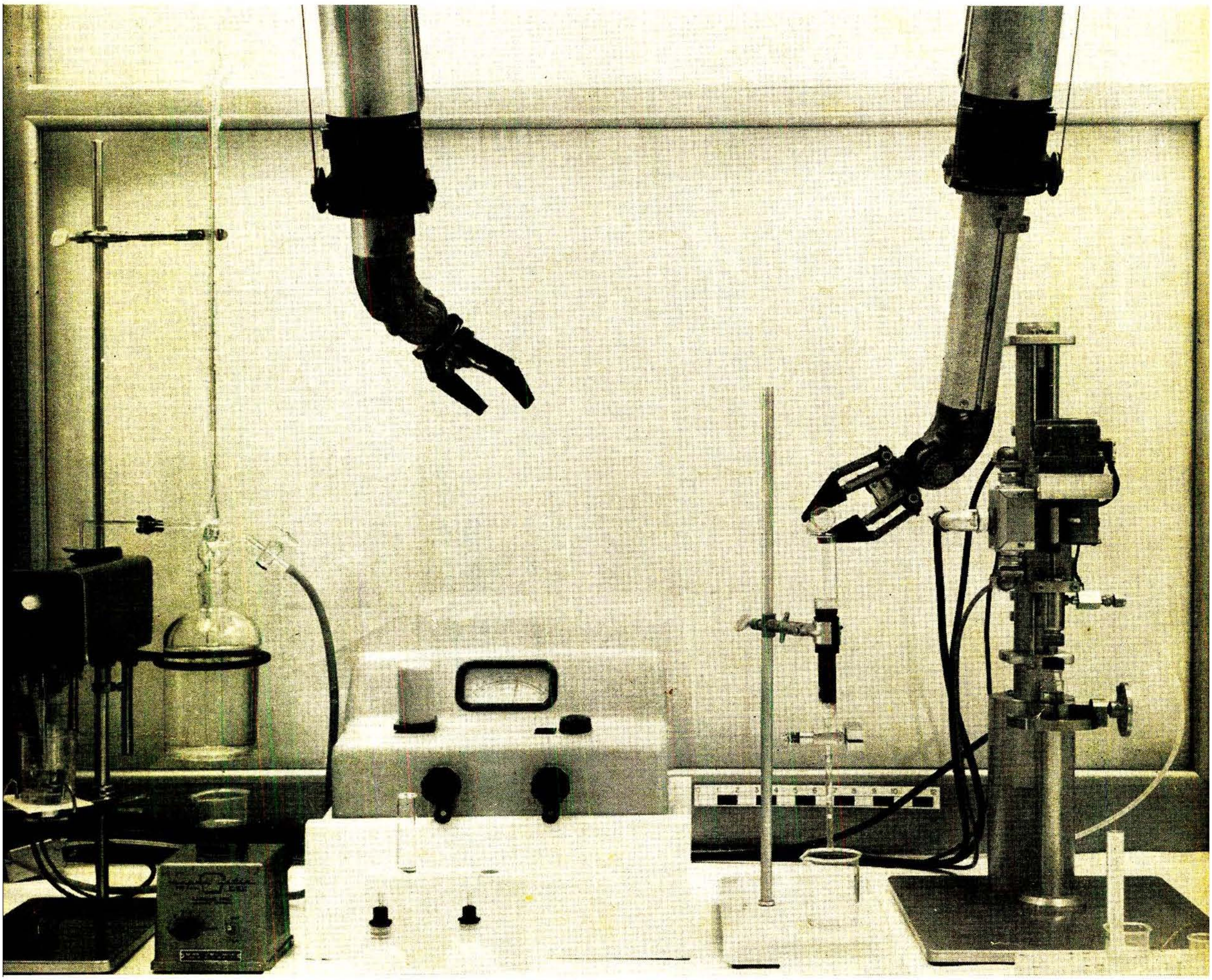
JUNE 1957

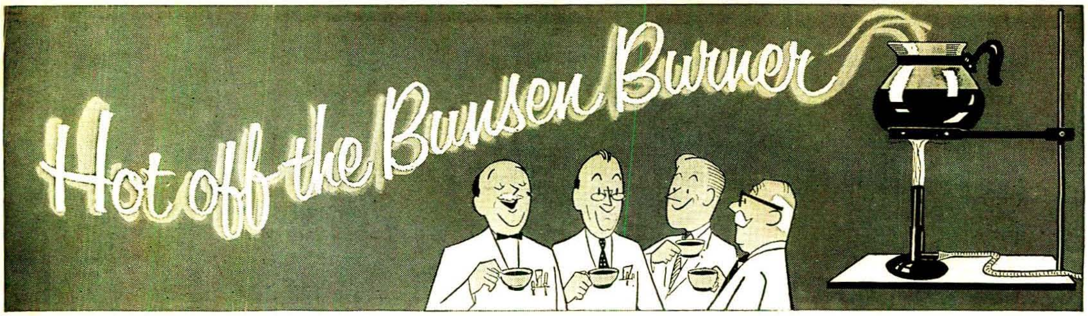
ANALYTICAL CHEMISTRY



ANALYTICAL INSTRUMENTATION MEETS ATOMIC AGE CHALLENGE

▶ New Rubbers from "Hot" Lab Research 49 A

▶ Analysts Attack Air Pollution Problems 864



Among chemists, the morning coffee-break is a well-established custom. During these informal symposia many worth-while data are exchanged. We should like to sit in and tell you about some of our 1,000 plus MERCK LABORATORY CHEMICALS.

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Every so often some histologist or pathologist gets to wondering if the tissue he's looking at under his microscope really contains fat. If doubt persists, a small bit of tissue is dunked in a solution of OSMIUM TETROXIDE MERCK REAGENT and the fat comes up black. This proves that the cells contain fat and not some artifacts due to poor fixing technic. Other familiar uses include hydroxylating lonesome double bonds and catalyzing certain oxidations with ceric sulfate. (A well-known example is speed-up of the balky reaction between arsenious acid and ceric sulfate.) OSMIUM TETROXIDE MERCK REAGENT is "the most," but keep its vapors out of eyes, respiratory tract, and away from skin. Otherwise—BLACK FAT!

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Magnification of blood sample from leukemia victim, showing extreme white cell-to-red cell imbalance. White cell level 250 times greater than normal.

Beckman®/DK Automatic Recording Spectrophotometer speeds research in leukemia

Seeking to stop leukemia, medical scientists have learned how to slow it down. Inhibitors have been found that temporarily stop the abnormal production of *leucocytes,* white blood cells. But, because the body develops resistance to these present inhibitors, white cell metabolism must be better understood and more selective inhibitors discovered to permanently stop abnormal production of leucocytes.

Leucocyte-inhibitor reaction is studied by introducing a radioactive assimilate into the environment of leucocyte samples, both in the presence and in the absence of an inhibitor. To determine what metabolic use the leucocytes make of the radioactive substance and what effect the inhibitor has on this process is a big analytical job.

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ANALYTICAL CHEMISTRY

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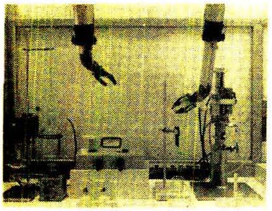

THIS MONTHS'S COVER

High radiation levels encountered in "hot" cells present challenging problems in analytical instrumentation. Ruggedness, accuracy, and resistance to radiation damage are typical requirements. Equipment used in the high radiation level, analytical facility at Oak Ridge National Laboratories includes (left to right) an autotitrator, magnetic stirrer, grating spectrophotometer, and servo-operated pipettor. Other facets of atomic age analytical instrumentation problems appear in the editorial, page 863, and the Laboratory of the Month, page 49 A. This subject will also be discussed at the Summer Symposium at Purdue June 13 to 15 (see program, April issue, page 21 A).

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Report for Analysts

News Section

Analyst's Column

Laboratory of the Month

Instrumentation

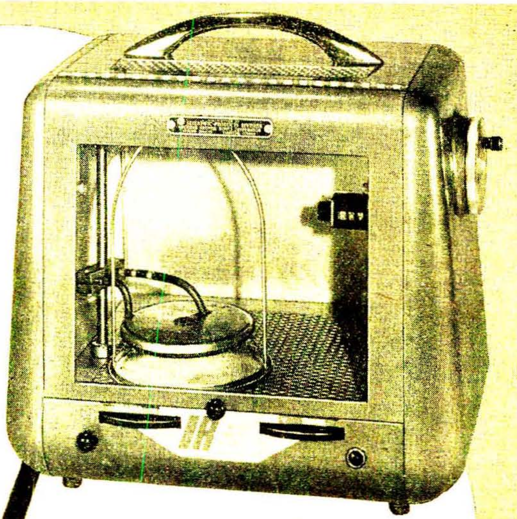
Crystallographic Data

Aids for the Analyst

CONTRIBUTED ARTICLES

Air Pollution Symposium

End of Symposium



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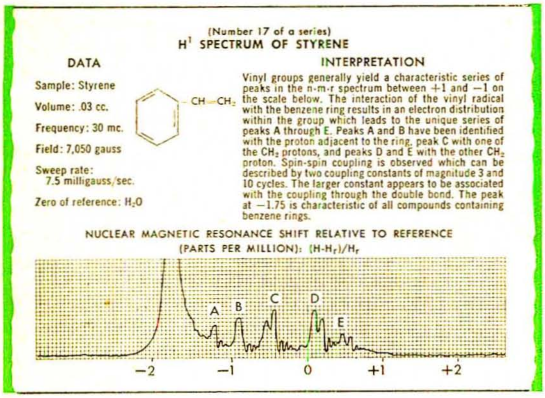
N-M-R at work ... *a 3 year progress report*

(Nuclear Magnetic Resonance)

38

17 of a series . . . 1955



(Number 17 of a series)

H^1 SPECTRUM OF STYRENE

DATA

Sample: Styrene

Volume: .03 cc.

Frequency: 30 mc.

Field: 7,050 gauss

Sweep rate: 7.5 milligauss/sec.

Zero of reference: H_2O

INTERPRETATION

Vinyl groups generally yield a characteristic series of peaks in the n-m-r spectrum between +1 and −1 on the scale below. The interaction of the vinyl radical with the benzene ring results in an electron distribution within the group which leads to the unique series of peaks A through E. Peaks A and B have been identified with the proton adjacent to the ring, peak C with one of the CH_2 protons, and peaks D and E with the other CH_2 proton. Spin-spin coupling is observed which can be described by two coupling constants of magnitude 3 and 10 cycles. The larger constant appears to be associated with the coupling through the double bond. The peak at −1.75 is characteristic of all compounds containing benzene rings.

NUCLEAR MAGNETIC RESONANCE SHIFT RELATIVE TO REFERENCE (PARTS PER MILLION): $(H-H_r)/H_r$

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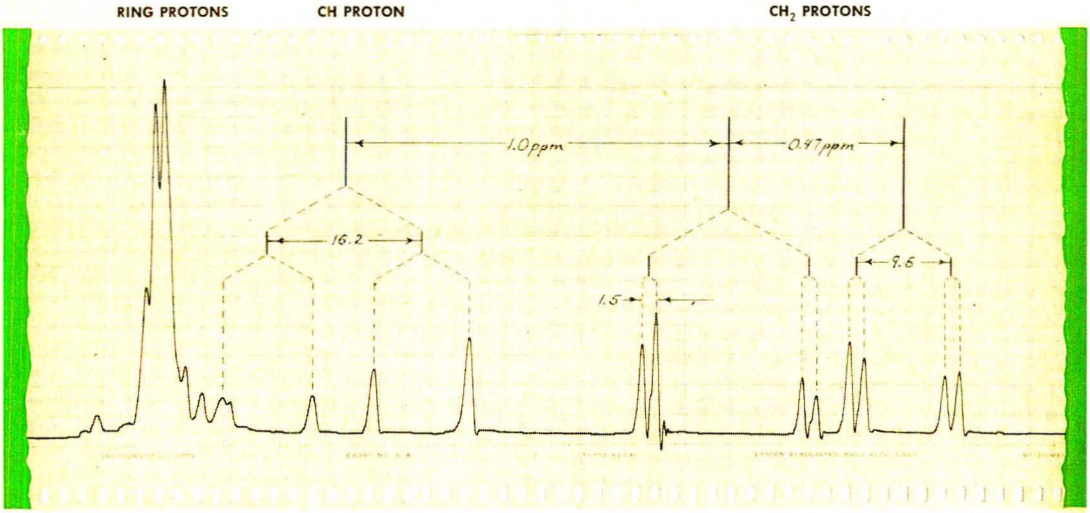
38 of a series . . . 1957 H^1 SPECTRUM OF STYRENE

INTERPRETATION: The application of a higher magnetic field (9400 gauss) and the greatly enhanced resolution obtained with the use of a flux stabilizer has shown that the interpretation given in No. 17 was only partially correct. The spectrum below shows twelve lines in groups of four, corresponding to each of the three vinyl protons coupled to the remaining two. The approximate values of the coupling constants are given below in cycles per second, and the chemical shifts are given in parts per million. It is thought that the largest coupling is associated with the protons which are *trans*— to one another.



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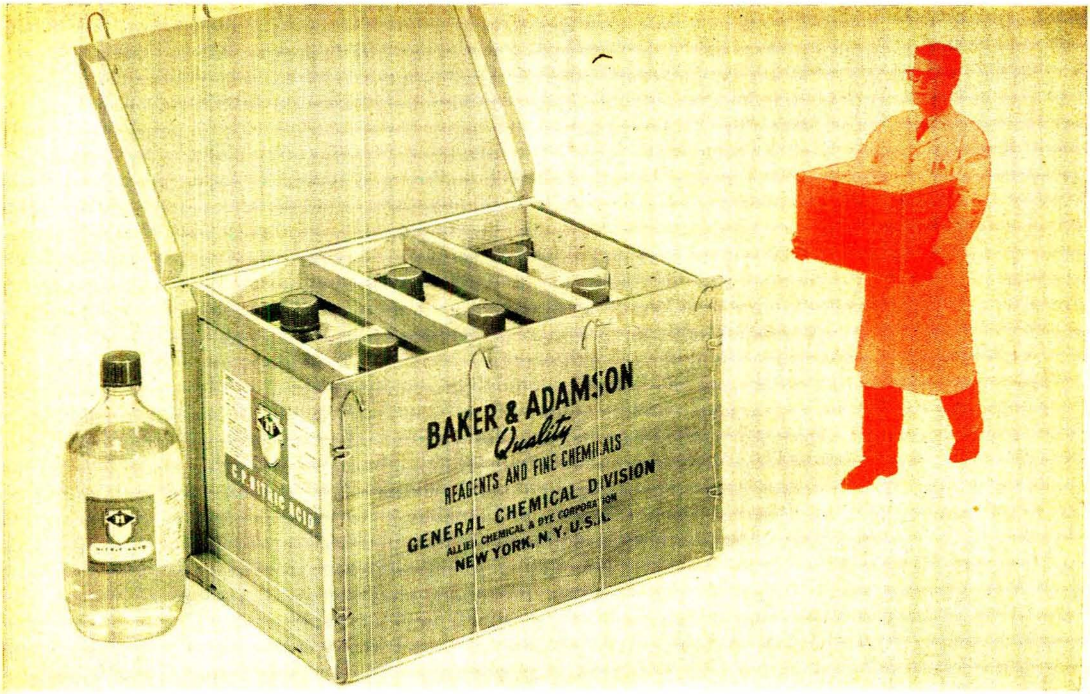

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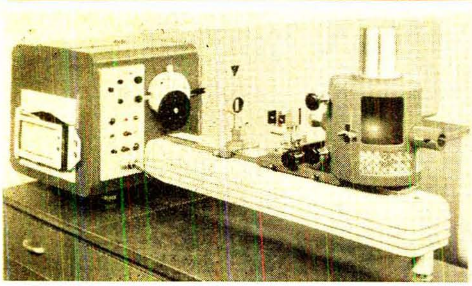


Figure 1. Bausch & Lomb's dual grating spectrograph may also be furnished with a single grating having twice the speed of the gratings normally supplied

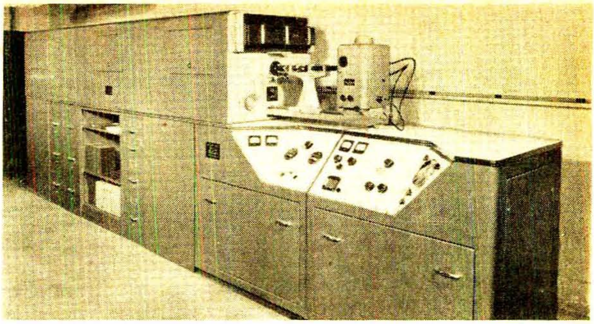


Figure 2. Jarrell-Ash Co. Ebert Spectrograph with the order sorter on the optical bar and the Varisource excitation unit underneath. The order sorter separates various spectral orders simplifying line identification

New Horizons for Emission Spectrochemical Analysis

The field of emission spectrochemical analysis is again on the move. Not content with their extensive role in industry and research, restless spectrographers are reaching out further into new frontiers of analytical chemistry. To appreciate these developments, the author is presenting a bird's-eye view of the over-all field today, summarizing those shortcomings which are so rapidly being overcome

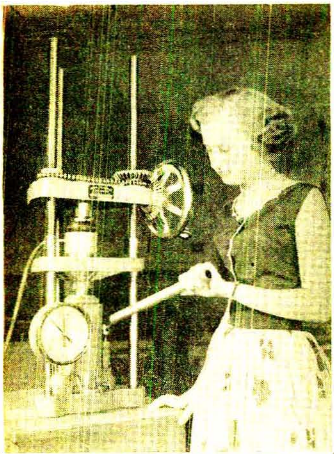
THE emission spectograph is at present capable of direct measurements down to 1 p.p.m. of many elements, especially metals which have simple spectra. For elements with more complex spectra, such as the rare earths, platinum, and trans-uranium groups, the sensitivity is not quite so good, approaching 0.5% concentration for a few. Various preconcentration techniques may be coupled with the spectrographic technique, however, to improve sensitivity. Simply ashing an organic substance, for example, will permit a hundredfold improvement in the limit of detection.

These detection thresholds are being pushed back further through advanced instrumentation and techniques. Two new spectrographs (Figures 1 and 2) with vastly higher dispersion and resolution than available heretofore are said to offer much more sensitivity. Increased dispersion and resolution result in far greater line-to-background or signal-to-noise ratios. One of these instruments may be ordered with an oversize grating measuring 4 × 4 inches, which increases the calculated speed of the instrument to $f/17$. It is claimed that the instrument so modified has an actual speed about twice that of a medium quartz instrument rated at $f/12$. Here then is a spectrograph combining speed and resolution, another big stride forward in trace-element technology.

In this trace-element safari, accessories not long ago considered laboratory relics are being revived. One is the hollow cathode source which, by entrapping atoms in a closed container, permits them to be excited over and over to enhance their limit of detection. Moreover, the hollow cathode operates at a low pressure and temperature, increasing the signal-to-noise ratio still further. Spectral lines from the hollow cathode source are sharp, without background or self-reversal, and may be detected at a concentration level some 100 times below that with a d.c. arc. (see Figure 3). The d.c. arc is normally considered the most sensitive source.

Techniques, too, are destined for revolutionary changes. G. H. Morrison, of the Sylvania Chemistry Laboratory in Flushing, N.Y., has recently announced an analytical method which has already proved immensely useful in evaluating transistor-grade silicon. Through the use of an ion exchange membrane (see Figure 4) followed by spectrographic analysis, the method is capable of detecting 0.001 p.p.m. of boron, slicing off three decimal points from existing methods. Of even greater significance, the system seems adaptable to many other elements in other matrices. Differing from conventional concentration techniques, Morrison's converts the matrix to a crystalline form so that

ARTHUR J. MITTELDORF, president of Spex Industries, Inc., manufacturer of spectrographic standards and accessories, graduated from Brooklyn College (1942) and did graduate work at the Polytechnic Institute of Brooklyn and Illinois Institute of Technology. He has worked for Bendix Aviation, National Lead Co., Armour Research Foundation, and Jarrell-Ash. His work has been primarily in the field of spectrochemistry. He has been active in promoting the interchange of spectrographic information among spectrographers. He is a member of the ACS, Optical Society of America, Society for Applied Spectroscopy, and an ASTM subcommittee on standardization of spectrographic equipment and tools.



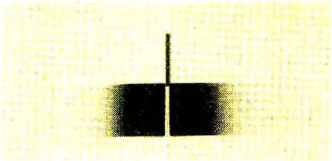


Figure 3. Comparison of hollow cathode discharge and d.c. arc discharge of the lithium lines at 6707 A., using a JAco-Ebert spectrograph in the 4th order at 0.77 A./mm. reciprocal dispersion

the wanted element may be extracted with water. Extremely low blanks are claimed with this technique (see page 892).

