature: 230 °C; m.p. of the pinacol: 201–3 °C; column temperature: 140 °C) produced acetophenone in 75% theoretical yield as ascertained by comparison of peak areas and retention times with those of standard acetophenone solutions.

These experiments add credibility to the formation of benzil in the electrolysis solution via Reaction 3. However, the shape of the current–time curve merits further consideration. One would not expect a current–time curve with a maximum to result from the simple decomposition of an electrolysis product yielding a new electroactive material. The increasing rate of the decomposition as indicated by the rising portion of the maximum suggests a reaction catalyzed by one or more of the reaction products—*i.e.*, an autocatalytic reaction. Because reverse aldol condensations are known to be base-catalyzed (*6*), Reaction 3 was examined with respect to the basicity of its products. It appeared that neither benzil nor acetophenone should catalyze the reaction, so the electrolytic product—the benzil radical anion—suggested itself as the catalyst. Because this catalyst is an electrolytic product, we suggest that the process be called electrolytic autocatalysis.

The plausibility of the above interpretation was supported by the following experiment: A solution of DBMH pinacol was prepared and electrolysis was performed at −1.2 volts *vs.* SCE. Because the $E_{1/2}$ of the pinacol is −1.69 volts, no reduction occurred. At this point a quantity of benzil equivalent to one fourth the amount of the pinacol present was added to the solution. The electrolysis was continued at −1.2 volts producing the blue benzil radical anion. After the electrolysis had proceeded for several minutes, the current began to increase and the solution became intensely blue. Finally the current passed through a maximum and decreased to the residual value. The quantity of electricity was equivalent to one electron per molecule of benzil plus one electron per molecule of pinacol—*i.e.*, DBMH pinacol decomposed to acetophenone and benzil and the latter was reduced. It should be noted that Reaction 3 did not commence until benzil radical anion was formed.

Current–time curves similar to Figure 3 were also obtained for the symmetrical β-diketones 1,3-bis(*p*-methoxyphenyl)-1,3-propanedione and 1,3-bis(*p*-fluorophenyl)-1,3-propanedione, and the color of both electrolysis solutions during the anomalous current increase again was blue. A combination technique was employed in obtaining the ESR spectra shown in Figures 5 and 6. To obtain these spectra, a solution of the β-diketone was electrolyzed to the first current minimum analogous to that in Figure 3. A sample of the electrolysis solution, which should contain the corresponding pinacol, was transferred to the ESR electrolytic cell and the spectra were obtained by the internal generation method.

The spectrum in Figure 5 was obtained from 1,3-bis(*p*-methoxyphenyl)-1,3-propanedione and is identical to the spectrum obtained from pure *p,p'*-dimethoxybenzil (anisil) upon internal generation. The observed coupling constants for anisil were 1.03 gauss for the *ortho* protons, 0.36 gauss for the *meta* protons and 0.10 gauss for the methoxy protons. Figure 6 shows the radical obtained from 1,3-bis(*p*-fluorophenyl)-1,3-propanedione. It is the expected *p,p'*-difluorobenzil radical with coupling constants of 2.32 gauss for the fluorine nuclei, 0.39 gauss for the *meta* protons, and 1.02 gauss for the *ortho* protons. These results indicate that the catalyzed pinacol decomposition is not peculiar to DBMH electrochemistry.

A less-pronounced anomalous current increase was obtained for the unsymmetrical β-diketone, 1-phenyl-1,3-butanedione. In this case one might wonder how this molecule would dimerize if at all—*i.e.*, would two radicals undergo phenyl–phenyl

(6) V. K. LaMer and M. L. Miller, *J. Amer. Chem. Soc.*, **57**, 2674 (1935).

coupling, methyl–methyl coupling, or mixed phenyl–methyl coupling? The above combination electrolysis technique was employed and two radicals were detected: 1-phenyl-1,2-propanedione and acetophenone radical anions. The former indicates that some mixed coupling occurs. Further research is being carried out on this system to discover whether any symmetrical coupling occurs. The observed coupling constants for 1-phenyl-1,2-propanedione are 3.35 gauss for the methyl protons, 1.81 gauss for the *para* proton, 1.55 gauss for the *ortho* protons, and 0.51 gauss for the *meta* protons which are quite similar to reported values (7). The acetophenone radical apparently results from the pinacol decomposition and the observed splitting constants are 6.93 gauss for the methyl protons and 4.28, 1.12, 6.52, 0.90, and 3.74 gauss for the ring protons in good agreement with reported values (8).

Electrolytic Autocatalysis. THEORY AND RESULTS FOR DBMH PINACOL DECOMPOSITION. Consider an electrochemical reaction scheme of the type

$$A + n_1e \xrightarrow{\beta_1} B \tag{4}$$

$$B \xrightarrow{k} C + D \tag{5}$$

$$D + n_2e \xrightarrow{\beta_2} E \tag{6}$$

where, in the case of DBMH, A is the β-diketone, B is the dimeric pinacol, C is acetophenone, D is benzil, and E is the benzil radical anion. The β's are the mass transfer rate constants and k is the decomposition rate constant. We assume that the reverse of Reaction 5 is very slow and that the potential of the electrode is in a region where the oxidation of B and/or E may be neglected and C is not electroactive.

The rate of Reaction 5 is considered to be a function of both C_B and C_E.

$$-\frac{dC_B}{dt} = kC_B{}^bC_E{}^e \tag{7}$$

The case in which $b = 1$ and $e = 0$ has been solved (9) but it pertains to the uncatalyzed decomposition of B. We shall consider the case in which $b = 0$ and $e = 1$—*i.e.*, the rate being zero order with respect to substrate, first order with respect to catalyst.

In addition to Equation 7 we have the rate equations

$$\frac{dC_E}{dt} = \beta_2C_D \tag{8}$$

$$\frac{dC_D}{dt} = kC_E - \beta_2C_D \tag{9}$$

Solving Equation 8 for C_D and differentiating with respect to time we have

$$\frac{dC_D}{dt} = \frac{1}{\beta_2}\frac{d^2C_E}{dt^2} \tag{10}$$

which on substitution with Equation 8 into 9 gives upon rearrangement

$$\frac{d^2C_E}{dt^2} + \beta_2\frac{dC_E}{dt} - \beta_2kC_E = 0 \tag{11}$$

Equation 11 is a homogeneous linear differential equation which when solved by means of its auxiliary equation gives

(7) G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Weiner, *J. Amer. Chem. Soc.*, **88**, 1998 (1966).
(8) N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 723 (1964).
(9) R. I. Gelb and L. Meites, *J. Phys. Chem.*, **68**, 630 (1964).

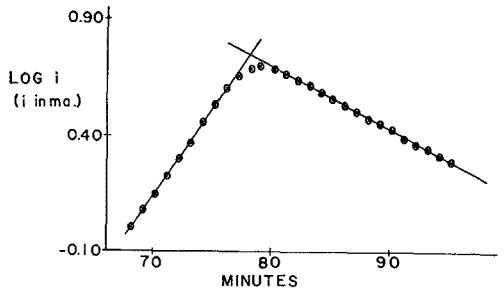


Figure 7. Plot of data from Figure 3 according to Equations 15 and 16

$$C_E = X\exp[(S_1 + S_2)t] + Y\exp[(S_1 - S_2)t] \tag{12}$$

where $S_1 = -\beta_2/2$ and $S_2 = (\beta_2{}^2 + 4\beta_2k)^{1/2}/2$. Initially no E is present so $C_E = 0$ at $t = 0$ and thus $X = -Y$. Rearrangement of Equation 12 gives

$$C_E = \{X\exp[(S_1 + S_2)t]\}\,[1 - \exp(-2S_2t)] \tag{13}$$

For large t, $\exp(-2S_2t) \ll 1$ and Equation 13 becomes

$$C_E = X\exp[(S_1 + S_2)t] \tag{14}$$

Equation 14 may be differentiated to give dC_E/dt which with Equation 8 gives C_D. In our system, reduction of A is complete before decomposition of B is significant so the current is given simply by $i = nFV\beta_2C_D$.

$$i = nFV(S_1 + S_2)X\exp[(S_1 + S_2)t] \tag{15}$$

Equation 15 is an expression for the current as a function of time for the autocatalytic decomposition of B with the reaction being zero order in C_B and first order in C_E.

It is expected that Equation 15 should apply to the rising portion of the current maximum. In this region a plot of ln i *vs.* t should give a line with slope of $S_1 + S_2$. The data from Figure 3 are presented in this fashion in Figure 7. An independent measure of β_2 would permit calculation of k from the slope just found.

We shall first assume that shortly after the maximum, decomposition of B is complete and the current–time curve represents the ordinary reduction of the remaining D. Thus the current should be given by

$$i = i_t\exp(-\beta_2t) \tag{16}$$

where i_t is a hypothetical initial current. Thus a plot of ln i *vs.* t for the descending portion of the curve gives β_2 directly; combining this with the value of $S_1 + S_2$ found for the rising part of the curve, one can then calculate the value of k.

It is important that β_2 be obtained under the same conditions of mass transfer that prevailed during the rising portion of the wave. In particular the stirring rate should be strictly constant throughout the experiment. It remains to be shown that the decomposition of B is complete shortly after the maximum. The concentration of E can be obtained at any time, t_2, through the integral

$$C_E = \frac{1}{n_2FV}\int_{t_1}^{t_2} id\tau \tag{17}$$

where t_1 is at the foot of the rising portion, a time when $C_E \approx 0$. Thus the quantity of E, C_EV, present at any time may be calculated from the integral of the experimental current–time

curve. The quantity of D, $C_D V$, can be obtained from the observed current and the relation $i = n_2 F V \beta_2 C_D$. Finally the quantity of B remaining is obtained from

$$V(C_B + C_D + C_E) = M_B^0 \quad (18)$$

where M_B^0 is the quantity of B present before decomposition as calculated from the amount of A used in the electrolysis. Equation 18 follows from the stoichiometry of the system, Equations 5 and 6.

The results of calculations of the quantities of B, D, and E as a function of time indicate that C_B approaches zero near the current maximum, leaving only C, E, and unreduced D in solution. Thus the assumption that β_2 may be obtained from a plot of ln i *vs.* t for the descending portion is valid.

The linearity of the ascending and descending branches of Figure 7 permits calculation of both β_2 and k and supports the validity of the pinacol decomposition scheme and the derived equations for electrolytic autocatalysis. To test the theory further, additional electrolyses were performed varying the quantity of DBMH, the stirring rate, and the temperature.

Table II shows the results of 10 experiments with values of the rate constant for the pinacol decomposition determined by the method just discussed. The values of k are relatively independent of stirring rate though they show a small dependence on concentration. As expected, k is strongly dependent on temperature.

The concentration dependence of k probably reflects an inadequacy in the theory, possibly in the simplifying assumption that the decomposition is zero order in pinacol concentration. The overall decomposition reaction must involve several steps and a rate equation as simple as that used in the derivation may not be adequate. However, computations of the various concentrations during the current–time maximum show that the rate equation used is superior to any other rate equation of comparable simplicity, in particular the case where the rate is first order both in pinacol and catalyst.

Table II. Kinetics of DBMH Pinacol Decomposition, 25 °C

DBMH, mg	k, min^{-1}
50[a]	0.60 ± 0.07
80	0.42 ± 0.03
100	0.39 ± 0.04
50[b]	1.38

[a] Including three different stirring rates.
[b] 40 °C.

Another factor which has not been taken into account in the theory is the fact that the blue solution during the pinacol decomposition slowly becomes green indicating that the benzil radical anion concentration is slowly decreasing. This decomposition of the radical anion has been verified during controlled potential reduction of solutions of benzil under otherwise identical solution conditions. This complication, of course, would affect the derived kinetic equations which assume that benzil radical anion does not decompose.

Nevertheless, the results in Figure 7 and Table II lend considerable credibility to electrolytic autocatalysis in the decomposition of the pinacol as the source of the unusual current–time maximum in the controlled potential reduction of DBMH and other β-diketones.

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Effect of Static Magnetic Field on Direct Current Polarography

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The effect of magnetic field on dc polarography has been investigated with a static magnetic field applied perpendicularly to the electrodes. Maxima of the second kind are decreased by the application of magnetic field. The factors influencing this effect are examined experimentally. As the mechanism of this phenomenon, the retardation of tangential motion on the electrode surface produced by the application of magnetic field is proposed. The effects of magnetic field on the first kind of maxima are also studied, and are divided into three groups by the magnetic field effect as its criterion. The origin of motion of electrolytic solutions around the dropping mercury electrode accompanied by the first kind of maxima is not unique. On the other hand, a small but distinct increase in the diffusion or migration current is produced by the application of magnetic field.

EFFECTS of external electric or magnetic fields on electrolytic reactions at the electrodes have been reported (*1–5*). Kryukova and Popovam (*1, 2*) reported the observation of polarographic maxima of the first kind produced by a static electric field applied perpendicularly to the dropping mercury electrode (DME). Imai, Inouye, and Chaki (*3*) studied the effect of an ac electric field on electrolytic reactions at the DME. Furthermore, Pekhteleva and Smirnov (*4*) reported the influence of transverse and longitudinal static magnetic fields on electrolytic reactions at the plane electrode, and showed that the electrolytic solution is hydrodynamically stirred by the magnetic field. Antweiler (*5*) tried, but failed, to observe the effect of magnetic field on maximum wave currents of the first kind in polarography. In a preceding paper (*6*), it was reported that the magnetic field influences dc polarography and the maximum wave currents of the first and second kinds decrease with the application of magnetic field. Experimental details and the interpretation of this effect will be given in this report. Furthermore, it will be shown that the diffusion or migration current is increased slightly by the application of magnetic field.

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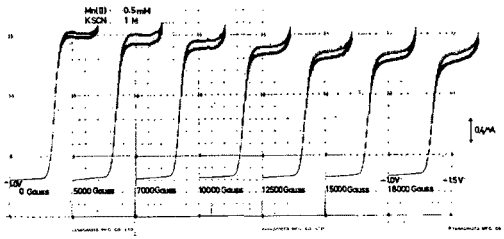


Figure 1. Dependence of polarographic current (the maximum of the second kind) on magnetic field strength

0.5m*M* Mn(II) and 1*M* KSCN

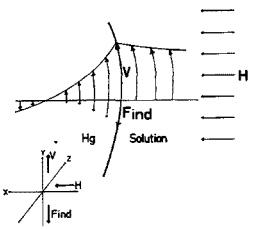


Figure 2. Tangential motion at interface of mercury and solution, and vector diagram of magnetohydrodynamics

V. Velocity of conducting fluid
H. Applied magnetic field
F_{ind}. Induced electromotive force

EXPERIMENTAL

Apparatus. Direct current polarograms were taken with the use of a Yanagimoto Polarograph Model PA-102. The static magnetic field varied from 0 to 18,000 Oe and was applied perpendicularly to the electrodes. The electromagnet used in this experiment was manufactured by the Japan Electron Optics Lab. Co., and has 30-cm diameter polepieces with a 60-mm gap. The homogeneity of the magnetic field is about 10^{-5} over the whole volume of the glass cell. All measurements were performed at 23.0 ± 0.5 °C.

Capillary. Capillary characteristics were as follows. The drop time of mercury (t) was 3.52 sec for a system of 0.2m*M* Mn(II), 1*M* KCl solution at a potential of −1.58 V, which was not altered by the applied magnetic field. The flow rates (m) were 0.736 and 0.740 mg/sec with and without magnetic field, respectively, for the above solution with an open circuit. The drop time and flow rate mentioned above were obtained with a 70-cm mercury height. Two other capillaries with similar characteristics were used occasionally.

Chemicals. Sample solutions used in this experiment were prepared from chemicals of analytical reagent grade. The water used for all solutions was deionized and distilled.

RESULTS AND DISCUSSION

Decrease in Maximum Wave Current. The effect of magnetic field is observed as a decrease in the maximum wave current. A typical example of the magnetic field effect on the maximum wave of the second kind is shown in Figure 1. For the second kind of maxima, this decrease in current is always observable. On the other hand, the appearance of the magnetic field effect for the first kind of maxima depends on conditions as described later. Two possible mechanisms for this effect are (i) the direct interaction of the applied magnetic field with induced or permanent magnetic dipoles arising from mercury drops and electrolytes, and (ii) the Lorentz force due to the interaction between magnetic field and the charge of electrons in mercury and/or that of electrolytes in motion. Mechanism (i) is eliminated, because the effect of magnetic field was similar in both cases for diamagnetic and paramagnetic samples, and the drop time of mercury does not change with magnetic field. Mechanism (ii) will be observed in two different ways—*i.e.*, one as a Hall effect, and the other a magnetohydrodynamic force. Of these two, the Hall effect can be eliminated, for ordinary diffusion current has to be reduced by the magnetic field for the Hall effect. It has been shown that the polarographic maxima are always associated with tangential motion at the surface of the DME (*2, 7*). Because the effect of magnetic field is observed as a reduction in maximum wave current, the most plausible mechanism for this is the suppression of the tangential motion due to the magnetohydrodynamic force.

Maxima of the Second Kind. Maxima of the second kind are of purely hydrodynamic origin and have been interpreted as due to the tangential motion of the surface of the mercury drop under the action of the high flow rate of mercury (*2, 7*). The polarographic limiting current for this maximum wave can be expressed as the sum of the Ilkovič diffusion and maximum wave currents, the latter being given by Equation 1 (*2, 8*),

$$i_{max} = KnFD^{1/2}Cr^{3/2}V^{1/2} \quad (1)$$

where K is a proportionality constant, n the number of electrons involved in electrochemical reaction at the surface, F the Faraday constant, D the diffusion coefficient, C the concentration of electroactive species, r the mean radius of a mercury drop, and V the velocity of the tangential motion at the mercury/solution interface as drawn in Figure 2.

It is assumed that the present system of mercury and electrolytic solutions at the interface can be treated as a magneto-fluid in a magnetic field. According to the theory of magnetohydrodynamics (*9*), a force $\mathbf{F}_{ind}$ acting on a conducting fluid in motion with a velocity $\mathbf{V}$ induced by a magnetic field $\mathbf{H}$ is given by

$$\mathbf{F}_{ind} = \kappa(\mathbf{V} \times \mathbf{H}) \times \mathbf{H} \quad (2)$$

where κ is the electroconductivity of the conducting fluid.

As shown in Figure 2, the direction of $\mathbf{F}_{ind}$ is opposite to that of $\mathbf{V}$,—*i.e.*, $\mathbf{V}$ is reduced by the magnetic field, resulting in a decrease in i_{max} of Equation 1. Since κ for mercury is very much greater than that for electrolytic solutions, this reduction is important only in the surface layer and inside the mercury drop.

For the validity of the assumption mentioned above, several experimental results were examined, which will be summarized in the following.

Dependence on Magnetic Field Strength. As shown in Figure 1, i_{max} decreases gradually as field strength increases, as suggested by Equation 2. By a rough calculation using Equations 1 and 2, it can be shown that the current observed is inversely proportional to the magnetic field strength. The details of this calculation will be published elsewhere.

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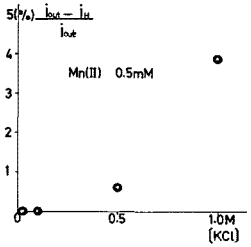


Figure 3. Dependence of magnetic field effect on concentration of supporting electrolyte

0.5 m*M* Mn(II)

DEPENDENCE ON CONCENTRATION OF SUPPORTING ELECTROLYTE. The magnetic field effect Δ_H is defined as follows,

$$\Delta_H = (i_{out} - i_H)/i_{out} \quad (3)$$

where i_H and i_{out} are the current intensities of the maximum waves with and without magnetic field, respectively. As the concentration of a supporting electrolyte is decreased, Δ_H defined in Equation 3 decreases. This is shown in Figure 3 taking Mn(II) as an example. As discussed above, the reduction in Δ_H implies that tangential motion becomes slow. Kryukova (*2*) reported that, at low concentrations of supporting electrolyte, tangential motion can only be observed at the potential of electrocapillary zero as shown in Figure 4. Her result is consistent with the present one in that tangential motion is negligible for low concentrations of supporting electrolyte at the decomposition potential of Mn(II) (about −1.6 V) as shown in Figure 3.

DEPENDENCE ON MERCURY RESERVOIR HEIGHT. As shown in Figure 5, Δ_H decreases with decrease in mercury reservoir height. There is a linear relation between the flow rate of mercury and the speed of motion at the mercury/solution interface. Hence, the speed of motion becomes negligible when the height of the mercury reservoir is low (*2*, *7*), resulting a decrease in Δ_H as suggested from Equation 2.

EFFECT OF AC ELECTRIC FIELD. When a transverse ac electric field (about 30 kHz) with a voltage of 0.5 ∼ 1 V/cm is applied to the DME, a rise in limiting current like the maximum of the second kind appears and is reduced by the application of magnetic field. This experiment shows that an ac electric field may cause tangential motion.

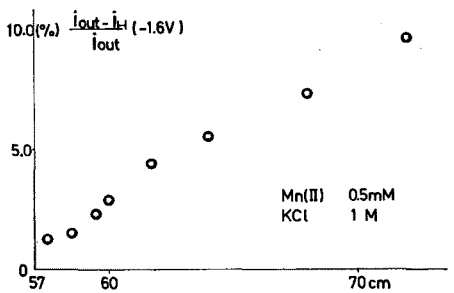


Figure 5. Dependence of magnetic field effect on mercury reservoir height

0.5m*M* Mn(II) and 1*M* KCl

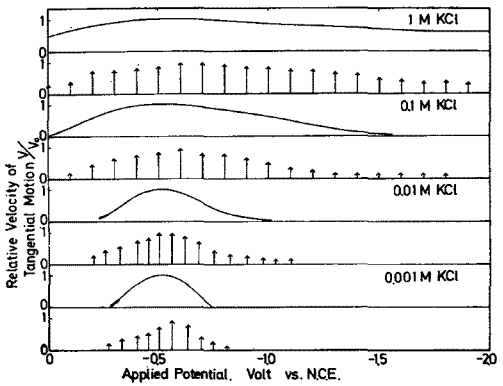


Figure 4. Relative velocity of motion of potassium chloride solution around a mercury drop

Arrows indicate experimental values, and curves are constructed from calculated values, both obtained by Kryukova *et al.* (*2*). v_o is velocity at potential of electrocapillary zero, v is velocity at any other potentials

EFFECT OF CAPILLARY ACTIVE SUBSTANCES. When surface active substances are added to solutions, the effect of magnetic field becomes small as shown in Figure 6. This is attributed to the retardation of the tangential motion by the presence of surface active substances. The magnitude of the effect of magnetic field is dependent on the ionic species. This result is interpreted in terms of the control of movement of the interface by capillary active ions.

Maxima of the First Kind. Sharp-shaped maxima observed in the rising portion of polarograms are generally designated as maxima of the first kind. Maxima of the first kind have been investigated by many workers (*7*). It is now well established that maxima of the first kind accompany the motion of electrolytic solutions around the DME. However, the origin of this motion still remains to be clarified.

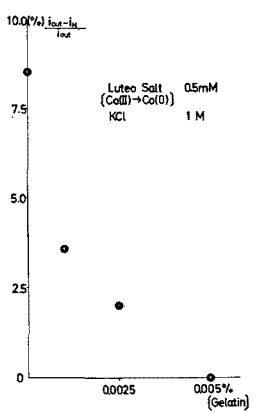


Figure 6. Dependence of magnetic field effect on concentration of surface-active substance

0.5m*M* Luteo salt [Co(II) → Co(0)] and 1*M* KCl

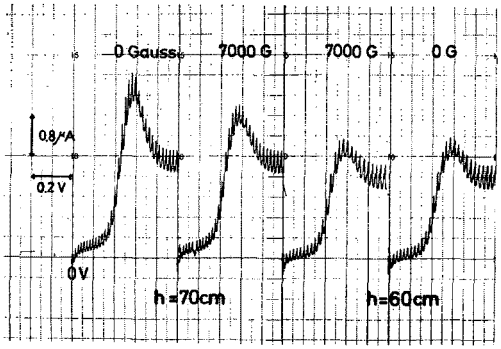


Figure 7. Relation between magnetic field effect on first kind of maxima and mercury reservoir height

1 mM $CuCl_2$ and 1M KCl

Frumkin and von Stackelberg (*2, 7, 10*) proposed the "surface tension theory," where they suggested that the uneven current density over the surface of a mercury drop produces a surface tension gradient and results in the motion of the mercury/solution interface. Barker and Faircloth (*11*) proposed that specific adsorption is the origin of the surface tension gradient. According to Heyrovský (*7, 12, 13*), however, it is outside the DME that the motion arises and not at the interface. From this observation, he concluded that the motion is due to the nonhomogeneity of the electric field in the neighborhood of the DME.

In the present work, the effects of magnetic field on the first kind of maxima are examined. The results may be divided into three groups—*i.e.*, the magnetic field effect is (i) observable only when the height of mercury reservoir is high, (ii) not observable at all, and (iii) observable, but almost independent of the height of mercury reservoir. These results suggest that the origin of the first kind of maxima is not unique.

GROUP (i). A typical example of group (i) is shown in Figure 7. In order that the magnetic field effect can be observed in group (i), the additional condition is required that the concentration of supporting electrolytes is high. The conditions for the magnetic field effect observed in group (i) is nothing but the conditions where maxima of the second kind are obtained. It has been shown that, under these conditions, maxima of the first kind often accompany those of the second kind (*7*). Therefore, the peak part observed with a 70-cm mercury height shown in Figure 7 should be taken as a superposition of the *real* maximum of the first kind, and a maximum of the second kind, the latter being reduced by magnetic field. With a 60-cm mercury height, only the *real* maximum of the first kind can be observed as shown in Figure 7. Because this maximum is little affected by magnetic field, the origin of this maximum is similar to that of group (ii), as described successively.

GROUP (ii). The magnetic field effect is always unobservable in this group. Examples for this group are systems of

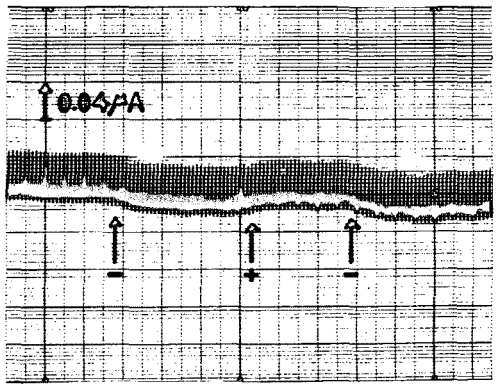


Figure 8. Limiting current increase upon application of a magnetic field of 7000 Oe

0.5mM $NiCl_2$ and no supporting electrolyte at −1.65 V constant
+ Application of magnetic field
− Switch off magnetic field

0.5 ~ 2.5mM O_2, Cu(II), Mn(II), Ni(II), Zn(II), Co(II), and Hg(II) at low concentrations (0 ~ 0.005N) of KCl or HNO_3, all of which have remarkable maxima. However, according to Frumkin and von Stackelberg (*2, 7, 10*), there is motion of the mercury/solution interface. If the interpretation proposed above to explain the magnetic field effect on maxima of the second kind is correct, the motion of the mercury/solution interface mentioned above should also be affected by magnetic field. This implies that Frumkin and von Stackelberg's explanation about the origin of maxima of the first kind is incorrect. One possible explanation is that motion does not exist on the surface of the mercury drop, and motion of the electrolytic solution is little affected by the magnetic field as discussed above. The absence of motion on the surface of the mercury drop in this case is consistent with the result obtained by Heyrovský (*12*).

GROUP (iii). Examples of this group are found in systems of 2mM Cu(II)–0.05~0.1N KSCN, 0.5~1mM Tl (I)–1M KCl and 1 mM Cu(II)–0.01N KCl. A few other systems belong to this group. The effect of magnetic field can be observed, even when the mercury reservoir is lowered. In addition to this, the ratio for the concentration of supporting electrolytes to that of depolarizers has to be properly chosen to observe the magnetic field effect. Kolthoff and Okinaka (*14*) reported that in dilute (<0.1M) KSCN solution, copper(II) yields cuprous thiocyanate which is adsorbed on the DME forming a monomolecular layer. At the reduction potential of this adsorbent, a remarkable maximum of the first kind appears. Barker and Faircloth (*11*) showed that there also is appreciable specific adsorption of the ion of thallium(I) from chloride solution giving maxima of the first kind. In the present work, both of these maxima are affected by the magnetic field as mentioned above. From the above considerations, it can be concluded that motion of the interface arising from the surface tension gradient of adsorptive-origin (*11, 15*) is an important origin of maxima of the first kind of group (iii).

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An Increase in Diffusion or Migration Current. In all investigations described above, the magnetic field effect on polarography has been observed as a decrease in the maximum wave current, and has been explained using the theory of magnetohydrodynamics. However, it has recently been found that the limiting current of migration or diffusion is also affected by the magnetic field. Contrary to the previous case, the present effect is observed as an increase in the migration or diffusion current as shown in Figure 8, and is small in magnitude compared with the previous one. Favorable conditions for observing this effect are a higher mercury reservoir height, the absence of surface active substances, and a lower concentration of supporting electrolyte. A possible mechanism can be obtained through the analogy of a magnetic mercury cathode (*16*)—namely, the magnetic field causes the electrolyte or the mercury drop to rotate or agitate like a rotor in a motor when the polarographic current flows. The third condition mentioned above may concern the removal of the tangential motion. However, explanations for the other two conditions remain to be worked out.

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CONCLUSION

By the use of a theory of magnetohydrodynamics, the mechanism of the effect of magnetic field on the second kind of maxima is explained in terms of the retardation of tangential motion of the mercury surface.

Using the magnetic field effect as a criterion, it is concluded that motion of electrolytic solutions accompanying maxima of the first kind is classified into two types of different origin. The first type of motion, originating at the surface of a mercury drop, is affected appreciably by a magnetic field. On the contrary, the second type of motion which arises in electrolytic solutions near the mercury drop, is little influenced by a magnetic field.

ACKNOWLEDGMENT

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NOTES

Fluorescence of Prostaglandin E_1

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PROSTAGLANDINS, originally isolated and identified from sheep seminal fluid, comprise a large group of naturally-occurring compounds found in most body organs and fluids. These are of great potential biologic interest because most have profound effects at very small dosages. Several recent reviews on the nomenclature, chemistry, physiology, and pharmacology of prostaglandins have appeared (*1–5*). The structure of prostaglandin E_1 (9-Keto-11α,15α-dihydroxy-prost-13-enoic acid) is shown in Figure 1. Because the structure of the prostaglandins suggested the possibility for several resonance forms of the molecule, this study was undertaken to determine their possible fluorescence.

EXPERIMENTAL

Prostaglandin E_1 (PGE_1) was weighed and dissolved in methanol at a concentration of 1 mg/ml and stored at 4 °C. Freshly-prepared dilutions of the stock solution were made in methanol at concentrations of 5 μg/ml and less. Aliquots of these were evaporated to dryness in 2-ml test tubes, under nitrogen, with a sand bath at 40 °C. One-half milliliter of

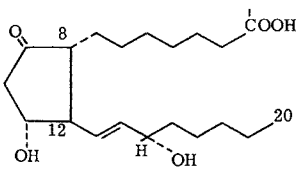


Figure 1. Structure of PGE_1

sulfuric acid–water reagent (70%, 30% v/v) was pipetted into these tubes which were then mechanically swirled. The samples and appropriate blanks of sulfuric acid were closed with ground glass stoppers and incubated for one-half hour at 65 °C. They were immediately immersed in 15 °C water for one-half hour. Fluorescence was determined on an Aminco-Bowman spectrophotofluorometer with quartz micro-cuvettes, previously acid cleaned and stored in concentrated nitric acid. The samples were activated at 366 mμ with a Xenon lamp source and read at 420 mμ. The stability of the instrument is checked with a standard solution of hydrocortisone.

All glassware was cleaned in concentrated sulfuric acid–dichromate solution and rinsed thoroughly with distilled water. Meticulous care and cleanliness were necessary to obtain reproducible and accurate results when measuring small quantities of the prostaglandins. In these studies, the turret of the spectrophotofluorometer was set at 3 and the sensitivity at 30.

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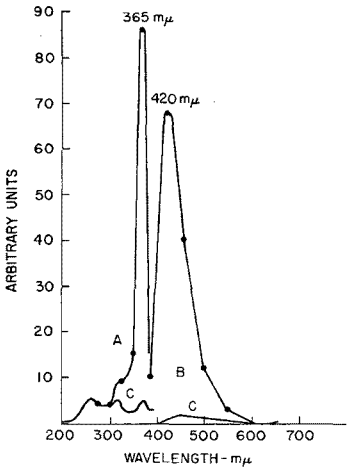


Figure 2. Uncorrected excitation (*A*) and emission spectra (*B*) of PGE_1 in 70% sulfuric acid-water (V/V) heated at 65 °C for 30 min. Emission set at 420 mμ to record excitation peak and excitation set at 365 mμ to record emission spectrum. Reagent blank 70% aqueous sulfuric acid, lower curves (*C*)

The sulfuric acid–water reagent deteriorated in a few days making it necessary to use a freshly-prepared, cooled reagent for very accurate work. The reason for the deterioration of the reagent was not studied but is very likely caused by hydration. Several batches and different commercial brands of reagent grade sulfuric acid were tested and blanks of these showed little variation in non-specific fluorescence.

RESULTS AND DISCUSSION

Fluorescence Spectrum. The uncorrected activation and emission spectra for prostaglandin E_1 are shown in Figure 2. The activation scan was obtained with emission set at 420 mμ. The emission scan was obtained with the activation at 365 mμ.

Increased concentrations of PGE_1 produced increased fluorescence as shown in Table I. With the equipment indicated, the limits of detection for accurate measurement are in the range of 0.2 to 0.5 μg of prostaglandin E_1.

Factors Affecting Fluorescence Development and Decay. The effect of incubation temperature on maximal fluorescence development was studied at 45, 65, and 85 °C. 65 °C was definitely superior.

The influence of various concentrations of sulfuric acid on fluorescence development, when the samples were incubated at 65 °C for one-half hour then read 30 minutes later, was investigated. There was little difference in fluorescence between 90 and 70% with a sharp decline between 70 and 60% sulfuric acid v/v in water. The lowest concentration of sulfuric acid that could be used to reproduce the induced fluorescence was chosen because higher concentrations of sulfuric acid tend to increase non-specific fluorescence in other materials. Studies on the effect of time of determination of fluorescence after incubation at 65 °C in 70% sulfuric acid-water (v/v) for one-half hour and cooled immediately in a 15 °C water bath indicated that any consistent arbitrary time could be used for reading all samples. For convenience, we chose the time of 30 minutes which was the earliest that we could get reproducible, concentration-related results.

Table I. Relationship of Fluorescence Intensity and PGE_1 Concentration in 70% Sulfuric Acid-Water (v/v) Incubated at 65 °C for 30 Min

PGE_1, μg	No. of samples	Fluorescence intensity, arbitrary units	
		Mean	Std. error
0.5	6	12.3	±1.0
1.0	10	31.3	±1.2
1.5	8	45.8	±2.3
2.0	8	59.5	±2.1
2.5	6	74.3	±2.6

The fluorescence of PGE_1, in 70% sulfuric acid-ethanol (v/v), was approximately one half of that observed with the corresponding aqueous sulfuric acid mixture.

Fluorescence of Other Prostaglandins. Preliminary studies on PGE_2, PGE_3, PGA_1, and PGB_1 indicate that these compounds fluoresce at absorption and emission spectra very similar to PGE_1. The emission spectrum of $PGF_1\alpha$ appears about 30 mμ longer than those of the other compounds. The relative fluorescence intensities (arbitrary units) of PGE_1, PGE_2, PGE_3, PGA_1, and PGB_1 appear similar with these same conditions.

Techniques for the extraction of prostaglandins from organs and body fluids are available and chromatographic techniques (column, thin-layer, gas–liquid and mass spectrograph) for their separations have been elucidated (*5*, *6*). Determination of the chromatographic thin-layer product by the relatively simple spectrophotofluorometric technique described herein could assist materially in these studies. Because of possible interfering fluorescent materials, suggestions are that the present technique be used only after isolation of relatively pure prostaglandins. For example, simple ether extracts of acidified (pH 3.0) human plasma contain several interfering compounds.

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Separation of Paraffinic Classes in Petroleum Distillates on a Cross-Linked Dextran

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WIDE-RANGE petroleum fractions can be separated into aromatics, olefins, and paraffin–cycloparaffins by liquid chromatography on silica gel (*1*). Further fractionation of the paraffins and cycloparaffins into *n*-paraffins and branched paraffins can be made by treatment with urea (*1*) or molecular sieves (*2*). However, complete removal of branched paraffins from cycloparaffins and separation of the various types of cycloparaffins are much more difficult. Methods which have been applied to these systems are thermal diffusion, azeotropic distillation, and liquid chromatography with added components (*3*). Although fractionation of fairly complex mixtures of branched paraffins and cycloparaffins has been obtained by these methods, the techniques have generally been limited to narrow distillation cuts. The separation of the cycloparaffins according to ring content is equally as difficult to achieve as the branched paraffins from cycloparaffins (*3*). Also, there does not appear to be an easy method for separating condensed cycloparaffins from noncondensed cycloparaffins in complex mixtures.

Mair *et al.* (*4*) investigated the separation of petroleum hydrocarbons with Sephadex LH-20. Sephadex LH-20, a methylated cross-linked dextran, has been used primarily for gel filtration, a technique which segregates compounds according to size. These workers studied a number of model compounds and demonstrated that Sephadex LH-20 separates *n*-paraffins from cycloparaffins and alkylbenzenes from cyclanobenzenes when the components are of similar molecular weight. Also separated were branched paraffin–cycloparaffin petroleum fractions near C_{21}. By combining and reprocessing, a final fraction containing 96% branched paraffins was obtained.

This investigation was undertaken to extend the Sephadex LH-20 separation of branched paraffins from cycloparaffins to wide-range petroleum fractions. During the study three other separations were also found to occur: condensed from noncondensed cycloparaffins, condensed cycloparaffins according to the number of rings, and separation of branched paraffins according to carbon number.

EXPERIMENTAL

Two batches of Sephadex LH-20 were prepared. The first was allowed to stand for 16 hours in contact with an excess of acetone and then transferred to a glass column 6 feet in length and 1 inch in diameter. A plug of glass wool 1/4 inch thick was added to the top of the packing to avoid disturbing the surface when adding the sample or solvent. The second batch was allowed to stand for 16 hours in contact with an excess of tetrahydrofuran and then transferred to a glass column 1 foot in length and 1 inch in diameter. The ends of this column were movable and covered with finely woven Teflon fabric to serve as diffusing plates. A solid pack was obtained by compressing the gel between the diffusing plates.

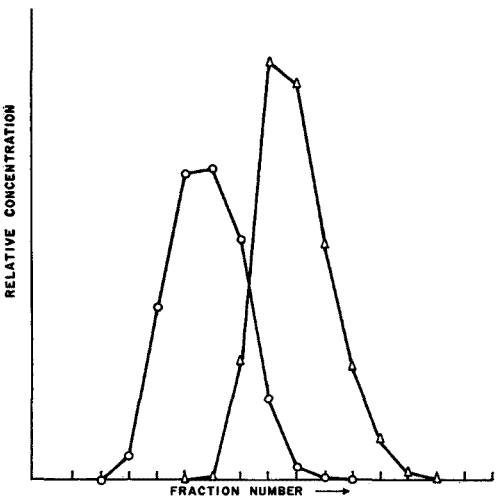


Figure 1. Separation of C_{11} to C_{16} branched paraffins from a C_8 cycloparaffin

○ **2-Methyldecane (C_{11})**
2,2,4,6,6-Pentamethylheptane (C_{12})
Heptamethylnonane (C_{16})
△ **1,2-Dimethylcyclohexane (C_8)**

A flow rate of 0.8 ml per minute was maintained in both columns throughout these studies, and the effluent was collected in 6-ml fractions. The fractions were monitored by means of gas–liquid chromatography, differential refractrometry, ultraviolet spectrophotometry, and mass spectrometry.

The 6-foot column containing the acetone expanded gel was used to study model compounds and the naphtha distillate. A charge of 1 ml was used for the model studies; 0.5 ml, for the naphtha studies. The 1-foot column containing the tetrahydrofuran expanded gel was used to study the crude distillate material. A charge of 0.5 ml was used.

To obtain representative branched paraffin and cycloparaffin mixtures, a naphtha distillate (C_9 to C_{15}) and a crude distillate (C_{14} to C_{26+}) were prepared as follows: The distillates were passed through Grade 923 silica gel and the effluent percolated through a column containing silica gel coated with silver nitrate (*5*). This was used to remove as completely as possible all olefinic, aromatic, and polar materials. The normal paraffins were then removed using 5 Å molecular sieves, as described by O'Connor and Norris (*2*). The nonnormal portions of the distillates were collected, and the sol-

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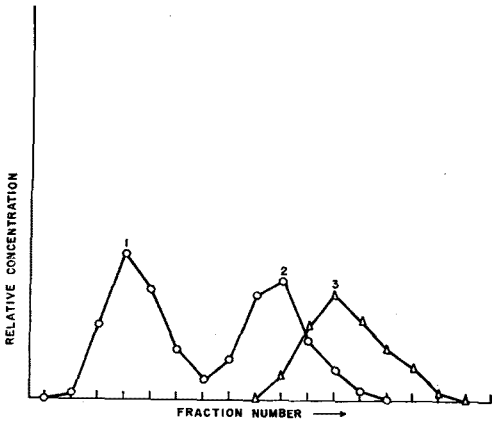


Figure 2. Simultaneous separation of branched paraffins according to size and of branched paraffins from cycloparaffins

○ (1) 5-*n*-Butylhexadecane (C_{20})
(2) Heptamethylnonane (C_{16})
△ (3) *n*-Decylcyclohexane (C_{16})

vent used in the molecular sieve separation was carefully distilled off. The non-normal mixtures were then considered ready for fractionation on the Sephadex columns.

RESULTS AND DISCUSSION

Several model systems were studied first to determine the feasibility of separating branched paraffins from cycloparaffins in wide-range petroleum distillates. A nearly complete separation of a C_8 branched paraffin from a C_3 cycloparaffin and of a more complex mixture consisting of C_6 and C_8 branched paraffins and two C_8 cycloparaffins is easily accomplished with one pass. Figure 1 shows a separation of a mixture of branched paraffins ranging from C_{11} to C_{16} from a C_8 cycloparaffin.

In Figure 2, a gel filtration separation of a C_{20} branched paraffin from a C_{16} branched paraffin is shown as well as the separation of both as a class from a C_{16} cycloparaffin. The gel filtration separation is not apparent in Figure 3 because the branched paraffins are presented as a composite system.

Wilk *et al.* (6) showed that Sephadex LH-20 resolves aromatic compounds according to the number of rings, the ring content increasing with elution volume. This same type of separation is obtained with cyclic paraffins. A one-ring cyclic paraffin was separated from a two-ring cyclic paraffin and both were separated from branched paraffins of similar molecular weight.

Figure 3 shows an unexpected separation. In this system 1,2-diphenylethane was almost completely resolved from 2,6-dimethylnaphthalene in one pass. This suggests the possibilities of separating condensed from noncondensed cycloparaffins in petroleum fractions. The studies on the naphtha and crude distillates show this to be true.

The separation of a five-membered ring cycloparaffin (cyclopentane) from a six-membered ring cycloparaffin (cyclohexane) was not complete. However, some separation did occur even though the differences in size and configuration were small. Based on experience with the other model compounds, recycling should improve the separation.

(6) M. Wilk and J. Rochlitz, *Z. Naturforsch*, **216**, 975 (1966).

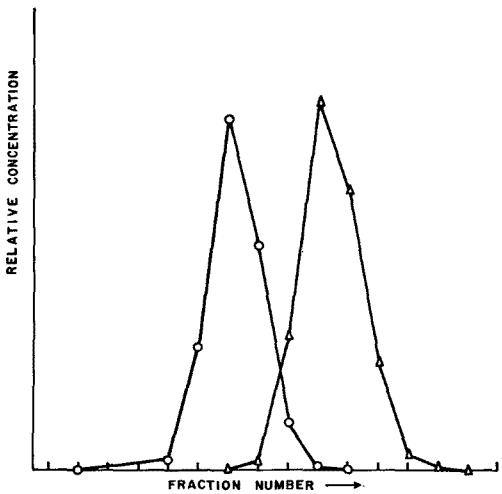


Figure 3. Separation of a condensed cyclic compound from a noncondensed cyclic compound

○ 1,2-Diphenylethane
△ 2,6-Dimethylnaphthalene

NAPHTHA DISTILLATE

The branched paraffin and cycloparaffin fraction of the naphtha was analyzed by mass spectrometry and gas chromatography before separation on Sephadex LH-20. The fraction contained 63.1% branched paraffins and 36.9% cycloparaffins with a carbon number range of C_9 to C_{15}. The cycloparaffin portion contained 27.7% noncondensed cycloparaffins and 8.7% condensed cycloparaffins.

The mass spectrometric results of the separated fractions are shown in Table I. The first 40 fractions contained only acetone and the next nine fractions naphtha and acetone. Three fractions—41, 42, and 43—contained only branched paraffins. Fraction 44, which represented less than 10% of the sample, contained 70.8% branched paraffins and 29.2% cycloparaffins. Fractions 45 and 46 were blended together before analysis. The composite showed only 2.9% branched paraffins and 97.1% cycloparaffins. Fractions 47, 48, and 49 were also blended before analysis and were found to contain only cycloparaffin.

The results in Table I also indicate a separation of noncondensed from condensed cycloparaffins. In fraction 44, the

Table I. Mass Spectrometric Analysis of Separated Fractions of the Naphtha Distillate

Reported as Mole Per Cent

	Fraction number			
	41–43	44	45 & 46	47–49
Paraffins	100	70.8	2.9	0.0
Noncondensed cycloparaffins	0.0	27.8	92.9	71.2
Condensed cycloparaffins	0.0	1.3	4.1	27.4
2-Ring condensed	0.0	1.3	4.1	25.9
3-Ring condensed	0.0	0.0	0.0	1.5
Benzenes	0.0	0.1	0.0	1.3
Naphthalenes	0.0	0.0	0.1	0.1

Table II. Gas Chromatographic Analysis of Separated Fractions of the Naphtha Distillate

Reported as Weight Per Cent

	Fraction number					
	41	42	43	44	45 & 46	47–49
C_9	0.0	0.0	0.0	0.0	0.4	0.3
C_{10}	0.0	0.0	0.7	4.3	7.4	1.3
C_{11}	0.0	2.6	20.2	34.6	24.3	13.9
C_{12}	1.5	18.2	35.8	25.4	26.0	35.2
C_{13}	23.8	45.8	28.7	19.0	24.3	26.4
C_{14}	16.9	46.4	27.3	11.1	12.5	14.1
C_{15+}	28.3	61.0	3.5	4.2	3.5	7.3

cycloparaffins are primarily noncondensed; whereas, the composite of fractions 47, 48, and 49 contained 27.4% condensed cycloparaffins.

A separation of the condensed cycloparaffins according to the number of rings is also shown in Table I. In fraction 44, the condensed cycloparaffins contain only two-ring compounds; whereas, in the composite of fractions 47, 48, and 49 both two-ring and three-ring condensed cycloparaffins appear. This type of separation was obtained with *n*-butylcyclohexane and decahydronaphthalene in the model compound studies.

The carbon number distribution data, as obtained by gas chromatography, are presented in Table II. A gel filtration type of separation is clearly shown in fractions 41, 42, and 43—*i.e.*, as the elution volume increases, the average carbon number of the isoparaffins decreases. With the elution of the cycloparaffins, the trend is reversed.

CRUDE DISTILLATE

A cursory look was taken at extending the separation into a higher molecular weight range. For this, the branched paraffin and cycloparaffin fraction from a C_{14}–C_{26+} crude distillate was used. The mass spectrometric analysis of this paraffin fraction showed 93.1% cycloparaffins and 6.9% branched paraffins with the cycloparaffins consisting of 54.8% noncondensed and 34.3% condensed.

The mass spectrometric results of the separated fractions showed that the initial fractions contained only tetrahydrofuran. The distillate appeared in six fractions. The first two were combined before analysis. The separations obtained were similar to, but not as complete as, those found for the naphtha using the longer column. The first three fractions contained both branched and cycloparaffins, but the last three contained only cycloparaffins.

A separation of noncondensed from condensed cycloparaffins is again indicated. A discrepancy was noted in the combined fractions 1 and 2 but as the elution continued through fractions 3, 4, 5, and 6, the percentage of noncondensed cycloparaffins decreased and that of condensed cycloparaffins increased.

A separation of the condensed cycloparaffins according to the number of rings is also shown. Except for the composite fraction 1–2, the ring content increased with elution volume.

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Quantitative Determination of Organic Halides in Dimethylsulfoxide

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NUMEROUS methods have been proposed for the determination of organic halides. The Carius, Pregl, and Schöniger methods make use of various oxidants to convert the organic halide to carbon dioxide, water, and halide ion, which is then determined titrimetrically or gravimetrically. These methods have been reviewed by Schöniger (*1*). Reduction methods include the use of potassium fusion (*2*) and sodium biphenyl (*3*). These are general methods for organic halides. Hydrolysis methods offer the possibility for the selective determination of certain halides in the presence of others. Rates of hydrolysis of organic halides in basic solution vary considerably, depending on the structure of the compound. In many instances it should be possible to find conditions such that one halide would react quantitatively while another would not react perceptively. With water and alcoholic solvents, however, the time and temperature required for quantitative reaction of many types of organic halides is excessive.

It has been shown that rates for the reaction of base with organic halides are greatly accelerated in dimethylsulfoxide (DMSO) (*4*). For example, the rate of reaction of methyl iodide with hydroxide ions is 5×10^6 faster in DMSO than in water. This may be explained by the decreased solvation of hydroxide ions in DMSO compared with protic solvents. Other aprotic solvents such as dimethyl formamide or dimethyl acetamide also possess large rate enhancing characteristics (*5*). However, these are not as stable as dimethylsulfoxide toward base and tend to hydrolyze. Therefore, dimethylsulfoxide appears to be the solvent of choice.

The procedures described below make use of the hydrolysis reaction with dimethylsulfoxide as the solvent and potassium hydroxide as the base. The reaction may be either or both of the following:

$$R{-}X + OH^- \rightarrow R{-}OH + X^- \qquad (1)$$

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(2) G. Kainz, *Mikrochemie ver. Mikrochim. Acta*, **39**, 1 (1952).
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(4) E. Tommila and L. Hamalainen, *Acta Chem. Scand.*, **17**, 1985 (1963).
(5) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

$$R{-}X + OH^- \rightarrow \text{Olefin} + X^- + H_2O \qquad (2)$$

In DMSO primary halides undergo reaction 1; secondary and tertiary halides undergo primarily reaction 2.

EXPERIMENTAL

Apparatus and Reagents. Dimethylsulfoxide and nitrobenzene were reagent grade.

Potassium hydroxide was a 40% water solution. Potassium hydroxide, 1*M*, was standardized against potassium acid phthalate with phenolphthalein as an indicator. Hydrochloric acid, 0.2*M*, was standardized against potassium hydroxide. Potassium thiocyanate, 0.4*M*, was a primary standard. Silver nitrate, 0.2*M*, was standardized against potassium thiocyanate. Ferric nitrate was a 10% solution in water. Nitric acid was reagent grade.

Organic halides were reagent grade of 98–100% purity.

Borosilicate culture tubes, 25 × 200 mm drawn in ampoules, or 50-ml Erlenmeyer flasks were used as reaction vessels.

Determination of Alkyl Iodides or Bromides. PROCEDURE 1. Weigh accurately approximately 2 meq of the sample into a weighing bottle. Transfer the sample to an ampoule with DMSO or to a flask if the sample is not volatile at 100 °C. Add 5 ml of 1*M* potassium hydroxide from a pipet and enough DMSO for a total volume of 30 ml. Seal the ampoule or cork the flask and place in a steam bath. After reaction is complete, remove the flask, cool, transfer the contents into a 125-ml flask with 50 ml of distilled water and acidify with nitric acid. Pipet 10 ml of standard 0.4*M* silver nitrate. Shake with 10 ml of nitrobenzene if chloride is being determined. Add 2 ml of 10% ferric nitrate and titrate with standard 0.2*M* potassium thiocyanate to a light orange end point.

PROCEDURE 2. The above procedure is used for the reaction. Titrate the excess phenolphthalein base after the reaction to the phenolphthalein end point with standard 0.2*M* hydrochloric acid. This procedure requires that both base and acid be standardized. A blank should be run under the same conditions as the sample. The blank titer is usually within 0.1 ml of 0.2*M* HCl of the normal acid–base titer. The acid–base titration can also be done potentiometrically. This is especially necessary for nitroaromatic halides which give colored solutions with base and DMSO thus prohibiting visual indicators.

Determination of Chlorides and Other Slow-Reacting Halides. PROCEDURE 3. A large excess, 5 ml of 40% potassium hydroxide, is mixed with 2 meq of halide and 25 ml of DMSO producing a two phase mixture. After reaction at 100 °C, the halide ion is determined as in Procedure 1 with the Volhard procedure.

Rate Determinations. Mix 4 meq of halide and 10 ml of 1*N* potassium hydroxide in a 50-ml volumetric flask and dilute to the mark with DMSO. Take 5-ml aliquots and seal in an ampoule. Place the tubes in a constant temperature bath at 55.5 °C. Determine the halide ion by the Volhard procedure after cooling the ampoule and acidifying the water solution.

RESULTS AND DISCUSSION

Aliphatic halides and polyhalides are generally determined in 30 minutes or less in DMSO at 100° C. Nitroaromatic halides require an hour or less. The results are summarized in Table I.

As a comparison Abdulla-Zade (*6*) used ethanolic potassium hydroxide at 125 °C for 2 hours to determine dichloroethane. The present method requires 30 minutes at 100 °C.

Unsubstituted aromatic halides such as chlorobenzene, bromobenzene, and iodobenzene were found to be completely unreactive toward 40% potassium hydroxide in DMSO after an hour at 100 °C. Substituted nitroaromatic halides reacted to produce a dark color (usually deep red) which did not completely disappear even after acidifying in water. This color is caused by the formation of a Meisenheimer adduct (*7*).

In order to demonstrate the selectivity of the method, rates for the reaction of base with *n*-butyl halides were run. The results are shown in Table II. It should be possible to determine binary mixtures of the compounds shown in Table II by using differential rate methods.

Crude rate runs demonstrated the feasibility of completely analyzing the following scheme:

$$\text{halobenzene} \xrightarrow{HNO_3} \text{mononitrohalobenzene} \xrightarrow{HNO_3} \text{dinitrohalobenzene}$$

Table I. Quantitative Hydrolysis of Organic Halides

Compound	Reaction time, min	Procedure	Found, %[a]
n-Butyl chloride	20	3	98.7 ± 0.1
n-Butyl bromide	10	2	99.2 ± 0.2
n-Butyl iodide	5	1	98.6 ± 0.2
Cyclohexyl chloride	60	3	99.4 ± 0.6
Benzyl chloride	10	1	100.5 ± 0.5
Isopropyl bromide	10	1	99.2 ± 0.2
tert-Butyl bromide	5	1	98.5 ± 0.5
1,3-Dibromopropane	10	1	98.7 ± 0.2[b]
Bromoform	15	1	99.0 ± 0.3[b]
Methylene dibromide	15	1	99.2 ± 0.2[b]
1,2-Dichloroethane	30	3	101.0 ± 0.5[b]
2,4-Dinitrochlorobenzene	instantaneous	2	99.5 ± 0.5
p-Fluoronitrobenzene	60	2	99.0 ± 1.0
p-Chloronitrobenzene	45	2	98.0 ± 1.0
o-Chloronitrobenzene	60	2	99.0 ± 0.3

[a] Average of two or more determinations.
[b] Based on all halogen atoms in the molecule.

Table II. Second Order Rate Constants for the Reaction of Base with *n*-Butyl Halides in DMSO at 55.5 °C

Compound	k (l · m^{-1} · sec^{-1})	Relative rate
n-Butyl chloride	1.68×10^{-5}	1
n-Butyl bromide	1.44×10^{-4}	38.4
n-Butyl iodide	3.94×10^{-3}	235

Table III. Analysis of Binary Mixtures

Compounds	Reaction conditions and procedure	Found, %
Chlorobenzene and *p*-chloronitrobenzene	45 min at 100 °C, procedure 3	99.2 of nitro
p-Chloronitrobenzene and 2,4-dinitrochlorobenzene	1 min at 25 °C, procedure 2	100.7 ± 0.1[a] of dinitro
1-Bromoethylbenzene and 2-bromoethylbenzene	1 min at 0 °C, procedure 1	98.2 ± 0.5[a] of 1-bromo

[a] Average of two determinations.

(6) G. A. Abdulla-Zade, *Azerb. Med. Zh.*, **10**, 74 (1956).

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Synthetic binary mixtures were made from 1 meq of each halide and the results recorded in Table III.

Any functional group that reacts rapidly with base in DMSO at 100 °C will interfere in procedure 2 in which the excess base is back titrated. Esters, aldehydes, or ketones with alphahydrogens, anhydrides, and acidic compounds such as carboxylic acids would interfere. However, if the Volhard method is used (procedures 1 and 3), there will be no interferences except with mixtures of halides.

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Determination of Trace Copper in Petroleum Middle Distillates with Cuprizone

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THE VERY LOW CONCENTRATIONS of copper usually present in refined petroleum middle distillates necessitate sensitive analytical methods. The amount of soluble copper in aviation turbine fuels is of considerable interest to the air transportation industry. Copper in the range of 150 ppb adversely influences the thermal stability of hydrocarbon fuels (*1*) as measured by the CFR fuel coker test (*2*).

The sources of soluble copper in middle distillates can be traced to carry-over from primary distillation of crude and other refining processes including amounts picked up from brass valves, fittings, and heat exchanger tubes, for example.

The use of cuprizone (biscyclohexanone oxaldihydrazone) as a spectrophotometric ligand for inorganic Cu(II) was first described by Nilsson (*3*). Wetlesen and Gran (*4*) applied cuprizone to the determination of copper in pulp and paper. The high sensitivity of cuprizone was reported by Peterson and Bollier (*5*). High selectivity was reported by Rohde (*6*) who employed cuprizone for determination of copper in a variety of nonferrous metals and alloys. These publications describe formation of the cuprizone–copper complex in aqueous solutions after chemical treatment of the sample matrix to obtain inorganic Cu(II) ions.

Both inorganic and organic Cu(II) can be successfully extracted and determined from petroleum middle distillates and other hydrocarbon solvents by complexing with solutions of cuprizone. The extraction with cuprizone is effected using methanol or other selected polar solvents. When 100 grams of sample are extracted, copper in the range of 0.02 to 2 μg per ml can be determined. The method is applicable to a wide variety of hydrocarbon fuels and solvents. Heavier stocks can be extracted after they are diluted in a suitable light solvent.

EXPERIMENTAL

Apparatus. Absorbance values were measured with a Bausch and Lomb Spectronic 20 using 1-cm cells.

Reagents. Cuprizone (biscyclohexanone oxaldihydrazone) solution, 0.2% prepared in anhydrous methanol. Warm gently to effect solution.

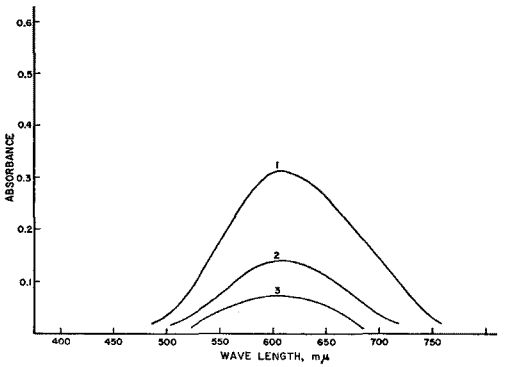


Figure 1. Absorption spectra of the copper-cuprizone complex in methanol

1. **Copper, 1.0 μg per ml *vs.* reagent blank**
2. **Copper, 0.46 μg per ml *vs.* reagent blank**
3. **Copper, 0.24 μg per ml *vs.* reagent blank**

Ammonium acetate buffer solution, 1 molar, is prepared in water and adjusted to pH 9.0 by addition of ammonium hydroxide before being diluted to volume.

Standard copper solution, 100 ppm in methanol, may be prepared from either inorganic or organo copper(II) certified reagents. Equivalent calibration curves were obtained from either class of copper reagent. Cupric acetate is recommended because of its solubility in methanol.

Procedure. Samples containing 0.1 to 2.0 μg of copper are weighed into a 250-ml glass-stoppered separatory flask. Usually 100-gram samples of middle distillate are transferred into the flask, followed by addition of 8 ml of 0.2% cuprizone solution and 2 ml of ammonium acetate buffer. The flask is shaken vigorously for 1 minute with venting to relieve pressure during the first half minute. Allow 15 minutes settling time. The settling time can be shortened by centrifuging. Withdraw the aqueous methanol phase into a 25-ml volumetric flask. Repeat the extraction with another 10 ml of cuprizone–buffer solution mixture. After making the second extraction, dilute to mark with methanol. Measure absorbance of the blue solution at 606 mμ against a reference solution of cuprizone reagent. Copper content is read from a straight line calibration curve. Beer's law is obeyed for the range 0 to 2 μg of copper per ml.

Sampling middle distillates for copper determination presents several difficulties. Nonreproducible analyses will often result from samples containing appreciable amounts of water. Copper-rich components have a strong tendency to

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Table I. Extraction of Copper from Petroleum Middle Distillates

A. 150 grams of kerosine extracted with 8 ml of cuprizone reagent in methanol and 2 ml of buffer

Extraction No.	Sample Cu content before extraction, ppb	Absorbance of extract	Copper extracted, ppb	Copper extracted, %
1	75	0.29	53	70.7
2	22	0.11	19	25.4
3	3	0.01	2	2.7
4	1	0.00	0	0.0
		Totals	74	98.8

B. 150 grams of kerosine extracted with 8 ml of methanol without complexing with cuprizone

Extraction No.	Sample Cu content before extraction, ppb	Absorbance of extract[a]	Copper extracted, ppb	Copper extracted, %
1	75	0.02	4	5.3
2	71	0.03	5	6.7
3	66	0.02	4	5.3
		Totals	13	17.3

[a] Absorbance developed after extraction by addition of 1 ml of 0.5% cuprizone and 1 ml of buffer.

concentrate in the water phase and are strongly surface active. Upon standing, a film of copper compounds is often adsorbed on the surface of the sample container. It is recommended that hydrocarbon samples be taken directly from the sampling point into smaller containers—*i.e.*, 4-oz bottles—and that the entire sample be extracted. Rinsing the empty sample container with the cuprizone-buffer solution used for the first extraction is recommended. To ensure against copper contamination, all glassware should be rinsed with warm 1:1 hydrochloric acid to remove any trace copper present prior to use.

The calibration curve is prepared from dilutions in methanol of the 100 ppm standard copper solution. Solutions in the range of 0.2 to 2.0 μg of copper per ml are recommended. Use of a 10-fold molar excess of cuprizone plus sufficient buffer solution to give pH 8 to 9 is emphasized for maximum color development and repeatability.

RESULTS AND DISCUSSION

The absorption spectra of the copper-cuprizone complex in aqueous methanol have an absorbance maximum at approximately 606 mμ. Typical curves are depicted in Figure 1. These curves closely resemble those of aqueous copper–cuprizone solutions reported by Smith (*7*).

The colored complex after extraction from middle distillates was stable for approximately 4 hours. After this time, there was a gradual fading of about 10% over a 24-hour period. Maximum color was produced 30 minutes after addition of cuprizone.

The extraction efficiency was determined by repetitive extractions of a prepared sample of oil-soluble organo copper (copper naphthenate) in kerosine previously analyzed to be copper free. Results shown in Table I*A* demonstrate that essentially all of the copper is removed after the second extraction. Results from Table I*B* show that the copper must be complexed with cuprizone to achieve effective extraction, as little copper is extracted by methanol alone.

The ligand-metal molar ratio was determined, according to the method of Yoe and Jones (*8*), to evaluate the composition of the complex. A series of methanol solutions containing a constant amount of copper with increasing quantities of cuprizone were prepared. Both reagent cupric acetate and pure copper wire were employed as copper source, each yielding equivalent results. The results, which are plotted in Figure 2, indicate breaks corresponding to the formation of a 4:1 complex between the ligand and the metal.

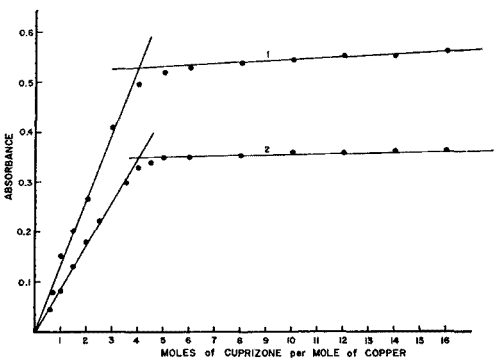


Figure 2. Molar ratio plots

Final concentration of copper

1. 3×10^{-5} molar
2. 2×10^{-5} molar

Several other water-miscible solvents that possess limited solubility in petroleum middle distillates were effective replacements for methanol. These include ethanol, pyridine, and *N*-methyl-2-pyrrolidone (NMP). This is by no means an exhaustive list. Solutions of cuprizone in NMP (General Aniline and Film) with the ammonium acetate buffer were especially effective for extraction and determination of trace copper in heavier petroleum stocks such as lubricating oils. Dilution of a viscous oil with a light hydrocarbon solvent prior to extraction minimizes viscosity problems.

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Volumetric Determination of Alcohols in Aqueous Solution with Bromine Chloride

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SEVERAL METHODS are known for determining alcohols in aqueous solution. These include gas chromatographic methods (*1*, *2*), volumetric methods based on back titration of excess oxidant such as permanganate, xenon trioxide, or ceric sulfate after oxidation of alcohol (*3–6*), and spectrophotometric analysis of the alcoholic complex with ammonium nitrate or vanadium oxinate (*7–10*). However, these methods are not always satisfactory regarding simplicity of procedure, precision, or applicable concentration range of alcohol.

It is known that halogens react as oxidants. Bugarszky (*11*) found that the oxidation of ethanol with bromine yields acetic acid and ethylacetate. Farkas (*12*) studied the oxidation of some other alcohols with bromine, and Kaplan (*13*) and Deno and Potter (*14*) investigated the oxidation mechanisms. We found that bromine chloride also oxidizes alcohols and has much stronger oxidizing power than bromine. The oxidation with bromine chloride of 1-butanol, 2-butanol, 1-propanol, 2-propanol, ethanol, and methanol in aqueous solution was examined. In appropriate conditions, the oxidation of primary and secondary alcohols, except methanol, with bromine chloride yields, quantitatively, an acid and a ketone, respectively. After oxidation of alcohols excess bromine chloride is titrated iodometrically.

This report describes a volumetric method which is simple, precise, and applicable to the quantitative determination of micro amount of alcohols in aqueous solution.

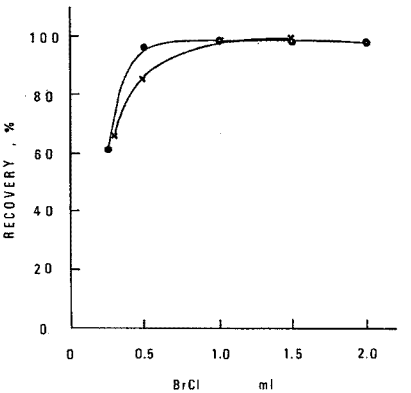


Figure 1. Effect of volume of bromine chloride solution on recovery

Sample size: 3 ml of 1.349 × $10^{-2}M$ solution; concd HCl: 0.2 ml; 20% KI solution: 4 ml; temperature: 1-butanol 50 °C; 2-butanol 20 °C time: 1-butanol, 3 hr; 2-butanol, 1.5 hr

o 1-Butanol
× 2-Butanol

EXPERIMENTAL

Reagents and Apparatus. Bromine chloride in aqueous solution was prepared by modifying Maruta's method (*15*). Potassium bromide, 79.34 grams, and 55.67 grams of potassium bromate were dissolved in water and diluted to one liter (bromine chloride solution). Addition of hydrochloric acid to this solution produces bromine chloride:

$$2KBr + KBrO_3 + 6HCl = 3BrCl + 3KCl + 3H_2O$$

Guaranteed reagents were used. Alcohol samples were distilled and the purities were examined by gas chromatography. Standard aqueous alcohol solutions of from 0.001349 to 0.1349 mole were prepared by weighing alcohols and diluting with water to volume. For example, to obtain a 0.01349 mole solution of 1-butanol, 100 mg of 1-butanol was weighed and diluted with water to 100 ml. Oxidations were carried out in a thermostat (±1 °C) using a 100-ml iodine flask, the stopper of which was sealed with 20% potassium iodide solution. The titrations with 0.1*N* sodium thiosulfate were made with a 10-ml semimicro buret.

Procedure for Primary Alcohols. Add 3 ml of aqueous sample solution and 1 ml of bromine chloride solution to a 100-ml iodine flask. The following steps must be carried out in a dark room. Add 0.2 ml of concentrated hydrochloric acid to the iodine flask. Stopper tightly and seal with 4 ml of 20% potassium iodide solution. Warm the mixture at 50 °C in a thermostat for 3 hours. After oxidation, the 20% potassium iodide solution which has been used to seal is dropped into the flask. Titrate the liberated iodine with 0.1*N* sodium thiosulfate. A blank is titrated with 3 ml of water. The amount of bromine chloride consumed in the oxidation is equal to the difference between bromine chloride before and after the reaction with alcohol.

Procedure for Secondary Alcohols. The procedure, including the use of a dark room, is the same except for oxidation temperature and time. The temperature is 20 °C and the time is 1.5 hours.

RESULTS

The volume of bromine chloride solution, the oxidation temperature, and the time must be standardized, because these factors affect the oxidation of the alcohols.

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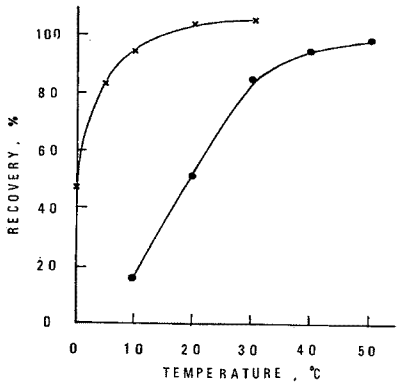


Figure 2. Effect of reaction temperature on recovery

Sample size: 3 ml of 1.349 × $10^{-2}M$ solution; BrCl solution: 1 ml; concd HCl: 0.2 ml; 20% KI solution: 4 ml; time: 1-butanol, 3 hr; 2-butanol 1.5 hr

o 1-Butanol × 2-Butanol

Volume of Bromine Chloride Solution. The effect of the volume of bromine chloride solution on the recovery was investigated by varying the volume from 0.25 ml to 2.0 ml against 3 ml of 1.349 × $10^{-2}M$ 1-butanol and 2-butanol solutions, Figure 1. One milliliter of bromine chloride solution is sufficient to complete the oxidation of the alcohols.

Oxidation Temperature. Reactions were carried out ranging from 0 to 50 °C and plotted against the recovery, Figure 2. Too high a temperature must be avoided because of the low bp of bromine chloride (5 °C) and a closed reaction system. Thus, the temperature is fixed at 50 °C for primary alcohols and 20 °C for secondary.

Reaction Time. A dependency of recovery on reaction time was investigated by changing the time from 15 minutes to 4 hours. Results are presented in Figure 3. A constant recovery was attained by warming more than 2 hours for

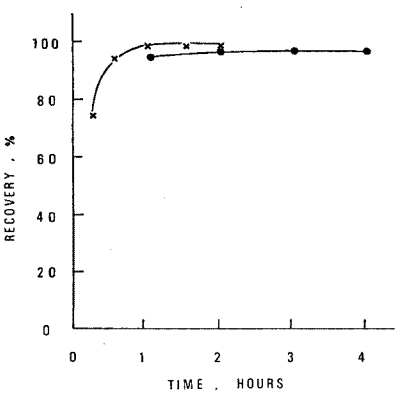


Figure 3. Effect of reaction time on recovery

Sample size: 3 ml of 1.349 × $10^{-2}M$ solution, BrCl solution: 1 ml; concd HCl: 0.2 ml; 20% KI solution: 4 ml; temperature: 1-butanol, 50 °C; 2-butanol, 20 °C

o 1-Butanol × 2-Butanol

Table I. Results of Primary Alcohol Determination

Concentration Taken (mol × 10^{-2})	Concentration Found (mol × 10^{-2})	Recovery, %	Average, %
	1-Butanol		
0.1349	0.1358	100.7	98.5
	0.1299	96.3	
0.3373	0.3245	96.2	97.0
	0.3299	97.8	
0.6745	0.6570	97.4	97.8
	0.6618	98.1	
1.349	1.352	100.2	100.2
	1.350	100.1	
2.698	2.720	100.8	99.9
	2.671	99.0	
3.373	3.299	97.8	97.7
	3.289	97.5	
4.047	3.849	95.1	96.2
	3.934	97.2	
5.396	4.484	83.1	83.0
	4.468	82.8	
	1-Propanol		
0.3328	0.3328	100.0	99.3
	0.3281	98.6	
0.8319	0.8061	96.9	95.8
	0.7870	94.6	
1.664	1.606	96.5	97.1
	1.626	97.7	
3.328	3.251	97.0	96.9
	3.222	96.8	
4.992	4.298	86.1	86.1
	4.293	86.0	
	Ethanol		
0.4341	0.4523	104.2	99.2
	0.4085	94.1	
1.085	1.061	97.8	97.2
	1.047	96.5	
2.171	2.078	95.7	96.6
	2.115	97.4	
3.256	2.901	89.1	89.1
	2.898	89.0	
4.341	3.716	85.6	85.2
	3.677	84.7	
6.512	4.383	67.3	66.8
	4.311	66.2	
	Methanol		
0.1560	0	0	0
	0	0	
0.3119	0.02370	7.6	12.7
	0.05520	17.7	
1.560	0.2605	16.7	15.2
	0.2122	13.6	
3.119	0.4179	13.4	18.7
	0.4335	13.9	
6.228	0.7349	11.8	12.4
	0.8034	12.9	

1-butanol and 1 hour for 2-butanol. Consequently, the time was standardized at 3 hours for primary alcohols and 1.5 hours for secondary alcohols. The volume of concentrated hydrochloric acid was fixed to 0.2 ml from a preliminary test.

Determination of Alcohols. The determination of primary and secondary alcohols is summarized in Tables I and II. The consumption of bromine chloride is two equivalents for primary alcohols and one for secondary. The plot of bromine chloride consumed against the amounts of alcohol used yields three curves which correspond to methanol, primary alcohols, and secondary alcohols, respectively. Data concerning different alcohols belonging to the same classification fall on the same curve as presented in Figure 4.