New photographic emulsions are also getting their share of attention. The same emulsions used to photograph a pretty young lady by the flickering light of her escort's cigarette lighter are beginning to aid the spectrographer in photographing the weak spectral lines produced by a few elusive atoms.

Individually, techniques and instrumentation such as those discussed offer a significant, but perhaps not startling, improvement in sensitivity. Used together, however, their power and effects compounded, they represent real progress in determining trace elements. A trace element may soon be regarded as one in the parts per billion range or below rather than parts per 100,000.

Extension of Scope

It is often stated that the spectrographic method is confined to the determination of the metals. These, plus such determinable nonmetals as phosphorus and fluorine, number about 70 elements. The rare gases, carbon, oxygen, nitrogen, hydrogen, and the halogens remain aloof, unwilling to have their noses counted spectrographically.

The hold-out elements are, however, gradually being brought into the fold. V. A. Fassel and associates at Iowa State College have recently developed a novel procedure for measuring the oxygen content of metals, a method which promises to outperform standard vacuum fusion techniques. The oxygen is released from the sample by using a d.c. arc in an enclosed chamber containing a fixed pressure of argon.

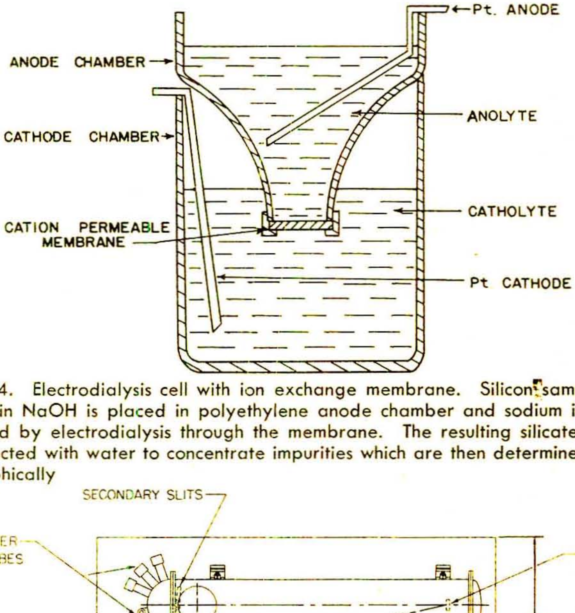


Figure 4. Electrodialysis cell with ion exchange membrane. Silicon sample dissolved in NaOH is placed in polyethylene anode chamber and sodium ions are removed by electrodialysis through the membrane. The resulting silicate matrix is extracted with water to concentrate impurities which are then determined spectrographically

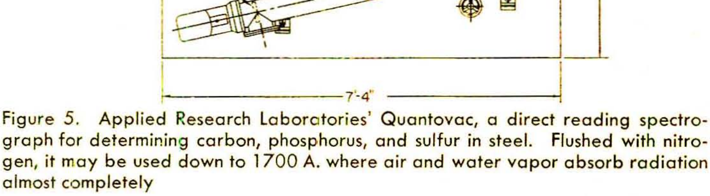


Figure 5. Applied Research Laboratories' Quantovac, a direct reading spectrograph for determining carbon, phosphorus, and sulfur in steel. Flushed with nitrogen, it may be used down to 1700 A. where air and water vapor absorb radiation almost completely

Intensity ratios of an oxygen line to an argon line are plotted as a function of the oxygen content. When methods like this find their way to production, higher-conductivity copper, less brittle steel, and titanium are certain to result.

Another approach toward determining several elements is by tracking them down in the far, or vacuum, ultraviolet. Reserved for pure research until just a few years ago, this region is being opened up through commercial instrumentation. One new spectrograph (Figure 5) skirts high vacuum problems by using a spectrograph flushed with nitrogen which is transparent down to around 1700 A. This instrument is specifically designed to determine photoelectrically the carbon, phosphorus, and sulfur content of steels. A second, more general instrument (Figure 6), may be used either photoelectrically or photographically from 500 to 2000 A. where there are strong lines of nitrogen, the halogens, oxygen, selenium, and the rare gases.

Improvement in Analytical Accuracy

At present, the best accuracy obtainable spectrographically is within ±1%, an order of magnitude poorer than the best wet chemical accuracy. This degree of accuracy, while satisfactory for the spectrographic monitoring of thousands of ingots of ferrous and nonferrous alloys poured every day, is not adequate for deciding exactly how much the producer owes the mine for a carload of tungsten ore sold on the basis of its metal content. Nor is it accurate enough for full understanding of physiological reactions which maintain body temperature, pulse rate, and blood composition, to better than ±0.5%.

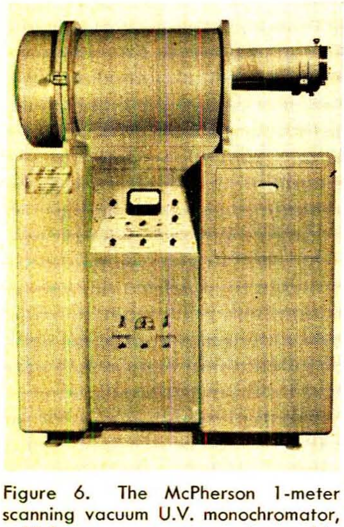


Figure 6. The McPherson 1-meter scanning vacuum U.V. monochromator, a high-vacuum spectrograph capable of photoelectric or photographic detection, is being used both in emission and absorption down to around 500A

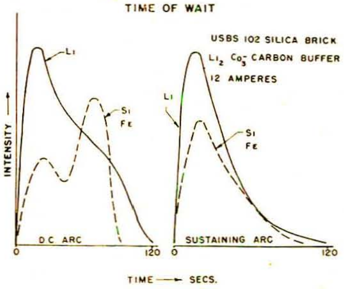


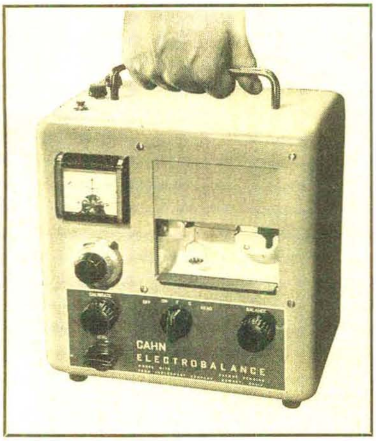
Figure 7. Comparison of typical moving-plate curves of the d.c. arc with those of the new National Spectrographic Laboratories' sustaining arc. The similarly shaped curves for lithium, silicon, and iron in the latter are related to the improved reproducibility claimed for the sustaining arc

Progress in improving spectrochemical accuracy has been continual over the years. More stable circuitry, more efficient sampling, better analytical techniques, the availability of purer materials, and more reliable standards have all aided in upping accuracy to its present values. There is every reason to believe that such slow but steady improvements will continue and will result in an extension of spectrochemical analysis to many new applications.

One interesting example of such an improvement is the sustaining arc source, a modified a.c. arc. This source is claimed to approach both the high sensitivity of the d.c. arc and the high precision of the spark source. In the past, high sensitivity and high precision were usually obtained at the expense of one or the other. With the sustaining arc, elements will often emit their spectral energy at the same rate (see Figure 7) where in contrast, they distill selectively in using a d.c. arc.

Development of Universal Analytical Methods

Paradoxically, the spectrograph has proved most effective in analyzing materials of known composition. When the spectrographer is told a particular sample is of 24S aluminum, he can quickly confirm this and, in but a few minutes, calculate the concentrations of the elements present. But hand a spectrographer a sample labeled merely "ore" and his analytical task is far more



difficult. Still lacking is a method whereby all their constituent elements can be rapidly and quantitatively determined in such complete unknowns.

In this area, progress has been made through the recent introduction of standards claimed to yield semiquantitative accuracy. Using a dilution technique whereby all samples and standards are essentially reduced to a common matrix, a method is specified with which the spectrographer can calculate concentrations accurately to ±30% of the amounts present.

Improvement in Speed of Analysis

We hear much about the speed of spectrochemical analysis: less than 1 minute by photoelectric and about 20 minutes by photographic techniques. Not many years ago, management was satisfied when the same analyses were performed in a day or so. In their relentless quest for reduced costs, management now talks about continuous (and instantaneous) process control analysis. An example is an instrument which would measure the nitrogen content of corn feed and thus provide automatic control of the protein content by hooking up the flow valves to a direct-reading spectrograph. Another is an instrument which would control the feed of nickel to an electric furnace and stop it just when the minimum concentration called for in the stainless steel specifications is reached.

Equipment manufacturers have already found some of the answers to these demands by management and, undoubtedly, have many more on the drawing boards. One manufacturer, for example, claims a significant advance in analytical speed with his new combination photographic-photoelectric in

Figure 8. Read-out console used with the Baird-Atomic, Inc. direct reading attachment converts their 3-meter spectrograph to a photoelectric instrument

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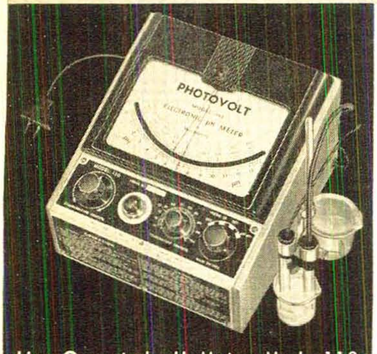

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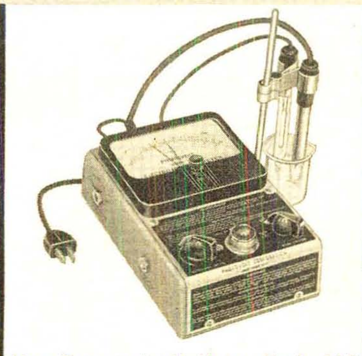
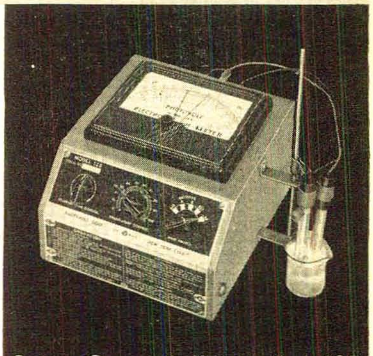
Scale Length 7", Precision 0.02
Price $200.00, see Bulletin 105

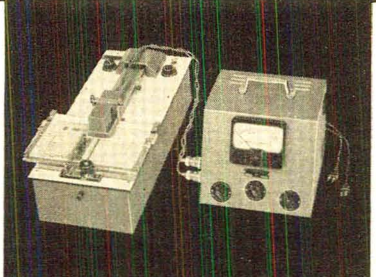


Line-Operated pH Meter Mod. 115
Scale Length 4", Precision 0.05
Price $130.00, see Bulletin 225

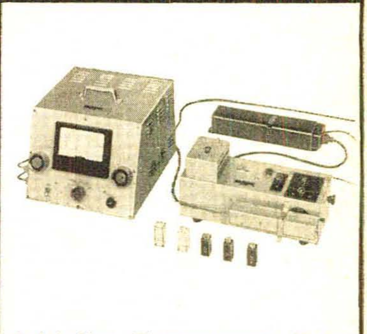


Battery-Operated pH Meter Mod. 125
Scale Length 5½", Precision 0.03
Price $160.00, see Bulletin 118

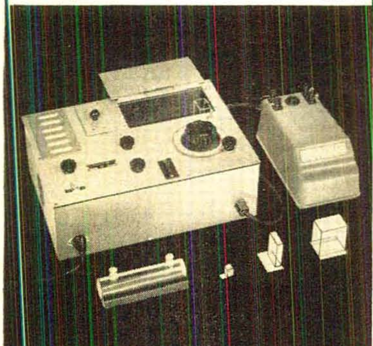
Reflection Meter Mod. 610
for Paper, Color Printing, Enamel,
Paints, Textiles, see Bulletin 605.



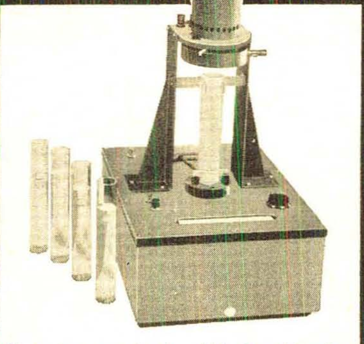
Electronic Densitometer Mod. 525
for Paper Electrophoresis and
Chromatography, see Bulletin 800



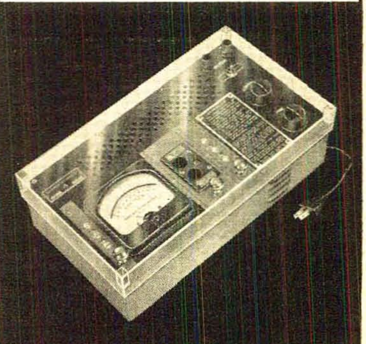
Multiplier Fluorescence Meter
Mod. 540, for Highest-Sensitivity
Fluorimetry, see Bulletin 392



Colorimeter Mod. 402-E, adaptable
for Nephelometry, Fluorimetry, and
Reflectometry, see Bulletin 420



Colorimeter Mod. 450 for Nessler
Tubes, for Water Analysis, Sugar
Whiteness Tests, etc., see Bull. 450



Colorimeter Mod. 401 for General
and Clinical Colorimetry and Turbidimetry, see Bulletins 406 and 409

Also: Multiplier Photometers, Exposure Photometers for Photomicrography, Hemoglobinometers, Glossmeters, Polarimeters, Foot-Candle Meters, Interference Filters, Mirror Monochromators

PHOTOVOLT CORPORATION

95 Madison Ave. **New York 16, N. Y.**

strument. While such instruments have been available in the past, the photoelectric part has lacked stability. This new one (Figure 8) uses a servo system to keep the exit slits centered on the spectral lines. It also features a device for rapidly locating a line photoelectrically. This instrument will aid research spectrographers in handling routine problems. Ordinarily used with a photographic plate, the spectrograph is converted to a direct reader for routine analysis by switching the cassette to a photoelectric detector box. It is claimed that, once calibrated, the box may be set up in as little as 10 minutes.

While photoelectric detection is unrivaled for speed, it seems that photographic detection will be necessary for nonroutine problems. Here a new development is rapid processing. Using hot, concentrated sprays, a plate may be completely processed and dried in less than 30 seconds. Moreover, reproducibility is said to be better than that using the best present-day spectrographic processing methods.

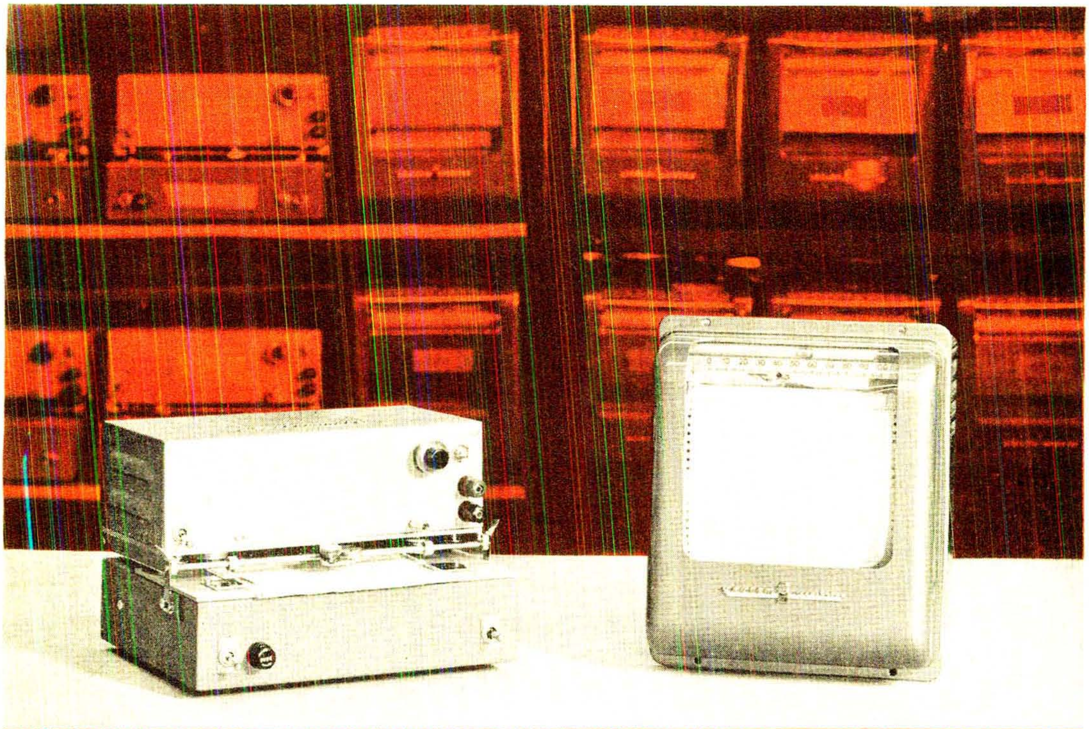
Any summary of the fundamental contributions of spectrographic analysis would encompass sciences as diverse as astronomy and zoology. Indeed, with regard to astronomy, our knowledge of the temperature, composition, velocity, size, age, and other characteristics of heavenly bodies is based largely on spectrographic data. In the field of medicine, the spectrograph has contributed vital information concerning the essentiality of such trace elements as zinc and cobalt. In geology, spectrographic analysis is an invaluable tool for correlating formations and discovering new mineral deposits.

In electricity, the spectrograph is aiding materially the rapid progress being made in semiconductor research. Another electrical area with great future promise is superconductivity—the ability of certain metals such as lead, to conduct electricity at temperatures near absolute zero with no resistance whatsoever. To date, this phenomenon is mainly an unexplained laboratory curiosity, although an application in digital computers is currently being explored.

An intriguing potentiality is the application to transmission of power. Already, electrical engineers have calculated that, if a metal is found which exhibits superconductivity at around −200° C., it will be economically advantageous to use it in certain long-distance power lines by cooling with a jacket containing liquid nitrogen. If such a metal or alloy is ever discovered, it is likely that the emission spectrograph will be credited with a tremendous assist.

Varian Strip Chart Recorders

POTENTIOMETER PERFORMANCE* AT MODERATE COST



Varian G-10 — Portable for laboratory or bench use where chart accessibility is of prime importance. Base price $340.

Varian G-11 — For panel, rack or portable use; designed for OEM, lab or field for long-term monitoring. Base price $450.

* The servo-balance potentiometer method has long been used in expensive recorders to achieve superior stability, sensitivity, ruggedness and high input impedance. Use of servo balancing systems assures full realization of these inherent advantages by providing ample power independent of the source being measured. Now Varian offers you recorders of moderate cost using this time-proven principle.

VARIAN SPECIFICATIONS:

- Spans as low as 10 mv
- Limit of error 1%
- Maximum source resistance 50K ohms or higher
- Balancing times: 1 second or 2.5 seconds on G-10; 1 second on G-11

WRITE TODAY FOR COMPLETE SPECIFICATIONS

Varian recorders are sold and serviced throughout the free world by representatives in principal cities.

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For further information, circle number 23 A on Readers' Service Card, page 77 A

RCA Electron Microscope Provides National Aluminate Corporation with the Satisfactory Way to Measure Size of Silica Particles in "Nalcoag."*

Silica particles in "Nalcoag." Magnification 65,000X.

The effects of various particle sizes in this product's stability and performance were known. But, until the RCA Electron Microscope was used, there was no satisfactory method of measuring the *size* of the particles. Now, with the electron microscope it's easy! And "Nalcoag" can be produced in the particle size most suitable for the use intended. This is a product improvement directly traceable to microscope studies. The RCA Electron Microscope is also used by this company for other particle size determination, for studies of diesel fuel and miscellaneous research.

Electron Micrograph of sludge particles in diesel fuel oil. Oil treatment has been improved considerably by new information obtained on the character of sludge-forming materials.

Hundreds of RCA Electron Microscopes are already in use. They have opened many new avenues of exploration in the field of chemistry, metallurgy, medicine, bacteriology and biology. The technique of operation is readily acquired by any competent technician. Compact, one-piece units, these amazing microscopes can provide useful photographic enlargements up to 300,000X.

For further information on the Electron Microscope, write to RCA, Dept. T-11, Building 15-1, Camden, N.J. In Canada: RCA VICTOR Company Ltd., Montreal.

**Registered trademark of National Aluminate Corporation for a colloidal silica, used as a binder in making molds for precision investment casting.*

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RADIO CORPORATION of AMERICA
Camden, N. J.

For further information, circle number 24 A on Readers' Service Card, page 77 A

Analytical Congress in Scotland

The Congress on Modern Analytical Chemistry in Industry will be held at St. Andrews University June 24 to 28. Sponsor is the Scottish Section, Society for Analytical Chemistry.

The program appears below:

Monday, June 24

Opening remarks by Chairman of the Scottish Section, Magnus Pyke.

Section I. Analysis in Modern Industry

Congress Lecture: "Analytical Chemistry in Industry." James Craik, Chairman, I.C.I., Ltd.