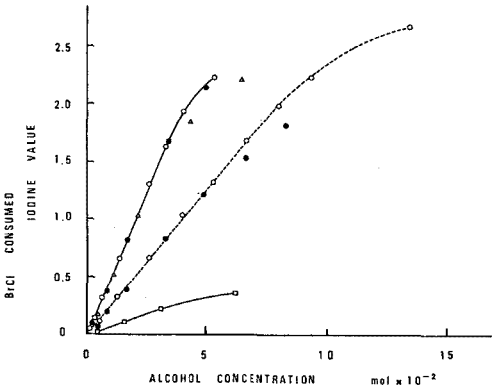


Figure 4. Relations between alcohol concentration and bromine chloride consumed

—— Primary
--- Secondary
○ Butanol
● Propanol
△ Ethanol
□ Methanol

Table II. Results of Secondary Alcohol Determination

Concentration Taken (mol × 10^{-2})	Concentration Found (mol × 10^{-2})	Recovery, %	Average, %
	2-Butanol		
0.1349	0.1438	106.6	109.7
	0.1520	112.7	
0.2698	0.2747	101.8	101.5
	0.2730	101.2	
0.5396	0.5488	101.7	100.3
	0.5337	98.9	
1.349	1.342	99.5	100.0
	1.356	100.5	
2.698	2.685	99.5	99.4
	2.676	99.2	
4.047	4.051	100.1	99.9
	4.035	99.7	
5.396	5.374	99.6	99.3
	5.342	99.0	
6.745	6.657	98.7	98.9
	6.678	99.0	
8.094	7.884	97.4	97.2
	7.843	96.9	
9.444	8.783	93.0	93.1
	8.802	93.2	
13.49	10.52	78.0	78.0
	10.52	78.0	
	2-Propanol		
0.3328	0.3415	102.6	101.4
	0.3331	100.1	
0.8319	0.8460	101.7	101.2
	0.8377	100.7	
1.664	1.657	99.6	99.4
	1.651	99.2	
3.328	3.308	99.4	99.4
	3.308	99.4	
4.992	4.802	96.2	96.1
	4.792	96.0	
6.656	6.057	91.0	91.4
	6.104	91.7	
8.320	7.130	85.7	85.3
	7.055	84.8	

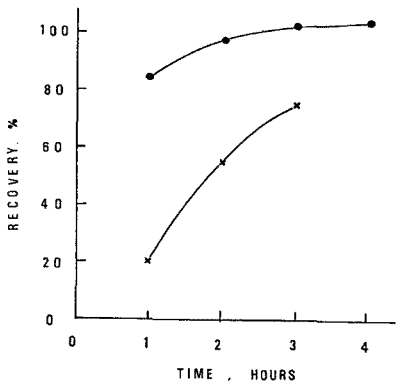


Figure 5. Comparison of oxidation rates between bromine chloride and bromine

Sample size: 97 mg of 98.6% 1-butanol; BrCl or Br_2: 600 mol % to alcohol; concd HCl: 3 ml; temperature: 20 °C

○ BrCl × Br_2

With regard to the precision, the coefficient of variation of recovery of the whole concentration range determined is 2.02% for the primary alcohols and 1.60% for the secondary.

The comparison of the oxidation rate of bromine with bromine chloride was investigated, and the result is presented in Figure 5. It is clear that bromine chloride is a more useful oxidant than bromine. Iodine chloride is unfavorable for it is difficult to use in water.

CONCLUSION

1-Butanol, 1-propanol, and ethanol can be determined in the range of 0.001349 to 0.03373 mole solution as presented in Figure 4. The detectable concentration range of ethanol is slightly less than that of other primary alcohols. Methanol can not be determined by this method. It is supposed that the oxidation of alcohols takes place by a C—H bond rupture in the methylene or methyne attached to the hydroxyl group (*12*, *13*). The resistance of methanol to this type of oxidation can be understood by the absence of such methylene or methyne group. While 2-butanol can be determined in the range of 0.002698 to 0.08094 mole solution, 2-propanol can only be determined in the range of 0.003328 to 0.04992 mole as presented in Table II and Figure 4. The detectable concentration range of 2-butanol is twice as wide as with other alcohols. It seems that a secondary alcohol can be oxidized more easily than a primary and that 2-butanol is more reactive than 2-propanol. Thus, the reactivity increases in the order: methanol $\ll$ ethanol $<$ propanol $<$ butanol.

The oxidation of alcohols with bromine chloride must be carried out in a dark room, for both primary and secondary alcohols give byproducts under light and yield recoveries exceeding 100%. With secondary alcohols, too high an oxidation temperature and too long an oxidation time should also be avoided, because the ketone obtained by the oxidation of an alcohol has an active α-methylene which can be easily substituted by halogens. Compounds which have a double bond, amino and carbonyl groups interfere with this method.

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Quantitative Analysis of Amines *via* Amine Boranes

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THE BORON–HYDROGEN bond of borane or diborane has been shown to be hydrolyzed quantitatively with many protic solvents (*1*). The conversion of the borane to a complex with an amine has been shown to stabilize the boron–hydrogen bond to hydrolytic or oxidative reaction conditions (*2–6*). These observations suggested a feasible analytical procedure for estimating the molar quantities of amine based on formation of amine boranes.

EXPERIMENTAL

Procedure. A weighed sample of the amine was placed in a flask which had been flushed with dry nitrogen. To this was added 20 ml of dry solvent (tetrahydrofuran in most instances) and the flask was attached to a gas buret. A similar apparatus was prepared in which no amine was added. To each flask was added a measured volume of solution of borane in tetrahydrofuran. After being stirred for 0.5 hour, the solution was treated with 2 ml of methanol. The volume of gas evolved from each reaction flask was measured and the volume from the reaction flask containing no amine was used to calculate the molarity of the borane–tetrahydrofuran solution. The evolution of hydrogen was usually complete within 5 to 10 minutes and any reaction after this time probably results from decomposition of the amine borane. Such complications were avoided by changing the solvent to one of higher dielectric constant or by lowering the temperature of the reaction during the analysis.

On the basis of the volume of hydrogen evolved from the flask containing amine, an estimation of the amount of excess borane present was made. The difference between this value and the moles of borane added gave the amount of borane protected as the amine borane and, therefore, indicated the number of equivalents of amine present. Typical results of this analytical procedure are given in Table I.

RESULTS

A procedure for the estimation of amines was developed which involved the treatment of the amine with an excess, but measured volume, of a standardized solution of diborane in tetrahydrofuran. The excess diborane was decomposed by the addition of water or alcohol, and the volume of hydrogen which was liberated was measured. A similar volume of the diborane solution was hydrolyzed to determine the titre of the solution. The difference in the volume of hydrogen evolved in the two experiments indicated the amount of amine borane which was formed and thus the molar equivalents of borane that were stabilized to hydrolytic conditions.

Because the nitrogen–hydrogen bond of amines is not broken by reaction with diborane (*1*) this analytical technique may be effective for primary, secondary, or tertiary amines. Such an analytical procedure could be used to determine the quantity of amines in a solution, the molecular weight (equivalent weight) of an amine, or the composition of a mixture of two amines of different molecular weights.

The analysis depends on the amine borane being kinetically stable to the hydrolytic conditions used to destroy the excess borane. With the strongly basic, unhindered amines, such as the cyclic amines, there was no difficulty in achieving selective decomposition; however, to increase the rate of hydrogen evolution a solvent of low dielectric constant, such as dioxane, was used. With less stable amine boranes formed with amines of large steric requirements or of weak basicity the selective hydrolysis was more difficult. The amineborane of the large amine, diisopropylethylamine, underwent partial hydrolysis in dioxane; however, a satisfactory analysis was accomplished by using tetrahydrofuran as solvent and a temperature of 0 °C for the methanolysis of the excess borane. With the weakly basic diethylaniline the amine borane was too unstable to be compatible with methanol in either solvent. These results are in agreement with hydrolysis rates reported for amine boranes (*3–6*). Varying the analytical procedure to fit the require-

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Table I. Typical Analytical Results

Amine	Amine, mmole	Borane, mmole	Hydrogen evolved, ml[a]	Hydrogen evolved, mmole[b]	Borane excess mmole[c]	Determined amine mmole[d]	Experimental error, %
1-Methylpiperidine	0.70	1.15	30.8	1.27	0.42	0.73	4.3
	0.76	1.15	27.7	1.15	0.38	0.77	1.3
α-Methylbenzylamine	0.75	1.07	22.7	0.94	0.31	0.76	1.4
N,N-Diisopropylethylamine	0.46	1.18	53.8	2.22	0.74	0.44	2.3
Piperidine	0.95	1.14	14.9	0.62	0.21	0.93	2.1

[a] Volume uncorrected for temperature and pressure.
[b] Corrected.
[c] mmoles $BH_3 = \frac{\text{mmoles } H_2}{3}$.
[d] mmoles amine = mmoles BH_3 Added − mmoles BH_3 excess.

ments of the amine under analysis permits the estimation of the molar quantity of aliphatic amines with a deviation of about 3% which compares favorably with other analytical procedures for amines (see Table I). Amines which form borane complexes of low stability, such as aniline derivatives, may be too easily alcoholized to permit analysis by this method (*3–6*).

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Chemical Microscopy of 10-Methylacridiniumchloride

Reactions with Platinum Metals and Gold

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BY MEANS OF chemical microscopy it has previously been shown (*1*) that an acid solution of acridiniumchloride, without benefit of any other complexing agent, could serve as a desirable reagent for the detection or identification of certain platinum metals and gold when present in acid solutions of their chlorides. The purpose of this paper is to report on the relative efficiency of the derivative 10-methylacridiniumchloride as a micro reagent for these same metals.

EXPERIMENTAL

The reagent solution was a 0.2*M* solution of 10-methylacridiniumchloride in 1*N* HCl; this appeared to be near the limit of solubility of the compound at room temperature. Just as in the previous experiments with acridiniumchloride, test solutions of the respective precious metal ions were prepared by appropriate dilution of stock solutions of gold(III), platinum(IV), palladium(I), iridium(III), rhodium(III), and ruthenium(III); the stock solution of osmium, however, was based on potassium osmate. All stock solutions were in 1*N* HCl, and all dilutions thereof were made with the 1*N* acid.

Individual tests under the microscope were carried out by allowing a 20-μl reagent drop to flow into a similar droplet of sample solution on a slide. Most observations were made through an 8-mm objective and a 10× ocular. Tests were considered satisfactory if appropriate crystals separated within 2 minutes.

RESULTS AND DISCUSSION

With an acidified osmate solution containing the equivalent of one part osmium in one or two thousand, the reagent caused a prompt separation of an abundance of bright yellow crystals (Figure 1). Many were in the form of plumulose, branched X's, and other aggregates. In plumules the barbs joined the shaft at an angle of approximately 45°. By polarized light the crystals appeared faintly dichroic, ranging from a very pale yellow to a slightly deeper shade. As samples were made more dilute there was a decreasing tendency to form the more complex branched aggregates, which were displaced by small yellow prisms. Two principal forms of the latter were observed; one type appeared as parallelepipeds having an extinction angle of approximately 30°, while another form resembled slender rods, pointed at both ends, and exhibiting parallel extinction. With an osmium content of only one part in 40,000, none of the plumulose aggregates separated. The reaction permitted the identification of osmium in samples containing as little as one part metal in 150,000, or 7 ppm.

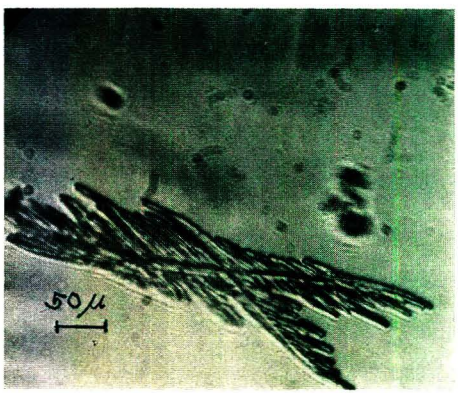


Figure 1. Crystalline derivative obtained by reaction of 10-methylacridiniumchloride with solution containing osmate

Using a 20-μl sample, this was equivalent to the identification of approximately 0.13 μg. For the purpose of merely detecting osmium, assuming the absence of interfering ions, the sensitivity of the reagent could be considered as 0.07 μg, because an adequate crystalline precipitate separated from solutions containing as little as one part osmium in 300,000. Because of the small dimensions of the crystals formed at high dilutions, a 4-mm objective should be employed. At high dilutions, the observations are also facilitated by the use of crossed polars.

Solutions of gold(III) chloride in HCl promptly reacted to form a yellow precipitate of very fine crystals (Figure 2). Even with a gold concentration of only one part in 50,000 a rather abundant precipitate appeared. In general, the crystals were so small that the use of a 4-mm objective was indicated. As a rule, crystals which appeared as elongated rectangles exhibited an extinction angle of 45°, while those with pointed ends showed parallel extinction. Identification was possible with a gold concentration below one part in 200,000, or the equivalent of 5 ppm.

Another metal for which the reagent showed a high sensitivity was platinum. The yellow precipitate contained small prisms occurring singly, or in the form of crosses, daggers, and some more complex aggregates (Figure 3); there were also occasional parallelepipeds. Many of the individual crystals exhibited parallel extinction, but angles of approximately 10° and 25° were also observed. Positive identifica-

(1) H. F. Schaeffer, *Microchem. J.*, **9**, 492 (1965).

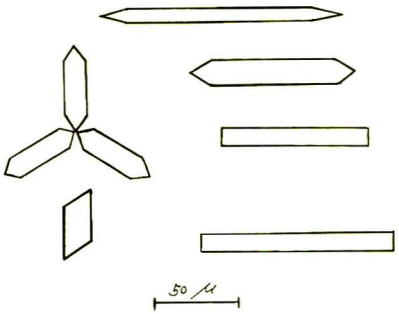


Figure 2. Crystals of derivative formed with gold

tion of platinum(IV) could be made at concentrations as low as one part in 200,000.

At a concentration of one part metal in a few thousand, solutions of palladium(II) chloride reacted to yield branched yellow aggregates (Figure 4). As opposed to somewhat similar crystals formed by osmium (see above), the barbs of the palladium derivative were perpendicular to the shaft. In addition to these aggregates there were also some smaller crystals in the form of thin parallelepipeds. In their most common orientation the latter crystals exhibited profile angles of approximately 60° and 120°. Extinction occurred when a shorter edge was parallel with one of the crossed polars. At higher dilutions the plumulose aggregates constituted a smaller proportion of the precipitate; when the palladium concentration dropped to one part in 25,000 or 50,000 the aggregates no longer were formed. However, by viewing through crossed polars the individual crystals still permitted identification of palladium at a concentration of one part in 100,000.

One distinguishing characteristic of the precipitate formed by iridium trichloride solutions was the orange color. The product contained branched aggregates (Figure 5) in which the branches were perpendicular to the central shaft. In addition to these aggregates there were also thin plates, which

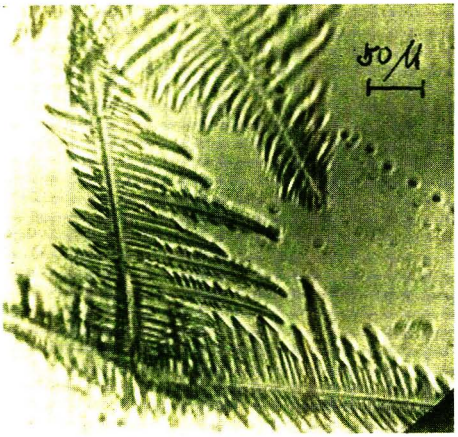


Figure 4. Palladium derivative

appeared as relatively long rectangles or laths. All of these thin plates exhibited parallel extinction. In some preparations a small proportion of the crystals were elongated hexagons, in which case extinction resulted when the long axis was parallel with the plane of polarization. As is frequently the case, there was a general tendency for the crystals to decrease in size as the sample concentration was lowered. Although a fair precipitate could be obtained with an iridium concentration of one part in 20,000, for the purpose of identification a concentration of one part in 10,000 should be considered the lower limit. At this dilution the use of a 4-mm objective is recommended.

With ruthenium(III) the reagent yielded a precipitate having a reddish brown macro appearance; viewed through an 8-mm objective the crystals showed a deep-yellow to amber color. The preparations were best observed through crossed polars. The crystals were in the form of thin leaves or plates, frequently irregular in shape. In some specimens the surface took the form of an elongated rectangle, with or without terminal notches; in other instances the plates appeared as parallelograms, with profile angles of approximately 45°

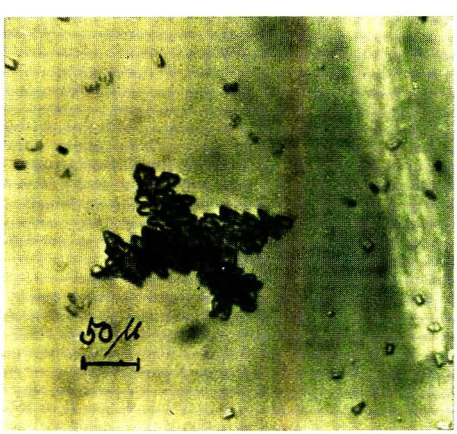


Figure 3. Platinum derivative

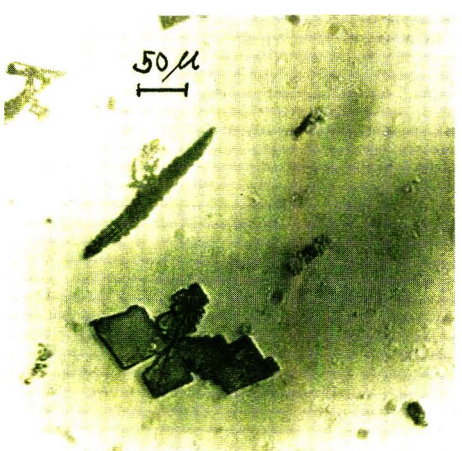


Figure 5. Iridium derivative

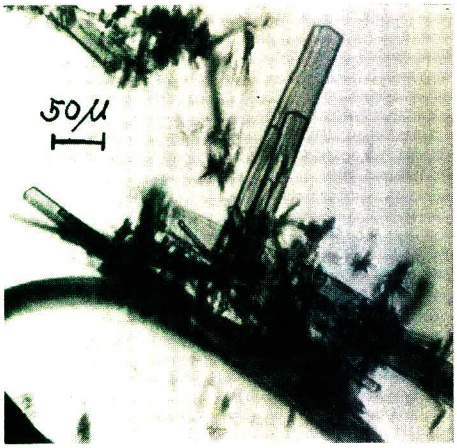


Figure 6. Ruthenium derivative

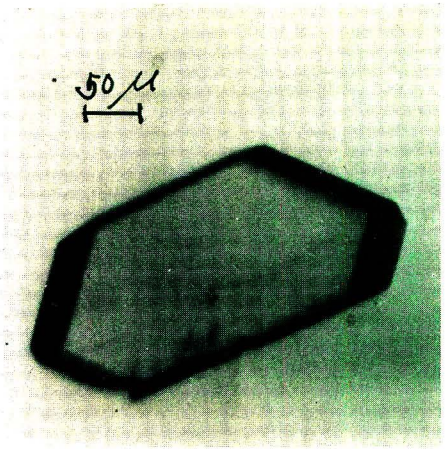


Figure 7. Derivative obtained with cupric ion

and 135°. There were also elongated hexagons (Figure 6). Generally, for all forms, extinction occurred with the long edge of a crystal parallel with the plane of polarization. Not infrequently some of the thin crystals were oriented in a plane perpendicular to the surface of the slide. Under favorable conditions ruthenium could be identified in samples containing as little as one part in 2000.

Rhodium(III) was the only member of the platinum group which failed to yield a crystalline product at the concentrations considered in this study. Even a 1% solution of $RhCl_3$ (approximately 4.7 parts Rh per thousand) failed to yield a precipitate with the reagent under the conditions of the experiment. Under these circumstances it was of interest to find that samples in which the concentration of gold, platinum, palladium, or iridium represented as little as one part in 10,000, good tests for the respective metals were obtained even in the presence of more than 20 times as much rhodium; furthermore, the presence of a moderate rhodium concentration did not interfere with tests for ruthenium.

Because copper may be a component of certain precious metal alloys, the effect of the methylacridiniumchloride reagent was tried on a 0.25*M* solution of cupric chloride in 1*N* hydrochloric acid. Under the conditions of the experiment no precipitate resulted. However, very interesting crystals of a copper complex were obtained by adding a few fine particles of solid cupric chloride to a reagent drop (Figure 7). It was also of interest to find that, in mixtures, the presence of Cu(II) ion caused no serious interference in the detection of gold, platinum, palladium, iridium, or osmium. To illustrate, when the concentration of any of the latter was equivalent to one part in 10,000, characteristic crystals separated upon addition of the reagent, even when the test sample contained 80 times as much cupric ion.

Table I. Sensitivity of Methylacridiniumchloride Reagent[a]

Metal identified	Maximum dilution	μg Identified
Au	2.0×10^5	0.10
Pt	2.0×10^5	0.10
Os	1.5×10^5	0.13
Pd	1.0×10^5	0.20
Ir	2.0×10^4	1.00
Ru	2.0×10^3	10.00

[a] Temperature range was 22–23 °C.

Table II. Comparison of Acridiniumchloride and Methylacridiniumchloride Reagents[a]

Lower Limits of Identification (in terms of μg of metal per 20-μl sample)

	Acridiniumchloride	10-Methyl-acridiniumchloride
Au	0.67	0.10
Pt	0.80	0.10
Os	1.00	0.13
Pd	1.33	0.20
Ir	1.33	1.00
Ru	...	10.00

[a] Temperature range was 22–23 °C.

CONCLUSION

As a reagent for the identification of precious metals at low concentrations, the 10-methylacridiniumchloride showed its greatest sensitivity for gold(III), osmium(VI), and platinum (IV) for which the limits of identification were in the range of 0.07–0.13 μg, while rhodium(III) yielded no precipitate at the concentrations studied (Table I). It was of interest to note that the presence of rhodium(III) or copper(II) did not interfere with the response of the other metals. Probably the most serious disadvantage of this reagent is the fact that it is not generally suited for identifying the precious metals in mixtures of each other. As shown in Table II, compared with acridiniumchloride, the 10-methyl derivative has been found the more efficient precipitant of the precious metals. In regard to the numerical data which have been cited in this paper, it is important to consider the fact that the crystalline complexes formed by both reagents are temperature-sensitive, so that in a very warm laboratory the minimum concentration to yield a satisfactory test is appreciably increased.

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Submicro Sampling and Solvent Extraction System for Rapid Gas Chromatographic Determination of Blood Alcohol

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GAS CHROMATOGRAPHY, by virtue of its ability to simultaneously separate and quantitate sample components, is uniquely suited to biomedical application. The use of the technique is, however, limited by the rather extensive pre-injection sample preparation which results in relatively long "per sample" analysis times.

The present study demonstrates a sampling system designed to take advantage of the inherent high specificity and sensitivity of gas chromatography to reduce manipulative steps in the analysis to a minimum. The procedure is applied to the determination of blood alcohol but is suitable for use in the determination of a wide variety of volatile components.

EXPERIMENTAL

Blood Alcohol Determinations. Blood ethanol levels are determined by a variety of gas chromatographic techniques (*1*, *2*), all of which require several chemical manipulations and measurements prior to the actual gas chromatographic analysis. In addition, they require (relatively) large samples of blood (which must be obtained by venipuncture), thereby negating any advantage derivable from the use of an extremely small aliquot of specimen in the actual chromatographic process. Use of the proposed sampling technique eliminates the volumetric measurements associated with aliquoting of sample and solvent and thereby reduces the demand placed on the laboratory. In addition, use of capillary ("finger prick") blood reduces requirements on the qualifications of personnel obtaining the specimen, as well as the actual amount of vital fluid obtained from the subject.

For purposes of this discussion, we can generalize biomedical blood analyses by gas chromatography as consisting of the following steps (the order may depend somewhat on the actual analysis being performed): 1. Sampling—venipuncture and collection of 1–5 ml of blood; 2. Measurement—taking an aliquot of blood for analysis; 3. Removal of water from sample; 4. Solvent extraction of sample constituents into volatile solvent; 5. Addition of internal standard substance to specimen; 6. Centrifugation to compact solids and to separate solvent layers; 7. Injection of aliquot into gas chromatograph; and 8. Analysis and interpretation of the results.

The present research combines steps 1 to 5 into a single operation performed at the time of sampling. The technique uses a micro sample; 25 μl of blood which may be obtained from a "finger prick" rather than venipuncture. This latter modification allows less skilled personnel to rapidly obtain the sample with considerably less discomfort and danger to the subject.

Instrumentation. An F and M (Hewlett Packard, Skokie, Ill.) model 402 dual column flame ionization detector, dual electrometer chromatograph was used. The recorder was a dual pen Moseley No. 7128-A (1 mV) with a disc integrator on one pen and an automatic attenuator on the other. The electrometer was normally in the $10^2 \times 1$ setting. The columns were 4-mm i.d. × 6-mm o.d., 6-foot glass columns (U-shaped) which were packed in our laboratory with 10% Igepal on Diatoport S., 80–100 mesh obtained from F and M. The columns were mounted in $^1/_4$-inch Swagelok fittings using silicone rubber "O" rings. Sample size was 0.4 μl—a compromise between usable peak size and minimum solvent elution time. The syringes were washed with acetone between injections, resulting in a small pre-ethanol peak on some chromatograms. Flame detector and flash heater temperatures were 140 °C, oven temperature was 110 °C. Flow rates were: helium (carrier) 60 ml/min, air 300 ml/min, and hydrogen 37 ml/min. Columns were routinely purged overnight at 110 °C and over weekends at 185 °C.

Sampling System. The sampling procedure developed for this study is based on the Unopette sampling system developed by H. W. Gerarde (*3*, *4*). In the conventional Unopette system, a 25-μl sample of blood is obtained from a finger prick site, using a disposable precalibrated capillary. The blood is drawn into a polyethylene reservoir containing premeasured aqueous diluent and preservative and the capillary is discarded. The reservoir is sealed with a plastic cone which had been used to protect the capillary. The sample is now ready for analysis by special micro techniques.

Unopettes for the study were prepared in our laboratory. For the determination of blood ethanol, Unopette reservoir contains *n*-butanol as a solvent with *n*-propanol (7.5 μg/ml) added as an internal standard. Anhydrous $CaSO_4$ (0.3 ± 0.05 gram) is also placed in each reservoir. The $CaSO_4$ serves two purposes: it adsorbs water from the solvent and subsequently from the blood specimen, and it provides a surface on which precipitated protein and blood cell membranes are adsorbed. Upon centrifugation of the Unopette reservoir, the drying agent and adsorbed substances pack into a firm mass which allows an aliquot to be drawn into the injection syringe without danger of plugging the needle. The $CaSO_4$ or solvent does not adhere to the polyethylene containers making them convenient for this purpose. The solvent, 0.7 ml of redistilled butanol (by 600-mm Vigreux column, center $^1/_3$ cut) with *n*-propanol internal standard added in bulk, is aliquoted into the Unopettes by a Lab Industries (Scientific Products, Chicago, Ill.) 0–1.0 ml repipette. The Unopettes are sealed with a plastic plug until use. When a sample is taken into the reservoir it is resealed with the capillary shield. Studies in our laboratory have demonstrated the nonreactivity and stability of the solvent system stored in the Unopettes. The criteria for evaluation of internal standard stability was the comparison of the ratio of internal standard to solvent peak area over a period of four weeks. The internal standard showed only random variation. The mean value of the ratio (area internal standard peak/area solvent peak) was 1.25 × 1024, while the standard deviation was 0.06 (5% relative). This study also confirmed the compatibility of the solvent-internal standard system with the polyethylene Unopette. Several commonly used solvents and internal standards, hexane, acetone, methyl acetate, etc. were either too volatile for prolonged storage or reacted with the Unopette. In view of the potentially long period which may elapse between preparation and use—*i.e.*, weeks or months—this criteria remains highly critical. Substances which can undergo slow chemical reactions are also un-

(1) R. Master, C. Barrais, and G. Legendre, *Trav. Soc. Pharm. Montellier*, **24**, 68–82 (1964).
(2) A. S. Curry, G. W. Walker, and G. S. Simpson, *Analyst* (London), **91**, 742–3 (1966).
(3) H. W. Gerarde, In "Proc. Intern. Symp. Microchem. Tech. (Aug. 16, 1961)," Wiley, New York, N. Y., 1962, p 1009.
(4) H. W. Gerarde and A. R. Walter, *Am. J. Med. Tech.*, **28**, Nov.-Dec. (1962), p 327.

suitable for use as internal standards. The ethyl and propyl esters are often used for internal standards in alcohol analyses because of their high volatility. Slow hydrolysis precludes their use when storage must be considered.

A typical gas chromatographic tracing for the analysis of a 0.10% (w/v) sample is shown in Figure 1. The impurities present in the solvent do not interfere with the analysis because the peaks are after the ethanol and internal standard peaks. Variations in the analytical results obtained by estimation of peak area using peak height, peak width at half-height times height, area measurement by polar planimeter, and by disc integrator measurement of area were investigated. Within a given day, the data showed good agreement when peak height alone was used. This is due in part to the similarity in the shape and size of the ethanol and *n*-propanol peaks which tends to minimize changes in instrumental parameters. Over several days, small changes in instrumental parameters would cause estimated ethanol concentrations determined by the ratio of peak height to vary slightly. For studies extending beyond one day, this variation was eliminated by using peak areas. In view of the small peak size, integration by polar planimeter was a superior technique to the use of the disc integrator.

RESULTS

Evaluation of the System (Blood Ethanol Determinations). The proposed system was evaluated with respect to three fundamental criteria: its ability to preserve blood ethanol levels after sampling, until analysis, while samples were stored in the Unopette; the accuracy of the method when compared to other accepted techniques for determining blood ethanol; and the precision of the method.

Because the proposed system represents a convenient method for sampling in the field, the capability of the system to preserve blood ethanol levels until analysis was investigated. Table I reports the data on four separate one-week studies which demonstrate the storage capability of the Unopette system. Series of blood samples were prepared by addition of aqueous ethanol solutions to pooled whole bloods. In all cases, the ratio of aqueous ethanol to blood ratio (v/v) was maintained at 1:19. This technique produces blood samples containing known amounts of ethanol but essentially unaltered either by excessive dilution or by local concentration effects created by adding pure ethanol. Series of specimens representing bloods at commonly encountered levels, 0.302, 0.211, 0.121, 0.000 (ethanol by weight), were prepared in this manner. Five samples were prepared from each pool. One sample at each concentration was analyzed on each of five days over a one-week period. The one week represents the conceivable range in elapsed times which might be encountered if specimens were collected in the field and returned to a central laboratory for analysis. The ratios of ethanol: *n*-propanol peak areas show only random variation over the test periods. The calculated ethanol contents of the various samples is based on the largest sample, 0.3016%, as a standard. The data in the table demonstrate the system's ability to preserve blood ethanol levels during storage between sampling and analysis.

Table I. Stability of Specimens Stored in Unopettes

Series No.	Mean[a] ratio	Ethanol Calcd[b]	Ethanol Obsd[c]	Error	Rel. error, %
1	0.696	0.3016	...		
	0.457	0.211	0.198	−0.013	6
	0.261	0.121	0.113	−0.008	6.5
	0	0	0	...	
2	0.581	0.3016	...		
	0.395	0.211	0.205	−0.006	3
	0.249	0.121	0.127	+0.006	5
	0	0	0	...	
3	0.596	0.3016	...		
	0.378	0.211	0.201	−0.010	5
	0.208	0.121	0.117	−0.003	7.5
	0	0	0	...	
4	0.586	0.3016	...		
	0.404	0.211	0.208	−0.003	1.5
	0.242	0.121	0.124	+0.003	2.5
	0	0	0	...	
				Mean	4.0

[a] Ratio ethanol *n*-propanol peak area.
[b] By dilution, data in weight % ethanol.
[c] By chromatographic analysis, weight % ethanol.

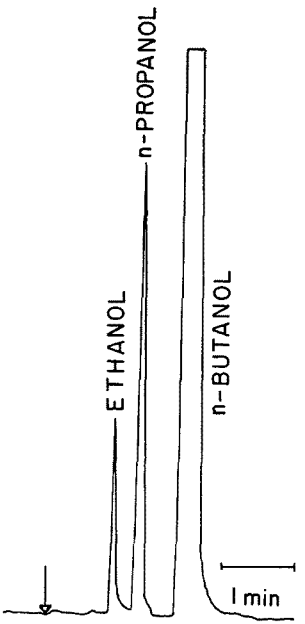


Figure 1. Typical chromatographic tracing

25 μl of blood, 0.7 ml *n*-butanol, 0.4 μl injected. Sample 0.100% ethanol (w/v). Sensitivity, ethanol, propanol $10^2 \times 1$ (with automatic attenuator) Butanol $10^2 \times 1024$

In the accuracy study, the proposed micro technique was evaluated by comparison to two other standard procedures: the macro gas chromatographic analysis (*5*) and alcohol dehydrogenase (*6*) methods. The four synthetic blood specimens (see previous section) were used in this study. In addition, 25 blood specimens analyzed at the author's laboratory in conjunction with the State's (Wisconsin) traffic safety program were analyzed by three techniques. For the comparison of the proposed method to the standard gas chromatographic procedure, the mean absolute error is 0.007%, and the mean algebraic error—*i.e.*, added with regard to sign—is 0.001%. In comparison to the enzymatic alcohol dehydrogenase technique, the mean absolute error was 0.005% and

(5) W. J. Cadman and T. John, presented at Pittsburgh Conference, Analytical Chemistry and Applied Spectroscopy, March 1958.
(6) L. Goldberg and W. Rydberg, "Automation in Analytical Chemistry," p 595, Mediad, Inc., New York, N. Y., 1966.

the mean algebraic error was +0.002%. Based on a typical sample value of 0.136%, the mean absolute errors are 5% (GC) and 4% (ADH), relative; well within the limits normally imposed on chromatographic assays.

The precision of the proposed technique was evaluated using a series of 20 specimens prepared from the same pool. The experiment was repeated a number of times on different days, and the data are summarized in Table II. The data are reported as ratio of ethanol to internal standard peak area. The conversion to per cent ethanol would show corresponding relative deviations. The average overall precision with respect to the mean value was 3%. From the precision study, we conclude that the method is capable of a routine precision of 3–4% (relative). This figure may be compared to the reported precision for other methods. For the macro gas chromatographic procedure, precision of 5% (*1*) and 6% (*2*) was reported; for alcohol dehydrogenase techniques, 5% (*7*). The distillation technique, the standard method for many blood alcohol determinations, has a precision of 4% (*7*).

An important general objective in some applications of the present research is to reduce the time required for individual analyses. In actual experiments in the laboratory, samples taken on site were shaken in the Unopette, centrifuged, injected, and quantitated (using visual chart reading and slide rule) in five minutes. By proper choice of solvent system and instrumental parameters, the technique is suitable for use in monitoring certain drug or metabolite (or anesthesia) levels during actual administration. Because of the required solvent elution time, approximately 12–13 minutes are required between successive injections on the same column. By using the dual column instrument, with a single electrometer and single recorder, samples could be run at the rate of 2 every 15 minutes. The ethanol-propanol section of the chromatogram emerges 3 to 4 minutes after injection.

(7) R. Bonnichsen and G. Lundgren, *Acta Pharmacol. Toxicol.*, **10**, 223–6 (1954).

Table II. Precision of Samples Taken in Unopette[a]

Series No.	Ratio[b] ethanol:propanol mean value	Std dev	Number of data
1	0.312	0.009	20
2	0.358	0.008	20
3	0.333	0.014	18
4	0.379	0.008	20
5	0.405	0.009	20
Av std dev		0.010	(3% relative)

[a] Sample from pool of 0.200% ethanol in blood. Experiment repeated five times on three different days. Chromatographic conditions specified in text.
[b] Ratio of peak areas.

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Determination of Amphetamine by Ultraviolet Spectrophotometry

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THE amphetamines are used principally as stimulants of the central nervous system. Side actions, overdosages, or illegal uses may occur which often result in a forensic requirement for evaluation of the drug level in biologic specimens. Paper chromatography (*1*), thin layer chromatography (*2*, *3*), and gas chromatography (*2*, *4–7*) have all been used to determine the amphetamines. Although the chromatographic methods are sensitive, they often lack the ability to provide the specificity required in analyses performed by the forensic scientist. When derivative formation is employed in the gas chromatographic determination of the amphetamines, the testing of a large number of specimens during a limited time interval becomes difficult.

Many nitrogen containing organic bases which absorb in the region of 260 mμ and have an aromatic ring as part of their chemical structure interfere with direct ultraviolet spectrophotometric methods (*6*, *8*) for determining amphetamine, and give a positive reaction in several colorimetric methods (*9–12*). With the latter, unpredictable variations of color development are frequently observed.

Amphetamine at concentrations often found in biologic specimens absorbs ultraviolet radiations weakly, and direct ultraviolet analysis of the unchanged drug in biologic materials is nonrewarding. At toxic levels of amphetamine, background absorption at 260 mμ induces a wide degree of variance in the final results, unless extensive purification of the biologic extract is achieved.

In this report a sensitive spectrophotometric method for quantitative analysis of amphetamine and certain related compounds is described. The procedure is applicable for screening biologic specimens for the presence of the compounds.

(1) A. Wickstrom and B. Salvesen, *J. Pharm. Pharmacol.*, **4**, 631 (1952).
(2) A. H. Beckett, G. T. Tucker, and A. C. Moffat, *ibid.*, **19**, 273 (1967).
(3) I. Sunshine, W. W. Fike, and H. Handesman, *J. Forensic Sci.*, **11**, 428 (1966).
(4) A. H. Beckett and M. Rowland, *J. Pharm. Pharmacol.*, **17**, 59 (1965).
(5) E. Brochmann-Hanssen and A. B. Svendsen, *J. Pharm. Sci.*, **51**, 393 (1962).
(6) L. Goldbaum, *Progr. Chem. Toxicol.*, **2**, 221 (1965).
(7) K. D. Parker, C. R. Fontan, and P. L. Kirk, ANAL. CHEM., **34**, 1345 (1962).
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(10) K. H. Beyer, *J. Amer. Chem. Soc.*, **64**, 1318 (1942).
(11) L. G. Chatten and L. Levi, ANAL. CHEM., **31**, 1581 (1959).
(12) E. Rathenasinkam, *Analyst* (London), **76**, 115 (1951).

Table I. Standard Curve Data for Amphetamine Reaction Product

Amphetamine in sample μg/ml	Absorbance in *n*-hexane[a]	Absorbance / Concentration
40.0	0.860	0.022
30.0	0.653	0.022
20.0	0.462	0.023
16.0	0.376	0.024
12.0	0.292	0.024
8.0	0.195	0.024
4.0	0.096	0.024

[a] Read at 287 mμ.

Table II. Compounds Yielding Absorbance at 287 mμ after Cerium Oxidation[a]

Compound	Absorbance in *n*-hexane[b]	Absorbance / Concentration
Amphetamine	0.46	0.023
Blank	0.01	...
1,2-Diamino-1-phenylpropane	0.52	0.026
Benzphetamine	0.08	0.004
Chlorphentermine	0.29	0.015
3,4-Dimethoxyphenylethylamine	0.01	...
Ephedrine	0.12	0.006
Hydroxyamphetamine	0.01	...
Mephentermine	0.39	0.020
Methamphetamine	0.21	0.011
Methoxamine	0.68	0.034
Methoxyphenamine	0.19	0.010
4-Methyl-2,5-dimethoxyamphetamine (STP)	1.00	0.050
Phenmetrazine	0.02	0.001
Phentermine	0.52	0.026
Phenylalanine	0.06	0.003
β-Phenylethylamine	0.39	0.020
Phenylpropanolamine	0.13	0.007
Tranylcypromine	0.16	0.008

[a] Each compound was determined from aqueous solution (0.8*N* HCl) to yield a corresponding concentration in *n*-hexane of 20 μg/ml.
[b] Average of three results.

EXPERIMENTAL

Apparatus. A Beckman DK-2A ratio-recording spectrophotometer with linear wavelength presentation was used for the ultraviolet absorption measurements. A Beckman IR-4 double beam infrared spectrophotometer was used for infrared spectra characterization of functional groups in the amphetamine product. A Barber-Colman Model 5000 equipped with a 10% SE 30 column (6 ft × 3.5 mm) on Gas Chrom Q (100–120 mesh) and a flame ionization detector was employed for gas chromatographic studies. Column temperature was 238 °C. The carrier gas was nitrogen flowing at a rate of 50 ml per minute.

Procedure. Ten milliliter amounts of oxalated blood or serum, 10- to 50-ml amounts of urine, or 10 grams of homogenized tissue are placed in a separatory funnel to which 5 ml of 1*N* NaOH and 200 ml of *n*-hexane are added. This mixture is shaken vigorously for three minutes. The *n*-hexane layer is removed and the recovered volume is recorded. Ten milliliters of 0.8*N* HCl are added to the hexane and this mixture is shaken for three minutes. After the layers have separated, 9 ml of the aqueous layer are placed in a 250-ml round-bottom flask along with 1.5 grams of anhydrous cerium sulfate (Fisher, purified grade) and 50 ml of spectro quality *n*-hexane. The contents are slowly refluxed with magnetic stirring for 30 minutes. After cooling, the *n*-hexane is removed and read against a blank through the region 250 to 360 mμ. If analysis at a single wavelength is required, determine the absorbance at 287 mμ. For the most accurate results, the blank should consist of a refluxed hexane solution prepared with the aqueous extract from an equivalent amount of biologic specimen known to contain no amphetamine. When therapeutic levels of the drug are indicated, the *n*-hexane containing the product should be evaporated to dryness by means of a rotary vacuum evaporator at 30 °C and the resulting residue suspended in 0.5 to 5 ml of spectro grade *n*-heptane depending upon the absorbancy observed for the *n*-hexane solution. The amphetamine content of the sample is calculated from a standard curve prepared by subjecting aqueous solutions of the drug in appropriate concentrations to the reflux system. The standard solutions of amphetamine product should be read against a blank of *n*-hexane. For gas chromatographic analysis, the residue from the evaporation of *n*-hexane is dissolved in 50 to 100 μl of *n*-heptane, after which an aliquot of 1–5 μl is injected into the chromatograph.

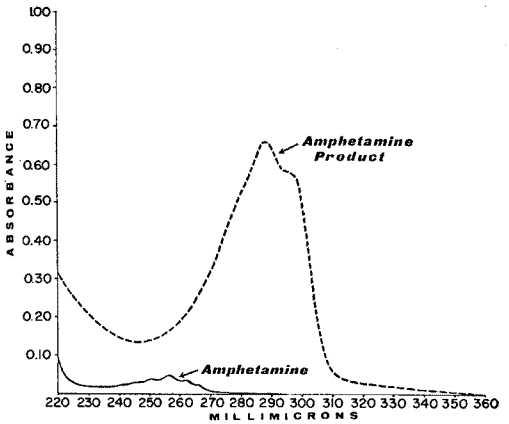


Figure 1. Ultraviolet absorption spectra of amphetamine in water, and of the cerium oxidation product in *n*-hexane, each corresponding to an amphetamine concentration of 30 μg/ml

RESULTS AND DISCUSSION

The reaction product of amphetamine has a well-defined ultraviolet absorption curve which has a maximum at 287 mμ and a minimum at 253 mμ in hexane. The absorbance at 287 mμ, illustrated in Figure 1, provides the increase in sensitivity of the present method over those procedures which rely on direct ultraviolet spectrophotometric analysis of unconverted amphetamine. At the levels investigated, a linear relationship exists between the absorbance of the reaction product and the concentrations of the drug in the original sample (Table I). The absorptivity/μg ratio of 0.024 for the product represents approximately a twenty-fold increase in sensitivity over the 0.0013 absorptivity/μg ratio observed for amphetamine.

Several other drugs which have the β-phenylethylamine group as part of their structure give a positive reaction with ceric sulfate and can be assayed by the proposed method (Table II). The products from several of these compounds have ultraviolet maxima and absorption curves identical to that of the amphetamine product. The method cannot distinguish spectrophotometrically between these drugs; however, at temperatures greater than 204 °C on the gas chromato-

graph, the reaction products have retention times on SE 30 which in most cases differ extensively from that of the amphetamine product (Table III). Of interest is that β-phenylethylamine, which interferes with amphetamine in the analysis of biologic samples that have undergone some degree of putrefaction, gives, after oxidation, a product yielding two chromatographic peaks considerably different in retention time from that observed for the amphetamine product.

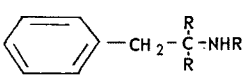
Amphetamine, methamphetamine, and 1,2-diamino-1-phenylpropane give products which have identical gas chromatographic retention times as well as ultraviolet spectrophotometric spectra. Oxidation of the amino group by the conditions of this method could yield from these three compounds an identical product. The report that methamphetamine is excreted in urine as amphetamine (*13*) overshadows certain specificity requirements for the two drugs not met by the procedure of this report.

Many basic drugs other than those containing the β-phenylethylamine group were investigated for possible interference with the determination of amphetamine. Such compounds were observed not to interfere.

Table IV summarizes the recovery of amphetamine which had been added in known amounts to whole blood and urine. The average recovery was 89% from blood and 97% from urine. Hydrochloric acid was observed to be the only acid which functions as a catalytic agent. The normality of 0.8 ± 0.2 is critical to the effectiveness of the procedure. Absorbance values in the optimum normality range of acid agree with those values given in Table I. The amount of cerium sulfate should not exceed the limits of 1.5 ± 0.25 gram. Cerium salts other than the sulfate yield lesser amounts of the desired product.

With five adult humans, each of whom received 5 mg of d-amphetamine by mouth, the highest concentration of unchanged amphetamine in the urine was found in samples collected during the period 4 to 8 hours following ingestion of the drug. The amount of amphetamine in urine samples collected at designated time intervals is shown in Table V. The drug can be detected in urine 48 hours after the ingestion of a single 5-mg dose, and during this time 25 to 44% of the drug was recovered. The results for this dosage level are in agreement with previous observations (*14*) that amphetamine excretion in urine occurs mainly in the first 24 hours and is essentially over 48 hours after administration.

The procedure is specific for those compounds which have a β-phenylethylamine group as part of their structure. Specificity requirements are: a β-methylene carbon, no hydroxy or methoxy substituent on the *para* position of the aromatic ring, and a primary or secondary amine group.



The beta carbon must exist as a methylene group presumably for oxidation to a carbonyl function. This is evidenced by the inability of tranylcypromine, ephedrine, and phenylpropanolamine to yield significant amounts of product (Table II). The observation that *para*-hydroxy-amphetamine, the primary metabolite of amphetamine, 3,4-dimethoxyphenylethylamine, and 3,4,5-trimethoxyphenylethylamine (mescaline) do not react implies that a hydroxy or methoxy substituent at the *para* position of the aromatic ring inhibits the desired reaction. Of further significance is that 4-methyl-2-,5-dimethoxyamphetamine (STP) and chlorphentermine give excellent yields of product. None of the hydroxyphenyl derivatives interfere with the analysis of amphetamine because they are insoluble in *n*-hexane, and are not removed from biologic materials in the initial extraction.

Several of the β-phenylethylamines that are converted to ultraviolet absorbing products have one or more alkyl sub-

Table III. Relative Retention Times of Reaction Products by Gas Chromatography[a]

Compound	Max UV absorption,[b] mμ	Ratio[c]
Amphetamine	287	1.00
Amphetamine (from urine)	287	1.00
1,2-Diamino-1-phenylpropane	287	1.00
Chlophedianol	247	0.39
Chlorphentermine	287	0.48
Diphenhydramine	247	0.25
Mephentermine	287	0.50
Methamphetamine	287	1.00
Methoxamine	286	0.70
Methoxyphenamine	245	1.05
4-Methyl-2,5-dimethoxyamphetamine (STP)	282	0.39; 0.44
Phentermine	287	0.50
β-Phenylethylamine	287	0.50; 0.77
Tranylcypromine	228	...[d]

[a] Conditions, see text.
[b] In hexane.
[c] Retention time of product from drug divided by retention time of amphetamine product.
[d] None observed.

Table IV. Recovery of Amphetamine after *In Vitro* Addition to Blood and Urine

Amphetamine added μg/ml	No. of detns.	Recovery, mean + std dev (μg/ml) Whole blood[a]	Urine[a]
50.0	9	45.4 ± 1.6	47.9 ± 1.9
25.0	9	22.1 ± 0.9	24.3 ± 1.0
10.0	10	8.9 ± 0.2	10.1 ± 0.3
5.0	7	4.3 ± 0.3	4.7 ± 0.4
Av recovery		88.6%	97.0%

[a] Ten milliliters assayed.

Table V. Amphetamine Recovered from Human Urine[a]

Time, hours	μg/ml I	II	III	IV	V
4	1.27	1.27	0.56	2.49	2.26
8	2.18	3.23	1.11	5.73	3.4
12	...[b]	1.48	0.80	1.07	1.45
16	1.37	...	0.24	0.58	1.35
20	0.52	0.97	0.34	1.21	1.09
24	0.29	0.72	0.52	0.55	0.78
32	0.44	0.21	...	0.08	0.22
40	0.03	0.18	...	0.02	0.15
48	0.01	0.04	0.16	0.11	0.07
Total recovered (mg)	1.25	2.02	1.64	1.86	2.21

[a] Each adult received 5 mg of d-amphetamine by mouth.
[b] Not determined.

(13) L. M. Gunne, *Biochem. Pharmacol.*, **16**, 863 (1967).
(14) G. P. Cartoni and F. DeStefano, *Ital. J. Biochem.*, **12**, 296 (1963).

stituent on the alpha carbon, and it is indicated that such groups at this point enhance the amount of product obtained. A carboxyl group at this same carbon inhibits the reaction. The latter is illustrated by the inability of the amino acid phenylalanine to afford a product with a measurable amount of absorption at 287 mμ (Table II). The requirement for a primary or secondary amine is indicated by the failure of benzphetamine to react. As a rule primary amines react much better than secondary amines. The requirements of the reaction establish a relatively high degree of specificity for the β-phenylethylamine structure.

The sensitivity limit of the method is approximately 0.5 μg/ml of specimen providing a 10-ml sample is used. The procedure of this report is as sensitive as the spectrophotometric methods for determining barbiturates (*15*). Barbiturates and amphetamines are often taken concomitantly, and now determination of both compounds at therapeutic levels in urine can be performed by spectrophotometric analysis.

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Spectrophotometric Determination of Microgram Amounts of Tantalum with Victoria Blue B

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SEVERAL spectrophotometric methods are available for the determination of small amounts of tantalum. Hydrogen peroxide (*1*), pyrogallol (*2*), gallic acid (*3*), and various fluorone derivatives (*4*), have been extensively employed as reagents for this determination. Methods for the determination of tantalum based on the formation of binary complexes in aqueous medium with reagents of this type, however, are basically relatively unselective. More selective methods have been reported for tantalum based on the formation and solvent extraction of ternary complexes of the tantalum with fluoride and methyl violet (*5*) and malachite green (*6*). This paper describes the application of the similar triphenylmethane type of dyestuff, Victoria Blue B (Basic Blue 26, Colour Index 44045), to the determination of microgram amounts of tantalum. Victoria Blue B forms a ternary complex with tantalum and fluoride in hydrofluoric-sulfuric acid medium. The complex is extractable into benzene. The complex has a somewhat higher molar absorptivity in benzene than the corresponding malachite green and methyl violet complexes, and a selective determination of tantalum is possible under the optimum conditions established in this study.

EXPERIMENTAL

Apparatus. Beckman model DB recording spectrophotometer fitted with Honeywell Electronik integrating recorder and matched 1-cm glass cells were used.

Victoria Blue B Reagent. The dyestuff (obtained from CIBA, Manchester, England) was purified by chromatography on an alumina column with isopropanol as solvent. An aqueous solution, $1.2 \times 10^{-3}M$, of the purified material was prepared by dissolving 0.600 gram of dyestuff in one liter of distilled water.

Thermogravimetric analysis of a sample of the chromatographically pure dyestuff revealed a progressive loss of weight of 4.7% between 20 and 80 °C. This corresponds to the presence of 1.5 molecules of water in association with each molecule of the dyestuff. Elemental analysis gave the following results: calculated for $C_{33}H_{32}N_3Cl$, C, 74.6%; H, 6.0%; N, 7.92%; found C, 74.2%; H, 5.9%; N, 7.6%.

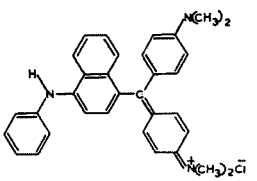


Figure 1. Victoria Blue B, $C_{33}H_{32}N_3Cl$

Tantalum Stock Solution. Dissolve 0.181 gram of tantalum metal (Specpure reagent, Johnson and Matthey, London, England) in 23 ml of 40% hydrofluoric acid and warm to assist dissolution. Dilute to 100 ml with distilled water and store in a polythene bottle. This stock solution is $10^{-2}M$ (1800 ppm) with respect to tantalum, and was diluted as required to give a final solution which was 2 ppm in tantalum and $0.01M$ with respect to hydrofluoric acid.

Hydrofluoric and sulfuric acids and salts of diverse ions used in interference studies were analytical reagent grade.

Preparation of Calibration Graph for Tantalum. When the tantalum complex was formed and extracted in glass separating funnels, poor reproducibility was obtained in the determination. This may possibly be attributed to the capricious adsorption and release of tantalum onto the glass surface in the dilute hydrofluoric acid solution. Polythene bottles were found satisfactory both for storage of reagents and for formation and extraction of the tantalum complex.

To each of a series of six 100-ml polythene screw-top bottles, transfer 3.3 ml of $18N$ sulfuric acid and 1.5 ml of $5N$ hydrofluoric acid. Add 0, 2, 4, 6, and 8 ml aliquots of standard tantalum solution (2 ppm) to the six bottles, and sufficient distilled water to make the volume 13 ml. Transfer 2 ml of stock $1.2 \times 10^{-3}M$ Victoria Blue B reagent solution to each bottle. Pipet 10 ml of benzene into each bottle, shake the solutions for *ca.* 30 seconds, and allow to stand to ensure complete phase separation. Remove an aliquot of the benzene phase from each bottle with a pipet and measure its absorbance at 635 mμ in a 1-cm glass cell against the blank solution (containing no tantalum) prepared simultaneously.

(1) P. Klinger and W. Koch, *Arch. Eisenhuttenw.*, **13**, 127 (1939).
(2) E. C. Hunt and R. A. Wells, *Analyst* (London), **79**, 345 (1954).
(3) H. Freund, K. H. Hammill, and F. C. Bissormette, U. S. Bureau of Mines, Investigation Report No. 5242, U. S. Government Printing Office, Washington D. C., 1954.
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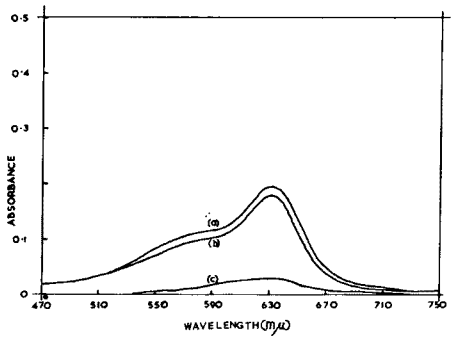


Figure 2. Absorption spectra for (*a*) tantalum complex against benzene, (*b*) tantalum complex against reagent blank, and (*c*) reagent blank against benzene (4 μg tantalum, 10 ml benzene)

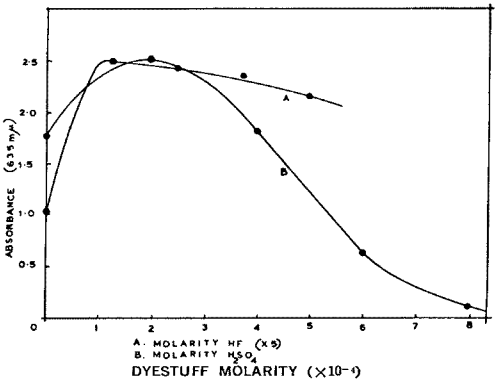


Figure 3. Effect of hydrofluoric acid (*A*) and sulfuric acid (*B*) concentration on net absorbance in benzene at 635 mμ

RESULTS AND DISCUSSION

Spectral Characteristics. The structural formula of Victoria Blue B is shown in Figure 1. The absorption spectra for the tantalum–Victoria Blue B complex and reagent blank are shown in Figure 2. The tantalum complex has a well defined absorption maximum at 635 mμ. Only a small amount of the excess Victoria Blue B reagent in the aqueous phase is extracted into the benzene phase under the optimum conditions established in this study. The reagent blank absorption maximum also occurs at 635 mμ in benzene.

Effect of Concentration of Hydrofluoric and Sulfuric Acids. Figure 3 shows the variation in the net absorbance in benzene with hydrofluoric acid concentration for the tantalum complex after subtraction of the reagent blank. Thus when the original aqueous solution is maintained at 2*M* with respect to sulfuric acid, the optimum hydrofluoric acid concentration is between 0.25 and 0.75*M*. Where possible, a medium 0.5*M* with respect to HF was employed. Similarly, when the hydrofluoric acid concentration is maintained at this value, the optimum sulfuric acid concentration is 2*M*. The relatively wide tolerance toward hydrofluoric acid minimizes problems encountered during the dissolution of samples for analysis.

Effect of Concentration of Victoria Blue B. The effect of the amount of reagent employed in the aqueous phase on the net absorbance in benzene at 635 mμ after extraction is shown in Figure 4. In the recommended procedure 2 ml of $1.2 \times 10^{-3}M$ reagent solution was selected to provide a concentration of $2 \times 10^{-4}M$ in the aqueous phase before extraction. This concentration represents a 30-fold molar excess of reagent over the maximum concentration of tantalum determined using the calibration graph under the optimum conditions. During these experiments the acidities were maintained at 2*M* H_2SO_4 and 0.5*M* HF.

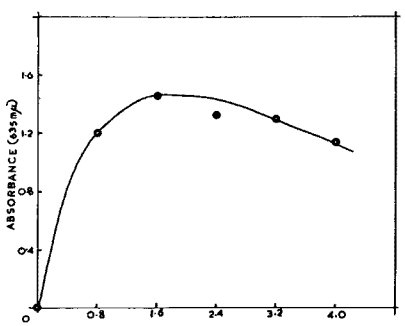


Figure 4. Effect of reagent concentration on absorbance at 635 mμ of tantalum complex against a reagent blank

Table I. Determination of Tantalum in Synthetic Samples

	Composition of Test Solution (ppm)												Tantalum (ppm)	
Sample	Al	Cu	Co	Cr	Fe	Mo	Mn	Nb	Ni	Ti	W	Zr	Present	Found
1						300					300		7.0	6.8
2		300			300				300				5.0	4.8
3		300			300				300	300			6.9	6.9
4		300			300			9.3	300				6.5	6.5
5					400		300						5.0	5.1
6				300				19		300			4.0	4.1
7			300					20		300		300	3.1	3.2
8	300					200				300		200	2.0	1.9
9					500	400							5.4	5.6

Calibration Graph and Range. The calibration graph is linear over the range 1 to 16 μg of tantalum in 10 ml of benzene. The optimum range for absorbance measurements on the spectrophotometer is 0.2 to 0.7 absorbance unit. With the recommended procedure these values correspond to 4.4 to 16 μg of tantalum in 10 ml of benzene. The effective molar absorptivity for the tantalum complex in benzene is 83,000 at 635 mμ.

Precision and Accuracy. In order to obtain a measure of the reproducibility of the determination of tantalum in pure tantalum solutions, the same amount of tantalum (4 μg) was determined 21 times over a period of several days. The average absorbance was 0.184 and the standard deviation 0.005 absorbance unit or 2.8%. Table I shows the results of analysis for tantalum of some simulated tantalum sample solutions which contained other ions. The table also includes the results for the determination of tantalum in several ferromolybdenum alloys.

Effect of Foreign Ions on Determination of Tantalum. Solutions were prepared containing 4 μg of tantalum and a 100-fold weight excess of each ion to be tested. The tantalum was then determined by the recommended procedure. An ion was considered to interfere when an error in the net absorbance for 4 μg of tantalum of greater than 5% was produced. The presence of a 100-fold excess of the following ions caused no interference: Al, Ag, As(V), Ba, Bi, Ca, Cd, Co, Cr(III), Cu(II), Fe(III), Mo(VI), Na, Ni, Pb, Sb(III), Sn(IV), Sn(II), Sr, Ti(IV), U(VI), W(VI), Zn, Zr, acetate, chloride, bromide, citrate, nitrate, silicate, and tartrate. The presence of a 100-fold excess of Ce(IV) and V(V) caused interference by oxidation of the Victoria Blue B reagent. The presence of the following ions at 100-fold excess gave rise to the error in absorbance given in parentheses: NH_4^+ (+19%), Hg(II) (+22%), Th(IV) (100%), and $B_4O_7^{2-}$ (100%). The presence of a 100-fold excess of niobium(V) caused a positive interference (+66%). The available niobium metal, however, contained *ca.* 0.02% of tantalum. After allowance for the contribution of the tantalum impurity to the absorbance, this error is reduced considerably. A 10-fold excess of niobium (tantalum free) can be tolerated without interference.

Nature of Complex. Victoria Blue B is blue (absorption maximum 635 mμ) in aqueous solution between *ca.* pH 1 and pH 12, and exhibits a yellow color (absorption maximum 475 mμ) in acid solution at pH lower than 1. In the recommended procedure for the determination of tantalum, therefore, the aqueous blank solution is yellow. The maximum absorbance of both the reagent blank and tantalum complex occurs at 635 mμ after extraction into benzene. The slope ratio method (*7, 8*) indicates a reagent : tantalum combining ratio of 1:1. The reagent–tantalum–fluoride ion association complex which is formed and extracted into benzene thus appears to result from the interaction of the protonated reagent cation with the tantalum–fluoro complex, TaF_7^{2-}, so that the empirical formula is represented by $RH^{2+}\,TaF_7^{2-}$. The mole ratio method (*9*) failed to give clear indication of the reagent : tantalum molar ratio, presumably owing to the low stability of the association complex.

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Determination of Bisphenol A and Impurities by Gas Chromatography of Their Trimethylsilyl Ether Derivatives

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BISPHENOL A (4,4′-isopropylidenediphenol) is an important chemical which is used in the production of polymers such as epoxy and phenoxy resins, polycarbonates, and polysulfones. Commercial bisphenol A generally exceeds 99% in purity and a product having a purity greater than 99.8% is normally considered a requirement for the synthesis of high polymers. The major, high boiling impurities in high purity bisphenol A, originally identified by Anderson, Carter, and Landua (*1*), are 2,4′-bisphenol A (2,4′-isopropylidenediphenol); Dianin's compound (4,4′-hydroxyphenyl-2,2,4-trimethylchroman), also called monophenol or codimer; and trisphenol [2,4-bis(α,α-dimethyl-4-hydroxybenzyl)phenol], also referred to as BPX. Despite the widespread use of bisphenol A as a raw material for the production of polymers, no quantitative method suitable for rapid analysis of this product was found in the literature.

Chromatographic procedures have most frequently been used for the analysis of bisphenol A. Paper chromatography was employed by Anderson, Carter, and Landua (*1*), Challa and Hermans (*2*), and Reinking and Barnabeo (*3*). Aurenge, Degeorges, and Normand (*4*), and Zowall and Lewandowska (*5*) used thin-layer chromatography for this analysis. However, quantitative results are difficult to obtain with these techniques. Gas chromatography has also been used for the analysis of bisphenol A. Direct methods have been reported by Tominaga (*6*) and Davis and Golden (*7*), but Gill was unable to determine bisphenol A directly because of serious peak tailing (*8*) and Anderson, Carter, and Landua (*1*) and Freudewald (*9*) observed decomposition when a direct procedure was employed.

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Table I. Analysis of Bisphenol A Synthetics by Gas Chromatography of TMS Ether Derivatives

Wt. % added				Wt % found[a]			
2,4′-BPA[b]	Dianin's	4,4′-BPA	Trisphenol	2,4′-BPA	Dianin's	4,4′-BPA	Trisphenol
0.20	0.10	99.50	0.20	0.20	0.11	99.49	0.20
0.10	0.11	99.79	...	0.10	0.10	99.80	...
0.48	0.19	98.85	0.48	0.48	0.18	98.91	0.43
0.09	0.05	99.77	0.09	0.09	0.05	99.76	0.10
0.05	0.01	99.89	0.05	0.06	0.01	99.88	0.05

[a] All results are averages of two or more determinations.
[b] BPA = bisphenol A.

The direct method of Tominaga is not desirable for the rapid determination of trace impurities in bisphenol A because the procedure requires an extraction with boiling xylene prior to chromatographic analysis. Furthermore, a different chromatographic procedure is required for the determination of di- and trinuclear phenolic impurities. Davis and Golden state that bisphenol A can be quantitatively determined by direct analysis providing an all glass inlet and column system is used (*7*), but these authors provide no quantitative data to support this claim nor do they indicate whether their chromatographic procedure is capable of determining separately the individual impurities in bisphenol A. Gill determined bisphenol A and associated impurities by gas chromatography after converting them to acetates by reaction with acetic anhydride. However, the Gill procedure has the disadvantage of being extremely time consuming. An analysis which determines each impurity individually takes over 2.5 hours. This paper describes a method for the analysis of bisphenol A and the determination of the major, high boiling impurities in bisphenol A by gas chromatography of their trimethylsilyl ether derivatives.

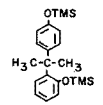
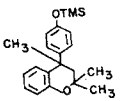
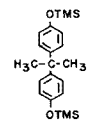
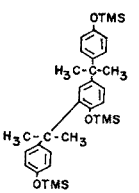
EXPERIMENTAL

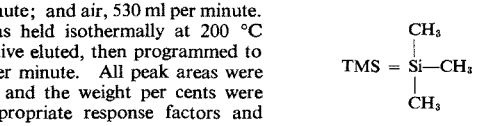
Apparatus. An F and M Model 810 dual column gas chromatograph equipped with a hydrogen flame ionization detector was used. The chromatographic columns were stainless steel, 6 feet × 0.25 inch, Siliclad treated, and packed with 1% OV-1 on 80 to 100 mesh Chromosorb G (HP), (Supelco, Inc.). The injection port and detector were maintained at 300 °C. Gas flows were: helium, 65 ml per minute; hydrogen, 65 ml per minute; and air, 530 ml per minute. The column temperature was held isothermally at 200 °C until the bisphenol A derivative eluted, then programmed to 275 °C at a rate of 20 °C per minute. All peak areas were measured with a planimeter and the weight per cents were calculated by using the appropriate response factors and normalizing.

Chemicals. Bis(trimethylsilyl)acetamide was obtained either from Supelco, Inc. or Applied Science Laboratories, Inc. and was used as received. Only reagent packed in glass sealed ampoules was used. The 4,4′-bisphenol A was the high purity product of Union Carbide Corp. and was recrystallized twice from benzene before use. The Dianin's compound, 2,4′-bisphenol A, and trisphenol were isolated from commercial bisphenol A by fractional crystallization and distillation.

Procedure. Approximately 100 mg of sample were weighed into a two-ml serum bottle, and the bottle was stoppered with a rubber septum cap. To aid the reaction a partial vacuum was pulled by evacuating air from the bottle with a 10-ml hypodermic syringe. One-half milliliter of bis(trimethylsilyl)acetamide reagent was then added to the serum bottle with a hypodermic syringe. The derivative preparation was shaken continually until the sample was completely dissolved (15 minutes). A 0.5-μl aliquot was then withdrawn and injected into the gas chromatograph.

Table II. Relative Retentions and Relative Responses for TMS[a] Ether Derivatives of Components of High Purity Bisphenol A Samples

Component	Structure of derivative	Relative retention	Relative response
2,4′-Bisphenol A		0.655	1.12
Dianin's compound		0.807	1.42
4,4′-Bisphenol A		1.00	1.00
Trisphenol		2.07	1.22



RESULTS AND DISCUSSION

In the determination of relatively nonvolatile (*e.g.*, trisphenol) or heat sensitive compounds (*e.g.*, bisphenol A) gas chromatographic analysis is frequently preceded by the preparation of stable, volatile derivatives. Trimethylsilyl (TMS) ether derivatives have been widely used for this purpose. Bis(trimethylsilyl)acetamide (BSA) is a relatively new silylating reagent which reacts with a variety of active hydrogen-containing compounds to form TMS derivatives (*10*). The phenolic hydroxyl groups of bisphenol A and of the major, high boiling impurities in bisphenol A are quantitatively converted to the corresponding TMS ethers within 15 minutes

(10) J. F. Klebe, H. Finkbeiner, and D. M. White, *J. Amer. Chem. Soc.*, **88**, 3390 (1966).

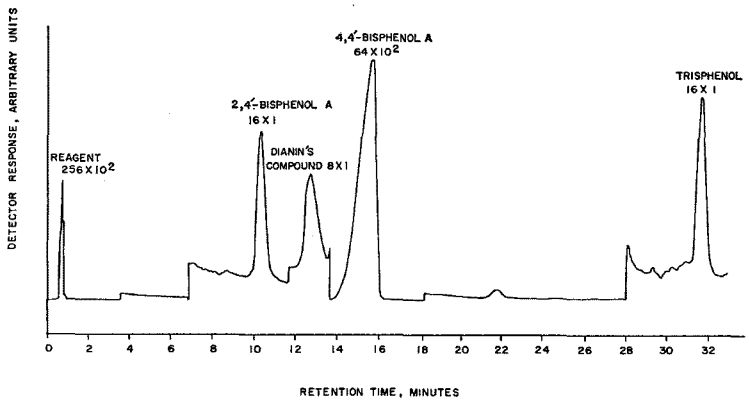


Figure 1. Chromatogram of the TMS ether derivatives of bisphenol A and of the major, high boiling impurities in bisphenol A

after the BSA reagent is added to the bisphenol A sample, providing the sample is completely dissolved in this time. The products of these reactions were verified by mass spectrometric analysis of traps of the individual gas chromatographic peaks. Each of the compounds gave a parent ion of the proper size for all OH's being replaced by $OSi(CH_3)_3$'s.

The emphasis in this work was on the analysis of high purity (>99%) bisphenol A. The method was developed with a hydrogen flame ionization detector because the concentration of impurities in high purity material is frequently below the detection limit of the thermal conductivity detector. The present procedure can readily determine impurities at the 50 ppm level without a concentration step. The separation of the Dianin's compound derivative from the 4,4'-bisphenol A derivative is critical to this analysis. The best results were obtained by operating the oven isothermally until the 4,4'-isomer derivative eluted, then rapidly programming the temperature to elute the trisphenol derivative. Chromatographing time for a complete analysis—*i.e.*, separate determination of each component—by this method is approximately 30 minutes and this time can be cut in half if it is not necessary to determine the low concentration of Dianin's compound which is normally present in high purity bisphenol A. To minimize analysis time, the excess BSA reagent is not removed from the derivative preparation prior to chromatographic analysis. The excess reagent and the derivatives burn at the detector to form silica, some of which is deposited on the collector electrode. These deposits adversely affect the response of the hydrogen flame ionization detector. Daily cleaning of the collector electrode mitigates this problem. This preventive maintenance takes less than 5 minutes a day.

Table I shows data which were obtained by analyzing synthetic mixtures of the major, high-boiling impurities in bisphenol A and illustrates the reliability of the method for the analysis of high purity material. The synthetics were prepared by accurately adding acetone solutions of the impurities to weighed amounts of twice recrystallized bisphenol A and evaporating the acetone with a stream of nitrogen. The derivatives were then prepared in the usual way. The relative retentions and the relative responses of the TMS ether derivatives of the compounds of interest are listed in Table II.

The results of a study on the precision of the method are summarized in Table III. These data were obtained from 5 successive analyses of a synthetic mixture.

Figure 1 shows a chromatogram of the TMS derivatives of a sample of high purity bisphenol A.

In addition to the high boiling impurities, low concentrations (<0.1 %) of water and phenol may also be present in high purity bisphenol A. BSA rapidly hydrolyzes in the presence of water and the TMS ether derivative of phenol elutes with the BSA reaction products under the conditions of the method. Therefore, these impurities can not be determined by the present procedure. If their determination is necessary, they can be measured by alternate procedures. The water content of bisphenol A can be determined by a Karl Fischer titration and the phenol can be determined by a separate gas chromatographic method (*8, 11*). Preliminary work in this laboratory indicates the feasibility of determining both water and phenol in bisphenol A by a single gas chromatographic method using a column packed with Porapak Q (Waters Associates, Inc.).

A troublesome problem encountered during the early part of this investigation was the sporadic appearance of extraneous peaks in the chromatograms. The source of these peaks was traced to BSA reagent which was purchased in silicone rubber stoppered serum bottles. BSA apparently reacts with impurities in the septum to form volatile compounds which elute under the conditions of the method. Similar ob-

(11) F. Kanne and K. Stange, *Z. Anal. Chem.*, **189**, 261 (1962).

Table III. Precision Study on the Gas Chromatographic Method for Analysis of High Purity Bisphenol A

Component	Wt. % added	Wt. % found (Average 5 analyses)	% std. dev. Absolute	% std. dev. Relative
2,4'-Bisphenol A	0.09	0.08	0.0044	5.6
Dianin's compound	0.05	0.03	0.0017	5.1
4,4'-Bisphenol A	99.77	99.81	...	...
Trisphenol	0.09	0.08	0.0051	6.2

servations were recently reported by others (*Chromatography Lipids*, August 1967, Supelco, Inc., Bellefonte, Pa.). This interference was eliminated by using BSA reagent purchased in glass sealed ampoules. Glass vials stoppered with septum, as recommended in the present method, can be safely used as reaction vessels for preparation of derivatives; however, prolonged exposure of the derivative preparation to the septa should be avoided.

ACKNOWLEDGMENT

The author thanks W. F. Beach, O. M. Garty, and J. W. Lewis for helpful discussions. The provision of pure samples of the impurities by A. G. Farnham and of twice recrystallized bisphenol A by P. Schnur is gratefully acknowledged.

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Indirect Spectrophotometric and Atomic Absorption Spectrometric Methods for Determination of Thiocyanate

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ABSORPTION SPECTROMETRIC METHODS for the determination of nonmetals are being investigated in this laboratory. This paper reports a study of indirect spectrophotometric and atomic absorption spectrometric methods for the determination of thiocyanate. These methods are based on the formation of a dithiocyanatodipyridine copper(II) complex which is extractable with chloroform. Spacu (*1–3*) has studied the precipitation of copper(II) as $Cu(py)_2(SCN)_2$ on both the micro and macro scales. The colorimetric determination of copper using this complex has been investigated (*4–7*). Colorimetric methods using the copper-pyridine reagent for the determination of thiocyanate have also been studied (*8–11*).

In utilizing the quantitative formation and selective solvent extraction of the complex, thiocyanate can be determined indirectly by the determination of copper in the complex. The determination of copper by atomic absorption spectrometric method is very sensitive (*12*). The indirect atomic absorption spectrometric determination of thiocyanate has a sensitivity of 0.05 ppm and has the advantage of speed, high precision, and simplicity.

EXPERIMENTAL

Apparatus. Absorbance measurements were made in 1.00-cm matched cells with a Cary Model 14 spectrophotometer. A reagent blank was used in the reference cell.

The atomic absorption measurements were made with a Beckman Model 1301 Atomic Absorption Accessory, a Beckman Model DB prism spectrophotometer equipped with a Beckman potentiometric recorder, and a Techtron burner assembly. The hollow cathode tube was neon filled and supplied by Beckman. A Thomas shaking apparatus was used for solvent extractions.