Analytical Research in the D.S.I.R. in Relation to Industry. G. R. Davies, Chemical Research Laboratory.

Modern Analytical Methods in the Iron and Steel Industry. B. Bagshawe, Brown Firth and Co., Ltd.

Steelworks Analysis Using Spectrographic Methods. D. Manterfield, Steel, Peech and Tozer, Ltd.

Tuesday, June 25

Chemical Problems in the Electrical Industry. Contribution of Analysis as a Research Service. R. C. Chirnside, General Electric Co., Ltd.

Application of Physical Methods of Analysis in the Gas Industry. A. B. Densham and G. Gough, North Thames Gas Board.

Some Recent Work in the Department of the Government Chemist. G. M. Bennett, Government Chemist.

Analytical Developments in a Pharmaceutical Laboratory. D. C. Garratt, Boots Pure Drug Co., Ltd.

Section II. Application of Some Newer Analytical Techniques in Industry

Congress Lecture: "Analysis and Food." L. H. Lampitt, J. Lyons and Co., Ltd.

Wednesday, June 26

Recent Progress in Separating Substances of High Molecular Weight. R. L. M. Synge, Rowett Research Institute.

Emission Spectroscopy in Industrial Analysis. M. Milbourn, I.C.I., Ltd.

Analytical Chemistry and Medical Science. A. T. James, Medical Research Council.

The Analyst and Infrared Spectroscopy. A. E. Martin and Howard Grubb, Parsons and Co., Ltd.

Modern Analytical Chemistry in Relation to the Plastics Industry. J. Haslam, I.C.I., Ltd.

Modern Analytical Chemistry and the Precious Metals. A. R. Powell, Johnson Matthey & Co., Ltd.

Analytical Research in the Nobel Division of I.C.I. A. F. Williams, I.C.I., Ltd.

Thursday, June 27

Process Analytical Control. B. W. Bradford, I.C.I., Ltd.

Section III. Developments in Analysis for New Problems in Industry

Congress Lecture: "New Analytical Reagents and Their Applications in Industrial Plant Control Operations." G. F. Smith, University of Illinois.

Use of Radioactive and Stable Isotopes in Industrial Analytical Problems. A. A. Smales, U.K. Atomic Energy Authority.

An Approach to Automatic Analytical Measurements. D. A. Patient, Baird and Tatlock, London, Ltd.

Friday, June 28

Polarography. G. C. Barker, G. W. C. Milner, and H. Shalgosky, U.K. Atomic Energy Authority.

Application of Gas Chromatography in the Petroleum Industry. A. I. M. Keulemans, Koninklijke Shell Lab., Amsterdam.

The Geochemical Approach to Prospecting for Minerals. C. F. Davidson, St. Andrews University.

Information has been received that registrations have been fully subscribed but that it is expected that the proceedings will be published in due course.

Further details are available from the Society for Analytical Chemistry, 14 Belgrave Square, London, S.W. 1, England.

Society for Analytical Chemistry Growing

Membership in the Society for Analytical Chemistry is now up to 1870, an increase of 28 over last year, members were told at the 83rd annual general meeting, held at London, March 1. J. H. Hamence was elected president for the forthcoming year, succeeding K. A. Williams.

During the previous year the society held six regular meetings and a meeting with the Food Group of the Society of Chemical Industry. Local sections and groups held 35 meetings.

A number of methods for the analysis of trade effluents were issued and a study of methods of assay for crude drugs was initiated.

New Microchemical Journal

The new *Microchemical Journal* is now being published by Interscience Publishers, Inc., under the auspices of the Metropolitan Microchemical Society. The editor is Nicholas D. Cheronis, Brooklyn College. Members of the editorial board are: John A. Means, Alfonso G. Mistretta, T. S. Ma, A. A. Benedetti-Pichler, and Bella Rosenfeld.

Two issues totaling about 360 pages are scheduled for 1957. Subscription price is $9.60. Members of the Microchemical Society get a preferred rate of $4.00.

In addition to publishing articles concerning the philosophy, ideas, and techniques of microchemical procedure as applied to all areas of the physical and biological sources, the journal will include abstracts of articles from a wide variety of journals.

Further details are available from Interscience Publishers, Inc., 250 Fifth Ave., New York 1, N. Y.

Beckman Instruments Establishes Process Instruments Division

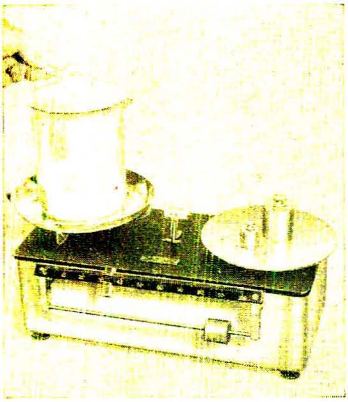
Beckman Instruments, Inc., has established a new Process Instruments Division with headquarters at Fullerton, Calif., and a manufacturing and engineering facility at Ronceverte, W. Va.

A rapid increase in sales of industrial and process control instruments has led to this step, Arnold O. Beckman, president, stated. Mark H. Howlett, former sales manager for scientific instruments, will head the new Process Instruments Division.

Fisher Acquires Machlett

Fisher Scientific Co. has purchased the laboratory apparatus and supply business of E. Machlett and Sons.

Machlett, a 60-year-old firm, will continue at its present location, 220 East 23rd St., New York, as a division of Fisher.



NEWS

New Will Corp. Plant

Will Corp., with headquarters in Rochester, N. Y., has announced the establishment of its 6th and newest laboratory supply and service center at South Charleston 3, W. Va. Will handles equipment, instruments, supplies, and reagent chemicals of 900 manufacturers. Other centers are located at Atlanta, New York, Baltimore, and Buffalo.

New Computing-Data Processing Firm Established

Datics Corp., a new organization offering services in electronic computing and data processing, has been established. The firm, located at 6000 Camp Bowie Blvd., Fort Worth, Tex., offers service in solving scientific and industrial problems on a contract basis. Kenneth L. Austin, president, has served with Douglas Aircraft, Consolidated Engineering, and ElectroData Corp.

Brooklyn Poly Offers Special Summer Course

Advanced professional instruction in use of specialized physical tools in chemistry and physics will be given at a "New Summer Laboratory Program for Industry." Sponsor is the Polytechnic Institute of Brooklyn. Courses will be

ANALYST'S CALENDAR

June 10 to 14	**Symposium on Molecular Structure and Spectroscopy,** The Ohio State University, Columbus, Ohio. *Contact:* Harald H. Nielson, Ohio State University, Columbus, Ohio. Ref. May, page 44 A
June 13 to 15	**10th Summer Symposium, ACS Analytical Chemistry Division and** ANALYTICAL CHEMISTRY, Purdue University, Lafayette, Ind. Ref. April Part I, page 21 A
June 16 to 21	**Annual Meeting, ASTM,** Chalfonte-Haddon Hall, Atlantic City, N. J. *Contact:* American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa. See page 28 A.
June 24 to 28	**Congress on Modern Analytical Chemistry in Industry,** St. Andrew's University, Scotland. See page 25 A.
July 10 to 17	**4th General Assembly and International Congress, International Union of Crystallography,** McGill University, Montreal, Canada.
July 16 to 25	**XIXth Conference and XVI Congress, International Union of Pure and Applied Chemistry,** Paris, France. See page 30 A.
July 26	**Conference on Control of Chemical Additives in Food.** Sponsors: Society for Analytical Chemistry, Association of Public Analysts (of Great Britain), Food Law Institute of the U.S., American Bar Association (Division of Food, Drug and Cosmetic Law), and Society of Chemical Industry (Food Group). Royal Institution, London, England. *Contact:* Society for Analytical Chemistry, 14 Belgrave Square, London, S.W. 1.

Coming Events

Aug. 7 to 9—Sixth Annual Conference on Industrial Applications of X-Ray Analysis, Denver Research Institute, University of Denver.

Aug. 20 to 22—Conference on Liquid Scintillation Counting, Northwestern University, Evanston, Ill. See page 34 A.

Aug. 26 to 30—Eighth Annual Infrared Spectroscopy Institute, Fisk University, Nashville, Tenn. See page 34 A.

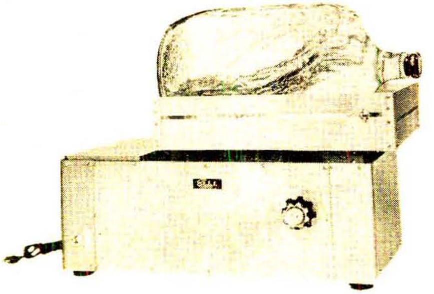
Aug. 28 to 30—International Symposium on Gas Chromatography, Instrument Society of America, Michigan State University, East Lansing, Mich.

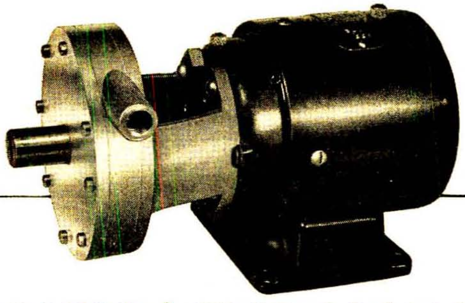
Sept. 8 to 13—132nd National Meeting, ACS, New York, N. Y.

Sept. 11 to 13—Fourth Ottawa Symposium on Applied Spectroscopy, Canadian Association for Applied Spectroscopy, Victoria Museum, Ottawa.

Oct. 14 to 16—Association of Official Agricultural Chemists, Annual Meeting, Shoreham Hotel, Washington, D. C.

Nov. 2 to 10—International Congress and Exhibition of Measuring Instrumentation and Automation, Nordwestdeutsche Ausstellungs-Gesellschaft m. b. H., Ehrenhof 4, Düsseldorf, Germany. See page 39 A.






Eastern
MIDGET
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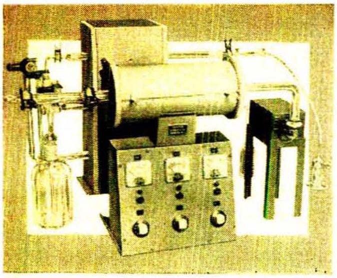

New, improved

OXYATOR

now permits **continuous operation** in the determination of Oxygen in metal

Research by Ledoux & Company has resulted in this new and advanced Model 3TG-2 Oxyator. Now for the first time, continuous operation has been made possible. This new and important feature incorporates the use of the multiple sample loading arm which permits the introduction of a new sample immediately upon the completion of the previous determination. The results are greater speed and lower costs in the determination of Oxygen in metals.

FEATURES:

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★ **Excellent Reproducibility**

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★ **Simplified Operation:** With proper training, technicians can obtain accurate results.

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Circle No. 28 A-1 on Readers' Service Card, page 77 A

held at various times between June 3 and August 12.

The schedule of courses is as follows:

June 3 to 7. Applied Infrared Spectroscopy.
June 3 to 7, 10 to 14, 17 to 21. New Polymerization Techniques and Stereospecific Polymers.
Evening lectures—same dates.
June 10 to 21. Industrial Applications of X-ray Diffraction.
July 8 to August 12. Application of Ion Exchange Resins and Membranes.
June 24 to 28. New Electrolytic Techniques.

Full details are available from Mrs. Doris Cattell, Summer Laboratory Program, Polytechnic Institute of Brooklyn, 99 Livingston St., Brooklyn 1, N. Y.

ASTM Meets June 16 to 21

Symposia on determination of gases in metals, spectrochemical analysis for trace elements, and determination of dissolved oxygen in water will constitute part of the annual meeting program of the American Society for Testing Materials. The meeting will be held at the Chalfonte-Haddon Hotel, Atlantic City, June 16 to 21.

In addition to 32 technical sessions, 50 or more of ASTM's main technical committees and subcommittees have also scheduled a host of meetings.

Papers of possible interest to analysts are set forth below. The program is still tentative.

Tuesday, June 18, 9:30 A.M.

Symposium on Determination of Gases in Metals

Two Apparati for Determination of Gases in Metals. D. L. GUERNSEY AND R. H. FRANKLIN, Massachusetts Institute of Technology.

Application of Vacuum Fusion to Gas-Metal Studies. W. G. GULDNER AND A. L. BEACH, Bell Telephone Laboratories.

Oxygen Determinations Using a Platinum Bath and Capillary Trap, W. G. SMILEY, Los Alamos Scientific Laboratory, University of California.

Bromination-Carbon Reduction Method for Determination of Oxygen in Metals. MAURICE CODELL AND GEORGE NORWITZ, Pitman-Dunn Lab., Frankford Arsenal.

Emission Spectrometric Determination of Oxygen in Metals. V. A. FASSEL, W. Z. GORDON, AND R. W. TABERLING, Institute for Atomic Research and Department of Chemistry, Iowa State College.

Tuesday, June 18, 2:20 P.M.

Symposium on Spectrochemical Analysis for Trace Elements

Emission Spectrometric Determination of Oxygen in Metals. V. A. FASSEL, A. GORDON, AND R. W. TABERLING, Institute for Atomic Research and Department of Chemistry, Iowa State College.

Trace Analysis by Means of the Graphite Spark. JAMES M. MORRIS AND FRANCIS X. PINK, Metal Hydrides, Inc.

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locates and measures radioactive constituents
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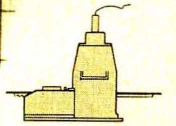

Now . . . you can use in your laboratory the same precise technique that tests the purity of isotope labeled compounds in Tracerlab's own radiochemical operations. With it, you can scan a chromatograph strip . . . then, lay it beside the resulting recording trace for direct identification of each location of radioactivity.

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2. SC-59 Shielded Manual Sample Changer
3. The Outstanding New TGC-14 Carbon Counter, or any other Tracerlab end-window Geiger, scintillation or proportional detector
4. SC-34A Precision Ratemeter or SU-3C Laboratory Monitor
5. Houston Technical Laboratories, or Esterline Angus Recorder.

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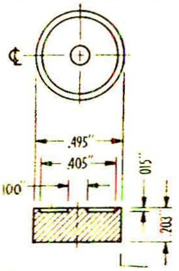

specially designed for testing of light oils and other materials where minimum penetration of the sample into the electrode is desired.

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National Carbon Company also supplies discs for rotation in the vertical plane: Disc L-4072 and Disc L-4075.

Disc L-4072 — Used when large volume of sample must be delivered to point of excitation.

Disc L-4075 — Used when a large volume of sample is not required at point of excitation.

All "National" spectroscopic electrodes and powders — materials and finished product — are tested by the cathode-layer method, most sensitive known in emission spectroscopy. There is no measurable ash in these products.

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For further information, circle number 29 A on Readers' Service Card, page 77 A

Thursday, June 20, 8:00 A.M.

Symposium on Determination of Dissolved Oxygen in Water

Study of the Accuracy of Methods of Testing for Dissolved Oxygen in High Purity Water. K. G. STOFFER, Arabian American Oil Co.

Polarographic Measurement of Dissolved Oxygen. W. W. ECKENFELDER, JR., AND BROTHER CONRAD BURRIS, Manhattan College.

The Beckman Oxygen Analyzer. THOMAS FINNEGAN AND ROSS C. TUCKER, Niagara Mohawk Power Co.

Evaluation of Hartmann and Braun Dissolved Oxygen Recorder. A. J. RISTAINO AND A. A. DOMINICK, U. S. Naval Engineering Experiment Station.

Determination of Dissolved Oxygen by Means of a Cambridge Analyzer. H. A. GRABOWSKI, Combustion Engineering, Inc.

Further details are available from the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa.

IUPAC Congress and Conference

The XVIth International Congress of Pure and Applied Chemistry, to be held in Paris July 18 to 24, promises to be a large meeting with 900 scientific papers sent in by authors of 38 nations. Lectures on physical, inorganic, and organic chemistry will be given in addition to the papers, and four symposia will be held on scientific bases of elastomers, fibers, and plastic tests; electrochemical methods of analysis; criteria for the purity of proteins; and geochemistry. The program for the symposium on modern electrochemical methods of analysis is given below.

Almost simultaneously with the congress, the XIXth Conference of the International Union of Pure and Applied Chemistry will take place July 16 to 25 in Paris. Meetings are scheduled for the committees of the sections on physical, inorganic, organic, biological, and analytical chemistry.

A number of excursions to places of interest in the area will be organized in connection with the congress, and a special program is planned for the ladies.

PROGRAM

July 23

Introduction. I. M. KOLTHOFF, Minneapolis.

Application of Electroanalytical Methods in Fused Salt Media. Chronopotentiometry. H. A. LAITINEN, Urbana.

Ampérométrie avec deux électrodes indicatrices. H. L. KIES, Delft.

Potentiométrie à intensité constante. R. GAUGUN, Paris.

Courbes intensité-potentiel dans les échangeurs d'ions. J. COURSIER, Paris.

Coulometric Determinations. F. CUTA, Prague.

Coulometrie und das Coulomb als uni-

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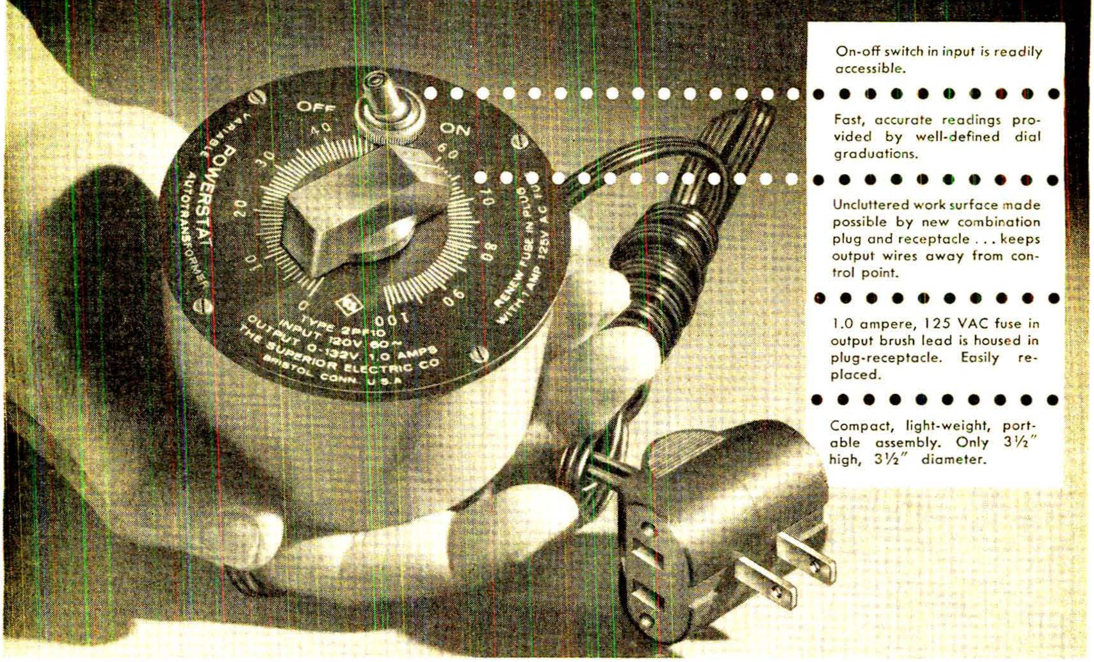

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For further information, circle number 31 A on Readers' Service Card, page 77 A

verselle Urtitersubstanz. P. S. Tutundzic, Belgrade.

Application de la goutte pendante de mercure à l'analyse quantitative de minimes quantités de différents ions. V. Kemula, Varsovie.

Anodic Stripping Voltammetry with Mercury Electrodes. Potential-step and Current-step Methods. G. Mamantov, P. Papoff, and P. Delahay, Baton Rouge.

July 24

Rotated Dropping Mercury Electrode. I. M. Kolthoff and Y. Okinaka, Minneapolis.

The Use of the Rotated Dropping Mercury Electrode in Polarographic Analyses and Amperometric Titrations of Micromolar Solutions. Nobuyuki Tanaka, Sendai.

Cinètique d'adsorption et processus à l'électrode. P. Delahay, Baton Rouge.

Electroseparation of Traçes of Elements Using Potentiostats. L. Rogers, R. C. DeGeiso, and C. F. Morrison, Jr., Cambridge, U. S. A.

New Techniques in Radiological Determinations Using Gamma Scintillation Spectrometry and Polarography. L. Love, San Francisco.

Eine neue Theorie der Elektrolyse und der Redoxydationen. A. Schleicher, Aachen.

Oszillopolarographische Mikroanalyse. R. Kalvoda, Prague.

Square Wave Polarography and some related techniques. G. C. Barker, Harwell.

Oszillopolarographische Analyse. von Pleticha, Prague.

Oszillopolarographische Analyse. H. Berg, Jena.

Anwendungmöglichkeiten der Hochfrequenzmesstechnik in der analytischen Chemie. F. Oehme, Jena.

Newer Methods for the Measurement of electrolytic Conductivity. V. S. Griffiths, London.

Titrimètre à haute fréquence. J. Courteix and Y. Conseiller, Paris.

Emploi du courant alternatif dans les méthodes électrochimiques d'analyse. I. Epelboin, Paris.

Instrumental Analysis Course at RPI

An intensive course in instrumental analysis is being offered by the Department of Chemistry, Rensselaer Polytechnic Institute, August 12 to 23.

This is the second year that this lecture-laboratory program has been offered to chemists and chemical engineers in industry and teaching.

Stephen E. Wiberley and Robert A. Osteryoung of RPI will direct the course. Lecturers will include experts in the fields of x-ray analysis, determination of organic structures by physical methods, spectrastructure correlations in the infrared, emission spectroscopy, and organic analysis by electrometric methods. Lab work will involve use of a wide variety of instrumentation.

Closing date for registration, which is limited, is August 1. Further details

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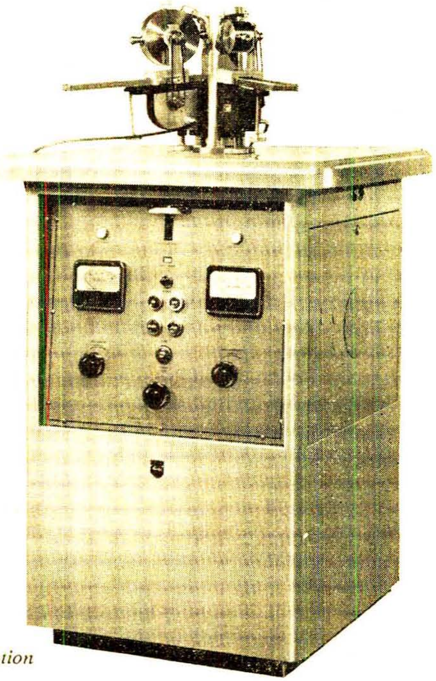

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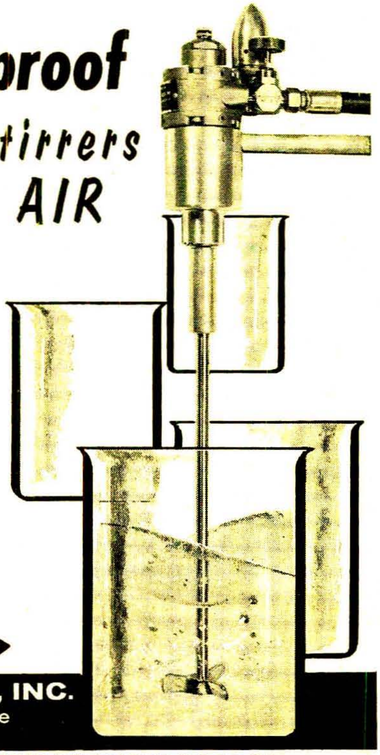


are available from Stephen E. Wiberley, Rensselaer Polytechnic Institute, Troy, N. Y.

Scintillation Counting Conference

Northwestern University will hold a conference on liquid scintillation counting at the Technological Institute, Evanston, Ill., August 20 to 22. A wide range of topics on the theory and application of liquid scintillators is covered by invited papers: coincidence counters, single channel counters, chemistry of liquid scintillators, and applications in biology and medicine, industry, archeology, physics, chemistry, and engineering.

Abstracts of nonsolicited papers should be sent to F. Newton Hayes, Program Chairman, Los Alamos, N.M., by June 1, 1957.

Instrumental Analysis Course at MIT

A one-week special summer program on new developments in instrumental analysis will be offered at the Massachusetts Institute of Technology, August 26 to 30. D. N. Hume and L. B. Rogers, professors at MIT, will direct the course.

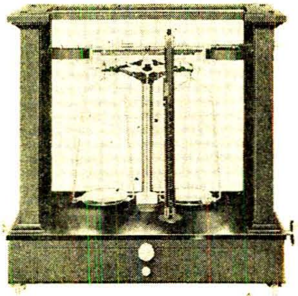
The lectures are aimed at the chemist who has had some experience with common instrumental methods. Topics covered in this advanced survey include: derivative and differential techniques; oscillographic and alternating-current polarography; current-voltage-time methods such as chronopotentiometry, gas chromatography, scintillation counting, spectrofluorometry, photometric titrations, and thermometric titrations. The lectures will cover basis principles and theory as well as typical applications in research and analysis.

Further details are available from the Office of the Summer Session, Massachusetts Institute of Technology, Cambridge, Mass.

Infrared Spectroscopy

Fisk University is sponsoring its Eighth Annual Infrared Spectroscopy Institute during the week of August 26 to 30. The institute is intended to introduce chemists, biologists, physicists, and engineers to infrared spectroscopy and its applications in industrial and academic research and in teaching.

Morning sessions will be devoted to introductory lectures, afternoons to laboratory work, and evenings to lectures on advanced topics. Laboratory facilities include single- and double-



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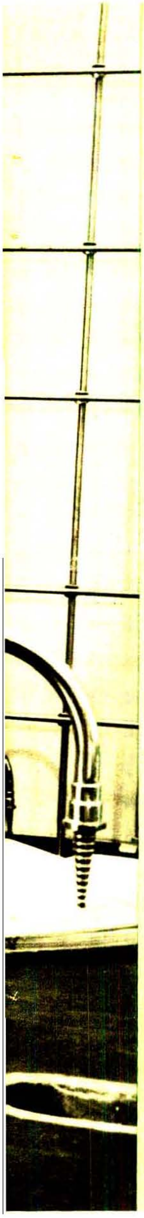

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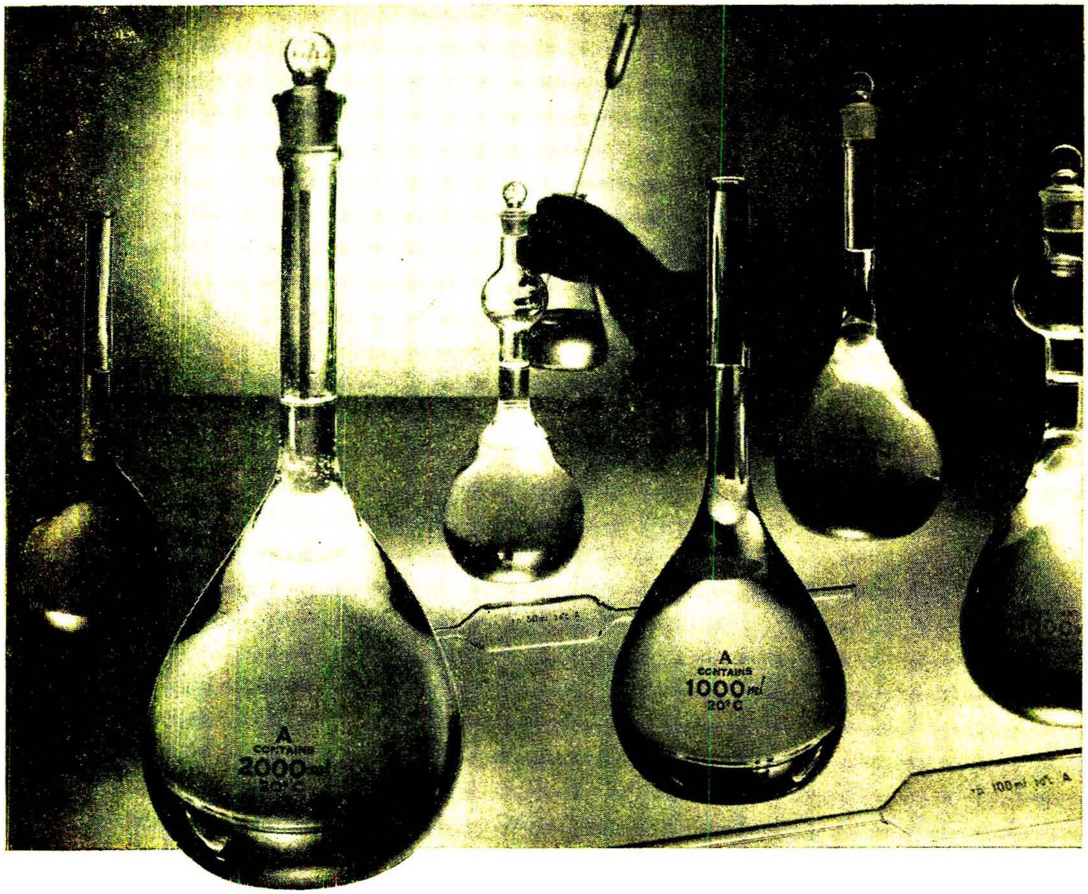
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New ACS Inorganic Division Seeks Papers

The new Division of Inorganic Chemistry of the AMERICAN CHEMICAL SOCIETY, which presented its first program at the recent ACS meeting in Miami, is interested in receiving papers for its program for the fall meeting at New York, September 8 to 13. It is also seeking new members.

Symposia are being organized on new industrial inorganic chemicals and high temperature inorganic chemistry. A symposium on the metal-carbon bond will be held jointly with the Division of Physical and Inorganic Chemistry. Deadline for papers and abstracts is June 1. These should be sent to L. B. Asprey, Los Alamos Scientific Laboratory, Box 1663, Los Alamos, N.M. Dues for membership in the new division may be sent to Dr. Asprey.

International Instrumentation and Automation Congress

The International Congress and Exhibition of Measuring Instrumentation and Automation will be held at Düsseldorf, Germany, November 2 to 10.

The exhibition will feature the latest developments in industrial measurement. The congress will foster exchange of technical views and experience between industrialists, scientists, and others involved in production control, manufacturing, and engineering operations.

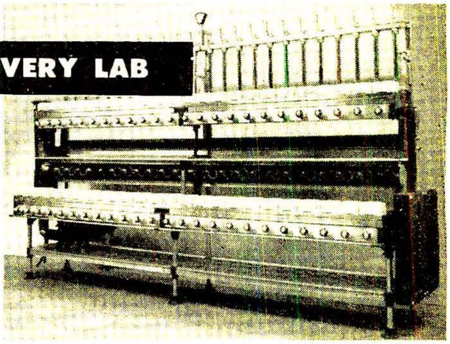
Further details are available from the Nordwestdeutsche Ausstellungs-Gesellschaft m. b. H., Ehrenhof 4, Düsseldorf, Germany.

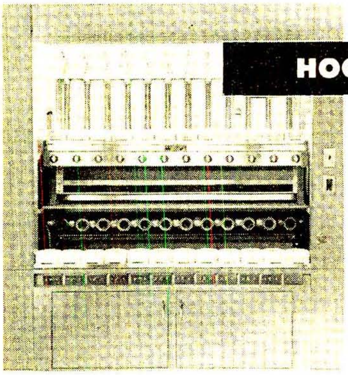
NEW BOOKS

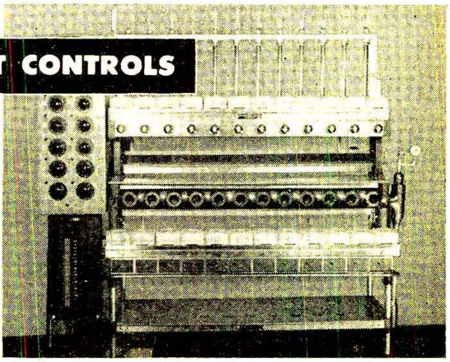
Elementary Qualitative Analysis. *E. B. Middleton* and *J. O. Page.* iv + 93 pages. The Exchange Store, College Station, Tex., 1956. $3.00.

This is a laboratory manual to be used by the student in an elementary qualitative inorganic analysis course. A schedule is outlined for the experiments to be conducted, and instructions for keeping a record of laboratory data are included.

Stepwise procedures are given for carrying out each recommended experiment with helpful annotations following the directions. In this manual, $(C_2H_5)_3$







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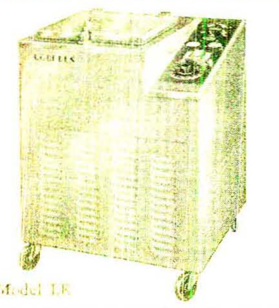

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Semimicro Qualitative Organic Analysis. Systematic Identification of Organic Compounds. *Nicholas D. Cheronis* and *John B. Entrikin.* 2nd edition. xiv + 774 pages. Interscience Publishers, Inc., 250 Fifth Ave., New York 1, N. Y. 1957. $9.00.

Rewritten, reorganized, and expanded to a great extent, this second edition is an up-to-date work on techniques and procedures for semimicro qualitative organic analysis. The authors have revised the chapters on laboratory techniques to include semimicro- and micromethods developed since the publication of the first edition, adapting the procedures to apparatus and equipment found in all organic laboratories. Several chapters have been rewritten and enlarged in order to incorporate recent developments. These include chromatographic procedures, physical constants of organic compounds, new reagents, separation of mixtures, and derivatives.

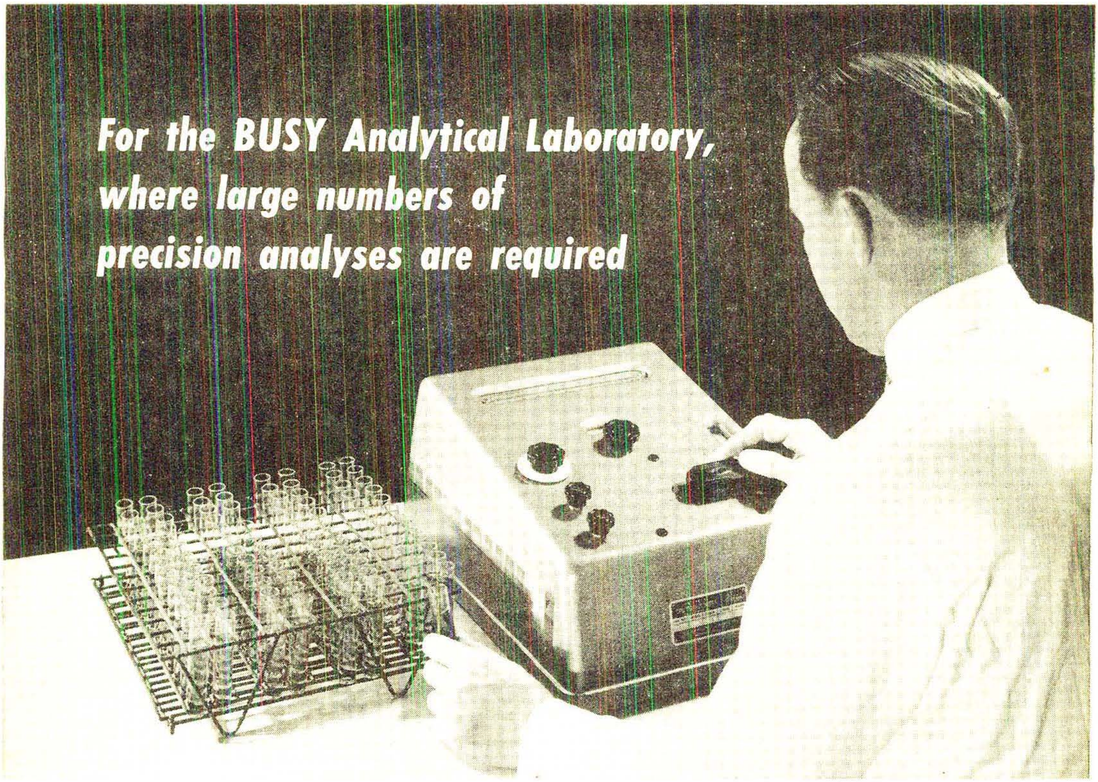
A complete new chapter has been added on the use of Davidson's acid-base indicators, and several hundred new compounds and derivatives have been inserted in the tables of physical constants for organic compounds. The bibliography has been expanded, and the problems and drill exercises have been increased.

With this revised edition, the authors provide a modern text on increasingly important semimicrotechniques for students of qualitative organic analysis, those studying more elementary organic chemistry, and industrial chemists and laboratory workers in related fields.

Introduction to Crystallography. *F. C. Phillips.* 2nd edition. ix + 324 pages. Longmans, Green and Co., Inc., 55 Fifth Ave., New York 3, N. Y. 1956. $6.00.

When the first edition of this book was published ten years ago, it was widely accepted as a useful introduction to the study of crystals. According to the author, this second edition retains most of the text intact with a few minor changes. The chapter on Space Groups has been modified where necessary to bring the symbolism into line with the standards in the new International Tables for X-Ray Crystallography.

The predominant feature of this new edition is the introduction of a new chapter on the Diffraction of X-Rays by Crystals. The inclusion of this phase ties together information given in previous chapters by presenting practical



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application of such information in the study of crystal structures.

The book, generously illustrated with specially drawn figures, is intended to serve as an introductory text for students of mineralogy, chemistry, and physics.

Guide to Qualitative Organic Chemical Analysis. *P. P. Linstead* and *B. C. L. Weedon.* xi + 169 pages. Academic Press, Inc. 111 Fifth Ave., New York 3, N. Y. 1956. $4.50.

Based on the teaching method established at the Imperial College of Science and Technology, London, this textbook outlines, in elementary manner, reliable methods for the detection and characterization of organic compounds.

Since the book is to be considered a "guide" for laboratory use, it is of necessity limited to procedures for identifying simple organic compounds. No attempt has been made to include the less common classes of organic compounds, or the various derivatives of fluorine and phosphorus. Special tests for alkaloids, steroids, and many heterocyclic compounds were also considered too specialized for the purpose of this book.

Within these self-imposed limits, the authors have come forth with a compact, concise book of equal value to the first year chemistry student and the post-graduate research worker looking for a reliable reference.

Modern Methods of Microscopy. *A. E. J. Vickers,* editor. iii + 114 pages + iv pages. Interscience Publishers, Inc., 250 Fifth Ave., New York 1, N. Y. 1956. $3.50.

This volume consists of a series of papers reprinted from *Research,* describing recent advances in the field of microscopy. An introductory paper on modern microscopy is followed by one on developments in electron microscopy. Development and applications of reflecting microscopes are discussed, as are fluorescence, phase contrast, and x-ray microscopy.

Interferometry is the subject of two more papers, and the metallurgical aspects of microscopy also get their share of attention in still another paper. The flying spot microscope and its use in particle analysis are outlined. The book is brought to a close with an article on the polarizing microscope in organic chemistry and biology.

Quantitative Chemical Analysis. *Robert B. Fischer.* xii + 401 pages. W. B. Saunders Co., 218 West Washington Square, Philadelphia 5, Pa. 1956. $5.50.

This text is designed as a basic course in the theory and practice of quantitative chemical analysis, presenting explanations of topics followed by suggested laboratory experiments. Divided into four parts, the book begins with an introduction containing a review of fundamental principles, descriptions of the types of quantitative analysis, the analytical balance, general unit operations and tools of quantitative analysis, and treatment of analytical data. Next follow sections on gravimetric methods, volumetric methods, and optical and electrical methods. The various methods may be covered in the order given or interchanged without any appreciable loss in continuity.

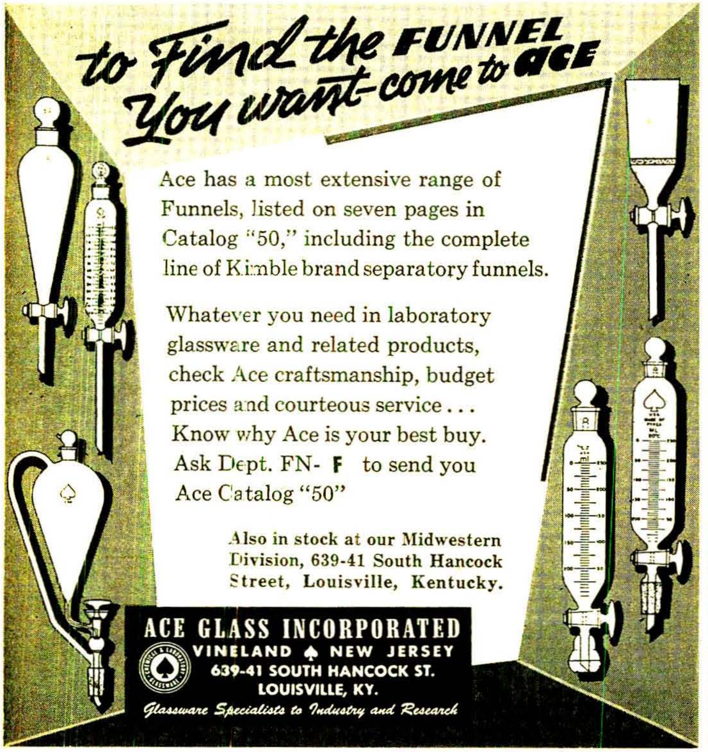
Sufficient laboratory work is given for a two-semester course, along with suggestions from the author for further variations. Each chapter is followed by a list of review questions, problems, and recommended additional reading. The appendixes at the end complete this volume, which can serve as text and laboratory manual in any beginning quantitative analysis course.