(1) G. Spacu, *Bull. Soc. Stiinte Cluj.*, **1**, 284 (1922).
(2) *Ibid.*, p 314.
(3) G. Spacu and J. Dick, *Z. Anal. Chem.*, **71**, 185 (1927).
(4) R. Biazzo, *Ann. Chim. Applicata.*, **16**, 96 (1926).
(5) J. B. Hester, *Chemist-Analyst*, **25**, 78 (1936).
(6) L. Chalk, *Analyst*, **55**, 187 (1930).
(7) C. Bennoit, *Ann. Chim. Anal. Chim. Appl.*, **12**, 66 (1930).
(8) J. Kruse and M. G. Mellon, ANAL. CHEM., **25**, 446 (1953).
(9) K. C. Bailey and D. F. Bailey, *Proc. Roy. Irish Acad.*, **37B**, 1 (1924).
(10) T. Moeller and R. Zogg, ANAL. CHEM., **22**, 612 (1950).
(11) Y. Y. Lur'e, *Zavodskaya Lab.*, **11**, 273 (1945).
(12) Beckman Instruments, Inc., *Flame Notes*, **1**, 88 (1966). Preliminary Information Sheet.

Reagents. COPPER(II) SOLUTION. Dissolve 0.252 gram of pure copper shot in dilute nitric acid and dilute to a liter with distilled water. One milliliter of this solution contains 0.252 mg of copper.

STANDARD THIOCYANATE SOLUTION. Weigh out 0.194 gram of potassium thiocyanate and dissolve in 1 liter of distilled water. Use standard silver nitrate as titrant and iron(III) indicator to standardize the thiocyanate. One milliliter of the thiocyanate solution contains 0.116 mg of thiocyanate.

All chemicals were reagent grade and all aqueous solutions were stored in polyethylene bottles.

Procedure. Weigh or measure by volume an amount of sample containing no more than 800 μg of thiocyanate in a total volume not exceeding 10 ml. The sample should contain no more than 360 μg when the atomic absorption spectrometric method is used. Transfer the sample solution to a 125-ml separatory funnel, add 20 ml of the copper(II) nitrate solution and mix thoroughly. Add 1 ml of pyridine and 20 ml of chloroform to the aqueous solution and shake for 6 minutes with an automatic shaker. After allowing 3 to 5 minutes for the layers to separate, collect the green organic layer in a polyethylene bottle.

SPECTROPHOTOMETRIC METHOD. Measure the absorbance of the organic extract at 407 mμ in a 1.000-cm cell using chloroform in the matched reference cell. Refer absorbance reading to a calibration graph.

ATOMIC ABSORPTION SPECTROMETRIC METHOD. Adjust the current applied to the hollow cathode tube at 10 mA. Adjust acetylene–air flame until a luminous flame is just observed. Use a slit width of 0.20 mm and adjust the monochromator setting until a maximum absorbance reading is obtained at the 324.7-mμ wavelength. Aspirate a standard solution corresponding to 232 μg of thiocyanate in the chloroform layer and adjust the restrictor to obtain maximum absorbance. Aspirate standard and unknown solutions using the absorbance readout of the recorder. Prepare a calibration graph.

In order to improve the sensitivity of the atomic absorption spectrometric method, evaporate the chloroform layer almost to dryness and then dilute to 25 ml with ethyl acetate. Aspirate the unknown solution and standard solutions using the absorbance scale of the recorder. Prepare a calibration graph.

RESULTS AND DISCUSSION

Spectrophotometric Method. THIOCYANATE CONCENTRATION. Figure 1 shows the visible absorption spectrum of the organic solution containing the dithiocyanatodipyridine

Table I. Interfering Diverse Ions

Ion	Spectrophotometric method, permissible amt., μg	Atomic absorption method, permissible amt., μg
Nickel(II)	20	20
Mercury(II)	20	20
Iron(II)	5	5
Silver(I)	20	20
Iodide	100	200
Nitrite	250	200
Permanganate	25	...
Vanadate	200	80
Iodate	...	500

copper(II) complex. The spectrum is characterized by the absorbance maximum at 407 mμ. Conformity to Beer's law was observed for 2.0 to 40.0 ppm of thiocyanate. The optimum concentration range is approximately 15 to 40 ppm of thiocyanate, corresponding to the 0.2 to 0.6 absorbance range. The molar absorptivity is calculated to be 790 l. $mole^{-1}cm^{-1}$. A reagent blank was found to have zero absorbance; therefore, chloroform was used in the reference cell. At less than 2 ppm, a negative deviation from Beer's law was observed, probably caused by unfavorable equilibrium conditions.

DIVERSE IONS. A study was made to determine the permissible amounts of various ions that may be present without interfering with the determination of ppm of thiocyanate. No attempt was made to determine the effect of the addition of more than 5000 μg of a specific ion, because this concentration is rather large compared to the concentration of thiocyanate being determined. Errors three times the relative standard deviation were considered negligible. Noninterfering ions include aluminum, ammonium, arsenate, bromide, carbonate, chloride, chromate, chlorate, cobalt(II), iodate, iron(III), lead(II), magnesium, molybdate, nitrate, perchlorate, phosphates, potassium, sodium, and zinc(II). The tolerances of interfering ions are listed in Table I, column two.

PRECISION. An estimate of the precision of the spectrophotometric method was ascertained from the results of eight samples each containing 29.04 ppm of thiocyanate. These samples gave a mean absorbance value 0.414 at 407 mμ. The standard deviation was 0.002 absorbance unit, or a relative standard deviation of 0.40%. In a series of determinations, about 25 minutes is required for each determination.

EXTRACTION OF COMPLEX. After testing various organic solvents, chloroform was found to be the most suitable extractant of the complex.

STABILITY OF COMPLEX. In a study of the stability of the complex in the chloroform layer, the absorbance remained unchanged for at least 2 hours. After standing for 7 days, a decrease in absorbance and a shift of the band to 401 mμ was observed.

Atomic Absorption Spectrometric Method. THIOCYANATE CONCENTRATION. The indirect atomic absorption spectrometric method is more sensitive than the indirect visible spectrophotometric method for thiocyanate. The calibration graph is linear up to 18.0 ppm of thiocyanate using chloroform as the solvent. The optimum concentration range is approximately 7 to 18 ppm of thiocyanate, corresponding to the 0.13 to 0.36 absorbance range. The reagent blank gave a reading of zero absorbance. The sensitivity is 0.2 ppm of thiocyanate. The most sensitive resonance line for copper is at 324.7 mμ (*12*).

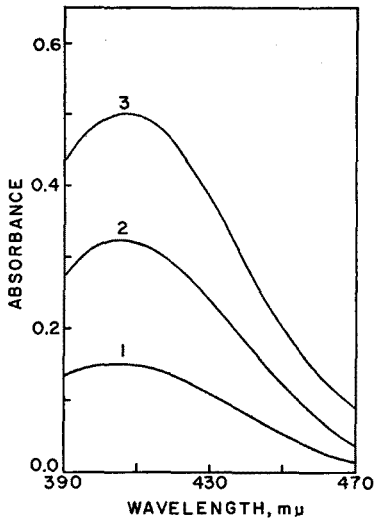


Figure 1. Absorption spectra for dithiocyanatodipyridine copper(II)

1. **11.6 ppm of thiocyanate**
2. **23.2 ppm of thiocyanate**
3. **34.8 ppm of thiocyanate**

PRECISION. An estimate of the precision of the indirect atomic absorption spectrometric method was ascertained from the results of eight samples each containing 11.6 ppm of thiocyanate. These samples gave a mean absorbance value of 0.254. The standard deviation was 0.005 absorbance unit, or a relative standard deviation of 1.87%.

DIVERSE IONS. The effect of a number of diverse ions on the determination of 11.6 ppm of thiocyanate was studied. Those ions which did not interfere at the 5000-μg level include: arsenate, bromide, carbonate, chloride, and nitrate. Minor interferences are chlorate at 3000 μg; sulfate, perchlorate, molybdate, and phosphate at 2000 μg, and chromate and tungstate at 1000 μg. The interfering ions are listed in Table I, column 3.

Modified AAS Method. An increase in sensitivity for the atomic absorption spectrometric method is obtained by evaporating the chloroform extract and diluting the residue to a volume with ethyl acetate. A calibration graph is linear 0 to 2.5 ppm of thiocyanate. The optimum concentration range is approximately 0.5 to 2.0 ppm of thiocyanate. The sensitivity limit is 0.05 ppm of thiocyanate. A reagent blank gave a small, reproducible absorbance reading which is probably due to the very slight solubility of copper(II) nitrate in the chloroform.

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Electroanalytical Determination of Molecular Fluorine in the Atmosphere

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General Dynamics Convair, San Diego, Calif.

FLUORINE is among the possible energetic oxidizers which may be used for propellant systems. A serious disadvantage is its toxicity, the threshold limit for which is 0.1 ppm by volume in air (*1*). A study of the atmospheric diffusion of fluorine from spills of liquid fluorine–oxygen mixtures was recently made (*2*). Instruments were required in this program to monitor the fluorine vapor concentration in air. Four types of instruments and methods were selected to monitor fluorine and hydrogen fluoride. Absorption and titration by wet chemical methods, conductometric methods (Davis HF indicator-recorder Model 11-7010-RP Special), Kr^{85} quinol–clathrate (Tracerlab Model FM-2 fluorine indicator-recorder), and electrochemical techniques were used. This paper describes the electrochemical fluorine detector-indicator instrument.

No suitable developed instrument was available to monitor fluorine specifically. We chose, therefore, to adapt the principle of the detector used by one of us (*3*) for balloon-borne measurements of ozone. In this instrument, air containing oxidant (O_3) oxidizes the I^- ion in a buffered KI solution in a cell containing platinum and silver electrodes. The iodine formed is reduced at the silver cathode. Insoluble AgI is produced on the cathode so that the iodide is removed from the reaction. This system was made specific for fluorine by substituting LiCl for the KI solution. Atmospheric oxidants do not affect the salt. Fluorine, however, oxidizes the chloride ion which undergoes the following electrode reactions:

$$\text{Anode } 2Cl^- - 2e \rightarrow Cl_2$$

$$\text{Cathode } Cl_2 + 2e \rightarrow 2Cl^-$$

For every molecule of fluorine, two electrons flow through the coulometric circuit and two atoms of chlorine are transferred from solution to cathode. Hence, the current generated may be calculated to be 0.14 μA times the flow in ml/min/ppm F_2 in the atmosphere. This current is easily measured when the flow rates are 100 to 300 ml/min. Theoretical details of coulometric halide determinations have been described (*4*). There are other methods and instruments available, but most do not distinguish the fluoride ion from the fluorine molecule concentration (*5–10*).

EXPERIMENTAL

Apparatus. A schematic diagram of the apparatus is shown in Figure 1. It consists of a bubbler fabricated from a 10/18 ⅋ joint. The inner joint bears a tube reaching to within a few millimeters of a 20-gage silver wire electrode which is fused into the bottom of the outer joint. The unit is then sealed so as to form a reaction cell about 13 to 15 cm long. The sensing element is thus a silver–silver chloride–chlorine galvanic cell. The second electrode is a 1-in. square of 80-mesh platinum gauze formed into a cylinder encircling a 4-mm dip tube. This acts as a bubbler. A Mast Model 2 AP-X piston pump and motor assembly (Mast Development Co., Davenport, Iowa) is attached to a side arm on the reaction tube by rubber tubing. This is used to suck air through the cell. A Teflon tube is attached to the inlet of the dip tube to bring in outside air for sampling. About 6 ml of unbuffered LiCl solution is sufficient to bring the liquid level above the platinum anode. The cell has a spontaneous EMF of about 0.25 V. This is balanced by an external EMF of the same magnitude so that no current flows in the absence of fluorine. The compensating EMF is selected by a voltage divider across a mercury cell. The current generated by the cell when fluorine passes through it is read on a 0 to 20 or 0 to 50 μA Rustrak Miniature Model 88 recorder or on a microammeter.

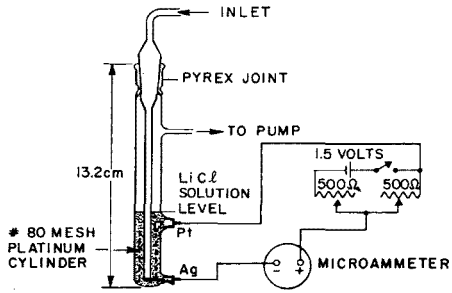


Figure 1. Schematic diagram of fluorine analyzer

For calibration purposes fluorine standards of air containing 5 to 50 ppm by volume of fluorine were prepared by diluting pure fluorine (approximately 98.0% F_2) with compressed air in clean passivated stainless steel tanks. The fluorine concentration was determined by absorbing a metered volume of the fluorine standard in 1% potassium iodide solution. The potassium iodide solution was then analyzed for fluoride by colorimetric analysis with thorium nitrate. Between calibrations no more than 25% of the mixture was used; this minimized the effects of fluorine release and adsorption from the tank walls.

The actual measured output of the instrument agreed with the theoretical output, and the electroanalytical principle was as accurate as other methods of analysis of fluorine at these low concentrations. Further calibrations were therefore limited to measurements of the pump flow rate.

(1) "Threshold Limit Values for 1962," American Conference of Governmental Industrial Hygienists, 1014 Broadway, Cincinnati 2, Ohio.
(2) "Atmospheric Diffusion of Fluorine from Spills of Fluorine-Oxygen Mixtures," General Dynamics Convair Rept GDC-DDB66-001, May 1966.
(3) M. Griggs, Ph.D. thesis, University of Oxford, Clarendon Laboratory, 1961.
(4) J. J. Lingane, "Electroanalytical Chemistry," 2nd ed., Interscience Publishers, New York, N.Y., 1958.
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(6) O. H. Howard and C. W. Weber, *ibid.*, **23**, 48 (1962).
(7) B. B. Baker and J. D. Morrison (to Southern Research Institute), U. S. Patent **2,870,067** (Jan. 20, 1959).
(8) M. G. Jacobson (to Mine Safety Appliances Co.), U. S. Patents **3,039,053** (Jan. 12, 1962), **2,861,926** (Nov. 25, 1958), **2,464,087** (March 8, 1949).
(9) G. H. Farrah (to Aluminum Co. of America), U. S. Patent **3,058,901** (Oct. 16, 1962).
(10) W. A. Darrah, U. S. Patent **2,278,248** (March 31, 1942).

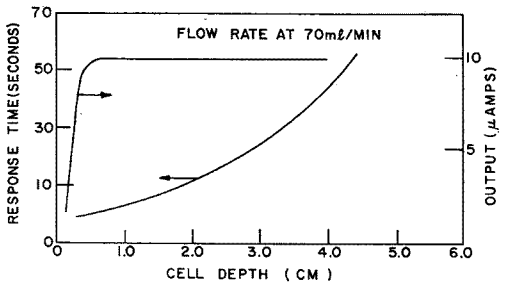


Figure 2. Effect of de pth of electrolyte on current output and response time

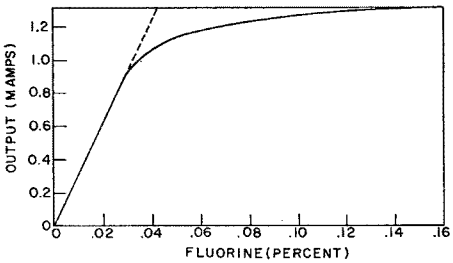


Figure 3. Effect of fluorine concentration on current output

The pump operated at a constant speed of about 220 ml/min. This volume was calibrated and checked for each pump as necessary. For monitoring low concentrations of fluorine—*i.e.*, when the instrument was over 1000 feet from a spill source—the recorder was converted to a maximum range of 10 μA for greater sensitivity.

DISCUSSION

Several considerations are important for an optimum design for the instrument. Lingane (*4*) has discussed the factors which afford good time response. For a minimum value of response time the volume of solution and the diffusion layer thickness must be small; the electrode area and diffusion coefficient must be large.

The diffusion coefficient of the chloride ion is larger than any other halide ion which might be used. The use of chloride rather than another halogen ion also achieves a specificity for the detection of fluorine. A high temperature also raises the coefficient for diffusion and makes the diffusion layer thinner, but no attempt was made to control these factors by temperature regulation except to avoid large changes in temperature.

The design and dimensions of the dip tube cell and platinum gauze provide vigorous stirring which keeps the diffusion layer thin. The bubbling is necessary to bring the chlorine into contact with the cathode so current can pass. The cylindrical fine mesh electrode permits continuous and free circulation of the liquid and affords a large reaction area and repeated contacts between solution and electrode so that no chlorine is lost. The size of the bubbles is such as to cause the solution close to the walls to pass into and out of the platinum cylinder more than 20 times per sec (*3*). The optimum stirring design was produced by a bubble tube 4 mm in diameter which reached to 1 to 3 mm from the bottom of the gauze cylinder.

A 0.1*M* KI solution buffered to pH 4 was first used for the electrolyte. This solution is affected by oxidants such as O_3 and NO_2 in air. KCl was therefore used to replace the KI solution. Ozone and NO_2 did not oxidize this solution. However, LiCl performed better than KCl and an unbuffered solution was more stable than a buffered solution.

Performance. The effect of the various parameters discussed above was determined experimentally. The operating conditions were then optimized. There is considerable leeway in design and in the mode of operation such as pumping rate, compensating voltage, and solution concentrations.

The compensating voltage may vary from -0.10 to about -0.35 without greatly affecting the current output. The best value is about -0.25 V because the current caused by fluorine is affected least at that value. The polarization of the electrodes by too low or too high a compensating voltage does affect the response time, however.

A salt concentration of about 0.2*M* furnishes uniform response time and fairly uniform current output over a considerable range, but a range of 0.2 to 0.6*M* is acceptable.

Figure 2 shows how current output and response time vary with the depth of solution in the cell. The greater the amount of solution, the longer the response time. The current output is constant even when the depth of solution is less than 1 cm. However, to maintain stability, the depth of solution used was always sufficient to immerse completely the platinum electrode. The capacity of the cell for fluorine was also increased thereby.

The relation between the flow rate or fluorine amount and the current output is a linear function. Figure 3 shows that the output is linear for fluorine concentrations to more than 1000 ppm. Very high or very low fluorine concentrations could be accommodated, if known ahead of time, by calibrating the constant speed pump for much lower or higher constant speed, respectively. The ammeter must be selected to encompass the appropriate range.

The instrument was satisfactory for measuring and recording fluorine concentrations over a wide range of values. The accuracy, reliability, operational life, simplicity, and servicing were all well within the requirements of an instrument for toxic-gas monitoring. It is sensitive only to fluorine of all atmospheric oxidants and needs no basic calibrations once complete fluorine absorption is assumed. At a constant pump speed the relation between current output and fluorine concentration is absolute because the instrument essentially counts fluorine molecules.

RECEIVED for review July 1, 1968. Accepted September 3, 1968.

An Alternative Combustion Technique for Tritium Scintillation Counting

SIR: Miniaturization of the Schöniger principle (*1*) for making certain radioisotopes available for scintillation counting was described by Gupta (*2*). The technique offers the advantage of removing all quantitative procedures after combustion, as the isotope remains wholly within the vial in which it will be counted. For material of low activity this is an added advantage.

When used for tritium determinations, the method has revealed three weaknesses. First, firing the specimens by the technique described has been, in our hands, uncertain. Second, liquid nitrogen for freezing the water of combustion is not always readily available. Third, and in our view the most serious criticism of the method in its present form, is the potentially appreciable amount of water, and therefore tritium, which may be lost, when vials are opened to introduce the scintillator solution. Naked eye observation indicates that part of the water vapor condenses, as combustion proceeds, on the cool inner surface of the neck and the foil lining the cap of the container. Brief immersion in any refrigerant, even liquid nitrogen, will not trap this. Neither will it condense the water vapor in the vial atmosphere, which is at ambient temperature or, if freezing is carried out immediately after combustion, possibly above ambient temperature.

The means proposed for avoiding these problems add to the reliability and possibly the accuracy of the method and thereby to confidence in it.

The first difficulty can be overcome by using India ink to blacken the carrier paper (*3*), followed after the ink has dried by a spot of 2–3% nitrocellulose (celloidin) in any volatile solvent. It has been found more convenient, however, to impregnate a sheet of pure cellulose tissue paper (weight about 1 mg per cm^2) with ink, dry it on aluminum foil lightly smeared with silicone oil to prevent adhesion, and then dip it into the nitrocellulose solution. When the solvent has evaporated, primers can be made by cutting the sheet into triangular slivers 2.5 mm wide at the base and approximately 8 mm long. About eight can be made from 1 cm^2 of prepared tissue, each weighing less than 0.5 mg. The apex of a primer is wedged between the cup and the basket, the broad end of the primer projecting vertically above the basket's rim. When correctly done, ignition is rapid and certain.

The second and third problems are interrelated and have been met by means of a deep freeze. First, all combustion water is collected on the bottom of the vial, in which the specimen has been burned, and then it is frozen there. This ensures absolutely minimal water loss when the scintillator is added.

To this end, vial holders of size suited to individual requirements are made by cutting holes in foam polyurethane sheet of the type used for thermal insulation. The diameter of the holes must be such that the vials are a neat push fit. The thickness of the plastic should be as near as possible the height of the vials with their caps screwed on. A thinner sheet, with the same face dimensions but without holes, is required for attachment to the holder during freezing.

As soon as combustion is complete, the vials are pushed, bottom foremost, into the holder. After the baskets have cooled (several minutes), the holder with vials in place is inverted and stood on a warm surface at about 40–45 °C—*e.g.*, the top of a drying oven. The condensed water on the vial neck and cap (now dependent and against the heat source) distills onto the cool bottom, which is in contact with the air at room temperature. After about 15 minutes the thin plastic sheet, which acts as the cover, is attached with rubber bands to the undermost—*i.e.*, the warm—side of the holder. The holder with vials and cover in position is placed at once in the deep freeze, *the exposed bottoms of the vials still pointing upwards.*

The unprotected bottom of each vial rapidly cools, and the water already there freezes. At the same time, water vapor in the vial atmosphere condenses on this surface, thus allowing any residual water on the warm neck, shoulder, and cap to evaporate and be transferred to the bottom. Convection currents aid in scavenging the water from the dependent parts of the vial, including the basket. Water transfer can continue as long as there is a temperature gradient, but is complete before thermal equilibrium is restored. In our practice, vials are left in the freezer (−85 °C or −120 °C) for 3 to 4 hours or overnight, but a shorter time would probably suffice at these temperatures.

Once distillation is complete, the cover is taken from the holder, and the vials are partially extruded, cap first, from their holes. They are then extracted individually for further treatment. Until their turn comes, vials remain in the deep freeze in an inverted position. As soon as a vial is removed, still inverted, the cap is quickly unscrewed and the basket is gently shaken out; under no circumstances should the basket come in contact with the frozen combustion water. The vial is now turned upright and the scintillator reagent added immediately. The sample is ready for counting, when the ice and any of the reagent components, which might have crystallized out, redissolve. It is hardly necessary to mention the need for gloves or towelling when handling the chilled vials, partly to prevent thawing and partly to avoid low temperature burns.

The amount of water vapor lost by displacement, when the scintillator is introduced, is clearly a function of the temperature.

At 20 °C each 25-ml vial contains approximately 0.4 mg of water vapor in its atmosphere—*i.e.*, about 10% of the total combustion water produced by an average biological sample burned to completion. At −29 °C this drops to about 0.0125 mg or 0.3% of the total (*4*). It is apparent that a freezing unit working at −30 °C or lower would provide adequate cooling for most purposes. Lower temperatures, of course, would bestow the advantage of lessening the risk of premature thawing, even if not greatly influencing water vapor loss. In this regard it should be remembered, that

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(2) G. N. Gupta, ANAL. CHEM., **38**, 1356 (1966).
(3) V. T. Oliverio, C. Denham, and J. D. Davidson, *Anal. Biochem.*, **4**, 188 (1962).
(4) Smithsonian Tables, W. E. Forsythe, Ed., Lord Baltimore Press, Baltimore, Md., 1954.

the water vapor mass remains constant at any given temperature, and is independent of the total amount of combustion water produced (assuming the latter is sufficient to saturate the atmosphere). It follows that the proportion of water vapor in the vial rises as the total amount of water falls. If the higher temperature ranges are used for freezing, it would be wise to minimize the relative displacement loss, when very small samples are being assayed, by bringing the total weight of the charge to be burned to 6 mg with fuel (see below).

The possibility of isotope being lost on the baskets, when they are shaken from the vials, has been investigated at count rates around 2000 cpm per burned specimen, and at a freezing temperature −85 °C. Provided baskets did not touch the ice in the vials, no increase over the background count was produced, when batches of 10 baskets were dropped directly into the scintillator solution. As no reason exists for thinking that baskets are preferentially dried, it is considered that the technique achieves virtually complete tritium trapping on the bottom of the vials.

Because it is imperative that a gas-tight seal should exist between the foil of the cap and the vial neck, it is advisable to inspect the foil and the lip of the vial for imperfections before use. Pin hole openings in the former can be closed by routinely smearing the surface with heavy silicone oil; this has been shown to have no quenching effect. A smear around the lip also effects lubrication, and a better seal between glass and foil, when the cap is being tightly screwed home.

In practice, baskets with shorter stems than those described by Gupta have practical and theoretical merits. First they are more stable. Second they are cheaper, being made from about 9-cm wire. Third, the closer the burning specimen is to the bottom of the container, the longer it remains surrounded with oxygen undamped by the combustion products being formed.

On trial the maximum amount of material (specimen, carrier cup, primer, and fuel) which could be burned was 7 mg, and for certain complete combustion, 6 mg. This figure is in agreement with that given by Kalberer and Rutschmann (*5*) using a 1-liter combustion flask—*i.e.*, 1 mg per 4 ml of oxygen. As primer, carrier cup, and fuel amount to approximately 2 mg, samples should not exceed 4 mg dry weight.

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(5) F. Kalberer and J. Rutschmann, Biochemical Department, Sandoz, Basel, supplied by Packard Instrument Co., Inc., U. S. A.,1967.

Automated Structure Elucidation of Several Kinds of Aliphatic and Alicyclic Compounds

SIR: The automated data acquisition and computer-aided interpretation of spectra is rapidly expanding (*1–3*). For instance, the determination of the amino acid sequence in oligopeptides was accomplished by the computer interpretation of high resolution mass spectra (*4, 5*). Aliphatic saturated normal and monomethyl substituted hydrocarbons from C_6 to C_{30} were also identified by computer-aided mass spectrometry (*6*). However, only one kind of spectrometer was tied into an electronic computer in every case.

Here we wish to report an actual attempt to feed physical data, acquired via computers from MS, NMR, IR, and UV, into a central computer which is programmed to structure elucidation based on a combination of all four types of data (Figure 1). The research up to date has been done with both aliphatic and alicyclic compounds containing less than fifteen carbons and only one oxygen, and with less than four sites of unsaturation. The whole system is composed of MS (JEOL, JMS-OISG, Mattauch-Herzog type), NMR (JOEL, JNM-C-60H), IR (Shimadzu IR-27G) and UV (Shimadzu MPS-50L) spectrometers, four smaller computers (slave computers 1, 2, 3, and 4; JEOL, Science Master EC-1, binary 16 bits, 4096 words, arithmetic time 200 μsec), and one larger computer (master computer, JEOL, JRA-5, binary 16 bits, 4096 words, arithmetic time 20 μsec) with an outer memory to automatically elucidate the molecular formulas and partial structures of these compounds.

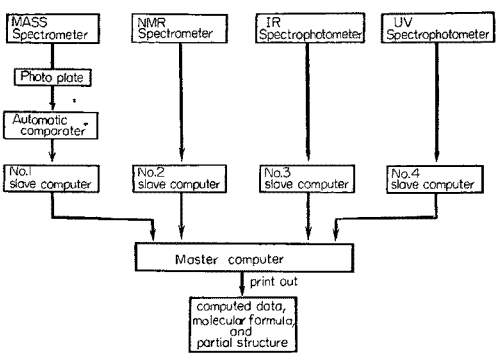


Figure 1. System for automated structure elucidation

The slave computer 1 connected with a comparater microphotometer (JEOL, JMA-1) calculates the possible combina-

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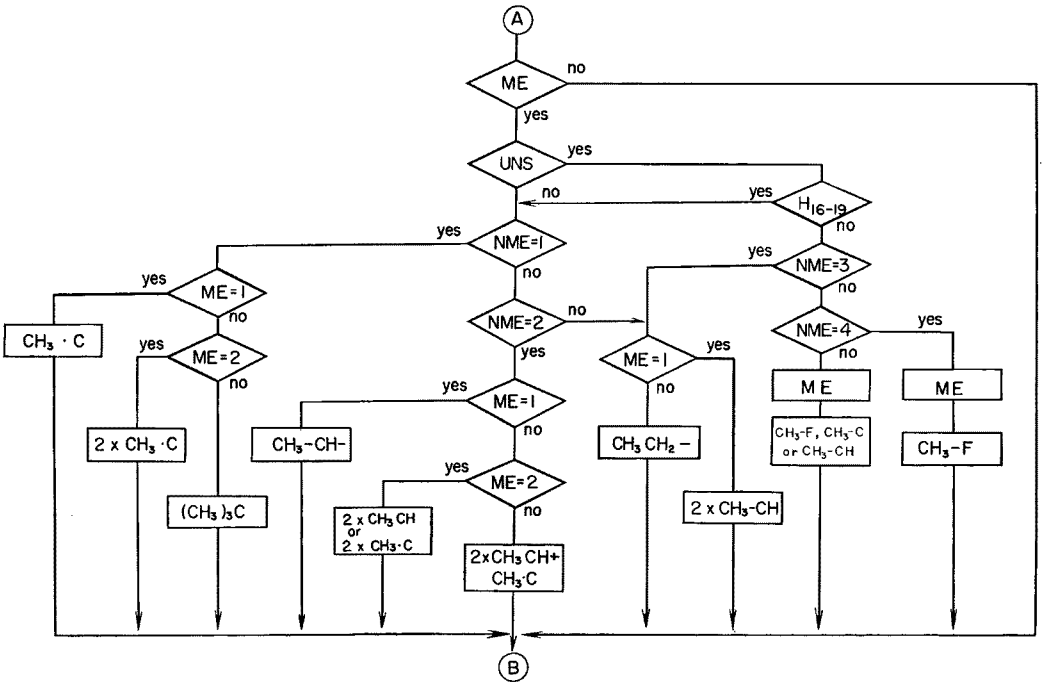


Figure 2. A part of program resident on the master computer

By this diagram the nature of methyl groups is clarified. CH_3C, CH_3CH, CH_3CH_2, and CH_3F represent methyl at tertiary carbon, methyl at secondary carbon, methyl at primary carbon, and methyl at olefinic linkage, respectively. Other abbreviations are as follows: ME, presence of methyl group; UNS, degree of hydrogen defficiency; NME, splitting number of methyl signal in NMR; and H_{16-19}, presence of proton assigned as index 16–19. NMR spectrum is divided into about 30 regions and each of them is temporarily called "index" by the authors

MASS DATA

C	H	O	INT
2	2	1	184
2	3	1	224
4	4	1	136
4	5	1	153
4	6	1	122
4	7	1	122
5	6	1	122
5	7	1	208
5	8	1	177
6	7	1	153
6	8	1	168
6	9	1	177
6	10	1	201

NMR DATA

NO	POSI	INT	AREA
1	369.6	35	185
2	368.4	43	137
3	367.0	30	105
4	137.2	11	214
5	128.0	198	1014
6	126.4	367	1369
7	124.2	17	152
8	113.4	183	707
9	112.0	176	536

TOTAL AREA= 4419

NO	POSI	AREA	COUPLING
1	368.3	427	J= 1.2(3)
2	137.2	214	
3	127.2	2383	J= 1.2(2)
4	124.2	152	
5	112.7	1243	J= 1.2(2)

IR DATA

NO	POSI	INT
1	3360	12
2	2984	88
3	2920	104
4	1714	84
5	1686	352
6	1614	348
7	1444	206
8	1378	174
9	1354	226
10	1268	30
11	1220	253
12	1162	239
13	1066	36
14	1020	63
15	962	171
16	896	24
17	820	77

UV DATA
UV POSI=220

Figure 3. Reproduction of data computed by the slave computers for mesityl oxide (1)