Structure Reports for 1940–41. *A. J. C. Wilson,* general editor. *M. C. Baenziger, J. M. Bijvoet,* and *J. Monteath Robertson,* section editors. Vol. 8. viii + 384 pages. N. V. A. Oosthoek's Uitgevers Mij., Utrecht, Netherlands, 1956. 80 Dutch florins.

Published for the International Union of Crystallography, this volume is intended to fill the gap between the last issue of Strukturbericht (1939) and the first issue of Structure Reports. The book describes structure determinations published during the period indicated, presenting all the structural data so completely that it is usually unnecessary to refer to the original papers.

The three sections of the book deal with metals, inorganic compounds, and organic compounds. Metal reports are arranged alphabetically, while inorganic and organic compounds are placed roughly in order of increasing complexity of composition.

Subject and formula indexes are included as a further aid in searching for compounds. The subject index contains an alphabetical listing by the names printed as the headings of reports. In the formula index, constituents are arranged in the alphabetical order of the chemical symbols. An additional index of carbon compounds is included, with primary classification by the number of carbon atoms and secondary classification by the number of hydrogen atoms.



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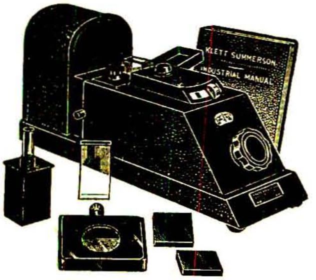

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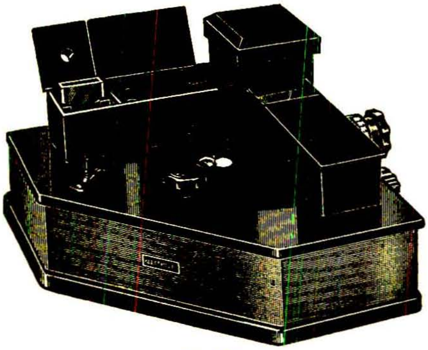

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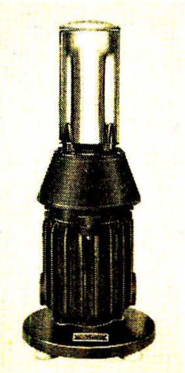

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the ANALYST'S column

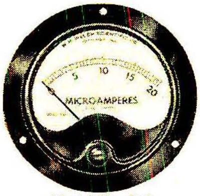
L. T. Hallett, Editor

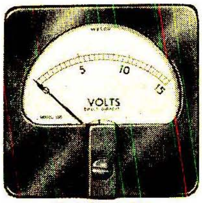
PRESENTATION of one system for classifying analytical methods (Report for Analysts, March 1957) has aroused interest on the part of some readers. One, who has another system, is A. A. Benedetti-Pichler (248–51 Thornhill Ave., Little Neck 62, N.Y.). He feels that a system of classification of analytical methods will not only display existing procedures in a readily remembered relationship, but also indicate new methods if it is based upon actually existing essential differences.

The method he uses appears in "Essentials of Quantitative Analysis" (Ronald Press, 1956).

A summary of his system appears below:

> Sampling should be considered not a part, but a prerequisite of analysis. Sampling and analysis stand in the relation of question and answer. Samples must be selected to contain the clues for the solution of the ultimate problem. This dictates the *procedure* of sampling.
>
> A separate classsification for qualitative and quantitative analysis is superfluous since both must proceed according to the same principles. The place of the precise measurement of quantitative analysis is simply taken by the observation of a phenomenon and an approximate estimation of its intensity when performing a qualitative investigation.
>
> The task of chemical analysis may therefore be divided into (A) the preliminary treatment of the sample and (B) the qualitative observation or the quantitative measurement of a property or phenomenon.
>
> The preliminary treatment may be completely omitted if the substance of interest is the only one in the sample that exhibits the phenomenon observed for identification or measurement. The presence of interfering substances or the use of a phenomenon of poor specificity may introduce the need for isolation of the substance of interest in addition to other preliminary operations


Model No. 350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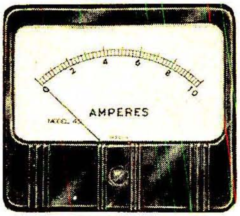
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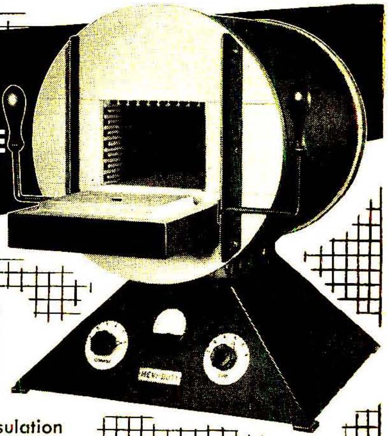

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P-E Analytical News

- *KBr sampling technique works with micro quantities*
- *Oil well logging with flame photometry*
- *Water is a good IR solvent above 6μ*

MICRO-SAMPLING WITH KBr

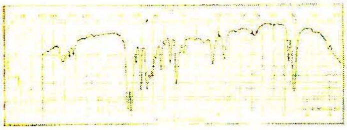
Here's an example of how the newly perfected potassium bromide (KBr) sampling technique can help analysts to examine micro quantities of material with infrared. The substances to be analyzed – in this case acetylsalicylic acid and caffeine – are uniformly mixed with KBr at about 1% concentration.

2.5 mg. of each of these mixtures is pressed into a 1mm. by 3mm. aperture in white blotting paper, 13mm. dia., between two polished steel plates by applying 25,000 pounds total force. The pressed disks obtained are placed, well centered, on the standard KBr disk holder for the Model 21 Infrared Spectrophotometer.

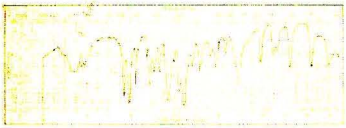
Since the sampling areas, in this case, are masked down to 1mm. by 3mm. with blotting paper, the windows transmit only about 25% of the radiation. Therefore a 25% transmission screen is placed in the reference beam and full scale spectra can then be recorded. Energy loss is compensated for by using a wider slit program.

Using this technique, the Model 21 and the new *Infracord infrared spectrophotometers produce excellent spectra of micro samples, and the samples can be placed directly in the sample space. The method was developed by Alexander D. Mebane, Ortho Research Foundation, Raritan, N. J.

*Trade Mark



Spectrum for Caffeine in KBr



Spectrum for Acetylsalicylic Acid in KBr

MUD, OIL AND THE FLAME PHOTOMETER

If you want to know something about the geological structure of an oil well, a remarkably accurate picture is given by the electrical characteristics of the materials through which the well is drilled. Unfortunately, mud can make a mess of the picture. The mud in this case is drilling mud, essential as lubricant and coolant for the drill bit, and containing salts and other electrolytes which can throw electrical measurements of strata all out of kilter.

The P-E Model 146 Flame Photometer can detect as little as 0.01 parts per million of sodium, 0.05 parts of potassium, 2 parts of calcium and 25 parts of magnesium. An accuracy of ±2% of full scale can be obtained in less than one minute.

The muds must be analyzed for sodium, potassium, magnesium and calcium ions so that their electrical effects can be corrected for, and a true picture of the geological structure obtained. This is where the Perkin-Elmer Model 146 Flame Photometer has been of great help. Filtrates pressed from the muds are fed directly into the "flame", with or without dilution depending on the expected ion concentration. Accurate results are obtained in minutes. The method is considered far superior to wet chemical analyses used before.

Still in the development stage is another application for P-E's new "flame" in oil well studies. Subterranean water held in the rock formations contain salts, hydrocarbons and other materials which tell a great deal about the oil-producing possibilities of the bed rock formation. The problem: to get samples of this water uncontaminated by drilling muds. Ways are being worked out, and the Flame Photometer will figure prominently in analyzing the water.

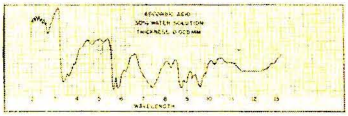
WATER CAN BE USED AS AN INFRARED SOLVENT

Confronted with infrared analysis of a water solution, many spectroscopists might say: Impossible! Water dissolves the rock salt cell windows and is so strongly absorbed in the region from 2μ to 15μ that it obscures most of the absorption bands of any material dissolved in it.

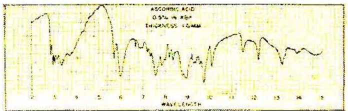
However, as early as 1949 some very excellent results were obtained with water as an infrared solvent, and great progress has been made since in the manufacture of optical crystals that resist water. Today there are at least 11 window materials that can be used. The most useful are probably sapphire (to 6μ), barium fluoride (to 13μ), and thallium bromide-iodide (to about 35μ).

Water is, of course, a strong absorber in the infrared. In the 3μ to 6μ region it is totally absorbing and no information can be gained about a sample. But above 6μ, spectra of sufficient intensity can be recorded by using concentrated water solutions in thin cells.

Why should we bother working with water solutions now that we have the KBr pressing technique? There is room for both. Sulfonates used in detergents, for example, do not mix homogeneously with KBr. Here, water solution work is preferable. And there are very large differences in the spectra of some materials in the liquid and solid phases. Note the two spectra for ascorbic acid below.



Spectrum for Ascorbic Acid, Liquid Phase



Spectrum for Ascorbic Acid, Solid Phase

Water solutions should not be discarded as impossible to work with in the infrared until attempts have been made to run their spectra in a thin cell equipped with appropriate windows.

Write us for a reprint of Helene Sternglanz's paper "Using Water as an Infrared Solvent" (APPLIED SPECTROSCOPY, 10-2-1956).

INSTRUMENT DIVISION
Perkin-Elmer *Corporation*
NORWALK, CONNECTICUT

We'll be glad to send you more information on any of these items. Or to put you on the mailing list for INSTRUMENT NEWS, a quarterly published by P-E to further research, material analysis and production through electro-optical instrumentation.

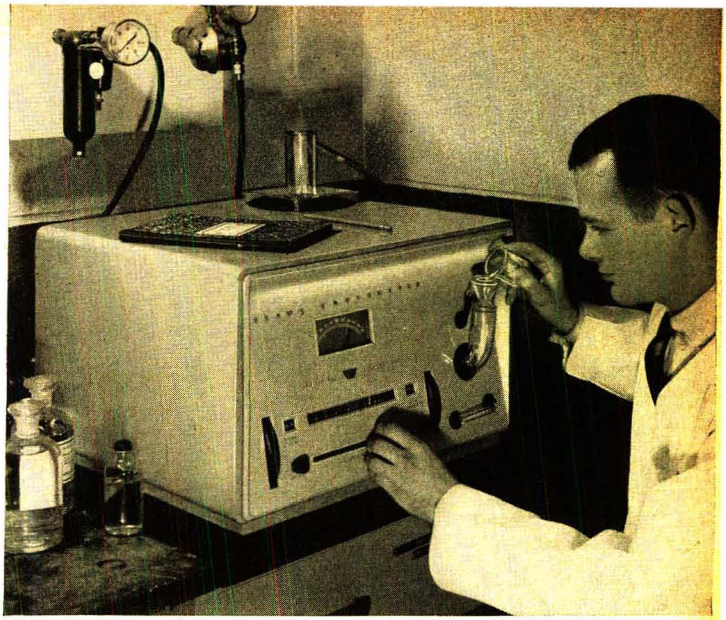
For further information, circle numbers 46 A-1, 46 A-2, 46 A-3, 46 A-4 on Readers' Service Card, page 77 A as disintegration, mixing, preparation of solutions, and aliquot partition.

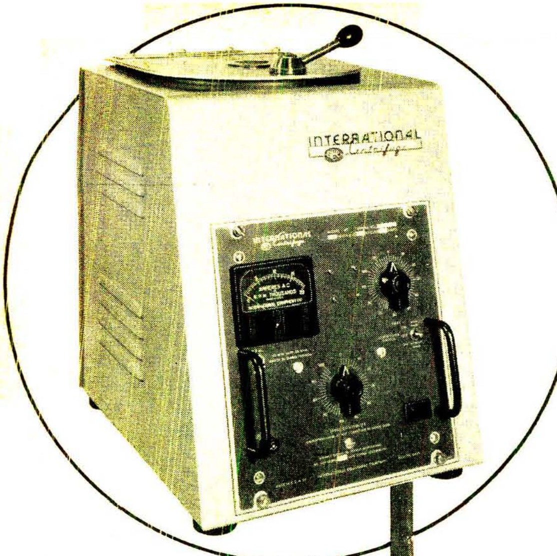
Separation, for the purpose of isolation, requires that the substances to be separated be present in different phases. Consequently, the task of separation involves two steps: the creation of separable phases and their mechanical separation. The latter is obviously best treated in the five sections which are naturally provided by the possible combinations of phases: solid-solid, solid-liquid, solid-gas, liquid-liquid, and liquid-gas. For the first step, there are only three ways of establishing a separable phase: mechanical addition of same, change of temperature (pressure) to obtain a transition, and causing a chemical reaction that is accompanied by the separation of a new phase.

Concerning the concluding operation of detection or determination, it is obvious that any kind of phenomenon or property may be used for observation or measurement. A classification of suitable phenomena will obviously use a grouping according to the three major divisions of natural science: physics, chemistry, and biology. The classification within the groups may follow the established subdivisions of these sciences or may be based upon a systematic listing of the theoretically predictable phenomena. Of the two choices, the latter seems especially attractive and appears in "Essentials of Quantitative Analysis" (pp. 197–202) as well as in "Instrumental Analysis" by Paul Delahay (Macmillan, 1957).

The classification of methods may be summarized as follows:

A. Sampling
B. Analysis
    I. Preliminary Treatment
        a. Disintegration
        b. Mixing
        c. Preparation of Solutions
        d. Aliquot Partition
        e. Separation
            1. Establishment of Separable Phase
            2. Mechanical Separation of Phases
    II. Observation or Measurement of Phenomena
        a. Physical Phenomena
        b. Chemical Phenomena
        c. Biological Phenomena





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*Note: speeds are obtained at 115 volts input to centrifuge; force is effective centrifugal force figured at the maximum radius of the material being centrifuged.

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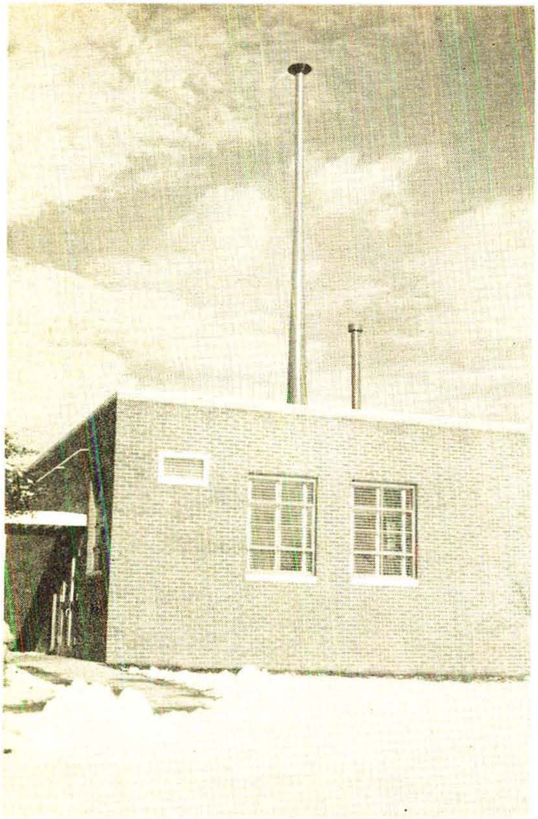
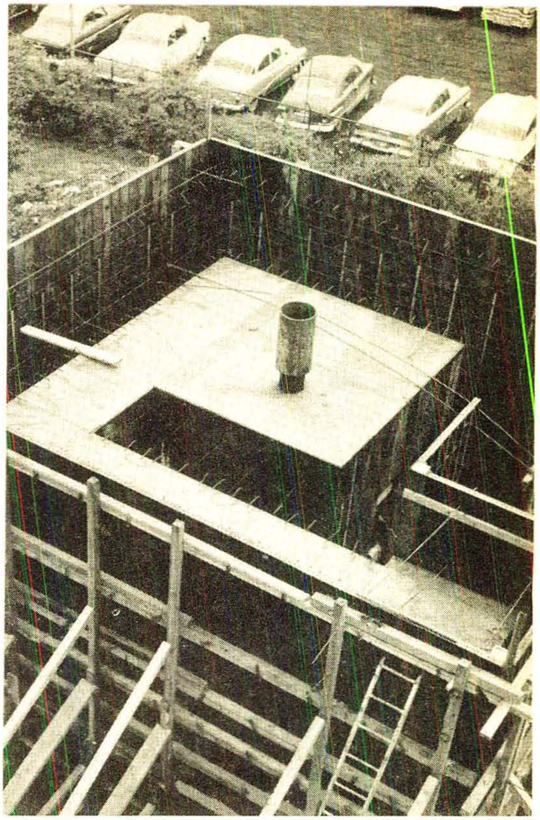


The air-conditioned radiation laboratory, 24 × 42 feet, is adjacent to the main research laboratory. The high stack is the exhaust for the fume hood; the short one connects to the "cave," via an underground duct, to exhaust ozone generated in the cave by gamma radiation. There are no radioactive wastes from cobalt-60



The cave which houses the cobalt-60 is a monolithic structure of reinforced concrete with 4-foot thick walls. A labyrinth of 4-foot aisles eliminates necessity for massive shielding doors. The shielding is effective for 10,000 curies of cobalt-60 or 1,000,000 curies of its fission by-product, cesium-137

LABORATORY OF THE MONTH

Radiation Opens Unexplored Avenues of Rubber Research

COBALT-60, a source of high energy gamma radiation, is the key element in Goodyear Tire and Rubber Co.'s new radiation laboratory.

The new $125,000 facility, located beside the main research building at Akron, is the first of its kind in the rubber industry. It was opened last December.

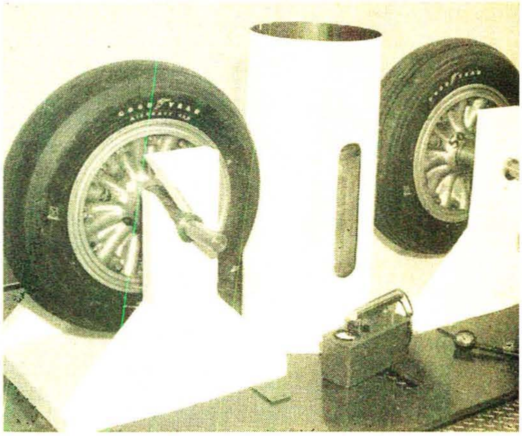
Main object of the fully equipped laboratory is to explore and develop rubber products which will perform satisfactorily in a radiation environment. Development of radiation-resistant airplane tires for atomic-powered aircraft is one important project.

Rubber is particularly susceptible to radiation. Excessive doses damage the rubber by leading to hardening and embrittlement. Cobalt-60 will facilitate tests on compounding practices and chemical activities.

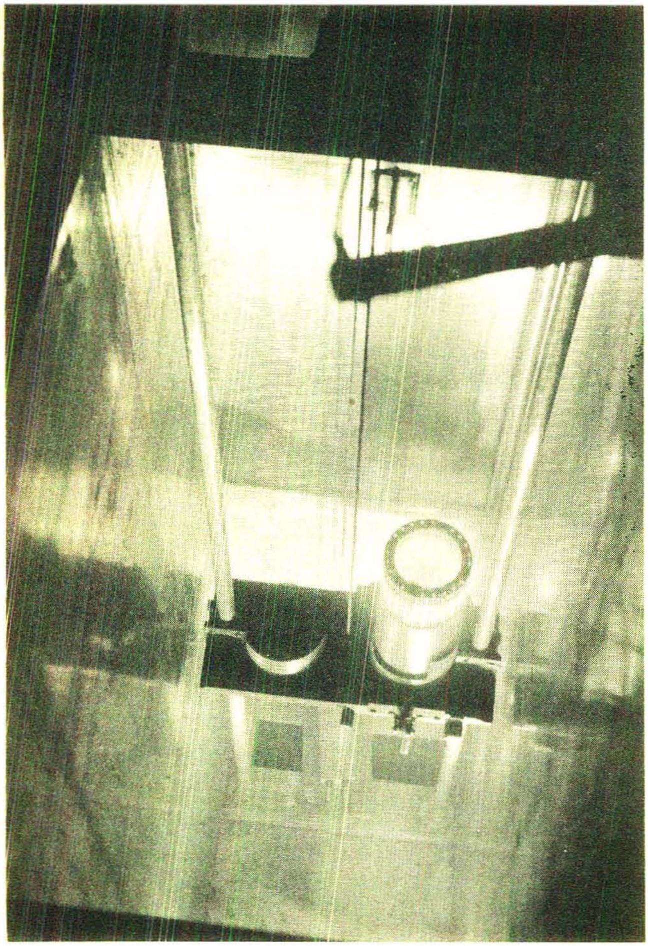
The high energy radiation will also be used to initiate chemical reactions, polymerization and vulcanization of rubber, and improve properties of plastics and resins. Vulcanization of most types of raw rubber can be done by irradiation without use of sulfur or heat.