The upper part of NMR DATA stands for the digitalyzed NMR spectrum. In the second-step calculation, slave computer 2 searches for the peaks with same J values based on these data, then nine peaks are reduced to five peaks as shown in the lower part of NMR DATA. The numerals in parentheses indicate the multiplicity of the peaks

```
COMPOSITION
C( 6)H(10)O( 1)
FUNCTIONAL GROUPS
CO(C)
CH=C
CH3(F)(X2) OR (CH3CO AND CH3(F))
CH3(F)(X1)
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Figure 4. Reproduction of data computed by the master computer for mesityl oxide (1)

tions of carbon, hydrogen, and oxygen and the intensities of all mass fragments from mass spectrum recorded on a photo plate. All NMR signals—positions, intensities, and areas—are digitalyzed through an analog-digital converter in slave computer 2. The coupling constant is also searched for by the slave computer. Each of the other slave computers (3 and 4)—those for the IR and UV spectrophotometers—determine positions and intensities of absorption bands. (The entire program resident on each computer will be reported in the near future.) All information thus given by the spectrom-

trans-Decaline (2)	COMPOSITION C(10)H(18)O(0) FUNCTIONAL GROUPS	2-Methylfuran (5)	COMPOSITION C(5)H(6)O(1) FUNCTIONAL GROUPS FURAN(2) CH3(F)(X1)
3-Methylcyclohexenone (3)	COMPOSITION C(7)H(10)O(1) FUNCTIONAL GROUPS CO(C) CH=C CH3(F)(X1)	3-Methyl-1-buten-3-ol (6)	COMPOSITION C(5)H(10)O(1) FUNCTIONAL GROUPS -OH CH2=CH CH3-C(X2)
Propargyl alcohol (4)	COMPOSITION C(3)H(4)O(1) FUNCTIONAL GROUPS -OH C(T)CH	Δ^3-Carene (7)	COMPOSITION C(10)H(16)O(0) FUNCTIONAL GROUPS CYCLOPROPANE(2H) CH=C CH3-C(X2) CH3(F)(X1)

Figure 5. Reproduction of data computed by the master computer for *trans*-decaline (2), 3-methylcyclohexenone (3), propargy alcohol (4), 2-methylfuran (5), 3-methyl-1-buten-3-ol (6), and Δ^3-carene (7)

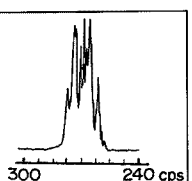
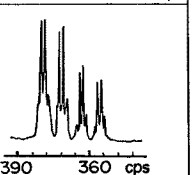
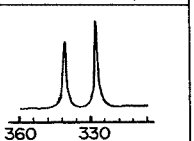
Dihydropyran (8)	COMPOSITION C(5)H(8)O(1) FUNCTIONAL GROUPS CH=C -O-	
trans-Crotonaldehyde (9)	COMPOSITION C(4)H(6)O(1) FUNCTIONAL GROUPS CHO(C) CH=C CH=C CH3(F)(X1)	
Camphene (10)	COMPOSITION C(10)H(16)O(0) FUNCTIONAL GROUPS CH=C CH=C CH3-CH(X2) OR CH3-C(X2)	

Figure 6. Reproduction of data computed by the master computer for dihydropyran (8), *trans*-crotonaldehyde (9), and camphene (10)

Some of functional groups (underlined) were miscomputed

eters and slave computers is fed into the master computer on which a program to elucidate the molecular formulas and partial structures of organic compounds is resident (Figure 2). The molecular formulas and partial structures are then printed out within several seconds.

An example will be shown. First of all, four kinds of spectra for this sample were measured. The mass spectrum was converted into a tabulated form by the comparater and slave computer 1. The positions (cps), intensities, and areas for all signals of NMR spectrum of this sample were given by slave computer 2. Then the computer continued further calculations based on these data to find out the chemical shifts and coupling constants. IR spectrum was expressed in numerals by slave computer 3. Slave computer 4 also detected an absorption maximum at 220 mμ (Figure 3). The master computer treated all the information to calculate the partial structures along the program already shown in Figure 2. In Figure 4, the first line stands for the molecular formula of this compound. CO(C) means this compound contains a conjugated carbonyl group. As another functional group, a trisubstituted olefin (CH=C) is present. Concerning methyl groups, the master computer suggests the presence of two possibilities, namely, three olefinic methyls [CH_3(F)] or an acetyl and two olefinic methyls. Although the latter is actually correct, our program was not able to distinguish between these two possibilities. However, from these partial structures it will not be difficult to build the molecular structure of mesityl oxide (1) as one of the most reasonable structures for the examined compound.

The printed out molecular formulas and functional groups of other samples are shown in Figure 5. For *trans*-decaline (2) only the molecular formula was given. For 3-methylcyclohexenone (3) the molecular formula and the presence of a carbonyl group with conjugation, a trisubstituted olefin, and an olefinic methyl were computed. For propargyl alcohol (4) a triple bond [C(T)CH] and a hydroxyl were suggested. For 2-methylfuran (5) a 2-substituted furan ring [furan(2)] and an olefinic methyl were suggested. For 3-methyl-1-buten-3-ol (6) a hydroxyl, a monosubstituted olefin (CH_2=CH) and two methyls at tertiary carbon (CH_3C) were suggested. Finally for Δ^3-carene (7) a cyclopropane ring with two hydrogens [cyclopropane(2H)], a trisubstituted olefin, two methyls at tertiary carbon, and an olefinic methyl were provided.

However, the nature of olefinic linkage of dihydropyran (8), *trans*-crotonaldehyde (9), and camphene (10) was miscomputed as shown in Figure 6. These inconsistencies are chiefly caused by the miscalculation of NMR spectra. In dihydropyran (8), CH=CH could not be observed because of a long ranged coupling of a proton at C-3. The *trans*-olefinic linkage of *trans*-crotonaldehyde (9) was not detectable because the *J* value of *trans*-protons is exactly two times the value of that between the methyl and the proton at C-3. Finally, the reason that two trisubstituted olefins were detected instead of terminal methylene in camphene (10) was that a pair of signals of the olefinic protons showed no coupling.

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Simple Tuning Device for Microwave Tapered Matching Cavity

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THIS REPORT describes a method of improving the coupling efficiency of the tapered microwave 2450 MHz cavity for sustaining a low pressure helium-plasma discharge as a source for the emission spectrometric gas chromatographic detector. McCormack, Tong, and Cooke (*1*) investigated the use of both tapered matching and coaxial microwave cavities for plasma source excitation as part of their development of an emission spectrometric detector for gas chromatography. They observed that greater sensitivity was attainable with the tapered matching cavity. Moye (*2*) also obtained greater sensitivity with the tapered matching cavity as compared to the Evenson type. The Evenson cavity has provision for both coupling and tuning adjustments to improve the efficiency of energy transfer to the plasma in the emission tube with a resultant reduction of energy reflected back to the magnetron. Moye (*2*) experienced considerable difficulty in keeping the Evenson cavity tuned.

The Evenson cavity was studied in this investigation. It was hoped that its potential for highly efficient energy coupling would permit excitation of difficultly excitable elements in a helium plasma at atmospheric pressure. A bidirectional power indicating meter (Micro Match meter Model No. 7253, Microwave Devices Inc., Farmington, Conn.) was incorporated in the system to optimize the tuning and coupling of the cavity. The meter scale was calibrated to read directly in watts for both forward and reflected microwave power. No emission lines other than those previously reported (*3*) were noted with halogen, phosphorus, or sulfur-containing compounds using this system, and it was still necessary to maintain the emission tube at a pressure of 1 cm of mercury.

The bidirectional meter was also used to measure the power coupling efficiency of a Raytheon UG 435/U tapered matching cavity. It was found to be very poor. Of the total forward generator output of 80 watts, about 50 watts were being reflected back to the magnetron generator. The high cost of an available tuning device prompted development of the present extremely simple modification.

Figure 1 illustrates the apparatus consisting of two irises, *A* and *B*, made of soft copper, 0.021 inch in thickness and having dimensions and shapes as shown. The two tabs of each iris must be bent downward along the dotted lines until they are 90° to the plane of the paper. The irises are then placed above the cavity slot with the tabs pointing down through the slot as shown. The discharge tube (*3*) (1.5 mm i.d., 6 mm o.d.) is located in front of iris *B* just touching its tabs. The slit in the center (from left to right) of each iris is 0.025 inch in width and can be cut out quite accurately with a sharp metal shears. The geometry of the irises is very important. Irises with many different shapes and dimensions were

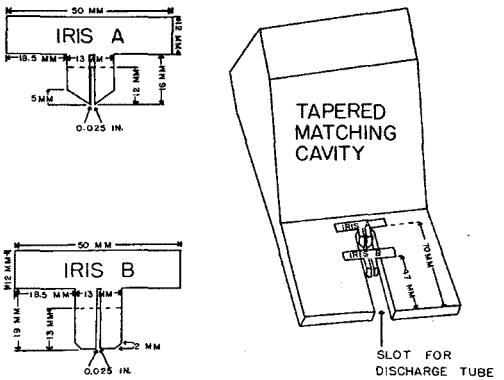


Figure 1. Cavity with irises for tuning

fabricated and studied. Those described showed optimum performance. The color of the copper irises darkens with use because of the intense heat of the adjacent plasma, but no deterioration in their function was evident. It should be noted that because of the large electric field in the vicinity of the cavity slot, the radiate power switch should be off when positioning the irises in the slot.

The irises serve to produce a tuned resonant cavity which provides maximum transfer of microwave energy to the plasma by increasing the electric field in the gas flowing through the discharge tube (*4–6*). Efficient coupling of microwave energy into the discharge was indicated by the bidirectional meter which measured only 2 watts of reflected power from 70 watts of forward power through the coaxial cable. Several operating advantages were observed with the modified cavity. The right-to-left positioning of the cavity relative to the discharge tube was much less critical in terms of observed line emission intensity. The plasma was able to be ignited at much lower generator power (30%). It was also operated at lower power (60%) than before with no observed decrease in emission intensity. The decrease in reflected energy and operating power levels promotes magnetron life by lowering its operating temperature. No cooling of the modified tapered cavity is necessary as with the Evenson type since no Teflon parts are incorporated which can deteriorate (*2*).

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Simplified Method of Preparing Column Materials for Gas–Liquid Chromatographic Separation of Some Pesticides

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PROCEDURES ranging from simple stirring to fluidized drying have been proposed to prepare column packing materials for gas–liquid chromatography (GLC) of organic chemicals (*1–6*) and organic pesticides (*7–14*).

Satisfactory separation of organochlorine pesticides was obtained with Anachrome ABS (*8, 9*), Chromoport XXX (*10*), Gas Chrom Q (*9, 11, 12*) and Chromosorb W (*13,14*) coated with silicones, but the packed columns required lengthy conditioning with repeated injections under specified temperature and gas flow. Gas Chrom Q coated with DC-200 and QF-1 required 3–5 days conditioning and did not separate Endrin from *o,p'*-DDT (*9*). McCully and McKinley (*14*) separated Endrin from *o,p'*-DDT by using Chromosorb W coated with SE-30 and QF-1. In our experience, variation between preparations can be attributed to uneven coating of the support due to inadequate mixing or to breakage of particles during stirring.

This report describes a simple method of preparing column materials to give reproducible chromatograms and to eliminate bleeding and lengthy conditioning.

EXPERIMENTAL

Coating the Support with Silicones. Materials and conditions used in preparation of columns are listed in Table I. SE-30 and QF-1 were dissolved in ethyl acetate (10 ml/gram of support) in a 500-ml round bottom flask (⅄ 24/40); SE-30 was broken into smaller pieces to hasten dissolution. The solution was gently heated (Variac at 25–30 V) and occasionally stirred for 1 hour or until the gum dissolved.

The support was added to the silicone solution; the slurry was refluxed on a heating mantle controlled by a Variac at 50 V and swirled occasionally for 1, 2, or 4 hours. With periodic swirling of the flask contents, ethyl acetate was evaporated (Variac at 50 V), under a gentle flow of nitrogen. The nitrogen flow was directed to the surface of the slurry by a piece of glass tubing bent in a V-shape and hung on the rim of the flask. The flask was tapped to dislodge adhering granules. The partially-dried granules were transferred to a crystallizing dish and heated (35 °C) until free of clumps. Drying was completed in an oven at 110 °C for 2 hours; portions of the coated material were then preconditioned at 230 °C for 2 or 4 hours, or at 250 °C for 1.5 hours.

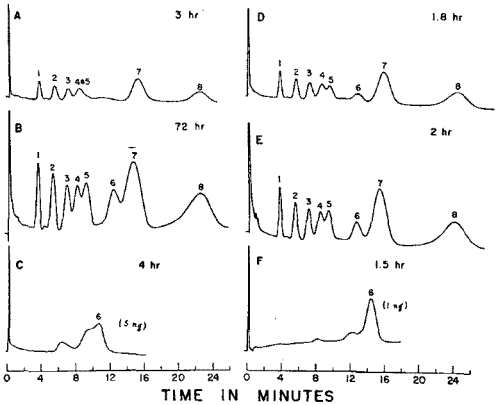


Figure 1. Typical chromatograms obtained from columns of Chromosorb W coated by refluxing SE-30 and QF-1 (10:0.4:0.6 grams) in ethyl acetate

Chromatograms *A*, *B*, and *C* were obtained from columns packed with unheated materials; chromatograms *D*, *E*, and *F*, materials heated at 230 °C. Number of hours from column installation to injection are indicated for each chromatogram. 1. Aldrin, 2. Heptachlor epoxide, 3. *p,p'*-DDE, 4. Dieldrin, 5. *o,p'*-DDT, 6. *p,p'*-DDT, 7. Endrin I, 8. Endrin II. *A*, *B*, *D*, and *E* are chromatograms of a solution consisting of compounds 1 to 4 (0.2 ng each), 5 and 6 (0.5 ng each) and Endrin (2 ng)

Packing the Glass Column with Coated Support. The silicone-coated support was packed under vacuum into the column, $4^1/_2$ feet × $^1/_4$ inch o.d. borosilicate glass tubing coiled to fit an Aerograph Hi-Fi Model 550. To ensure tight and even packing, the material was poured in small portions and final packing of the column was under −25 psi pressure.

RESULTS AND DISCUSSION

Coated materials heated at 230 °C for 2–4 hours before being packed (Table I: columns 9, 11, 13, and 15) did not contaminate the electron capture (EC) detector (tritium source) and produced discrete resolution of pesticides as soon as the operating temperature was obtained. Typical chromatograms obtained with these columns are shown in Figure 1 (*D, E, F*), Figure 2 (*I, J, K*), and Figure 3 (*N, O*). Heating the materials increased the recovery or sensitivity 5 times for the organochlorine and approximately 10 times for the organophosphorus pesticides studied.

Portions of the same coated materials but packed without heating (Table I: Columns 10, 12, 14) bled and contaminated the EC detector. Most importantly, the unheated materials did not satisfactorily separate the pesticides and the sensitivity of detection was low even after cleaning the EC detector.

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(5) H. H. Wotiz and S. C. Chattoraj, ANAL. CHEM., **36,** 1466 (1964).
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(13) J. R. Brown, *Canadian Med. Assoc. J.*, **97,** 367 (1967).
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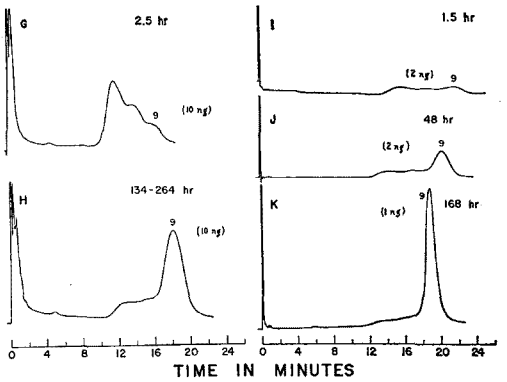


Figure 2. Typical chromatograms of methoxychlor obtained from columns of Chromosorb W coated by refluxing SE-30 and QF-1 (10:0.4:0.6 grams) in ethyl acetate

Chromatograms *G* and *H* were obtained from columns packed with unheated materials; chromatograms *I* to *K*, materials heated at 230 °C. Number of hours from column installation to injection are indicated for each chromatogram

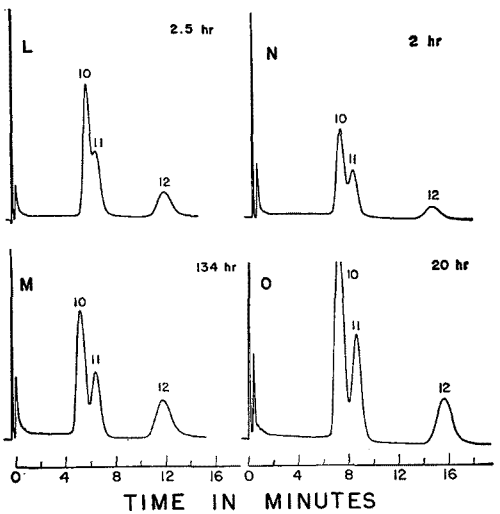


Figure 3. Typical chromatograms obtained from columns made of Chromosorb W coated by refluxing SE-30 and QF-1 (10:0.4:0.6 grams) in ethyl acetate

Chromatograms *L* and *M* were obtained from columns packed with unheated materials; chromatograms *N* and *O*, materials heated at 230 °C. Number of hours from column installation to injection are indicated for each chromatogram. 10. Malathion (20 ng), 11. Parathion (2.5 ng), 12. Carbophenothion (0.125 ng)

Table I. Materials and Conditions Used in Preparation of Columns

	Column Materials					Treatment, hr		Chromatogram[b]	
	Column support (Chromosorb)			Coating, grams				1st inj. from installation,	
Column	Type	Mesh	Wt, gram	SE-30	QF-1	Reflux	Heating[a]	hr	Quality
1	W	60–80	9	0.4	0.6	1	0	22.5	Unsatisfactory
2	W	60–80	10	0.4	0.7	1	0	19.2	Unsatisfactory
3	W	60–80	10	0.5	0.6	1	0	64.2	Unsatisfactory
4	W	80–100	10	0.4	0.6	1	0	20.8	Unsatisfactory
5[c]	W	60–80	9	0.4	0.6	1	0	1.8	Unsatisfactory
6	W	80–100	10	0.5	0.6	1	0	23.8	Unsatisfactory
7[c]	W	60–80	10	0.4	0.7	1	0	18.7	Unsatisfactory
8	W	60–80	10	0.5	0.6	1	0	0.8	Unsatisfactory
9[d]	W	80–100	20	0.8	1.2	1	2.0 (230 °C)	0.8	Satisfactory
10[d]	W	80–100	20	0.8	1.2	1	0	3.2	Unsatisfactory
11[d]	W	80–100	20	0.8	1.2	1	4.0 (230 °C)	0.7	Satisfactory
12[d]	W	80–100	20	0.8	1.2	2	0	2.8	Unsastifactory
13[d]	W	80–100	20	0.8	1.2	2	4.0 (230 °C)	0.7	Satisfactory
14[d]	W	80–100	20	0.8	1.2	4	0	1.5	Unsatisfactory
15[d]	W	80–100	20	0.8	1.2	4	2.0 (230 °C)	0.6	Satisfactory
16	W	80–100	10	0.4	0.6	1	0	2.3	Unsatisfactory
17[e] (HMDS)	W	80–100	20	0.8	1.2	1	0	1.5	Unsatisfactory
18[e] (HMDS)	W	80–100	10	0.4	0.6	1	0	4.0	Unsatisfactory
19	G	80–100	20	0.8	1.2	1	0	0.9	Unsatisfactory
20	G	80–100	20	0.8	1.2	1	1.5 (250 °C)	3.0	Unsatisfactory
21	G	80–100	20	0.4	0.6	1	0	3.8	Unsatisfactory
22	G	80–100	20	0.4	0.6	1	1.5 (250 °C)	1.0	Unsatisfactory

[a] Further heating in an oven at higher temperatures before packing, in parenthesis.

[b] The chromatographic analyses were performed with an Aerograph Hi-Fi electrometer (Model 500-C) and oven (Model 550) with tritium-coated detector under constant conditions: 190–195 °C oven, 230 °C injection block, approximately 75 ml/min N_2, 190 °C detector temperature, and with electrometer attenuation 8-X at range 1.

[c] Columns 5 and 7 are duplicates of Columns 1 and 2, respectively.

[d] Portions of the same materials used for columns 10, 12, and 14 were heated, as indicated, before being packed into columns 11, 13, and 15, respectively.

[e] (HMDS), Hexamethyl disilazane-treated Chromosorb.

Conditioning for several days was necessary to obtain chromatograms comparable to those obtained with the heated materials only a few hours after installation. Typical chromatograms from the unheated materials are shown in Figure 1 (*A*, *B*, *C*), Figure 2 (*G*, *H*), and Figure 3 (*L*, *M*).

Column materials that were not heated before packing (Table I: Columns 1–8, 10, 12, 14, 16) did not separate Dieldrin from *o,p'*-DDT or Malathion from Parathion. Partial degradation of *p,p'*-DDT and Methoxychlor was continuously observed; satisfactory recoveries of these compounds were obtained only after lengthy conditioning of the columns. The use of different sizes of solid support and proportions of the coating material did not improve column performance; the 80 to 100-mesh support was preferred because it could be tightly packed into a glass column.

The columns made of silanized Chromosorb W coated with SE-30 and QF-1 (Table I: Columns 17, 18) gave unsatisfactory resolution of some organochlorine and organophosphorus pesticides. Malathion retention time was greatly decreased as compared to those of Parathion and Carbophenothion; the multiple peaks produced indicated breakdown.

Although columns made of Chromosorb G coated with SE-30 and QF-1 (Table I: Columns 19, 20, 12, 22) gave good resolution of the test compounds, the recoveries based on peak heights were very low when compared to those from Chromosorb W columns. The *p,p'*-DDT breakdown was negligible. Heating of silicone-coated Chromosorb G in an oven at about 250 °C for 1.5 hours did not improve the recovery of pesticides.

In separating organochlorine and organophosphorus pesticides, Chromosorb W coated with DC-200 and QF-1 (20:0.8:1.2 grams) and heated at 230 °C for 2 hours before packing was comparable to that coated with SE-30 and QF-1.

ACKNOWLEDGMENT

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Calibration of the Methanol and Glycol Nuclear Magnetic Resonance Thermometers with a Static Thermistor Probe

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IN NUCLEAR magnetic resonance, the temperature of a sample is commonly obtained by measuring the chemical shift of methanol or of 1,2-ethanediol (glycol). During our work with proton exchange (*1*) most of the experimental error was attributed to the temperature measurement, and a more accurate and direct method was desired.

A thermistor probe [U. S. Patent applied for (Figure 1)] fitting inside a 5-mm sample tube was built. A probe holder [Patent applied for (Figure 2)] conveniently holds the probe in place, and the probe does not touch the walls of the sample tube. Thus, the tube can spin freely around the stationary probe. The lower part of the probe is made from tubing of polyperfluoroethylene to provide thermal insulation. A resistance bridge and meter (Atkins 3F01A-C/AB/AC/AD/AE, Atkins Technical, P. O. Box 14405, University of Florida Station, Gainesville, Fla. 32603) provides a direct temperature reading spread out over 4 scale ranges. The meter may be placed as far from the probe as desired. The accuracy is ±1 °C or better between −50 and +150 °C, and the reproducibility is 0.2 °C.

An alternate way to support the probe is shown in Figure 3. A sleeve bearing of polyperfluoroethylene permits the sample tube to spin while the probe rests on it. It is desirable to reinforce the rim of the thin glass sample tube with a compression ring, made by perforating the top of a pressure cap.

To prevent lifting of the sample by the nitrogen flow, a cylindrical polyperfluoroethylene spinning weight of 38 grams is used (*2*, *3*).

The thermistor contains oxides of the transition metals, and is paramagnetic. It affects the field homogeneity whenever it is in contact with the liquid, and retuning of the Y-fine homogeneity control is necessary when the probe is raised or lowered. With the thermistor 20 mm above the receiver coil, the observed line width is 1.6 Hz.

A temperature gradient occurs in the spinning sample tube. In a spinning methanol sample at −40 °C, the lowest temperature occurs at the bottom. The temperature was measured 10 and 30 mm above the bottom, and the difference was 1.0 °C. Without spinning, the difference is slightly larger. The first position coincides with the center of the receiver coil. The spectrometer is a Varian A60, with a V6031 probe and a V6040 temperature controller.

The stationary temperature at the coil changes slightly when the probe is inserted into the liquid, because heat leaks through it. The effect was studied at −40 °C from the chemical shift of methanol. Insertion of the probe raises the final temperature at the coil by 1.0 °C, irrespective of the depth of insertion. For a probe which had a thinner tip by omitting Part 4 of Figure 1, the effect of insertion was only 0.7 °C, but it was more difficult to keep the tip straight, and this probe had no other advantage.

For optimum accuracy of the temperature measurement, the probe is in contact with the liquid while taking the spectrum, then lowered to the position of the receiver coil to measure the temperature. On the other hand, for optimum resolution, the probe is raised above the surface of the liquid while taking the spectrum.

It is necessary to keep the polyperfluoroethylene tip of the probe straight to avoid interference with the spinning. A slight curvature is easily straightened out manually by bending in the opposite direction. The tip is protected when not in use. It is inert to all solvents and dilute acids and bases.

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(3) A. L. Van Geet, *Rev. Sci. Instrum.*, in press.

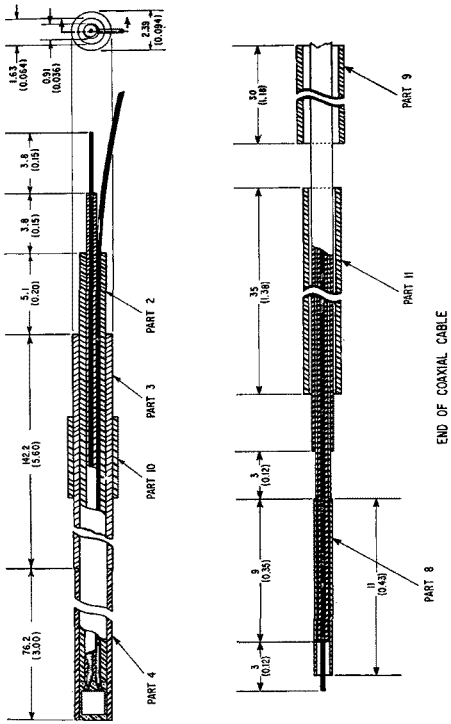


Figure 1. Static thermistor probe

Parts *8*, *9*, *11* are tubes of polyperfluoroethylene, and are used to connect the probe (left) to the coaxial cable (right). Part *3* is a brass tube (different cross-hatching). Part *10* is an adjustable stop to limit the depth of insertion

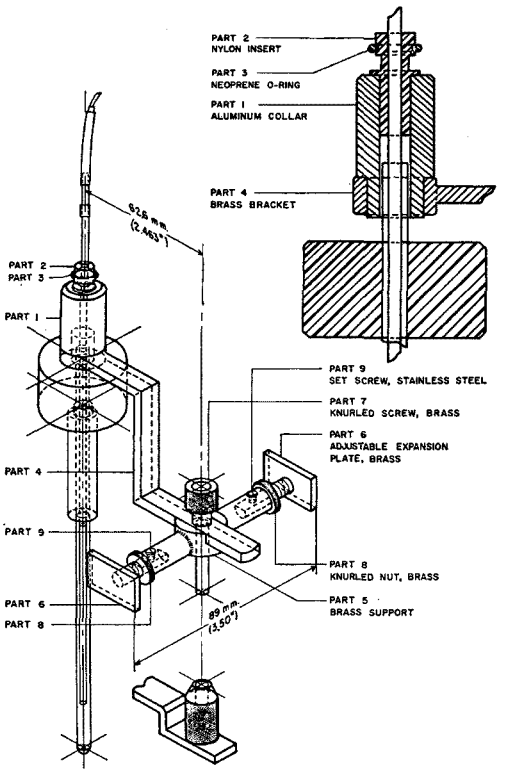


Figure 2. Clamp for static thermistor probe

Thermistor probe is supported by nylon insert *2* of aluminum collar *1*, and does not touch the glass sample tube. The sample tube fits inside the cavity of collar *1* without touching it. The lower part of brass support *5* fits accurately inside the center hole of the vertical-position knurled nut (bottom) of the Varian NMR probe. The adjustable expansion plates *6* press against the faces of the magnet coils, and hold the clamp in place

A spinning thermistor probe has also been built (*3*). This probe spins along with the sample tube, and the tube remains closed with a pressure cap.

CHEMICAL SHIFT OF METHANOL AND ETHYLENE GLYCOL

The chemical shift $\Delta\nu$ (in Hz) between the CH_3 and the OH group of methanol cannot be represented by a straight line over the entire temperature range of 220–330 °K. A quadratic equation fits the data with an error (RMS) of 0.6 °K (convenient graphs are available from the author).

$$T = 435.5 - 1.193\,|\Delta\nu| - 29.3\,(10^{-2}\Delta\nu)^2 \qquad (1)$$

The coefficient of the quadratic term is small, and over a temperature range of 60 °K, the data can be fitted to a straight line with errors of 0.8 and 0.4 °K, respectively:

$$220\text{–}280\ ^\circ\text{K}: \quad T = 478.6 - 1.906\,|\Delta\nu| \qquad (2)$$

$$260\text{–}320\ ^\circ\text{K}: \quad T = 464.0 - 1.775\,|\Delta\nu| \qquad (3)$$

At the limits of these ranges, the straight line approximations still agree with Equation 1 within 0.6 °K.

The chemical shift between the CH_2 and OH groups of glycol fits a straight line perfectly with an error of 0.3 °K over the range 310–410 °K:

$$T = 466.0 - 1.694\,|\Delta\nu| \qquad (4)$$

At room temperature, these results agree with the calibration charts supplied by Varian Associates within 1 °K. At 220 °K, the Varian chart gives a temperature 4.2 °K lower, and at 410 °K, it gives 3.4 °K lower.

The results are probably accurate within 1 °K, and were obtained with a Varian A60 spectrometer. The sweep width was calibrated by the sideband method using an audio oscillator and a frequency counter. The probe was calibrated by comparison with a vibrating quartz thermometer (Dymec 2801 A, Hewlett-Packard), and below 370 °K the corrections were within 1 °K.

Neuman and coworkers (*4*) also find that the Varian temperatures for the glycol are low. They placed a copper–constantan thermocouple inside a piece of tapered glass tubing sealed at the bottom, and clamped the top of the tube to a ring stand. The tube, which had an outside diameter of *ca.* 1 mm, was lowered into the spinning sample tube containing glycol. In this way, they find (*5*): $T = 466.5 - 1.691\,|\Delta\nu|$, in excellent agreement with Equation 4.

(4) R. C. Neuman and V. Jonas, *J. Amer. Chem. Soc.*, **90**, 1970 (1968).
(5) R. C. Neuman, University of California, Riverside, private communication, 1968.

PARTS AND ASSEMBLAGE

1. Thermistor (Atkins P99-3, bottom left in Figure 1) with two copper wires (AWG 32, 0.20-mm o.d.), attached. Insulate one of the wires with Teflon "spaghetti" tubing, Size 32, "Thin Wall", 0.28-mm i.d., 0.65-mm o.d., available through electronic and plastic supply houses. Twist the two wires a few turns.
2. Teflon Tube (Figure 1), perfectly straight, Length 221.0 mm, Size 20, "Standard Wall", 0.91-mm i.d., 1.65-mm o.d. Made by Chemplast (150 Dey Rd., Wayne, N. J. 07470) and Alpha Wire (711 Lidgerwood Ave., Elizabeth, N. J. 17207).

   Teflon tubing may be straightened by heating at 150 °C for at least 3 days while stretched by 5% or more. After stretching force has been removed, heat for at least 1 hour to remove strain. The brass telescope tubing of Part *3* is convenient to keep the Teflon tube straight while heating.

   To prepare the Teflon surface for cementing, the bottom 90 mm is immersed in Chemgrip Treating Agent (Chemplast) which is a suspension of sodium metal. A shortened NMR tube is an ideal container. Wash out and dry. Slide Part *2* over Part *1*.