The 1000-square-foot building, in addition to the "cave" which houses the cobalt-60, has a well-equipped physics and chemistry laboratory for preparation of materials and test specimens and for evaluating results and products of irradiation research.

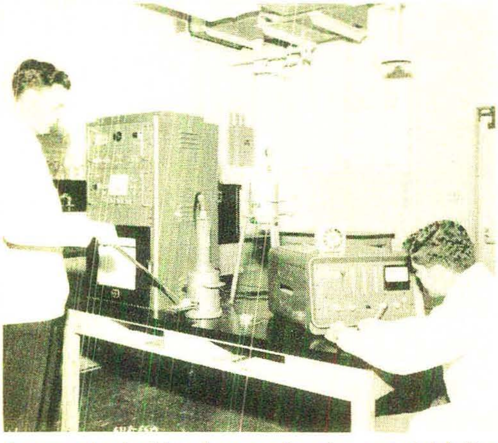
The design of this installation removes practically all limits on the size and number of samples which can be irradiated at one time, eliminates remote control manipulations, and eliminates need for underwater operations.



To study damage resulting from intense gamma radiation, airplane tires, mounted near the cobalt-60 source, are rotated slowly to improve the uniformity of the irradiation. The cobalt-60 is raised into position from the well during experiments. An additional shield is placed around the source as an extra protection in case of blowouts

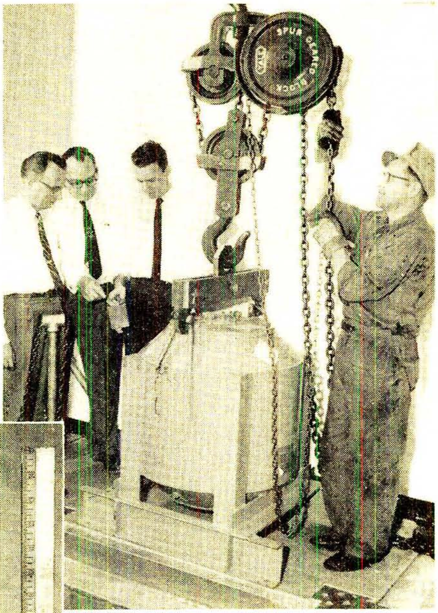


The cobalt-60 source and elevator are shown through the clear shielding water in the aluminum-lined well. The well is 3 by 6 feet and 17 feet deep. Holes in the rack are for addition of cobalt-60 to keep the source up to strength, since it decays to half value in 5.3 years. A stainless steel cable raises and lowers the elevator. An aluminum counterweight equal to the weight of the source and its pedestal is on the left. In emergencies, the lever at the top can be tripped from outside ◄ the cave to drop the source in the well



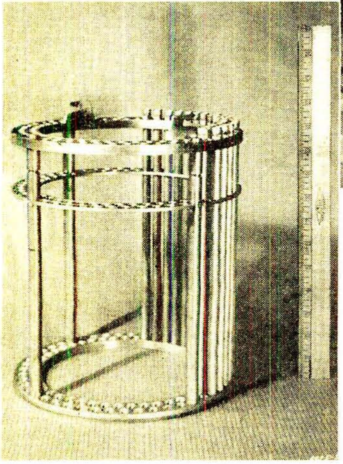
A research physicist places radioactive material (white disk) in scintillation detector which measures gamma ray spectrum, while lab technician at right keeps a check on amount of radioactivity. Effects of radiation on rubber and other materials are now being studied in Goodyear's new radiation laboratory

S. D. Gehman watches through radiation-resistant window while operating elevator winch which raises radioactive cobalt-60 from bottom of well. T. C. Gregson checks intensity of radiation on monitoring instrument. Mechanical interlock prevents door to radiation chamber from being opened while cobalt-60 is in "up" position

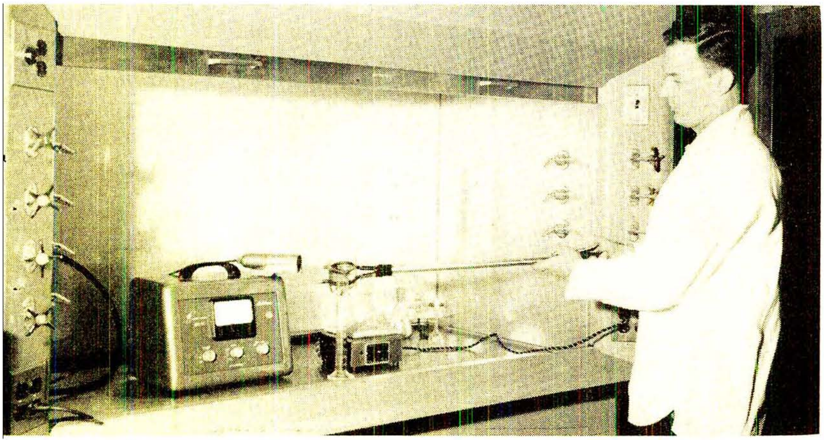


The cobalt-60 source is a cylindrical aluminum rack in which are mounted 72 0.5-inch diameter aluminum tubes. Each tube is loaded with 9 aluminum-clad slugs of cobalt 60, 1 inch long and 0.25 inch in diameter. Ears on the rack permit transferring it to or from the shipping container, under water, by means of a long handled tool

▼



The cobalt-60 source, inside an 8000-pound lead shipping container, is ready to be lowered into the tank. It is then transferred, while under water, to the elevator in the tank



The stainless steel hood allows researchers to conduct experiments with the highest degree of safety. Dangerous fumes are carried away by a specially designed ventilating system, while materials that are spilled can be washed away. The monitor checks radiation levels and subsequently detects any contamination. T. C. Gregson, Goodyear physicist who helped design the laboratory, is shown doing an isotopic dilution analysis of a radioactive material

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Precision	0.05 mg	0.02 mg	0.002 mg

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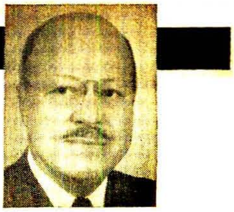
INSTRUMENTATION



by Ralph H.
Müller

Image storage tubes hold promise for many scientific applications

The development of image storage tubes has been stimulated by developments in television technology. These devices have been used extensively in television, radar, and computing machines, but they seem to hold great promise in other fields. An important survey of image storage tubes has been made by H. G. Lubszynski, Research Laboratory, Electric and Musical Industries, Ltd. [*J. Sci. Instr.* **34,** 81 (1957)].

Image storage tubes are devices capable of storing a halftone picture directly. In general the information contained in a halftone picture is written into the storage tube in the form of a charge image on an insulating target. At a later time it can be read out and displayed on a cathode-ray tube. Digital storage tubes which are used for storing mathematical information are in a different class. They require intermediate encoding and decoding devices to store and reproduce the information contained in a halftone picture.

The author discusses the principles of several types of storage tubes: several British types and the RCA storage Orthicon, the Graphecon, and the Metrechon. The details of these devices are too complex to warrant extensive discussion here. They are elegant extensions of television tube techniques embodying the principles of electron optics. The circuitry for writing pictorial information and subsequent read-out is similar to television practice. The application possibilities, however, are of immediate interest to every scientist and technologist. The author gives the impression that scientific applications have lagged, despite the high state of development of these devices. First of all, it is necessary to decide the relative advantages of storage tubes and photography, because the photographic plate is the simplest form of storage. When new information is coming in constantly, one is driven to motion-picture techniques and a point is soon reached when a definite decision can be made. It is already true that the sensitivity of modern image storage tubes is superior to that of photographic emulsion.

One important use of image storage tubes is the improvement of signal to noise ratio of a weak picture by integration. The integrated information can be scanned off and the resulting video signal amplified and used to give a bright display with high contrast. Great promise is held for applications in fluoroscopy wherein a short exposed picture may have to be examined in detail. Certain image storage tubes can be provided with windows transparent to ultraviolet, x-ray, or infrared radiation and made to store relatively short-exposed pictures for subsequent prolonged reading.

The tubes are suited for slowly changing pictures with high speed play-back, or for fast transients followed by slow read-out. This review article is an excellent summary of the art and should stimulate the reader to seek new and untried applications.

Polarographic Determination of Oxygen

The polarographic determination of oxygen has been a useful method for many years, particularly in following the mechanism of respiration and photosynthesis. An interesting instrumental development vastly increases the utility of this technique. F. S. Brackett, J. H. Daniel, and R. G. Crickard [*Rev. Sci. Instr* **28,** 182 (1957)] describe a recorder for oxygen concentration and rate of exchange, in which a polarographic square wave method is adapted to servo-pen recording. Cam-driven microswitches provide the square potential pattern and also the programed timing on which the rate evaluation is based. The 3-second time resolution, which their system affords, reveals transient details which cannot be observed in ordinary concentration recording. According to these investigators and others, the static platinum electrode is superior to other polarographic methods in rapidity of response. There are inherent time limitations imposed by the interruption periodicity, but in this scheme the time has been reduced to 3 seconds.

Schematics and complete circuit diagrams describe the square wave switching, and the sequential operation of rate condenser, amplifier, and recorders.

Full scale on the oxygen concentration recorder usually corresponds to equilibration with 25% oxygen and represents an input of 2.5 to 3 μa. for the electrodes commonly used. A threefold expanded scale is used for low oxygen values, corresponding to a full scale of about 1 μa. The rate-recording system responds only to change in output potential and this provision accounts for one of the most unusual features of the system. It is true that the rate-recording system makes a more severe demand on the residual noise level by a factor of some 100-fold; hence the tracings are slightly more erratic than the direct recording of oxygen concentration. This is more than offset by the accurate delineation of transients in oxygen concentration, which are almost imperceptible in the direct concentration recording. The authors illustrate several striking examples of oxygen evolution, both direct and for rate of exchange for a system containing algae Chlorella, when the suspension is alternately exposed to dark and light.

We have long had the feeling that studies in cell respiration warrant the full resources of modern instrumentation. This is a fine example of such application. Indirectly, it is a faint indication that Heyrovský's science of polarography is not hopelessly committed to endless studies of new chemical systems to be "polarographed." There is much we can learn from old systems if they are examined by refined techniques.

Optical Problems of a Satellite

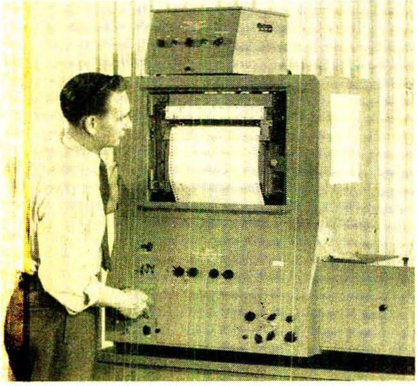
We happen to be among those queer creatures who are cold to science fiction stories. Their weird extrapolation of future possibilities always strikes us as inadequate; and is this not the fate of all scientific prediction? Despite this we are compelled to report on required reading of a serious topic which is almost in the "Buck Rogers"

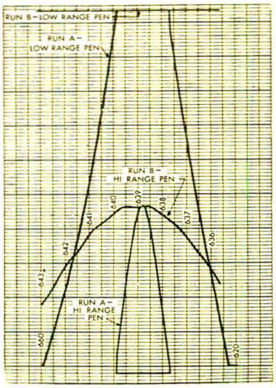
Cary / instrument abstracts

Applied Physics Corporation/Pasadena/California

At Eastman Kodak

Cary Model 14 Spectrophotometer measures absorbance to 7.1 without correction for stray light.





Run A represents the normal check of a Fabry-Perot interference filter similar to those used in densitometry of color films where the passband and shape of the filter curve is important up to densities of 7.0. This particular filter curve showed a nonsymmetrical peak at 639 mu. For a closer examination of this peak a second expanded curve of this wavelength region, Run B, was made in super-position on the first curve.

In the Laboratories of the Eastman Kodak Company interest in absorbance values over seven—less than .00001% transmission—is more than idle curiosity. Recently, Kodak physicists, using one of their Cary Model 14 Spectrophotometers, were pleased to find they could measure densities to 7.1 without correction for stray light.

In contrast, there are numerous instances where months of hard work were wasted because unsuspected stray light of single monochromator instruments caused large errors sometimes even below 1.0 absorbance.

Double monochromators cost more to design and build. But they provide advantages that can be had in no other way.

Besides low stray light, the double monochromator adds the dispersion of its separate sections and is arranged to cancel severe optical aberrations, giving increased resolution.

In the Model 14, a silica prism and a 15,000 line diffraction grating add the higher ultraviolet dispersion and the low stray light of the prism to the excellent visible and infrared dispersion of the grating. Each complements the other to produce exceptional performance from 1860 to 26,500 Angstroms.

All Cary instruments are truly direct reading. Freedom from stray light provides one of the most dramatic examples of what this can mean to a user, but there are others. Some of the unusual features of Cary Recording Spectrophotometers which contribute to accuracy by helping avoid corrections are listed at right.

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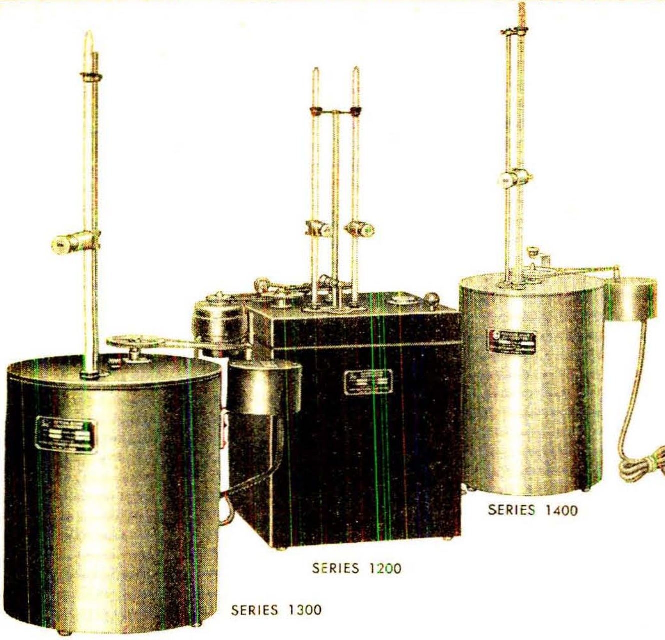
class. All of this is to be found in one of our most sedate and respected journals—i.e., the *Journal of the Optical Society of America*. R. Tousey of the U. S. Naval Research Laboratory discusses some of the optical problems of the satellite [*J. Opt. Soc. Amer.* **47,** 261 (1957)].

According to a Presidential announcement of some two years ago, the United States will launch several small instrumental satellites as part of its participation in the International Geophysical Year. The average satellite is a sphere, to be 20 inches in diameter and to weigh in all not over 21.5 pounds. It will be propelled by a three-stage rocket, the components of which will be fired in sequence. The ultimate orbit will be an ellipse with a perigee of not less than 200 miles, and an apogee perhaps as great as 1500 miles. The launching will be such that the orbit crosses the equator at an angle of about 35°, as a consequence of which the satellite should reach 35° north and south latitude once each revolution. The velocity required to balance the centripetal gravitational force is some 18,000 miles per hour; hence the satellite will complete one circuit of the earth in 90 to 110 minutes, with the exact period depending on the heights of perigee and apogee. It will be visible to the eye during periods corresponding to the intersection of two zones—i.e., each of the visibility belts corresponding to some 40°N and 40°S latitude and the longitudinal twilight zone.

Precise tracking will be made by radio and with cameras. The satellite will contain a radio system known as Mintrack, which is a transmitter operating at 108 mc. at a power of 10 to 50 μw. Direction-finding receiving stations of the type used by radio astronomers will be set up, more or less along the 75th meridian of longitude. The satellite must cross this "fence" once each revolution. It is predicted that the angle accuracy can be better than 1 minute of arc. The aid of radio amateurs has also been enlisted in this program. Precise photographic measurements will be still more accurate and these are being set up by the astrophysicists. These measurements can be expected to furnish accurate data for the oblateness of the earth and for the calculation of atmospheric density above 200-mile altitude.

Fascinating problems have arisen in designing coatings of the sphere, to minimize excessive heating by solar radiation or excessive cooling when the earth shields the satellite from the sun. This article emphasizes optical problems and one of the chief concerns is the continuous recording of the Lyman



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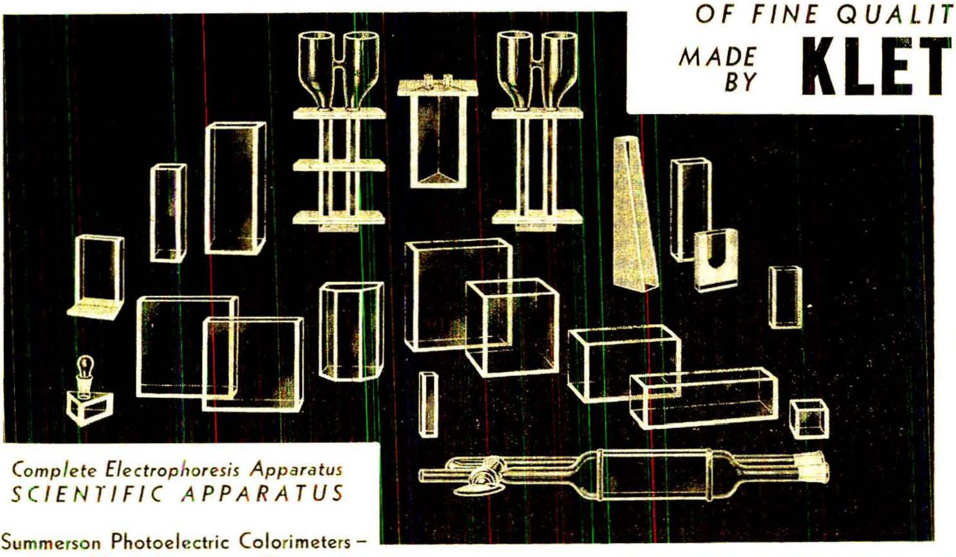

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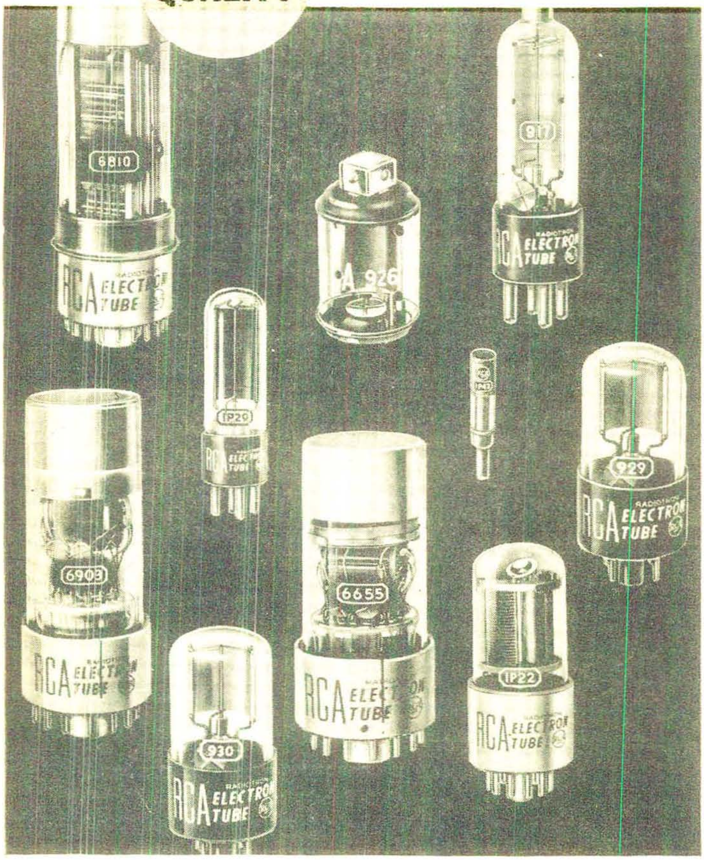
alpha radiation in the far-ultraviolet spectrum of the sun. The device for this purpose is a nitric oxide–filled ionization chamber fitted with a lithium fluoride window. Nitric oxide has a photoionization threshold at 1340 A., which is longer than Lyman alpha, but is far enough in the ultraviolet practically to eliminate all of the solar spectrum. Since the satellite will be spinning, it is necessary to know the aspect angle between the ion chamber and the sun. This information is supplied by an ordinary phototube responding to the visible spectrum. It should be possible to receive Lyman alpha measurements 16 times a day.