3. Brass Tube, perfectly straight, Length 142.2 mm. Telescope Tubing, 1.65-mm i.d., 2.38-mm o.d.
4. Teflon Tube, perfectly straight, Length 76.2 mm, Size 14, "Lightweight," 1.70-mm i.d., 2.30-mm o.d. Treat 5 mm of the top and the bottom part with Chemgrip Treating Agent. Slide Part *4* over Part *2*. Slide Part *3* over Part *2* against Part *4*.
5. Brass Supporting Tube (not shown), Length 69 mm, 2.4-mm i.d., 3.2-mm o.d. Slide over Part *4*.
6. Identical to Part *5* (not shown). Slide over Part *3*.

   Apply epoxy cement, Chemgrip-HT (Chemplast), to thermistor and into tubing. Apply cement to the joint of Parts *3* and *4*, and into tubing. Be certain the cement does not touch Parts *5* and *6*. Cure at 150 °C while keeping Parts *3* and *4* straight.

   Starting at 4 mm above the top of Part *2*, remove the insulation of the copper wire, as shown in Figure 1. The other wire is cut 20 mm above the top of Part *2*.
7. Belden 8700, Miniature Coaxial Cable. Length 1.20 meters. Prepare as shown in Figure 1 at right.
8. Teflon Tube, Length 11 mm, Size 22, "Lightweight," 0.80-mm i.d., 1.15-mm o.d. Slide over inner insulation of Part *7*.
9. Teflon Tube, Length 30 mm, Size 12, "Standard Wall," 2.20-mm i.d., 3.00-mm o.d. Prefit over brass tube, 2.38-mm o.d., then slide over Part *7*.
10. Teflon Tube, Length 5 mm, Size 12, "Standard Wall." Slide over Part *3*.
11. Teflon Tube, Length 35 mm, Size 14, "Lightweight" (see Part *4*). Slide over Part *7*.

    Solder inner conductors together, and slide Part *8* over the joint. Solder the uninsolated wire of Part *1* to the shield of Part *7*, leaving small bead of solder. Use minimum heat to avoid damage to polypropylene insulation. Slide Part *11* against Part *3*. It should fit snugly over the bead of solder. Slide Part *9* over Part *11*, and partially over Part *3*.

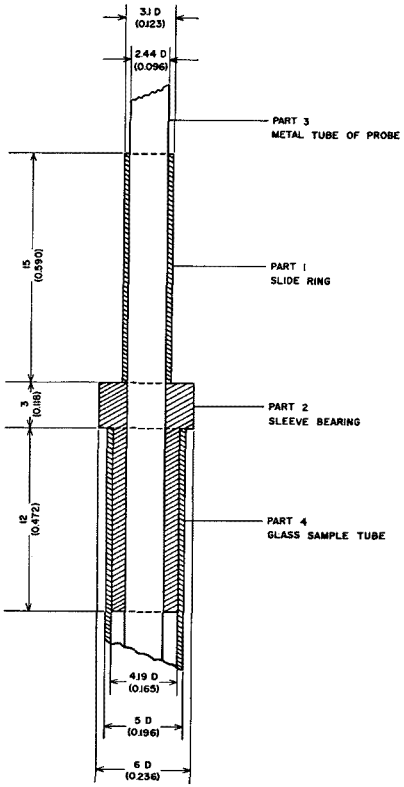


Figure 3. Sleeve bearing for static thermistor probe

Slide ring *1* fits snugly around brass tube *3* of the probe, and sits on the sleeve bearing *2*, permitting free rotation. It is made of electrical "spaghetti" tubing of polyperfluoroethylene, size AWG 11, "Standard Wall", i.d. 2.35 mm, o.d. 3.1 mm. The probe *3* fits freely and without any binding in the bearing *2* which is machined out of polyperfluoroethylene

12. Connector (not shown), Amphenol 80-MC2M, 2 pens, shielded. Connect to top of Part *7*.

ACKNOWLEDGMENT

The thermistor thermometer clamp was designed and made by Arthur C. Baase.

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Use of a Primary Beam Filter in X-Ray Fluorescence Spectrometric Determination of Trace Arsenic

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SEVERAL STUDIES have shown that a filter foil of a suitable element placed in the primary X-ray beam can improve sensitivity of X-ray fluorescence determination by absorbing radiation which normally contributes to background. Salmon (*1*) used nickel, brass, and aluminum filters to suppress the background of characteristic radiation from a tungsten X-ray tube target and from copper, nickel, and iron impurities in the target. Jenkins and de Vries (*2*) describe application of a titanium filter to improve detectability for chromium by eliminating the background of characteristic radiation from a chromium target tube. Theoretical considerations in selecting filters have been discussed by Caticha-Ellis, Ramos, and Saravia (*3*).

Most applications of filters have dealt with reducing the background of scattered characteristic lines of the X-ray tube target or target contaminants. The present application and the work of Reference *3* illustrate that the technique may be of more general value in improving detectability and analytical precision. In the determination of arsenic, for example, scattered characteristic radiation does not interfere; but a filter can sharply reduce background from the continuous spectrum of white radiation generated in the X-ray tube.

EXPERIMENTAL

Apparatus. A Norelco Universal Vacuum spectrometer is used for the measurements. The instrument is operated with helium atmosphere, lithium fluoride analyzing crystal, 5-mil spacing entrance collimator, scintillation detector, and pulse-height analyzer. A full-wave rectified generator supplies 40 mA at 50 kV to a type FA-60 tungsten-target X-ray tube.

A modification of the spectrometer permits either of two filter foils to be placed over the X-ray tube window without removing the sample changer head assembly. Two hinged aluminum filter frames are mounted on the window mask holder and can be moved in or out of position by rod linkages extending through the spectrometer housing.

Samples are contained in Type EP-16 Caplugs (Protective Closures Company, Inc., Buffalo, N. Y.) covered with 0.25-mil Mylar film.

Reagents. Standards are prepared by dissolving Eastman triphenylarsine ("Eastman Grade") in either Eastman "Spectro Grade" benzene or a mixture of C_{11} to C_{14} paraffins. Neutron activation analysis shows the arsenic content of both solvents to be less than 50 ppb.

Procedure. To correct for matrix effects (see following section), the total count rate, R_T, at the As $K\alpha_{1,2}$ analytical line is divided by the count rate, R_S, at the coherently scattered W $L\beta_4$ tube line. R_T is taken as the average of two 200-second counts made before and after a 100-second count to determine R_S. The calibration curve is a plot of the ratio R_T/R_S *vs.* the arsenic content of standards in parts per million.

(1) M. L. Salmon, "Advances in X-Ray Analysis," Vol. 6, University of Denver, Plenum Press, New York, N.Y., 1963, pp 301–12.
(2) R. Jenkins and J. L. de Vries, "Practical X-Ray Spectrometry," Springer Verlag, New York, N.Y., 1967, p 169.
(3) S. Caticha-Ellis, A. Ramos, and L. Saravia, "Advances in X-Ray Analysis," Vol. 11, Plenum Press, New York, N.Y., 1968, pp 105–13 (in press).

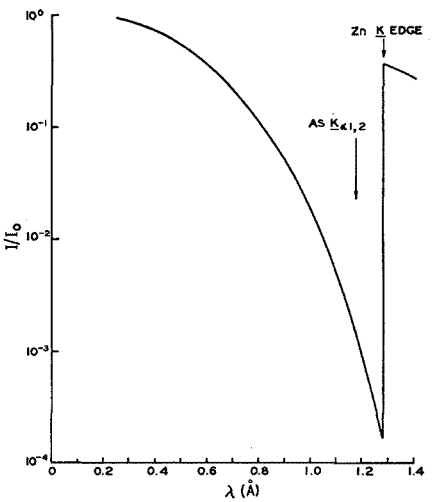


Figure 1. Transmission of X-rays through a 28.6 mg/cm² zinc filter

RESULTS AND DISCUSSION

An important point in choosing the material for a filter which is to absorb background radiation at wavelength λ is that the absorption edge of the material occur at a wavelength longer than λ. This ensures that shorter wavelength radiation which excites the analytical line at λ will be attenuated less than background at λ. Figure 1 illustrates how a zinc filter meets this requirement where λ is the As $K\alpha_{1,2}$ line at 1.177 Å. Here the filter's transmission (I/I_o) as a function of X-ray wavelength has been calculated from a tabulation of mass-absorption coefficients in Reference *2*. In Table I, values of I/I_o for four available thicknesses of zinc foil are given for 1.177 Å X-rays which are coherently scattered and for 1.153 Å X-rays which are incoherently scattered to appear as 1.177 Å background radiation. For a hydrocarbon sample, intensities of the coherently and incoherently scattered X-rays are approximately equal (*4*).

The degree to which the filter reduces the intensity of As $K\alpha_{1,2}$ fluorescent radiation from the sample by absorbing short wavelength exciting radiation is much more difficult to estimate accurately. For this reason the optimum filter thickness is determined experimentally (Table II). The criterion used in comparing different thicknesses is a detection limit C_L, defined as the arsenic concentration required to give a net response equal to three times the expected standard deviation of the background measurement. This background measurement is the background count rate (R_B) at the analytical line divided by the scattered tube line count rate (R_S). As shown

(4) C. M. Johnson and P. R. Stout, ANAL. CHEM., **30**, 1921 (1958).

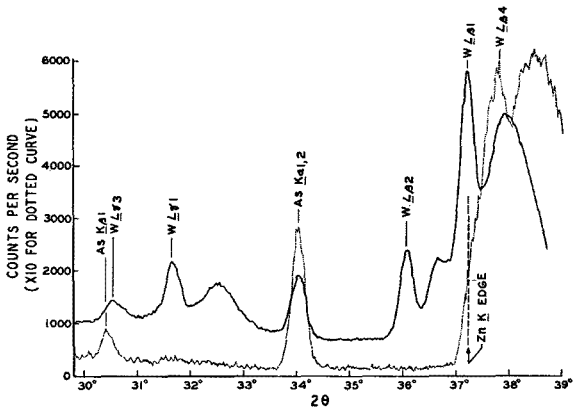


Figure 2. 2θ scans of 100 ppm arsenic in benzene

——— Without filter

· · · · With 28.6 mg/cm² zinc filter

by Liebhafsky *et al.* (5), the standard deviation of the ratio R_B/R_S is given by

$$\sigma_B = \frac{R_B}{R_S}\sqrt{\frac{1}{R_B t_B} + \frac{1}{R_S t_S}} \quad (1)$$

where t_B and t_S are counting times at the analytical and scattered lines, respectively. The detection limit then becomes

$$C_L = \frac{3R_B}{MR_S}\sqrt{\frac{1}{R_B t_B} + \frac{1}{R_S t_S}} \quad (2)$$

(5) H. A. Liebhafsky, H. G. Pfeffer, E. H. Winslow, and P. D. Zemany, "X-Ray Absorption and Emission in Analytical Chemistry," John Wiley and Sons, Inc., New York, N.Y., 1960, p 279.

Table I. Transmission of X-Rays through Zinc Foils of Varying Thickness

Foil thickness		I/I_o	
mg/cm²	Mils	λ = 1.153 Å	λ = 1.177 Å
10.2	0.56	0.12	0.10
18.4	1.02	0.019	0.015
28.6	1.58	0.0023	0.0015
36.8	2.04	3.7×10^{-4}	2.1×10^{-4}

where M is the slope of the calibration curve. In calculating C_L, a total counting time of 500 seconds is distributed between t_B and t_S so as to minimize σ_B.

For the case of no filter in Table II, R_S is the count rate of coherently scattered W $L\gamma_1$ radiation (1.099 Å) from the X-ray tube target. Earlier work in our laboratory had shown that a ratio technique based on this line compensates effectively for matrix effects. When the zinc filters are placed over the X-ray tube window, however, the W $L\gamma_1$ line is attenuated so severely that its intensity can no longer be measured with good precision in a reasonable time. In this case the coherently scattered W $L\beta_4$ line (1.302 Å), lying on the long wavelength side of the zinc K edge (1.283 Å) is used as the ratio line. Table III gives results of a test of the technique's effectiveness in compensating for absorption by oxygen and sulfur in the sample. Both elements reduce the counting rates of As $K\alpha_{1,2}$ X-rays, but W $L\beta_4$ X-rays are absorbed to very nearly the same degree, effectively compensating for the interelement effect.

In a further test of the tube line ratio technique, 9.36 ppm arsenic was added to an oil sample which contained 0.13 ppm arsenic initially, according to neutron activation analysis. A content of 9.81 ppm arsenic was found, in good agreement with the 9.49 ppm known to be present.

Table II. Detection Limits for Arsenic with Varying Thicknesses of Zinc Filters

Filter thickness, mg/cm² Zn	Analytical-line background		Scattered tube line		Net counts per second, As $K\alpha_{1,2}$ per ppm	Calibration curve slope M, ppm^{-1}	Detection limit C_L, ppm
	R_B, cps	t_B (s)	R_S, cps	t_S (s)			
0	1316	308	3396	192	17.5	0.0051	0.46
10.2	172	380	1702	120	8.75	0.0051	0.27
18.4	45	415	1060	85	5.39	0.0051	0.20
28.6	14	439	728	61	3.30	0.0045	0.17
36.8	12	434	528	66	2.30	0.0044	0.23

Table III. Interelement Effect Compensation by Tube Line Ratio Technique

As added, ppm	Interfering element	As $K\alpha_{1,2}$, cps	W $L\beta_4$, cps	As found, ppm
44.7 (standard)	None added	163	736	...
40.3	3.7% S	94.2	477	39.2
47.1	4.0% O	159	706	45.4

Table IV. Determination of Arsenic in Oils

Sample	ppm As, X-Ray	$\sigma_{X\text{-ray}}$, ppm	ppm As, NA
A	0.42	0.10	0.40
B	4.19	0.13	5.5
C	36.2	0.6	37.6

Results given in Table II indicate that the 28.6 mg/cm² filter is optimum of those tested and that it should improve the detection limit relative to no filter by a factor of 2.7. Superimposed 2θ scans in Figure 2 illustrate this filter's effect in reducing the background of scattered radiation to give an 18-fold improvement in net peak-to-background ratio for the As $K\alpha_{1,2}$ line. The 36.8 mg/cm² filter is seen in Table II to give only a small incremental reduction in background and a higher value of C_L, relative to the optimum filter. A pulse height scan indicates that the background observed with the thickest filter is primarily second order scattered radiation which cannot be entirely eliminated with pulse height analysis and upon which the filters have little effect.

Taking the 28.6 mg/cm² filter as optimum, a calibration curve was prepared and several measurements were made to determine the filter's effect in improving precision and accuracy. To conform with the fixed time counting capabilities of the instrument, the 500-second total counting time for these tests was distributed slightly differently from that indicated as optimum in Table II. A 100-second count on the W $L\beta_4$ or W $L\gamma_1$ tube line was taken in between two 200-second counts on the As $K\alpha_{1,2}$ line to minimize the effect of instrumental drift. The calibration curve prepared with the 28.6 mg/cm² filter was linear to 100 ppm As, the highest level measured. The curve's slope was 4.54×10^{-3} ppm^{-1}, and the intercept on the R_T/R_S axis was 0.0189.

To compare precision attainable with and without the filter, series of eight measurements were made on a 0.72 ppm arsenic standard. When the filter was used, the standard deviation of the data was 0.09 ppm, compared with a standard deviation estimated from counting statistics alone of 0.07 ppm. Without the filter, the observed standard deviation rose to 0.29 ppm, compared to an estimated 0.16 ppm based on counting statistics.

Further information on precision and accuracy is presented in Table IV. The means of results and standard deviations are listed for sets of six measurements on three oils with widely varying arsenic contents. Neutron activation (NA) analyses, accurate to an estimated ±10% of the amount, are also given.

Based on results in Table IV and measurements on the 0.72 ppm arsenic standard, analytical precision using the filter is estimated to be 0.1 ppm or 3% of the amount, whichever is greater. The results of the interelement effect and standard addition tests, and two of the three comparisons with neutron activation analysis, indicate that accuracy is approximately equal to this precision.

These measurements show that a primary beam filter can improve detectability and precision in the general case where background is largely scattered white radiation. The degree of potential improvement will depend upon initial intensities of fluorescent and scattered background radiation, and upon the spectral distribution of shorter wavelength exciting radiation.

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Determination of Trace Contaminants in Air by Concentrating on Porous Polymer Beads

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WITH the ever increasing need for the determination of trace contaminants in complex mixtures, the development and use of selective detectors (*1*) has become very important in gas chromatography. The selective detector eliminates superfluous peaks from the chromatograms and thus makes the qualitative and quantitative analysis of complex mixtures much easier. However, the best detector for a particular analysis often cannot be used because of its lack of sensitivity. Various concentrating techniques, most of which employ cryogenic trapping, have been reported in the literature, and have been reviewed by Altshuller (*2*). A method has been developed for concentrating gas samples at room temperature on porous polymer beads which eliminates the use of cold traps or cold columns, and gives on-column injection. The gas sample is concentrated on the same column that is subsequently used for the gas chromatographic analysis.

For the determination of chlorinated and brominated hydrocarbons, three selective detectors are available, electron capture, stacked thermionic flame, and microcoulometer. The electron capture detector has the disadvantages of having only a very narrow linear range, requiring a separate calibration factor for each halogenated compound, and being relatively insensitive to many chlorinated compounds. A compound which captures electrons weakly and whose chromatographic peak falls adjacent to a strongly capturing compound is completely obscured by a much smaller quantity of the strong electron capturer. There are very few papers in the literature where the stacked thermionic flame detector has been used for routine determinations.

It was felt that the microcoulometer was potentially the best detector for chlorinated hydrocarbons, because its response (*3*) should be directly related through Coulomb's law to the number of chlorine atoms in the molecule. There are two drawbacks to the microcoulometer, slow response and lack of sensitivity. The range of detection of the microcoulometer has been reported (*3*) to be from 0.1 to 1000 μg of chloride ion. Because trace analysis in gas chromatography is usually considered to be in the range of 1 ppb to 10 ppm by volume, the sensitivity of this detector is not sufficient with

(1) E. Cremer, "Advances in Gas Chromatography," Preston Technical Abstracts Co., Evanston, Ill., 1967, p 52.
(2) H. P. Altshuller, *J. Gas Chromatogr.*, **1**, (7) 6 (1963).
(3) D. M. Coulson and L. A. Cavanagh, ANAL. CHEM., **32**, 1245 (1960).

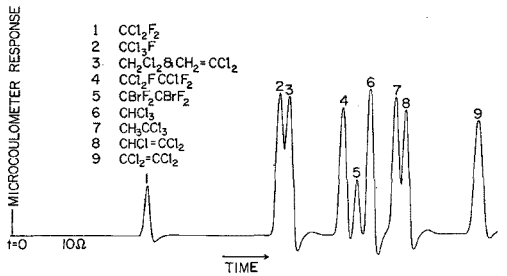


Figure 1. Coulometric response for halogenated hydrocarbons in 2- ± 1-ppm range using 100-ml sample loop

the normal chromatographic air sample of 5 to 10 ml. In order to obtain the required sensitivity, a concentrating technique is needed.

It had been reported previously by Hollis (*4*) that the retention times of low molecular weight hydrocarbons and halogenated hydrocarbons were quite long on porous polyaromatic polymer bead columns as compared to gas–liquid chromatographic columns. These long retention times make it possible to concentrate air samples on the chromatographic column at room temperature, and subsequently elute the components as symmetrical peaks by temperature programming. The sample components apparently remain as a narrow band on the column until its temperature is raised above ambient. The slow response of the microcoulometer is not of consequence, as it is compensated for by the long and varied retention times of the low molecular weight halogenated hydrocarbons on the porous polymer beads. Also the fact that water does not interfere and is eluted as an early peak without tailing, eliminates the necessity of drying the sample before injection.

EXPERIMENTAL

Equipment and Chemicals. The on-column concentrating technique was developed using Porapak Q and S obtained from Waters Associates, Inc. The 80–100 mesh Porapaks were packed in 6-foot × $^1/_4$-inch stainless steel columns. The chromatograph used was a Microtek MT-220 equipped with a Dohrmann Microcoulometer operating in an oxidative mode with a silver cell. The chromatograph was also equipped with a multifunctional programmer and Carle 8-port sampling valves. The standard gas mixtures were prepared in Alloy Products Corp. gas bottles made of stainless steel having a volume of 1.7 liters. The chlorinated hydrocarbons were purchased from Chem Service Inc. The chlorofluorocarbons were obtained from DuPont.

The gas mixtures were prepared by dilution techniques. In the case of liquid halogenated compounds, the calculated volume of the liquid was injected with a microsyringe, through a septum, into an evacuated gas bottle. The bottle was then pressurized to 300 psia with air or helium. For lower dilutions, aliquots of the original mixtures were further diluted.

Procedure. The halogenated compounds that have been determined by this technique in the 10-ppb-by-volume range are given in Table I. Care must be taken to prevent adsorption in the sample loop and sample valve. There was no apparent sample loop adsorption because of the high volatility of the compounds analyzed and the length of time for the injection.

(4) O. L. Hollis, ANAL. CHEM., **38**, 309 (1966).

Table I. Halogenated Hydrocarbons Determined by On-Column Concentrating

Compounds	Boiling point, °C
CH_3Cl	−24
CCl_2F_2, (Freon-12)	−29.79
$CH_2=CHCl$	−13.9
CH_2Cl_2	40.2
$CClF_2—CClF_2$, (Freon-114)	3.77
CCl_3F, (Freon-11)	23.77
$CH_2=CCl_2$	37
cis-$CHCl=CHCl$	60
trans-$CHCl=CHCl$	48.3
$CCl_2F—CClF_2$, (Freon-113)	47.57
$CBrF_2—CBrF_2$, (Freon-114B-2)	47.26
$CHCl_3$	61.2
CH_3CCl_3	74.0
$CHCl=CCl_2$	87.2
$CCl_2=CCl_2$	121.2

The type of porous polymer beads selected and the particular temperature program used depends on the mixture to be analyzed. A portion of the air sample to be analyzed is put in a 100- or 500-ml sample loop. Care must be taken that the column oven is equilibrated at some temperature between 30 to 50 °C. This equilibration temperature must be the same for each analysis or the retention times of the components of the standard and the sample will vary slightly. The sample is injected into the column over a 5-minute period, with helium used as a carrier. The sample valve is left in the inject position throughout the entire analysis. The flow rate of the carrier gas must be great enough to transfer the sample from the sample loop to the column in the allotted time. The temperature of the column is then raised at the maximum heating rate to 100 °C and held at this temperature for 5 minutes. The appropriate temperature program for the mixture is then followed to elute the sample. The program used for the mixtures in this paper was 10 °C/minute from 100 to 120 °C, 2 °C/minute from 120 to 136 °C, and 10 °C/minute from 136 to 166 °C. The column then was heated at the maximum rate to 210 °C and held there until the tetrachloroethene was eluted.

After analyzing numerous air mixtures, it becomes necessary to "clean" the porous-polymer-bead column of higher molecular weight compounds present in the mixtures. This is accomplished by raising the column temperature to 210 °C at night so that the helium carrier purges the column. It is necessary to do this in order for the retention times of the standards to remain constant. The purging of the column could also be accomplished by backflushing the column.

RESULTS AND DISCUSSION

A mixture of some of the compounds in Table I in the 2.0-±1-ppm range (except for the CCl_2F_2) is shown in Figure 1. The elution time for the tetrachloroethene is 38 minutes on Porapak S. A 100-ml sample loop was employed for this analysis. Figure 2 shows a chromatogram of a sample in the 20- ±10-ppb range using a 500-ml sample loop. The CCl_2FCClF_2 peak is too large because of the contamination of the sample bottle valve with this compound in its manufacture. The brominated compound is not quantitative in the silver cell because of the formation of the hypobromite. In making standard samples in the ppb range, difficulties are often encountered, particularly with CCl_2FCClF_2 because of contamination from the dilution gas and equipment.

The technique of on-column concentration of large air samples has also been used with a hydrogen flame detector.

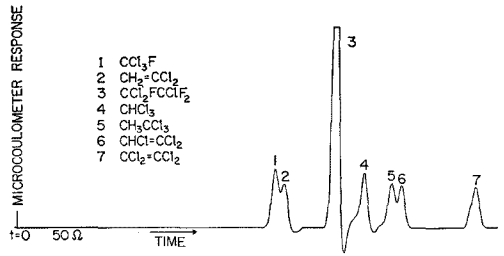


Figure 2. Coulometric response for halogenated hydrocarbons in 20- ± 10-ppb range using 500-ml sample loop

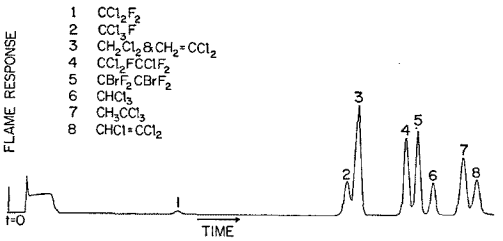


Figure 3. Flame ionization response for halogenated hydrocarbons in 1-ppm range using 100-ml sample loop

Table II. Accuracy and Precision of On-Column Concentrating Technique with Porapak Q Column

Compound	Prepared standard, ppm	Determined by coulometric detector, ppm
$CH_2=CCl_2$	1.0	0.96, 1.04, 1.02
$CCl_2F—CClF_2$	1.0	0.99, 1.01, 0.99
$CHCl_3$	1.0	0.98, 0.92, 1.01
CH_3CCl_3	1.0	0.95
$CH_2=CHCl$	2.5	2.5

Figure 3 shows the flame response to a mixture in the 1-ppm range using a 100-ml sample loop. There is an initial upset in the flame base line when the large volume samples are injected, but this settles down before the first peak is eluted.

The on-column concentrating technique for gas samples eliminates the need for cold traps and cold columns. It is conceivable that much larger samples could be used, limited only by the physical length of time required to put the sample on the column.

The base line of the microcoulometer is not affected by the temperature programming of porous polymer beads, although there is a slight degradation of the polymer at the high temperatures. Because no chlorinated product is evolved in this degradation, the detector does not respond.

The quantitative accuracy and precision of the on-column concentrating technique were determined by standards containing only one halogenated compound in air. The standards were prepared to have a concentration of 1.0 and 2.5 ppm by volume. The response of the standards when chromatographed using the on-column concentrating technique was related through Coulomb's law and the concentration was determined. This value was then compared to the prepared concentration. These data are presented in Table II. The data show that the method is quantitative and thus there is no loss of sample on the column or elsewhere. The greatest problems in determining the quantitative accuracy of the method are encountered in preparing the standards in the ppb range and not in the determinations.

The on-column concentrating technique has been used routinely in studying trace contaminants in closed environmental systems and in air pollution studies at this Laboratory.

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Abbreviations used: col., column; corr., correction; corresp., correspondence; EDTA, ethylenediaminetetraacetic acid; NMR, nuclear magnetic resonance spectrometry; rev., review; symp., symposium. Numbers followed by the letter "A" refer to pages in the advertising section; those followed by the letter "R" refer to pages in the April review issue.

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(1) P. D. Zemany, General Electric Co., Schenectady, N. Y., personal communication, 1960.
(2) C. D. Popov, *Zh. Fiz. Khim.*, **50**, 1234 (1963).
(3) American Instrument Co., Silver Spring, Md., *Bull.* 2778H (1956).
(4) L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd ed., Methuen and Co., London, 1958, p 20.
(5) L. Roe and J. R. Doe, AEC Report 66-170, Los Altos, Calif., Feb. 1964.
(6) A. B. Doe, U. S. Patent 2542356 (1952).
(7) J. A. S. Adams and W. J. Maeck, ANAL. CHEM., **26**, 207 (1954).
(8) N. Doe, Abstracts 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept. 1966, No. U 74.

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ANALYTICAL CHEMISTRY has compiled the following list of terms frequently used in papers on spectrometry. The list includes definitions and abbreviations, and represents usage preferred by ANALYTICAL CHEMISTRY and endorsed by its advisory board. Sources used in the compilation are: *Chemical Abstracts*, H. K. Hughes, *et al.* [ANAL. CHEM. **24**, 1349 (1952)], and the ASTM Committee E-13 on Absorption Spectroscopy (E 131–66 T).

Absorbance, A. (Not optical density, absorbancy, or extinction.) Logarithm to the base 10 of the reciprocal of the transmittance $A = \log_{10}(1/T)$.

Absorptivity, a. (Not k). (Not absorbancy index, specific extinction, or extinction coefficient.) Absorbance divided by the product of the concentration of the substance (in g/l) and the sample path length (in cm),

$$a = \frac{A}{bc}$$

Absorptivity, Molar, ϵ. (Not molar absorbancy index, molar extinction coefficient, or molar absorption coefficient.) Product of the absorptivity, a, and the molecular weight of the substance.

Angstrom, Å. Unit of length equal to 1/6438.4696 of wavelength of red line of Cd. For practical purposes, it is considered equal to 10^{-8} cm.

Beer's Law. (Representing Beer-Lambert law.) Absorptivity of a substance is a constant with respect to changes in concentration.

Concentration, c. Quantity of the substance contained in a unit quantity of sample. (In absorption spectrometry it is usually expressed in grams or moles per liter.)

Frequency. Number of cycles per unit time.

Infrared. The region of the electromagnetic spectrum extending from approximately 0.78 to 300 microns.

Micron, μ. Unit of length equal to 10^{-6} meter.

Millimicron, $m\mu$. Unit of length equal to one thousandth of a micron. Almost but not exactly equal to 10 angstroms.