If these fantastic probes into the nature of our outer space seem remote from the concern of the analyst, let us recall that Sir Norman Lockyer analyzed the solar atmosphere and found helium long before it was discovered on the earth. To those diligent analysts who are using the best resources of instrumental analysis in analyzing the smogs of Los Angeles and the rest of our afflicted municipalities, this all adds further information because solar and cosmic radiations create ozone and this reacts in diverse ways with man-made pollutants. This may be the Geophysical Year, but it is a new era in which all fields of science will be enriched.

Thermistor Reproducibility

We are increasingly disturbed by private and published reports on small but definite discrepancies in the behavior of thermistors. These have arisen from attempts to reproduce, with high precision, the temperature resistance function. In most technical and industrial applications, such discrepancies are trivial and negligible. Analysts are notoriously meticulous and these troubles persist. There was a time when, from personal experience, we were convinced that strict reproducibility was obtained only if the thermistor was subject to constant and uninterrupted electrical (and presumably thermal) excitation. It seems that this is not the complete answer. We are studying this intensively. A possible clue seems to lie in more complete aging of a thermistor. During manufacture, they are subjected to prolonged baking and the aging shows an initially high rate. Some of these things may be settled at the Symposium of Thermal Titrations to be held at the New York meeting of the ACS. That symposium will settle the proper terminology for such titrations, but we are bold enough to express the hope that more will also be known about thermistor behavior.



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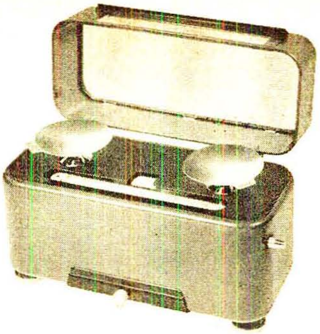

Model IL-9

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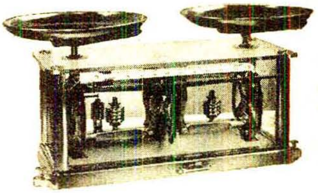

Model IL-1

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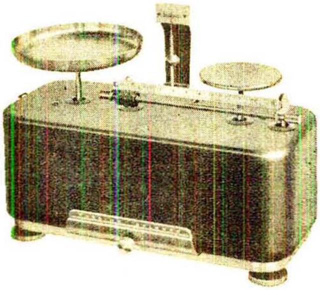
260 mg.



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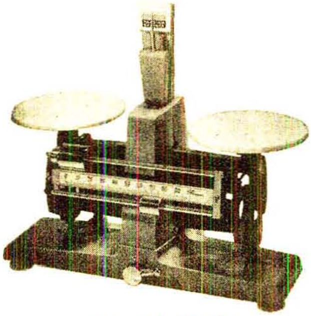
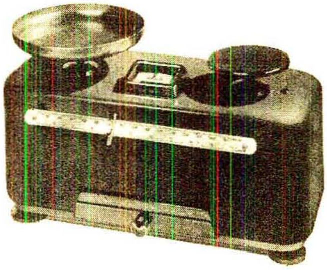


Model IL-7

Capacity: 2 kilo (5 lbs.)
*Sensibility Reciprocal:
200 mg.



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New

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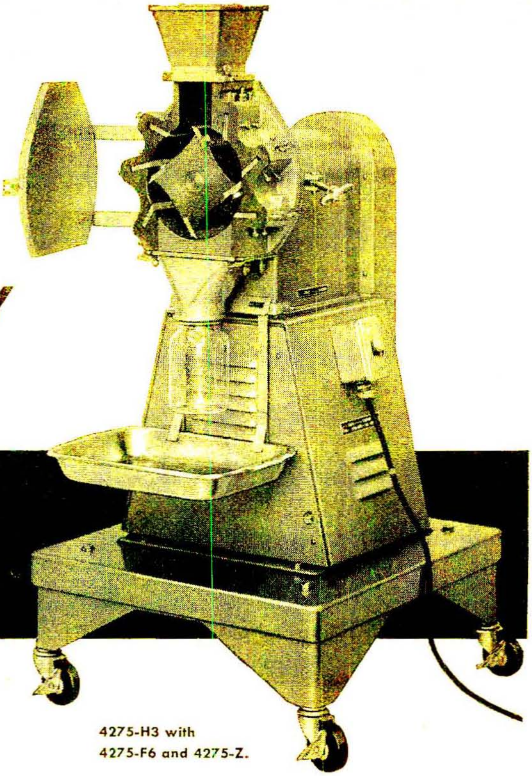

With harder knife edges for cutting Teflon, resins, etc.

New portable stand

4275-H3 with 4275-F6 and 4275-Z.

WILEY LABORATORY MILL, Standard Model No. 3. Principal advantages of new Model No. 3 are: harder cutting edges on the knives, making it suitable for a broader range of materials, including Teflon, polyethylene resins, titanium scrap, etc.; quieter performance with less vibration; and improved appearance, i.e. baked gray enamel with parts subject to abrasion chromium plated.

As in the earlier model, four hardened steel knives on a revolving shaft work with a shearing action against six knives bolted into the frame. The shearing action of the cutting edges, between which there is always a clearance, tends to avoid changes in the sample such as temperature rise, loss of moisture, liquefaction, contamination, etc., making this mill satisfactory for many materials which can not be reduced by other mechanical means. A sieve is dovetailed into the frame so that none of the material comes from the grinding chamber until it can pass through the mesh.

Furnished with interchangeable receivers, i.e. either a deep, cast aluminum drawer with rounded inner corners, or a chute for collecting the sample directly in a standard screw neck glass jar, or in a bag, table drawer, etc. Either receiver slides into a new, spring-loaded holding device.

4275-H3. Wiley Laboratory Mill, Standard Model No. 3, motor driven, mounted on enclosed base, with chute for collection of sample. With $\frac{1}{2}$ h.p. continuous duty motor, 1725 r.p.m.; starting switch with thermal overload cutout; V-belt, belt guard; three sieves with openings of $\frac{1}{2}$ mm, 1 mm and 2 mm diameter, respectively; jars; set of four wrenches; gun-type grease injector and 1 lb. of lubricant. For use on 115 volts, 60 cycles, single phase, a.c. Power consumption 800 watts. Without Stand or Tray Attachment. 886.00

4275-R3. Ditto, but with drawer of cast aluminum alloy in place of chute and jars. 876.50

4275-F6. Spillage Tray Attachment, for use with above. Consists of bracket, which can be attached without tools, and Stainless steel tray $14\frac{3}{4}$ inches x $10\frac{5}{32}$ inches x $2\frac{1}{4}$ inches deep. Can be adjusted for drawer or glass jars, sizes 1 pint to 2 quarts, inclusive. 18.80

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ANALYTICAL CHEMISTRY

EDITORIAL

June 1957, Vol. 29, No. 6

Analysts Meet Challenge of Nuclear Age

The past decade of the atomic era has presented analysts with a multitude of challenging problems in such areas as techniques, instrumentation, and new methods.

Reactor elements, for example, can tolerate only extremely minute traces of certain impurities such as boron in graphite and impurities in fuel slugs. Conversely, this has required analysts to come forth with analytical techniques and methods to determine these traces. Determinations on the order of parts per 20,000,000 are common.

Nuclear programs call for metals and alloys which have extraordinary resistance to high temperatures, thermal shock, and corrosion. Some of the new alloys which meet these physical requirements present a host of problems to analysts. In some cases it is even difficult to dissolve these materials.

In the area of instrumentation, especially in "hot" cells, there are truly fantastic problems. Remote control manipulation is one of the more obvious ones. Corrosion, shielding, insulation breakdown, and maintenance are added headaches for the instrumentalist.

Rapid growth of the nuclear field will result in a need for additional hot cells, possibly on a scale beyond anything envisioned at present. This, in turn, presents problems of cost and difficulties of extensive shielding and expensive custom-built instrumentation.

Possibly the analyst can help develop techniques, similar to those used in the petroleum industry, where analyses can be made on process streams, thus reducing the need for high-level hot analytical cells. Such a development will become even more essential as the level of radioactivity in nuclear materials is increased.

The Summer Symposium, sponsored by the Division of Analytical Chemistry and ANALYTICAL CHEMISTRY a decade ago on the subject of nuclear energy and the analyst, and the forthcoming one on the same subject at Purdue University, show that the analytical chemists have accepted the challenge presented by the atomic age. During the past decade they have met the problems with a high degree of success. It seems likely that future problems will be approached and met successfully.

AIR POLLUTION

A group of papers from the Symposium on Air Pollution, Division of Analytical Chemistry, 130th Meeting of American Chemical Society, Atlantic City, N. J., September 1956

Critical Comparison of Collection Efficiencies of Commonly Used Aerosol Sampling Devices

CONRAD SCHADT and R. D CADLE
Stanford Research Institute, Menlo Park, Calif.

▶ The extent to which the theory of particle collection techniques could be applied to commonly used field instruments has been determined. The instruments included sedimentation chambers, an MSA electric precipitator, a Greenburg-Smith impinger, Millipore filters, the Cassella thermal precipitator, and an impactor. The aerosols used for determining efficiency were nearly monodisperse—that is, the particles were nearly all the same size. The use of such aerosols greatly simplifies the problem of comparing the efficiencies of the instruments for collecting particles of different sizes. Perhaps the most interesting feature of the results obtained has been the marked discrepancies often observed between theoretical and observed efficiencies. Possible reasons for these discrepancies are discussed.

Many aerosols, smokes, or dusts are of great importance today in connection with air pollution problems, recovery of valuable materials otherwise lost from stacks, and in processes requiring the formation of aerosols, such as spray painting. The need to study these various aerosols has resulted in the use of many sampling methods and devices to collect aerosol particles for measurements of mass, particle size distributions, and other physical and chemical properties.

The collection efficiencies of the various sampling devices often vary greatly for different aerosols and different conditions of operation. This makes the selection of sampling devices for any particular laboratory or field program of aerosol studies a difficult problem. Fortunately, most of the numerous devices in use can be classified according to a few basic principles of operation. The purpose of the experimental program on which this paper is based is to present information on each of these types of devices which will serve as a guide for the selection of sampling instruments for various field or laboratory programs.

The following sampling devices were used in this study:

Thermal precipitator
Jet impactor
Greenburg-Smith impinger
Electrostatic precipitator
Membrane filter (Millipore filter)
Sedimentation box

EXPERIMENTAL

Equipment. The thermal precipitator was a modified commercial unit, manufactured by C. F. Casella & Co., Ltd., London, England. The usual wire heating filament was replaced for these studies with a ribbon filament. The aerosol was drawn past the hot filament by allowing water to flow from a tank to which the precipitator head is attached. The particles were collected on microscope cover slides located on opposite sides of the hot filament. Important dimensions of the precipitator are:

Filament width	1.4 mm.
Length of exposed filament (normal to direction of air flow)	10 mm.
Distance from filament to each cover slide	0.15 mm.

Temperature gradients were determined using a copper-constantan thermocouple made from 1-mil wire.

The jet impactor consisted of a single rectangular jet opposite a microscope-slide collecting surface. The jet was mounted in a metal housing which had a track to hold the microscope slide at the proper distance from the jet. Air was drawn through the jet by applying a vacuum to the metal housing. The instrument had the following dimensions:

Jet length	11 mm.
Jet width	0.20 mm.
Distance from jet to collecting surface	0.53 mm.

This impactor is not commercially available, but is similar to a single stage of the cascade impactor manufactured by C. F. Casella & Co., Ltd., London, England.

The Greenburg-Smith impinger (*4*) was constructed in the glass shop of Stanford Research Institute. The following are the dimensions of the unit used in the tests:

Diameter of collecting tube	60 mm.
Jet diameter	2.3 mm.
Distance from jet to flat bottom	5 mm.
Liquid level	50 mm.

The electrostatic precipitator was an MSA Electrostatic Sampler, Model F, made by Mine Safety Appliances Co., Pittsburgh, Pa.

Membrane filters (*3*) are commercially available from the Millipore Filter Corp., Watertown, Mass. Two types of Millipore filters were tested, AA (aerosol assay) and HA (hydrosol assay).

A sedimentation box was constructed of Styrafoam (for thermal insulation) and the interior was lined with sheet aluminum (for an electrically conducting surface). This surface was electrically grounded during experiments. The top of the box was hinged so that it could be opened for rapid filling with aerosol and so that collecting slides could be readily inserted or removed. Microscope slides with and without electrically conducting layers of Aquadag (Acheson Colloids Co., Port Huron, Mich.) were used as collecting surfaces for subsequent microscopic examination. The inside dimensions of the box were 25.4 cm. high and 35.6 × 40.6 cm. cross section.

Two aerosol photometers were used to measure relative aerosol concentrations: an NRL Smoke Penetration Meter, on loan from the Chemical Corps, and a Sinclair-Phoenix forward-scattering smoke photometer. The NRL instrument was used for most of the measurements, as it was the only one available at first, and the Sinclair-Phoenix was used for the most recent tests, when it was the only one available.

A cascade impactor made by C. F. Casella & Co., Ltd., was used with the latter photometer to provide information on particle size of glycerol aerosols.

Particle Preparation. The stearic acid (Eastman Kodak Co.) was redistilled before use. Aerosols of stearic acid were prepared using a La Mer condensation-type generator (*10*). Particle sizes were determined using the "Owl" (*9*) and microscopic examination of collected particles. Most of these aerosols exhibited higher order Tyndall spectra, indicating that they were nearly monodisperse. The sodium chloride was reagent grade and was not further purified. Aqueous solutions were dispersed using an aspirator-type aerosol generator similar to that described by Cadle and Magill (*1*). The newly formed aerosols were passed through a bed of glass beads to remove the larger particles. Evaporation of the water droplets left an aerosol of sodium chloride crystals. Size distributions of the aerosol particles were determined by preparing electron micrographs of particles collected with the thermal precipitator. The size of the suspended salt crystals was varied by varying the concentration of the salt solution. A typical size distribution is shown in Figure 1.

Reagent grade glycerol was used to prepare glycerol aerosols. Aqueous solutions were dispersed in the same manner as the sodium chloride solutions, using the aspirator-type aerosol generator previously described (*1*). Size distributions of the aerosol particles were determined from samples collected with a Casella cascade impactor. The size of the glycerol droplets was varied by varying the concentration of the glycerol solution.

Carbonyl iron was obtained from the General Dyestuff Corp. Chemical analysis showed that it contained 97.3% iron. The iron dust was dispersed with an air nozzle designed for use with powders (*1*). A single particle size distribution was used, which was determined by microscopic examination of the collected particles (Figure 1).

Test Procedure. A typical run with a thermal precipitator consisted of generating the aerosol, drawing it through the precipitator using a predetermined flow rate and thermal gradient, and measuring the widths of the deposits of the two cover slides.

The other sampling instruments were tested in a 10-cubic meter test chamber in which aerosols were formed. The sedimentation box was opened and aerosol was gently blown into the box with a fan operated at very low speed. The lid was closed and the particles were allowed to settle 8 to 24 hours, depending on particle size. Microscopic counts were then made and concentrations calculated from these data and from the volume of the box.

The jet impactor, Greenburg-Smith impinger, electrostatic precipitator, and membrane filter were each tested in the following manner. Aerosol was drawn through the device at a predetermined flow rate. The aerosol which passed through was sampled by an aerosol photometer, which compared this aerosol concentration with that in the test chamber. These measurements gave the relative amount of aerosol which passed through each sampling device. Some additional runs were made by placing Millipore filters in series with other devices to collect the particles passed. Direct Millipore filter samples were also taken and microscope counts were made on both sets. Comparison of these counts gave the relative number of particles passed by each sampling device.

RESULTS AND DISCUSSION

Thermal Precipitator. Epstein has developed an extension of radiometer theory which is generally considered the best explanation of thermal force (*2*). This theory considers adsorption and desorption of gas molecules and "thermal creep" of the molecules along the surface of the particle in the thermal gradient. The thermal gradient and the thermal conductivities of the particle and of the gas surrounding it determine the temperature distribution in the particle. Thermal force is given by

$$F_t = \frac{9\pi D_p}{2}\left(\frac{k_a}{2k_a + k_i}\right)\frac{\mu^2}{\rho T}G \qquad (1)$$

Good agreement with this theory was obtained by Rosenblatt and La Mer (*6*) using tricresyl phosphate, and by Saxton and Ranz (*7*) using paraffin oil and castor oil. All these materials have fairly low thermal conductivities (Table I). Equation 1 shows that for materials with large thermal conductivities the thermal force would be small. One might therefore expect to experience difficulty in collecting materials with high thermal conductivities by the method of thermal precipitation. Such difficulty has not been reported in the literature although this instrument has been in use for many years. Therefore, experiments were performed with materials covering a wide range of thermal conductivities (Table I).

Table I. Thermal Conductivities

Aerosol Material	Thermal Conductivity, Cal./Cm. Sec. ° K.
Air	5.9×10^{-5}
Stearic acid	3.0×10^{-4}
Glycerol	6.37×10^{-4}
Sodium chloride	1.55×10^{-2}
Iron	1.61×10^{-1}
Tricresyl phosphate	4.8×10^{-4}
Castor oil	4.32×10^{-4}
Paraffin oil	2.97×10^{-4}

Flow rates and thermal gradients were so chosen that the width of the deposit was less than the width of the region of thermal gradient (taken as the width of the filament). The width of the deposit was then controlled by the flow rate and by the time required for the particle nearest the filament to travel to the cover slide. Thermal forces were calculated assuming uniform thermal gradient, laminar flow, and the Stokes-Cunningham equation for fluid resistance to a particle in motion.

Stearic acid and glycerol, materials with relatively low thermal conductivities similar to those of the materials in the references cited above, experienced calculated thermal forces which were consistent with theory. However, sodium chloride and carbonyl iron, which have much higher thermal conductivities, experienced thermal forces,

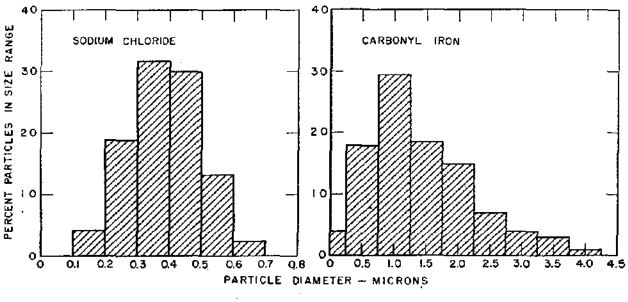

Figure 1. Particle size distributions

respectively, about 40 and 30 times the theoretical values (Table II). The comparison of theoretical with experimental values is shown by the parameter, F_t/GD_p, which is a constant according to theory for a given material. From the practical viewpoint of thermal sampling of aerosols, these results represent a fortunate disagreement with theory for materials of high thermal conductivity, as these materials can be sampled with greater success than would otherwise be the case. A possible explanation of the discrepancy lies in the uncertainty of the thermal conductivities of the solid particles. It is also conceivable that some other phenomenon becomes relatively important for those cases where Epstein's thermal force has a very small value.

Jet Impactor. The collection efficiency of the impactor was studied as a function of aerosol material, particle size, and jet velocity. The results were compared with theoretical efficiencies in terms of a dimensionless inertial parameter, ψ. The theoretical efficiency increases rapidly with increasing values of $\sqrt{\psi}$ from 0% at 0.35 to 100% at about 0.7 for a rectangular jet (*5*). This parameter is defined as

$$\psi = C\rho_p V_o D_p^2/18\mu D_c \qquad (2)$$

Collection efficiencies obtained for glycerol aerosols of 0.5- and 1.0-micron diameter exhibited a smooth, continuous variation with ψ, although the curves were shifted toward higher than theoretical values of ψ (Figure 2).

The collection efficiency data obtained with stearic acid aerosols (Figure 3) generally indicate a rather erratic behavior of the impactor. Collection efficiency for 0.3-micron particles shows that, as the velocity approaches sonic, the efficiency falls off. For the larger particles most ψ values are relatively high, and the theoretical collection efficiencies are 100%. The efficiencies generally increase with increasing ψ, except when velocities approach the sonic region, thus showing a qualitative but not quantitative agreement with theory.

For sodium chloride particles of 0.2-micron diameter (Figure 4), the efficiency increases with increasing ψ values up to a jet velocity about 75% of sonic velocity, and then decreases for higher values. For 0.4-micron sodium chloride particles the efficiency varies inversely with ψ, showing no agreement at all with theory.