Sample Path Length, b. (Not l or d). Internal cell or sample length, usually given in centimeters.

Spectrograph. Instrument with an entrance slit and dispersing device that uses photography to obtain a record of spectral range. The radiant power passing through the optical system is integrated over time, and the quantity recorded is a function of radiant energy.

Spectrometer, Optical. Instrument with an entrance slit, a dispersing device, and with one or more exit slits, with which measurements are made at selected wavelengths within the spectral range, or by scanning over the range. The quantity detected is a function of radiant power.

Spectrometry. Branch of physical science treating the measurement of spectra.

Spectrophotometer. Spectrometer with associated equipment, so that it furnishes the ratio, or a function of the ratio, of the radiant power of two beams as a function of spectral wavelength. These two beams may be separated in time, space, or both.

Transmittance, T. (Not transmittancy or transmission.) The ratio of the radiant power transmitted by a sample to the radiant power incident on the sample.

Ultraviolet. The region of the electromagnetic spectrum from approximately 10 to 380 $m\mu$. The term without further qualification usually refers to the region from 200 to 380 $m\mu$.

Visible. Pertaining to radiant energy in the electromagnetic spectral range visible to the human eye (approximately 380 to 780 $m\mu$).

Wavelength. (One word.) The distance, measured along the line of propagation, between two points that are in phase on adjacent waves—units Å., $m\mu$, and μ.

Wavenumber. (One word.) Number of waves per unit length. The usual unit of wavenumber is the reciprocal centimeter, $cm.^{-1}$ In terms of this unit, the wavenumber is the reciprocal of the wavelength when the latter is in centimeters in vacuo.

Guide for Measures of Precision and Accuracy

It is important to know what an author means when he writes of precision and accuracy. The following definitions are applicable when one operator provides a series of test results and no prior information on the method is used. They are endorsed by ANALYTICAL CHEMISTRY—after careful study by members of its Advisory Board and on advice of qualified statisticians—and suggested when results reported are suitable for statistical treatment (based on 5 or more determinations).

Series. A number of test results which possess common properties that identify them uniquely.

Mean. The sum of a series of test results divided by the number in the series. Arithmetic mean is understood.

Precision Data. Measurements which relate to the variation among the test results themselves—i.e., the scatter or dispersion of a series of test results, without assumption of any prior information. The following measures apply:

VARIANCE. The sum of squares of deviations of the test results from the mean of the series after divisions by one less than the total number of test results.

STANDARD DEVIATION. The square root of the variance.

RELATIVE STANDARD DEVIATION. The standard deviation of a series of test results as a percentage of the mean of this series. This term is preferred over "coefficient of variation."

RANGE. The difference in magnitude between the highest test result and the lowest test result in a series.

Accuracy Data. Measurements which relate to the difference between the average test results and the true result when the latter is known or assumed. The following measures apply:

MEAN ERROR. The average difference with regard to sign of the test results from the true results. Also equal to the difference between the average of a series of test results and the true result.

RELATIVE ERROR. The mean error of a series of test results as a percentage of the true result.

Recommendations for Infrared Spectra of New Compounds

Infrared spectra of *new* compounds described in research articles will be published in the Coblentz Society's spectrum collection according to an agreement between ANALYTICAL CHEMISTRY and the Coblentz Society. It is anticipated that this policy will benefit the scientific community by providing for publication of a larger number of spectra than journal space can permit and by offering systematic indexing of these literature spectra in a single collection. Reference to location of the spectra in the Coblentz Society collection will be provided in the article concerned. *Partial spectra for discussion of a narrow region of the spectrum will continue to be published in the journal article.*

Review. The spectra will be reviewed by the Coblentz Society according to specifications established for the National Standard Reference Data System [ANAL. CHEM., **38,** (9), 27A (1966)]. Only those spectra which are good enough to pass Class III requirements will be published.

Information to be Submitted. Spectra considered for this program are for essentially pure compounds in the region of 2.5 to 15 microns. Spectra of all purified end-products and of key intermediates in a synthesis should be submitted. The spectra of intermediates will not be published if the compounds were impure, but they should be available to the reviewer. Spectra of any model compounds prepared for comparison will be very useful. Other pertinent data such as elemental analysis and NMR or UV spectra should be included along with the structures and *approved* names of the compounds. This information and spectra should be submitted to the journal editor with the original article.

Absorption Range. Sample thickness and concentration should be chosen to yield at least 60% absorption by the strongest band; for most compounds the strongest band should not absorb more than 99%. These recommended absorption intensities will generally be provided by a 10% solution in a 0.1-mm cell, or by a 0.01-mm capillary layer.

The transmission background at 5 to 5.5 microns should be about 90% with a range from 75% to 100% acceptable. It is seldom justified to allow the transmission maximum in this region to be less than 60%.

The difference in background transmission at 2.5 and 5.5 microns should not be more than 30% for an uncompensated spectrum. Any reference beam attenuation should be recorded by placing the attenuator in the sample beam and marking % T at the short wavelength end of the spectrogram.

Instrumentation. Whenever a choice is available to the chemist, a spectrometer with linear wavenumber presentation and grating resolution is recommended. Linear wavelength spectra and prism resolution are acceptable.

Commercial spectrometers should be functioning at manufacturer's specifications. Data demonstrating instrument performances should be included. A single beam spectrogram would serve for most spectrometers to show energy level, resolution, and wavelength calibration from H_2O and CO_2 absorption bands. A better calibration can be obtained from indene [*Spectrochim. Acta,* **20,** 1175 (1964)].

Sample Preparation. Solutions in inert solvents, thin films, or mulls in inert media are generally preferred but pellets may be used when special needs appear to justify them. Path length, concentration, and solvent used should be recorded on the spectrogram. Solvents used for deposition of films or in final purification steps should also be reported.

Format. Suggestions from the editor of the Coblentz Society's spectra are:

(1) Send original spectrometer charts or unretouched photographs.
(2) Do not ink curves by hand.
(3) Run the spectra on paper supplied with large numbers which will be legible after reduction of chart to 10 inches.
(4) Provide compound name, structure, empirical formulas, and purity.
(5) Provide sample state and spectrometer operating conditions.
(6) Submission of the spectra is assumed to constitute permission for their publication in the Coblentz Society collection. If there are any limitations or specific credits to be given, please state them. State whether the submitted originals can be retained or must be returned.
(7) No draftsman's lettering is required on the charts, but all information should be legible and the face of the spectrum should be free of unnecessary markings.

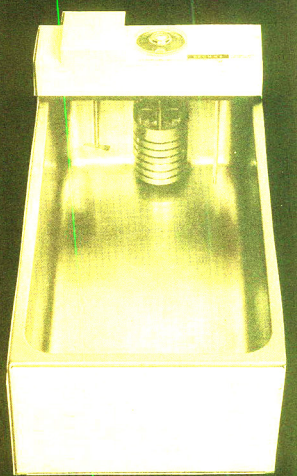
Editor's Note: The above information applies only to complete spectra of new compounds. Partial spectra of known compounds that relate to an article will continue to be published with the article according to our customary procedures (See "Manuscript Requirements Guide" or "ACS Handbook for Authors").

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Analytical Chemistry

DECEMBER 1968

Valid through May 1969

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416 417 418 419 420 421 422 423 424 425 426 427 428 429 430
431 432 433 434 435 436 437 438 439 440 441 442 443 444 445
501 502 503 504 505 506 507 508 509 510 511 512 513 514 515
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3	28	53	78	103	128	153	178	203	228	253	278	303
4	29	54	79	104	129	154	179	204	229	254	279	304
5	30	55	80	105	130	155	180	205	230	255	280	305
6	31	56	81	106	131	156	181	206	231	256	281	306
7	32	57	82	107	132	157	182	207	232	257	282	307
8	33	58	83	108	133	158	183	208	233	258	283	308
9	34	59	84	109	134	159	184	209	234	259	284	309
10	35	60	85	110	135	160	185	210	235	260	285	310
11	36	61	86	111	136	161	186	211	236	261	286	311
12	37	62	87	112	137	162	187	212	237	262	287	312
13	38	63	88	113	138	163	188	213	238	263	288	313
14	39	64	89	114	139	164	189	214	239	264	289	314
15	40	65	90	115	140	165	190	215	240	265	290	315
16	41	66	91	116	141	166	191	216	241	266	291	316
17	42	67	92	117	142	167	192	217	242	267	292	317
18	43	68	93	118	143	168	193	218	243	268	293	318
19	44	69	94	119	144	169	194	219	244	269	294	319
20	45	70	95	120	145	170	195	220	245	270	295	320
21	46	71	96	121	146	171	196	221	246	271	296	321
22	47	72	97	122	147	172	197	222	247	272	297	322
23	48	73	98	123	148	173	198	223	248	273	298	323
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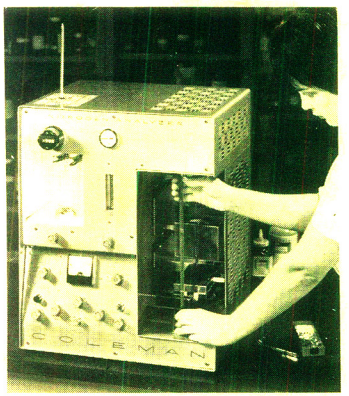


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416	417	418	419	420	421	422	423	424	425	426	427	428	429	430
431	432	433	434	435	436	437	438	439	440	441	442	443	444	445
501	502	503	504	505	506	507	508	509	510	511	512	513	514	515
601	602	603	604	605	606	607	608	609	610	611	612	613	614	615
616	617	618	619	620	621	622	623	624	625	626	627	628	629	630
631	632	633	634	635	636	637	638	639	640	641	642	643	644	645

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2	27	52	77	102	127	152	177	202	227	252	277	302	
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11	36	61	86	111	136	161	186	211	236	261	286	311	
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13	38	63	88	113	138	163	188	213	238	263	288	313	
14	39	64	89	114	139	164	189	214	239	264	289	314	
15	40	65	90	115	140	165	190	215	240	265	290	315	
16	41	66	91	116	141	166	191	216	241	266	291	316	
17	42	67	92	117	142	167	192	217	242	267	292	317	
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19	44	69	94	119	144	169	194	219	244	269	294	319	
20	45	70	95	120	145	170	195	220	245	270	295	320	
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22	47	72	97	122	147	172	197	222	247	272	297	322	
23	48	73	98	123	148	173	198	223	248	273	298	323	
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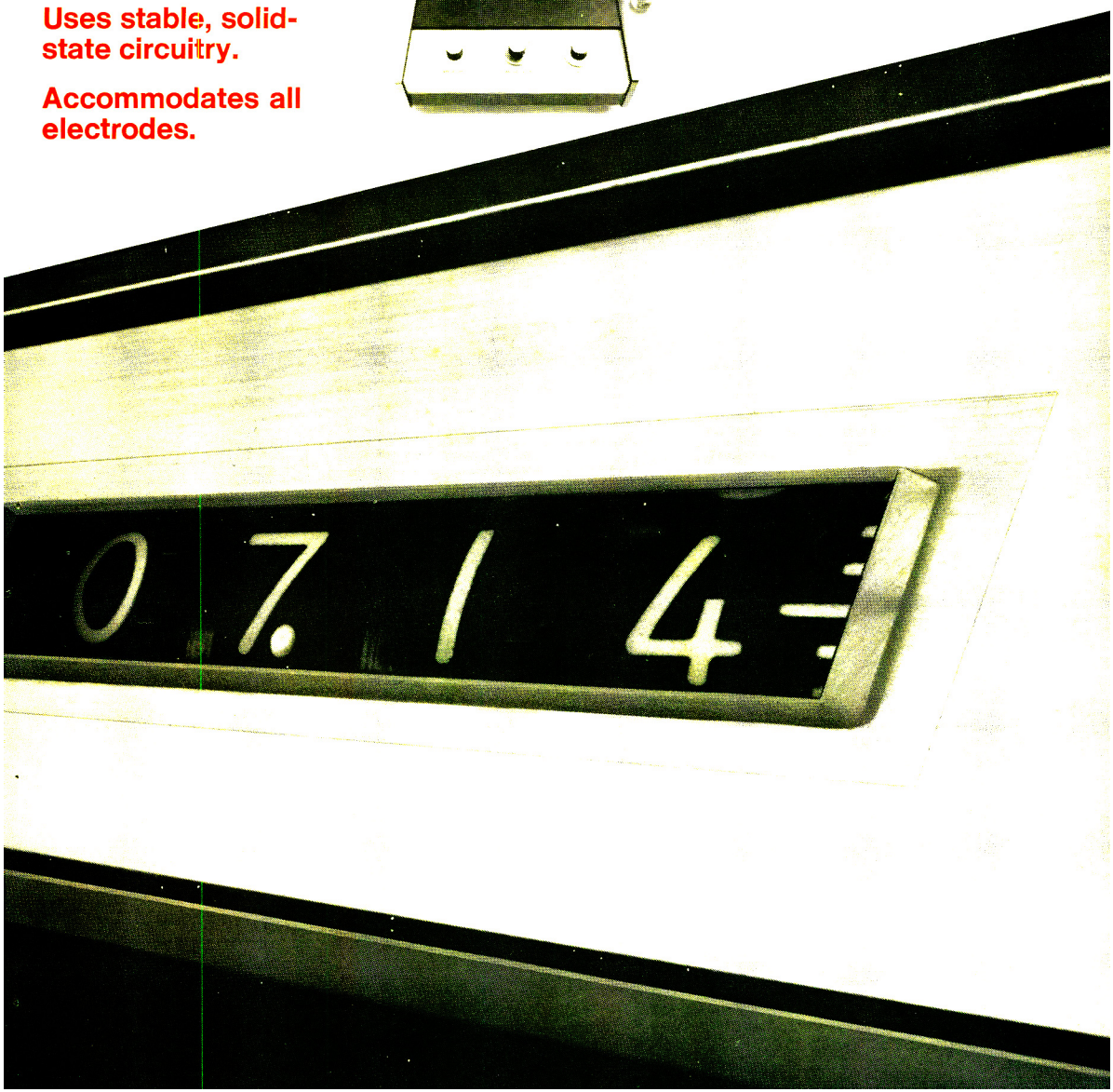
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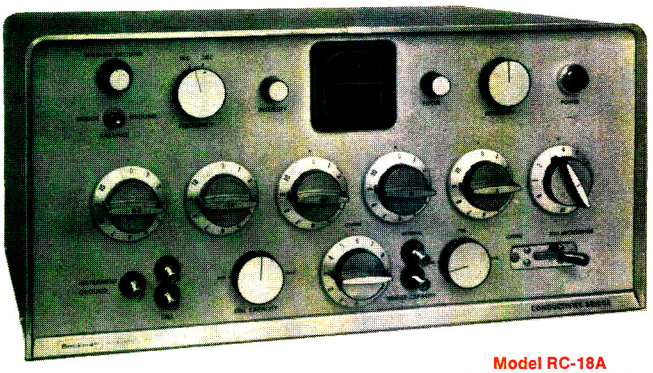
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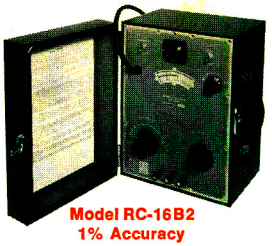
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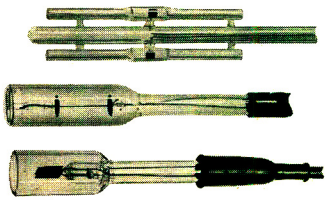




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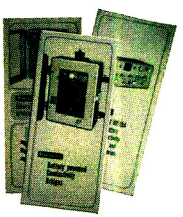
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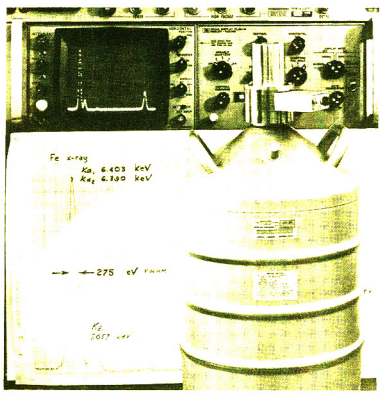
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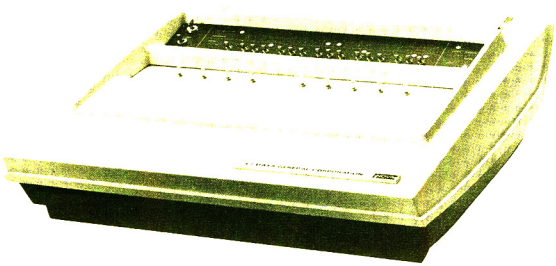
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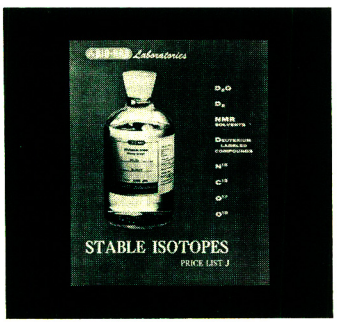
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D compounds

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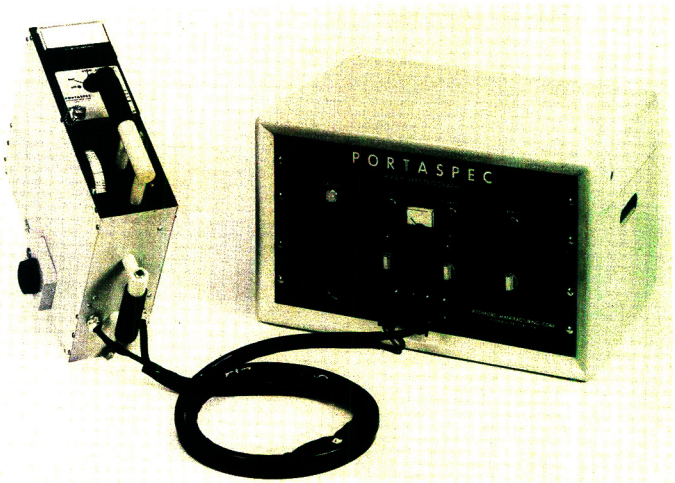
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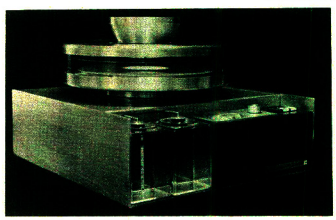
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The Digicord is a solid state pH meter featuring a rapid, positive, numerical display for reading accuracy. Parallax is eliminated and the entire pH range can be expanded without switching. Drift is less than 0.002 pH unit in any eight-hour period. There is no ac polarization of electrodes and almost perfect linearity. Photovolt Corp., 1115 Broadway, New York, N. Y. 10010 **405**

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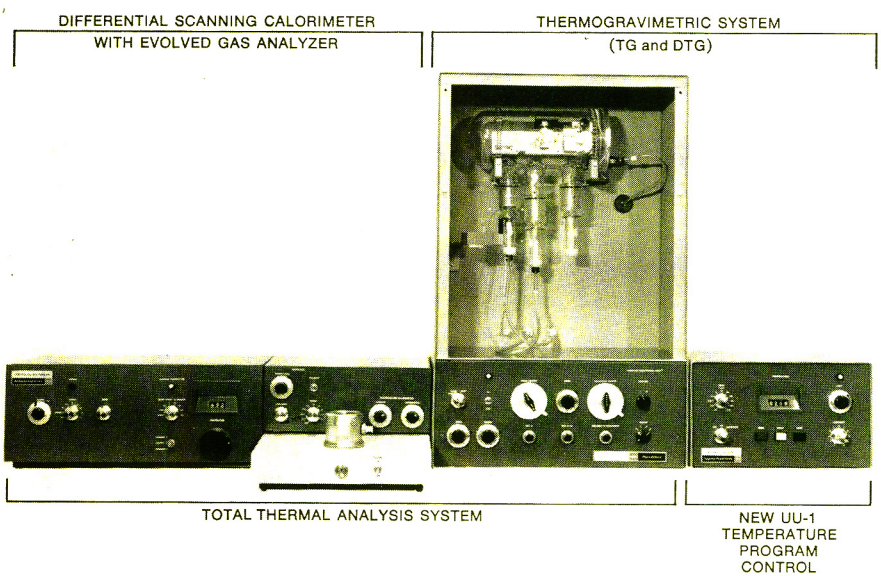
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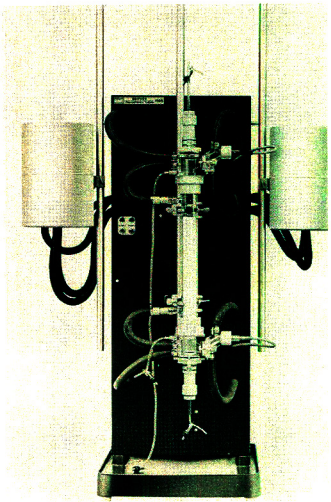
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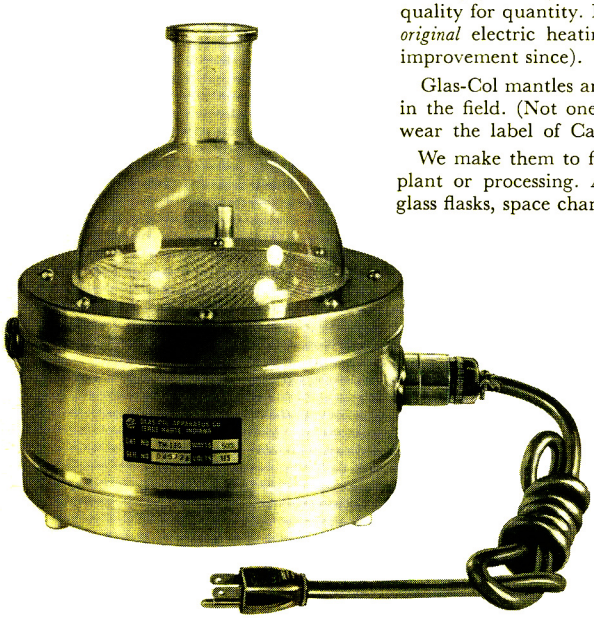
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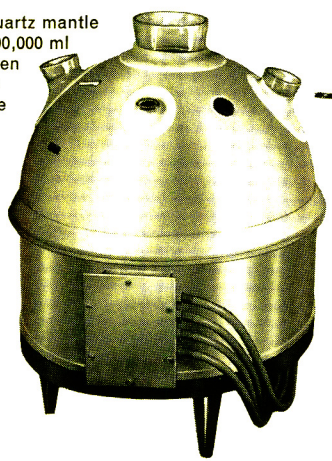




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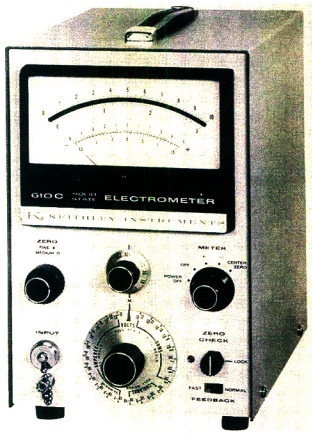
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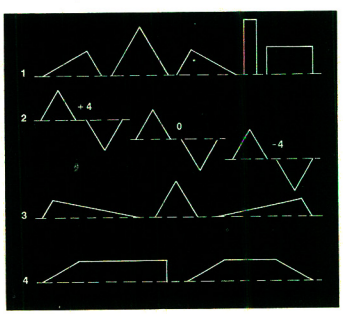
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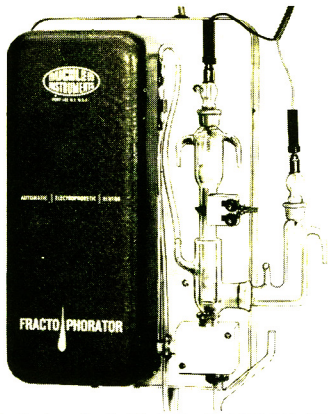
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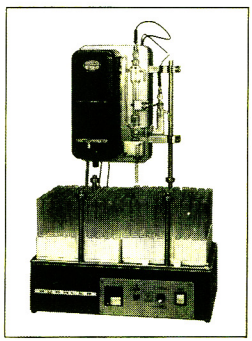
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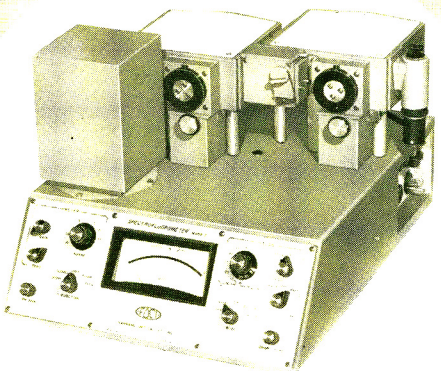
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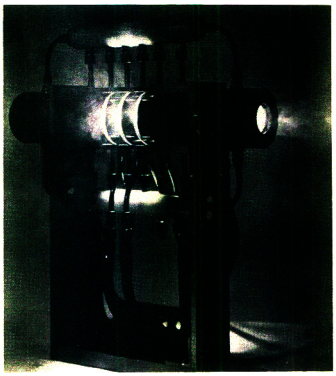


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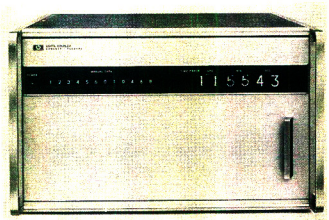
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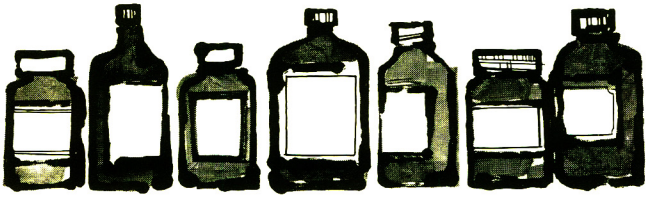
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2,2,6,6-Tetramethyl-3,5-heptanedione (EASTMAN 9900)
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4,5-Dimethyl-o-xylene-α,α'-dithiol (EASTMAN 10524)
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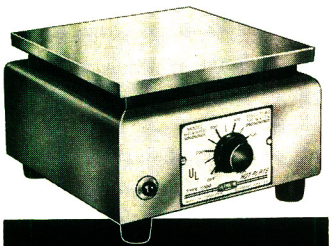
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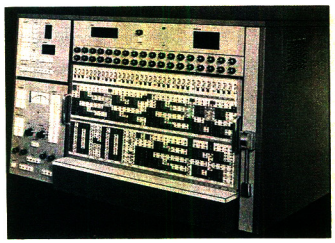


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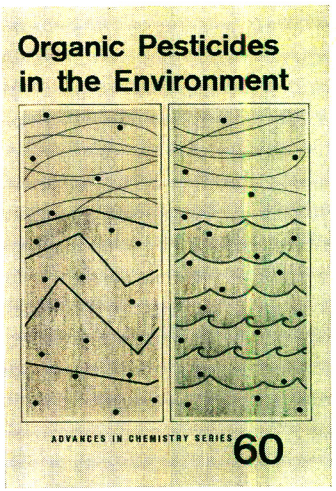
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Wavelength to Compound Correlation Chart

One side of this circular slide chart translates wavelength to compound. The cursor is set to any given wavelength and the chart automatically identifies most of the compounds producing adsorption bands at that wavelength. The flip side presents wavelengths of the main absorption bands of 61 classes of chemical compounds. The formula for wavelength to wavenumber conversion is also given. Barnes Engineering Co., 30 Commerce Rd., Stamford, Conn. 06902 **416**



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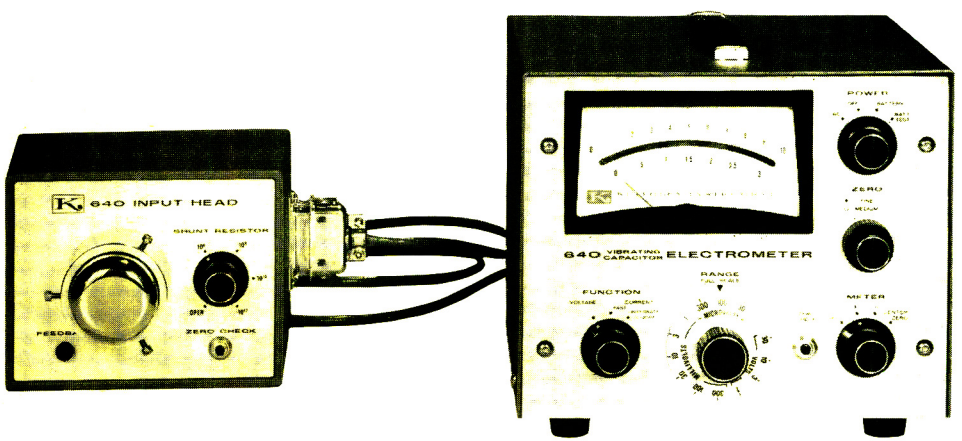
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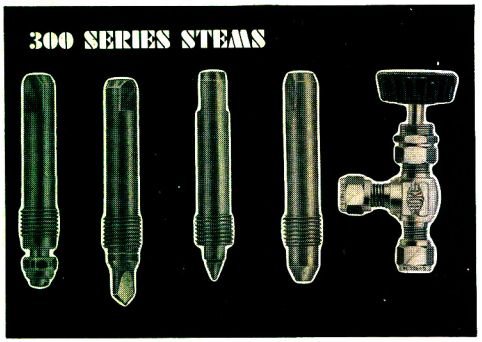
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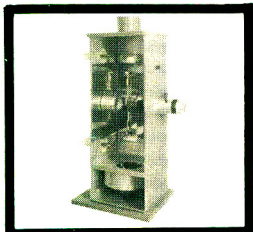
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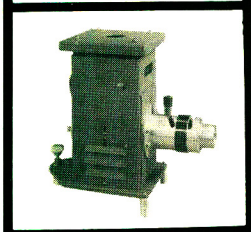
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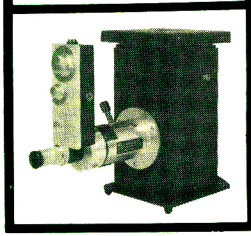
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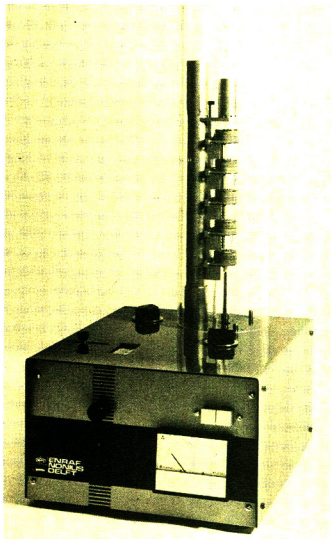
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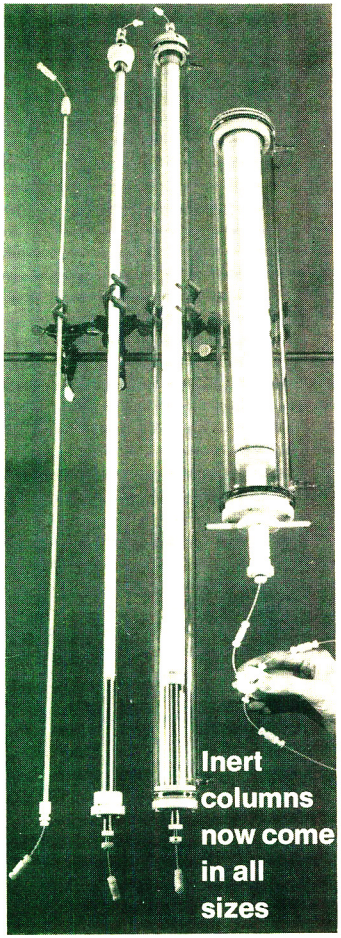
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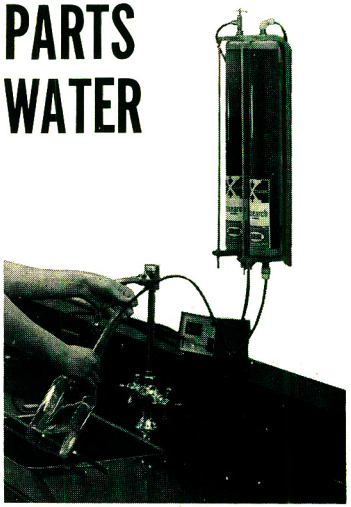
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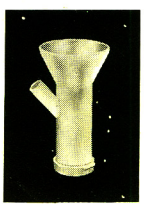
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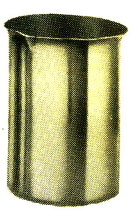
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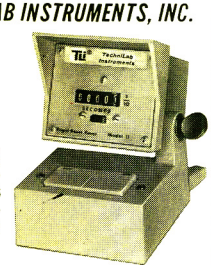
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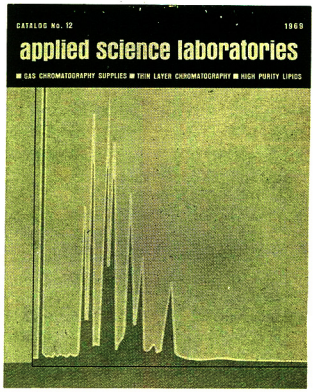
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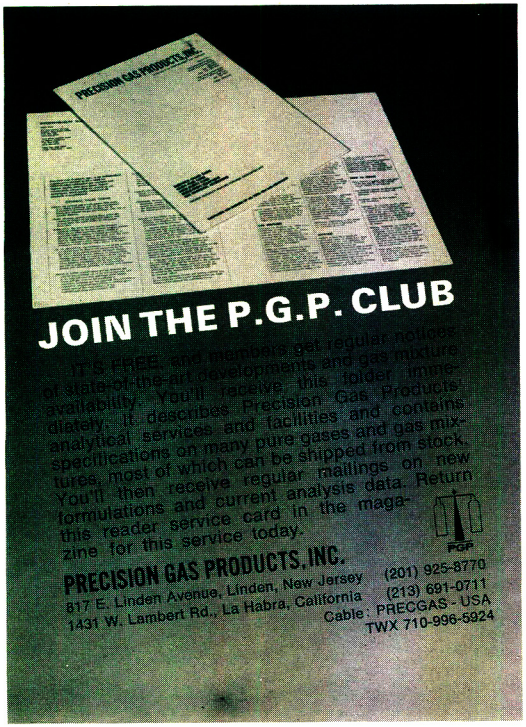
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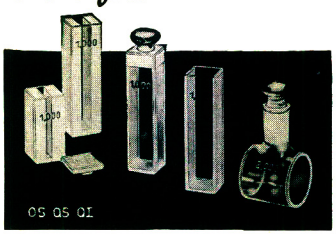
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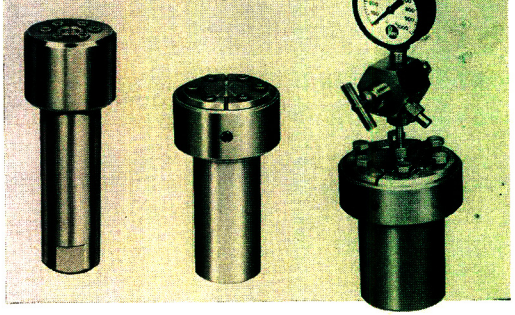
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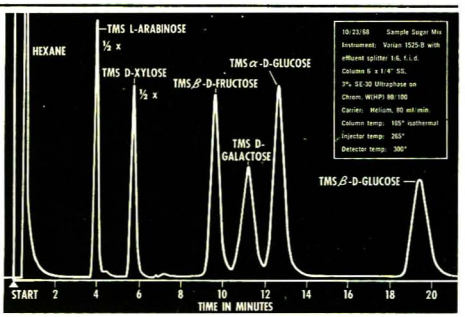
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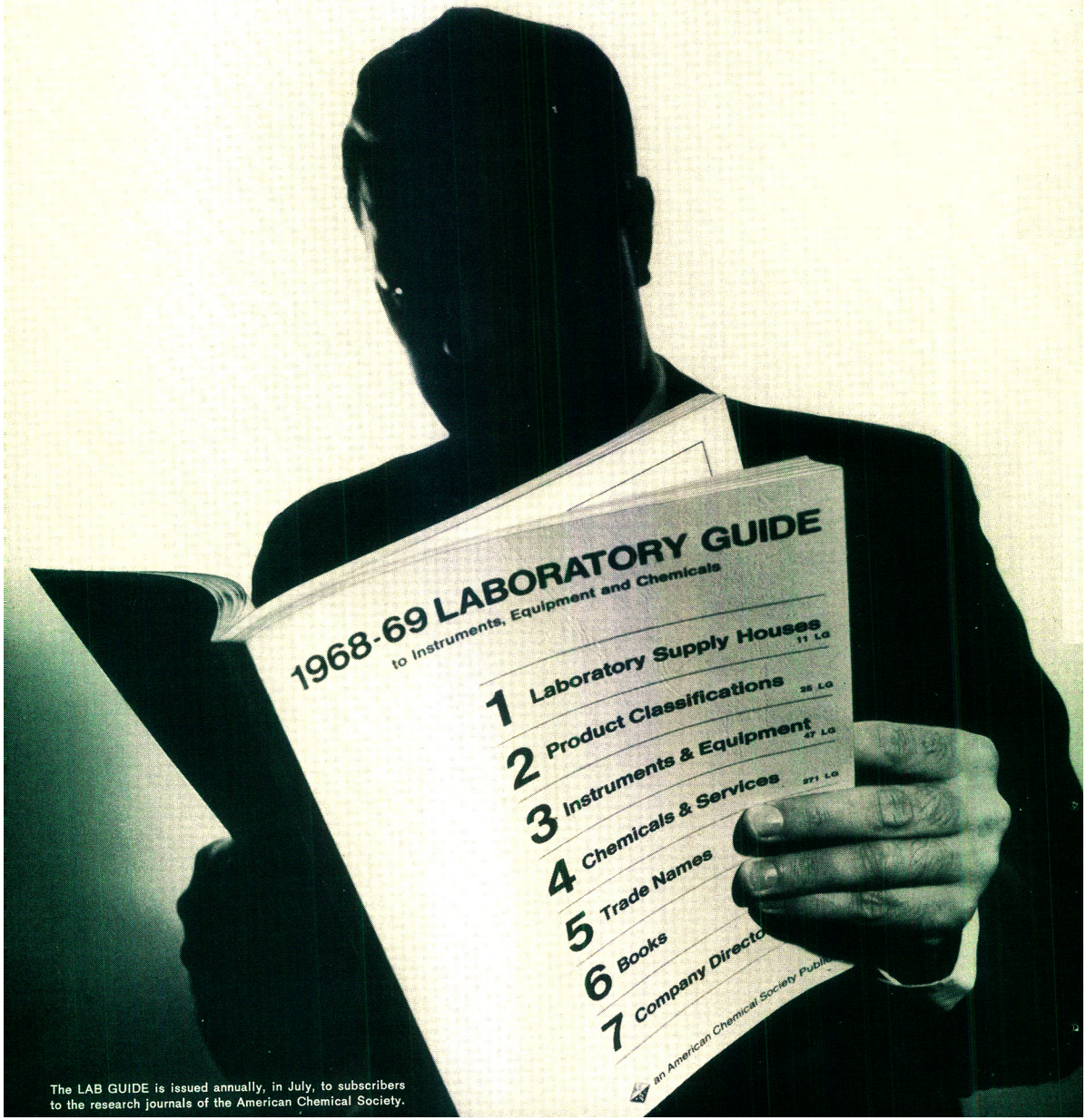
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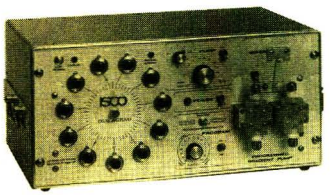
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MANUFACTURERS' LITERATURE

Heating Equipment. A 12-page catalog describes and illustrates the latest laboratory heating equipment and controls by Electrothermal Engineering Ltd., London, England. Electro-thermal Sales Corp., 14 Landing Rd., Roslyn, N. Y. 11576 **601**

Gas Chromatography Systems. The 1600 series gas chromatograph, system modules, and accessories are described in a 24-page catalog. HCL Scientific, Inc., 1800 Broadway, P. O. Box 4223, Rockford, Ill. 61110 **602**

Smoke Inspection Guide. Model 110, consisting of a specially developed strip of photographic film with four measurement sections and a protective case, is described in Bulletin 804, two pages. Environmental Research Corp., 3760 N. Dunlap St., St. Paul, Minn. 55112 **603**

Temperature Controller. Bulletin 1240/DB 4.5, two pages, presents Model 72C, a compact, nonindicating, temperature controller with a time proportioning mode of control. Barber-Colman Co., Rockford, Ill. 61101 **604**

Germanium Detectors. Specifications of lithium drifted germanium detectors, dewar–detector configurations, and options are presented in a six-page brochure. Isotopes, Laboratory Products Division, 50 Van Buren Ave., Westwood, N. J. 07675 **605**

Pulse Height Converter. Design and operational features of Model 461A are described in Bulletin 58A, 12 pages. Technical Instruments, Inc., 441 Washington Ave., North Haven, Conn. 06473 **606**

Laser-Raman Spectrometry. A 16-page catalog includes descriptions of laser options, sample illuminator with holders for gaseous, liquid, and solid samples, double spectrometer, detection, amplification, and recording equipment and accessories for the Ramalog, a laser-Raman spectrometry system. Spex Industries, Inc., 3880 Park Ave., Metuchen, N. J. 08840 **607**

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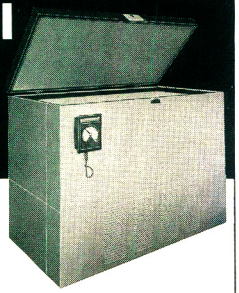
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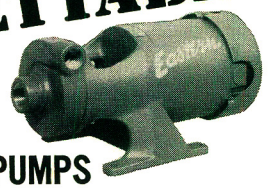
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MANUFACTURERS' LITERATURE

Concentration Converters. Bulletin 7139 provides complete descriptions and specifications for both a digital and a standard concentration converter. The instruments can be used in IR and UV studies, fluorometry, atomic absorption, colorimetry, and all analyses requiring transmittance in absorbance conversion. Beckman Instruments, Inc., 2500 Harbor Blvd., Fullerton, Calif. 92634 **608**

Digital Spectrogram Recorder. Model DSR-1, a system for converting analog data from potentiometric recorders into digital form for computer analysis, is described in an eight-page brochure. Conrac Corp., 1600 S. Mountain Ave., Duarte, Calif. 91010 **609**

Lab Scaffolding. Climpex miniature lab scaffolding equipment is featured in the 1968 Planchets Catalog. Gelman Instrument Co., 600 S. Wagner Rd., P. O. Box 1448, Ann Arbor, Mich, 48106 **610**

Power Supplies. The company's complete line of power supplies and related devices is presented in Catalog No. 154, 40 pages. Electronic Research Associates, Inc., 67 Sand Park Rd., Cedar Grove, N. J. 07009 **611**

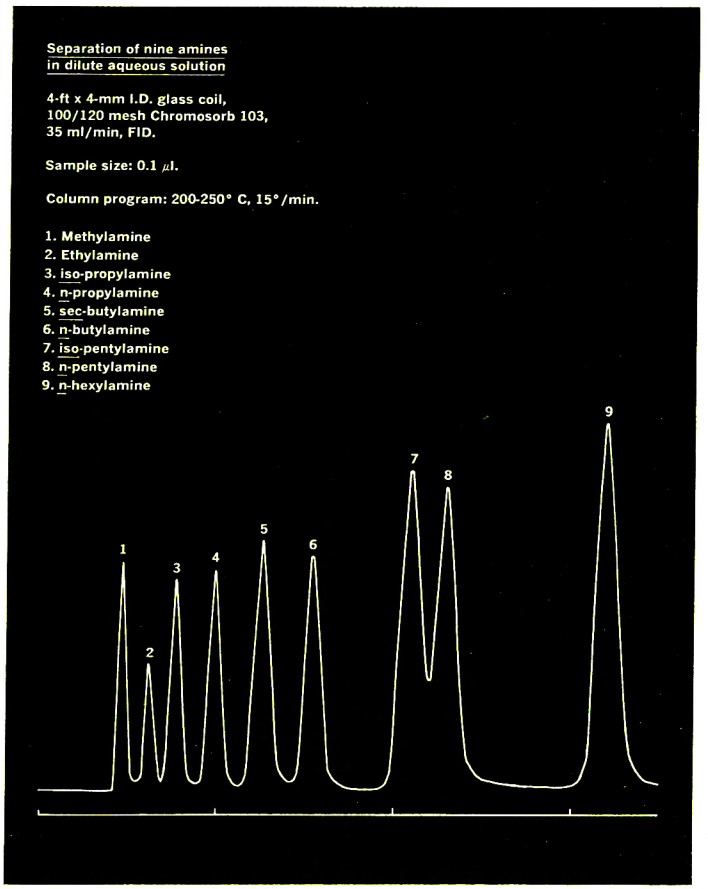
Boron Fluoride Monoethylamine. This material, as it relates to glass laminates, heat distortion temperatures, chemical resistance, electrical properties, fillers, and exposure experience, is discussed in an eight-page technical bulletin. The Harshaw Chemical Co., Division of Kewanee Oil Co., 1945 E. 97th St., Cleveland, Ohio 44106 **612**

New Metals Line. A new 95-page Advanced Materials catalog introduces 25 metals and six stock alloys now available in the VP line. VP grade metals and alloys are a high purity grade prepared by vacuum melting, vacuum annealing, distillation, or related processes. They are of higher quality than the usual commercially available metals. Materials Research Corp., Orangeburg, N. Y. 10962 **613**

Electron Microscopy Bibliography. This publication covers instrumentation design and practical applications in scanning electron microscopy. The bibliography is separated into 12 classifications. Electron Optics Division, Engis Equipment Co., 8035 Austin Ave., Morton Grove, Ill. 60053 **614**

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MANUFACTURERS' LITERATURE

Carbon-14 Amino Acids. Uniformly ^{14}C-labeled amino acids of moderate and relatively high specific activity are listed in this folder. International Chemical & Nuclear Corp., Chemical & Radioisotope Division, 801 N. Lake St., Burbank, Calif. 91502 **615**

Centrifuges. Catalog 80, eight pages, presents both floor- and bench-model super-speed centrifuges for batch and continuous flow with various forces, capacities, and rotors. Lourdes Instrument Corp., Old Bethpage, N. Y. **616**

Omnigraphic Recorder. Model 6650, a bidirectional incremental plotter, is presented in Bulletin No. 568-6650, six pages. Houston Instrument, Division of Bausch & Lomb, 4950 Terminal Ave., Bellaire, Tex. 77401 **617**

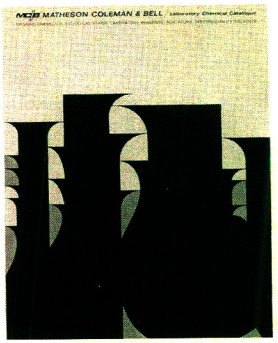
Literature Search Program. Bulletin FLSP describes a computer cataloged and indexed bibliography of more than 10,000 scientific papers dealing with theory, application, and instrumentation in the fields of liquid scintillation counting, gamma counting, pulse height analysis, and gas and liquid chromatography. Packard Instrument Co., Inc., 2200 Warrenville Rd., Downers Grove, Ill. **618**

Liquid Scintillation Counting. A 24-page booklet entitled "An Introduction to Liquid Scintillation Counting" has been recently introduced. It was prepared for scientists not yet familiar with the fundamentals of this scientific tool. N. V. Philips' Gloeilampenfabrieken, Analytical Equipment Department, TQ III-2, Eindhoven, The Netherlands **619**

Spectrometry Instrumentation. "This is Jarrell-Ash" is a 36-page bulletin describing and illustrating optical emission instruments, spectroscopic instruments for research, atomic absorption/flame emission instruments, X-ray diffraction, spectrometric supplies, and diffraction gratings. Fisher Scientific Co., J308 Fisher Bldg., Pittsburgh, Pa. 15219 **620**

Electronic Kits. Over 300 kits for every interest and budget are included in this 116-page, 1969 Heathkit catalog. Heath Co., Benton Harbor, Mich. 49022 **621**

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MANUFACTURERS' LITERATURE

Macrotome. A precision cutting device for semiconductors, laser crystals, ceramics, and other hard and brittle materials is presented in a four-page booklet. Materials Research Corp., Orangeburg, N. Y. 10962 **622**

Chemical Catalog. Over 200 chemicals for research and development are listed in this four-page, 1969 catalog. The Ames Laboratories, Inc., 200 Rock Lane, Milford, Conn. 06460 **623**

Glass and Plastic Laboratory Ware. PL-68L, a 64-page catalog, presents several pages of new products and a new general pricing schedule. Owens-Illinois, Kimble Products, P. O. Box 1035, Toledo, Ohio 43601 **624**

Radioactive Compounds. Catalog 70, 76 pages, lists radioactive compounds, sources, nuclides, and accessories. Tracerlab, Division of Laboratory for Electronics, Inc., 1601 Trapelo Rd., Waltham, Mass. 02154 **625**

Electrobalance. Both manual and recording electrobalances and major accessories for both are presented in a six-page condensed catalog. Cahn Division, Ventron Instruments Corp., 7500 Jefferson St., Paramount, Calif. 90723 **626**

Numerical Displays, Counters, etc. Catalog '69, six pages, describes numerical displays, counters, memories, tubes, and accessories. Integrated Circuit Electronics, Inc., P. O. Box 647, Waltham, Mass. 02154 **627**

Pulse Instrumentation. Condensed Catalog 1968–69, four pages, illustrates and describes general purpose pulse and digital data generators. Datapulse, Inc., 10150 W. Jefferson Blvd., Culver City, Calif. 90230 **628**

Resistance Alloys. Properties and performance characteristics of Hoskins Alloy 750, Alloy 815, and Alloy 875, Fe–Cr–Al electrical resistance materials, are described in a new 16-page catalog. Hoskins Manufacturing Co., 4445 Lawton Ave., Detroit, Mich. 48208 **629**

Sephadex LH-20. Brief descriptions of recently published articles and illustrated examples of separations using Sephadex LH-20 are presented in Technical Data Sheet No. 13, four pages. Pharmacia Fine Chemicals, Inc., 800 Centennial Ave., Piscataway, N. J. 08854 **630**

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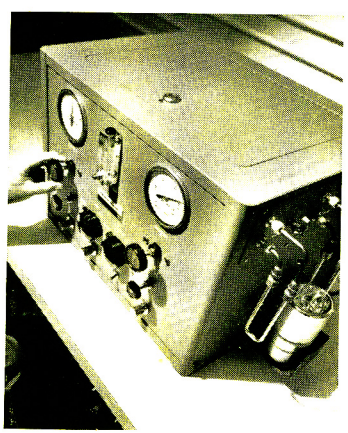
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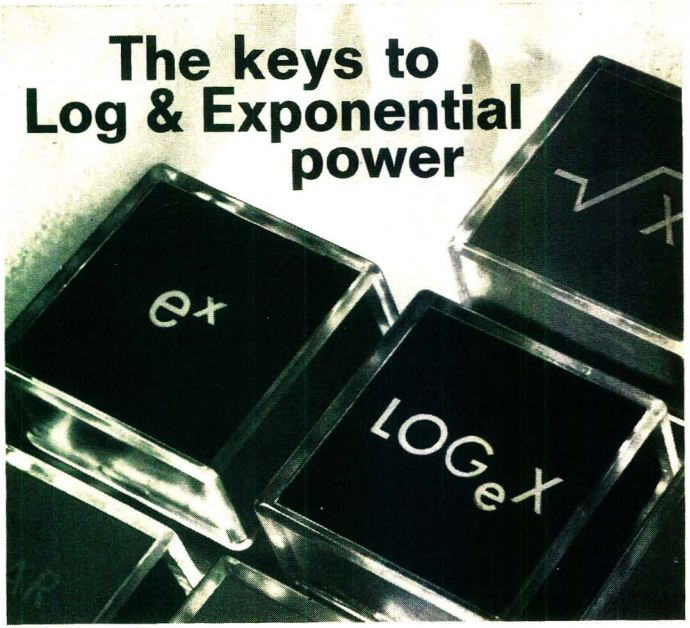
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MANUFACTURERS' LITERATURE

Thermocouple Guidebook. Bulletin TT-335, 40 pages, covers design philosophy, materials selection, and suggestions for thermocouples and thermowells. Pall Trinity Micro Corp., Route 281, Cortland, N. Y. 13045 **631**

Microcalorimetry. System 10700 for both batch and flow microcalorimetry is described in a 10-page brochure, 10700-EO1. LKB Instruments, Inc., 12221 Parklawn Dr., Rockville, Md. 20852 **632**

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.

Research Analysis Notes, Vol. 1, No. 1. The technical communications in the first issue of this new periodical discuss the ignition theory in atomic absorption and the reflection penetration theory in infrared spectrometry. Research Analysis Associates, Inc., 165 Dodge Ave., Stratford, Conn. 06497

Instrument News, Vol. 19, No. 1. Model RMH-2, an ultra-high resolution mass spectrometer, and Model 203, a fluorescence spectrometer, are discussed in this issue. The Perkin-Elmer Corp., Main Ave., Norwalk, Conn. 06852

Gas-Chrom Newsletter, Vol. 9, No. 4. Products introduced in this issue include ^{14}C labeled amino acids and lipids. Arachidonic acid 1-C-14 and methyl arachidonate 1-C-14 are new lipid radiochemicals. Applied Science Laboratories, Inc., State College, Pa. 16801

Ace Bulletin, Vol. 9, No. 2. A complete photochemical system for laboratory scale photochemical reactions, a fully jacketed Adjusta-Chrom recycling column, and a general-purpose portable all-glass evaporator stripper are among the new products discussed. Ace Glass Inc., Vineland, N. J. 08360

Technical Journal, No. 4, 1968. The topics discussed in this issue include a system approach to effluent disposal, the treatment of industrial waste water, and calibration methods for instruments that measure contaminants in our atmosphere. Leeds & Northrup, Sumneytown Pike, North Wales, Pa. 19454

Arcs & Sparks, Vol. 13, No. 2. ITT Cannon Electric of Santa Ana, California is presented and Lester W. Strock is the Featured Spectroscopist. Ultra Carbon Corp., P. O. Box 747, Bay City, Mich. 48706

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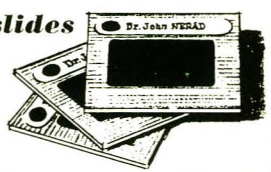
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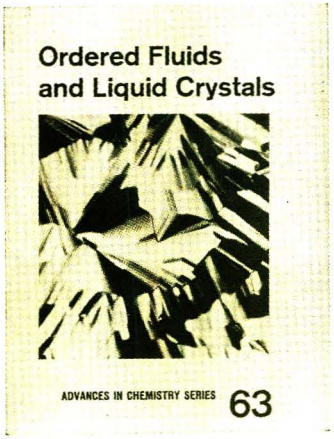
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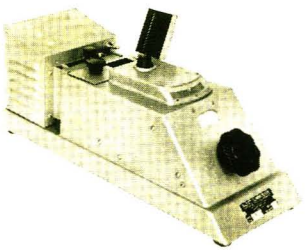
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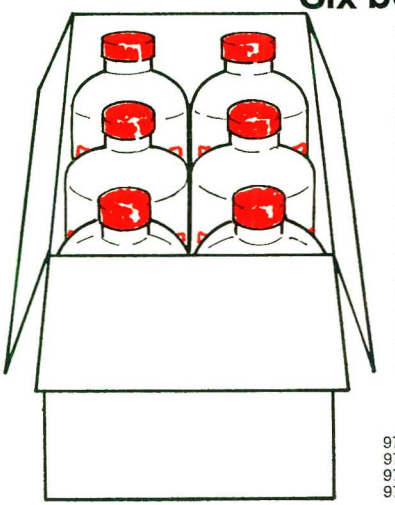
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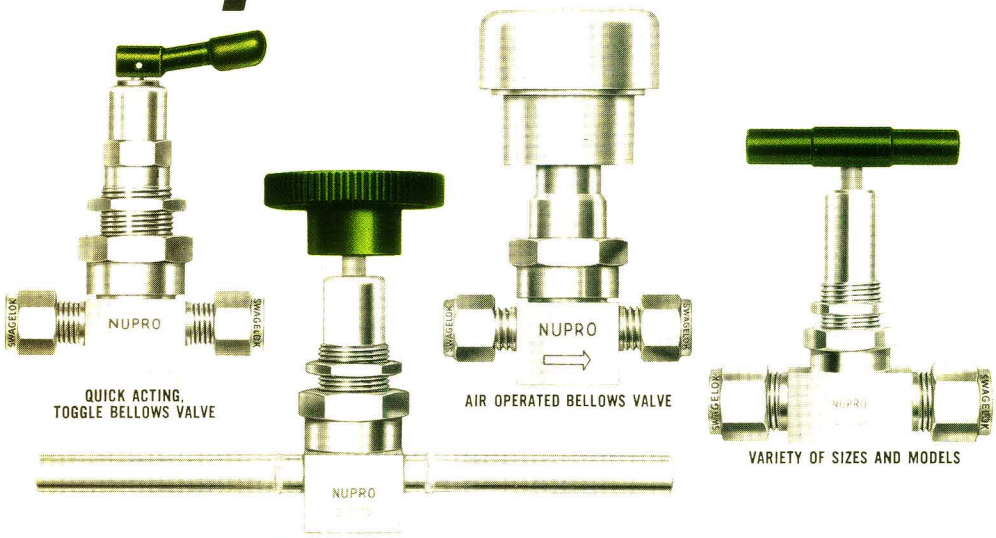
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