Examination of the slides on which the sodium chloride and stearic acid aerosols were collected showed varying sparse and dense deposition of material over a large area of the slide for each of these materials (Figure 5). This indicates that particles were initially collected by impaction, but as they

Table II. Thermal Precipitator

Aerosol Material	Particle Diameter, Microns	Sampling Rate, Cc./Min.	Thermal Gradient, ° K./Cm.	Width of Deposit, Cm.	$(F_t/GD_p) \times 10^7$	
					Experimental	Theoretical
Stearic acid	0.30	2.2	8270	0.037	2.9	7.36
		3.0	1600	0.056	13.3	
		3.0	2230	0.065	7.9	
		4.0	8270	0.047	4.1	
	1.0	2.2	2230	0.075	6.6	
		2.2	3200	0.090	3.8	
		2.2	4230	0.055	4.8	
		3.0	2230	0.12	6.1	
		8.7	4230	0.14	7.4	
	2.0	3.0	2230	0.11	7.1	
		3.0	9800	0.06	2.9	
		7.5	6730	0.11	5.3	
		15.0	6730	0.16	7.5	
	5.0	3.2	2230	0.15	5.4	
		3.2	4230	0.10	4.6	
		6.7	4230	0.15	6.3	
		6.7	6730	0.11	5.9	
Sodium chloride	0.2	2.5	2230	0.13	3.0	0.197
		5.0	2230	0.11	7.0	
		7.1	8270	0.068	4.3	
		7.3	5360	0.092	5.0	
		7.7	4230	0.055	10.9	
	0.4	3.2	2230	0.13	4.8	
		3.2	5360	0.075	3.4	
		6.4	8270	0.066	5.2	
		16.7	8270	0.12	7.4	
Iron	1.4	0.5	5400	0.060	0.86	0.0191
		0.5	5400	0.095	0.54	
		1.0	5400	0.14	0.74	
		1.0	8300	0.084	0.80	
		1.0	8300	0.085	0.78	
		2.0	8300	0.13	1.04	
		5.0	8300	0.17	1.94	
Glycerol	0.5	2.5	4230	0.062	4.5	4.08
				0.074	3.7	
			5400	0.049	4.4	
				0.045	4.8	
			8300	0.015	9.4	
				0.025	5.6	
	1.0	2.5	4230	0.132	2.4	
				0.137	2.3	
			5400	0.105	2.3	
				0.105	2.3	
		5.0	8300	0.072	4.4	
				0.072	4.4	

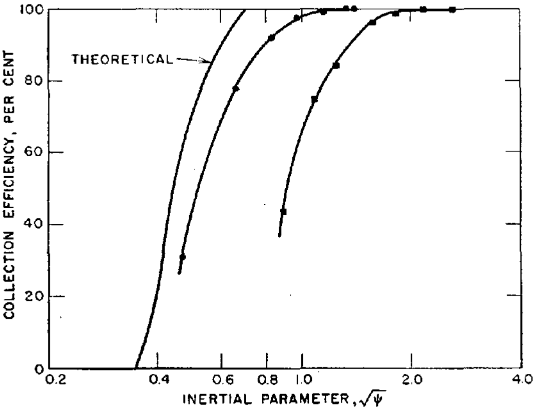

Figure 2. Collection efficiency of jet impactor with glycerol aerosols

● 0.5 micron
■ 1.0 micron

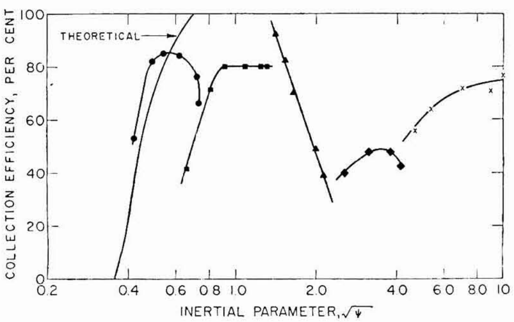

Figure 3. Collection efficiency of jet impactor with stearic acid aerosols

● 0.3 micron
■ 0.6 micron
▲ 1.0 micron
◆ 2.0 microns
× 3.0 microns

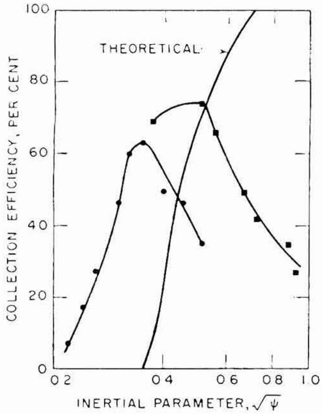

Figure 4. Collection efficiency of jet impactor with sodium chloride aerosols

● 0.2 micron
■ 0.4 micron

piled up on top of each other, they began to break loose, thus resulting in a much lower over-all collection efficiency than the initial efficiency. Additional evidence to support this contention was obtained by attempting to weigh the total material collected for successively larger and larger samples.

It was not possible to collect enough mass of sodium chloride or stearic acid aerosol to weigh with an analytical balance, whereas weighable amounts of glycerol aerosol could readily be collected.

If the physical nature of these materials is considered—glycerol particles as liquid, stearic acid particles as supercooled liquids (before collection), and sodium chloride particles as crystals—it appears that this is the order in which their adhesion and cohesion might vary, and this is the observed order of the agreement of their collection efficiencies with impactor theory. Glycerol showed good qualitative agreement even in the region of sonic velocities. Stearic acid was in fair qualitative agreement, and sodium chloride was in poor agreement.

While these results are not meant to test impactor theory, since this is a field-type instrument, they indicate the need for a great deal of information as to what happens after initial impaction of particles.

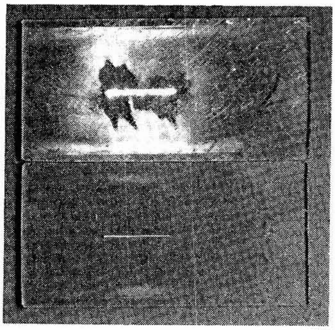

Figure 5. Jet impactor samples

Greenburg-Smith Impinger. This device can be classed as a modified form of the jet impactor which operates under liquid. One might expect to find some similarity to a jet impactor. Accordingly, ψ values were calculated and compared with the measured collection efficiencies. The data obtained with this instrument (Figures 6 and 7) show a smooth variation of efficiency with ψ and excellent qualitative agreement with theory. However, as particle size increases, higher ψ values are required for corresponding efficiencies. This instrument did not exhibit the sensitivity to aerosol material that the jet impactor did when glycerol, stearic acid, and sodium chloride were compared. The difficulty experienced with the jet impactor in collecting appreciable quantities of material would not be expected here.

Electrostatic Precipitator. This instrument was tested throughout its available voltage range and at various flow rates up to about 2 cubic feet per minute, its normal operating rate. Varying the voltage from 8 to 16 kv. had no measurable effect on the efficiency, and even at maximum flow rate the efficiency was very high for all aerosols, 98% or better (Table III). The Sinclair-Phoenix smoke photometer (*8*), which was available only for the glycerol tests, allowed investigation of the region of efficiency beyond 99%, and showed that for lower flow rates efficiencies of 99.99% are obtainable. The electrostatic precipitator has not shown any observable sensitivity to the nature of the aerosol material. It is probably a good general purpose instrument whenever the form in which the material is collected is acceptable.

Table III. Electrostatic Precipitator

Aerosol Material	Particle Diameter, Microns	Flow Rate, Cu. Ft./Min.	Collection Efficiency, %
Stearic acid	0.3	2.5	99
	0.6	2.5	99
	1.0	2.5	99
	2.0	2.5	98
	5.0	2.5	99
Sodium chloride	0.2	2.2	99
	0.4	2.2	99
Glycerol	0.5	0.33	99.96
		0.66	99.94
		1.00	99.87
		1.33	99.84
		1.66	99.80
		2.3	99.68
	1.0	0.17	99.99
		0.33	99.98
		0.66	99 94
		1.00	99.91
		1.33	99.86
		1.66	99.86
		2.3	99.82

Membrane Filters. All the aerosols which have been considered above were sampled with these filters. The collection efficiencies of both types, aerosol assay and hydrosol assay, were greater than 99% for all aerosols. This was the limit of measurement for all except the glycerol aerosols, which were measured with the new photom-

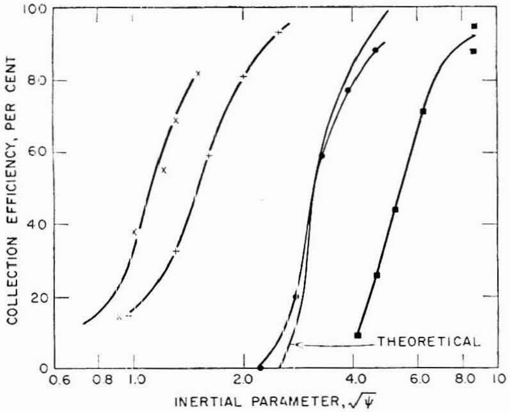

Figure 6. Collection efficiency of Greenburg-Smith impinger with sodium chloride and glycerol aerosols

Sodium chloride	Glycerol
× 0.2 micron	● 0.5 micron
+ 0.4 micron	■ 1.0 micron

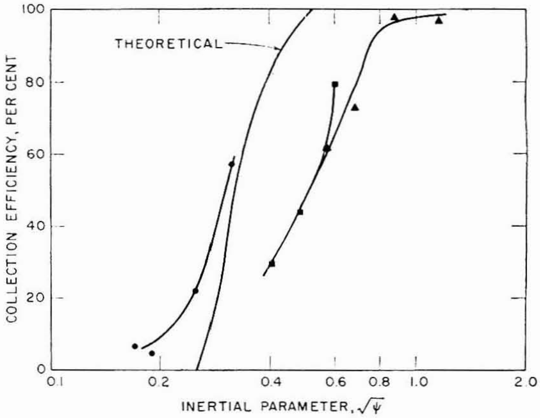

Figure 7. Collection efficiency of Greenburg-Smith impinger with stearic acid aerosols

● 0.6 micron
■ 1.0 micron
▲ 2.0 microns

eter previously described. The efficiencies measured with this instrument were greater than 99.995%, which was the practical limit of measurement.

Sedimentation Box. Sedimentation or settling of particles on slides and subsequent microscope counting are often used as an absolute method of determining particle concentration in an aerosol. This method has been compared with results obtained from the same aerosols with Millipore filter samples (Table IV).

Table IV. Sedimentation Box

Aerosol Material	Particle Diameter, Microns	Particle Concn., No. of Particles/Liter × 10^5	
		Sedimentation	Millipore filter
Stearic acid	2.0	7.3	1.35
		5.8	0.89
	4.0	7.1	4.1
	5.0	0.94	1.4
Sodium chloride	0.4	188	170

Stearic acid aerosols of 1- and 2-micron diameter produced very erratic, uneven distribution of deposit on the slides in the sedimentation box. Concentrations of 2-micron particles determined by the sedimentation technique were considerably higher than those determined from Millipore filter counts. For particles of 4 and 5 microns the agreement of the two methods was fairly good.

With 0.4-micron sodium chloride excellent agreement was obtained with filter counts. Very even distribution of particles was observed on the slides. The differences between the two materials may have been due to electric charge on the stearic acid particles.

SUMMARY

Three of the sampling devices tested did not show any sensitivity to the nature of the material being collected: Millipore filters, electrostatic precipitator, and Greenburg-Smith impinger. The thermal precipitator showed some sensitivity to thermal conductivity of the material being collected, though far less than that predicted by theory. Materials of high thermal conductivity were somewhat harder to collect. The jet impactor was sensitive to the adhesive and cohesive properties of the material being sampled. The tendency was to blow the material off the slide after collecting a very small amount. The sedimentation method may be sensitive to electrical charge on particles, which is a function of both the material and its treatment.

Some of the experimental results obtained by the methods of impaction and thermal precipitation are different from what would be theoretically predicted. These data have been obtained with field instruments, which are not designed to test theories. The results show the need for additional information in determining the performance characteristics of the various sampling devices, and they indicate the need for caution in the operation of the instruments and interpretation of the results.

NOMENCLATURE

$C = 1.00 + 0.16 \times 10^{-4}/D_p$, empirical correction factor for resistance of the gas to the movement of small particles, dimensionless
D_c = diameter of round jet or width of rectangular jet, cm.
D_p = effective diameter of aerosol particle, cm.
F_t = thermal force on particle, dynes
G = thermal gradient, ° K./cm.
k_a = thermal conductivity of gas, cal./° K. cm. sec.
k_i = thermal conductivity of particle, cal./° K. cm. sec.
T = absolute temperature, ° K.
V_o = velocity of aerosol jet, cm./sec.
μ = viscosity of gas, poise
ρ = density of gas, g./cc.
ρ_p = density of particle, g./cc.

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Automatic Long-Path Ultraviolet Spectrometer for Determination of Ozone in the Atmosphere

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▶ An ozone spectrometer was constructed and applied to atmospheric measurements in order to compare oxidant-ozone relationship for varying degrees of Los Angeles smog. Absorption by ozone of ultraviolet radiation in the region from 250 to 300 mμ is used as a basis for measurement of concentrations between 0 and 100 parts per hundred million (by volume). Automatic recording made 24-hour data feasible. Night-time values which do not exceed 2 or 3 p.p.h.m. furnish a basis for instrument calibration. Values up to 35 p.p.h.m. were obtained during August 1955.

Man's interest in ozone began more than 100 years ago when Schönbein, who was responsible for its discovery, claimed its presence in atmospheric air (*28*). It is interesting to note that his "ozonometer" consisted of paper soaked in potassium iodide and starch and that for years data thus obtained were subject to the criticism that the chemical reaction used was not specific to ozone.

As early as 1925 it was recognized that another oxidant, nitrogen dioxide, was also usually present in the air in concentrations of the same order as ozone (*11*, *27*). In fact, Paneth and Edgar stated in 1938 (*21*) that attempts to identify ozone by specific reagents had been unsuccessful, so that some chemists were even inclined to deny altogether the presence of ozone in the air. After rejecting the direct spectroscopic method as feasible but too difficult and costly for routine measurements, they set out to make the old chemical method (*16*, *32*) more reliable. Their technique was applied in several determinations, but the large amount of surface ozone measurements made since 1938 have used the method or Regener (*22*) or variations of it. This includes methods that are now more or less automatic, such as that described by Gluckauf and coworkers (*12*) and Bowen and Regener (*3*).

However, starting in 1931, several investigators, using the characteristic strong absorption of ozone in the ultraviolet (2200 to 3000 A.), with artificial light sources producing radiation in this band, made direct measurements of the ozone content near the earth (*5–8*, *13*, *14*, *30*). These latter determinations were stimulated by the uncontestable revelation of the presence of ozone in the atmosphere by spectroscopists studying the radiation from the sun and stars (*9*, *10*). It was soon recognized that most of the ozone thus measured was concentrated in the higher atmosphere (*31*). By 1941 both the chemical and spectroscopic methods agreed to values of 0 to 3 parts per hundred million (by volume) as the normal but variable concentration of ozone in the lower atmosphere (*20*). Concentrations of nitrogen dioxide of 0 to 2 p.p.h.m., at least in some areas, also occurred simultaneously.

The situation in Los Angeles in 1954 regarding identification of ozone in the smog had many features which were similar to those of the early days in normal clean atmospheres. The early clue to the presence of more than ordinary levels of ozone or oxidant was given by the excessive cracking of stressed rubber in the Los Angeles Basin as compared to other locations. Haagen-Smit followed this lead and, using the rubber cracking (*4*) and phenolphthalein reagent (*19*) methods, made quantitative estimates of ozone and oxidant during smog attacks (*15*). Furthermore, by a set of brilliantly conceived experiments, he discovered the mechanism of ozone formation in laboratory experiments with irradiated mixtures of nitrogen dioxide and organics.

Stanford Research Institute, using a modification of the classical potassium iodide technique (*17*), made estimates of the oxidant concentration in smog. They also used the method of Paneth and Edgar (*20*) on a smog atmosphere and have recently reported their results (*18*). Regener and his coworkers (*24*), in collaboration with the Stanford Research Institute, obtained direct spectroscopic evidence of ozone in the Los Angeles smog.

The situation as of the middle of 1954 can be summarized as follows. There was qualitative evidence of the presence of ozone in Los Angeles smog. The concentrations certainly exceeded the normal clean air surface values of 0 to 3 p.p.h.m., and may at times have reached 100 p.p.h.m. There was a real need to make the ozone-oxidant relation quantitative over the full range of oxidant values reached in smog attacks. Therefore, it appeared desirable to build an ultraviolet spectrometer for the measurement of ozone concentration, based on the same principles as Regener's instrument (*23*) but adapted for continuous automatic operation.

APPARATUS

The first approach was to consider the use of a photoelectric instrument

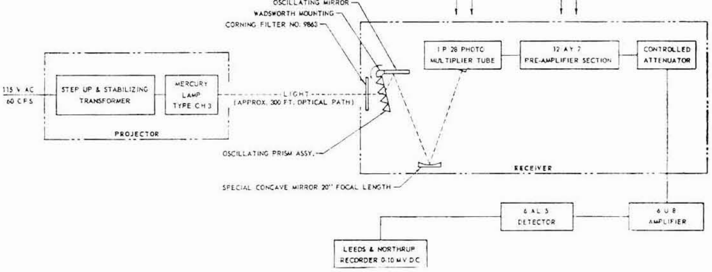

Figure 1. Block diagram of ultraviolet recording spectrometer

devised by Stair, Bagg, and Johnston (*29*) under the sponsorship of the Army Ordnance Department. However, as they noted, their apparatus was not suited to daylight operation as originally set up. Baum, who had carried out an intensive study of the attenuation of ultraviolet light over a long atmospheric path in 1950 (*1*, *2*), advised the use of Regener's principle of measurement. Essentially, the use of narrow bands of radiation for each of the wave lengths needed for the ozone determination required the use of a dispersion system. Accordingly, a photoelectric spectrometer in two sections was designed (*25*).

Figure 1 shows a block diagram of the entire apparatus. The projector unit houses a type CH3, high-pressure mercury lamp mounted in horizontal position. It has a 6-inch aperture faced with a quartz plate. The lamp is placed at the focus of a spherical mirror. The lamp, mirror, and housing were assembled permanently because adjustments for focus and tilt proved unnecessary. It was also found that the lamp radiation was adequately modulated by the alternating current supplied, so that mechanical modulation or chopping was unnecessary. However, it was found necessary to provide voltage regulation for the lamp because line voltages generally available at field locations would be variable and the projector intensity is used as a radiometric standard of reference. Ordinary voltage-stabilizing transformer equipment would not operate the high-pressure mercury lamp in proper fashion; laboratory investigation culminated in the addition of a separate autotransformer to set the level of the regulated voltage.

The receiving unit consisted of the prism spectrometer, the photomultiplier detector and associated electronics, and a strip-chart recorder. The spectrometer has an exit collimator 5½ inches in diameter and 20 inches in focal length faced with a Corning filter No. 9863. The prism is a Fresnel-type assembly of four 60° fused quartz prism elements. The slit width was 0.03 inch and subtended about 5 mμ at 300 mμ. Synchronous motors drive the wave length and program cams. The wave length cam provides a sweep from 254 to 365 mμ in approximately 45 seconds. The programming cam provides two such sweeps about 1 minute apart every 15 minutes. The recorder was adjusted to full-scale deflection (10 mv.) at 365 mμ with one-fortieth attenuation. The attenuator cuts out a little below 300 mμ. Figure 2 shows a schematic diagram, and Figure 3, a photograph, of the optical system. The circuitry involved in the detection, amplification, and recording of the received radiation is the same as that shown by Stair and coworkers (*29*, Figures 4 and 5), except that the amplifier was modified to be tuned to 120 cycles per second instead of the 510 cycles per second used by Stair. The electronics comprise a high-voltage supply for the photomultiplier tube and a tuned amplifier (together with its power supply) for additional amplification of the modulated signal. The spectral radiant energy of the mercury arc, as modified by its transmission through a Corning glass filter No. 9863, is measured by a Type 1P28 photomultiplier. The emission of the lamp, the transmission of the filter, the spectral sensitivity of the photomultiplier tube, and the combined effect are shown in Figure 4.

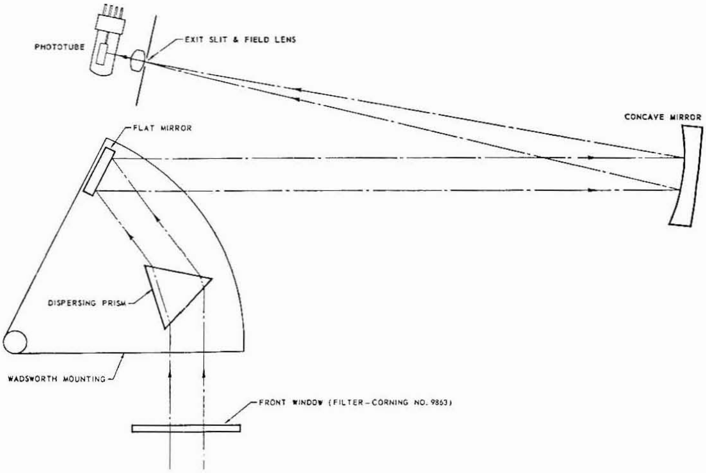

Figure 2. Schematic diagram of optical system

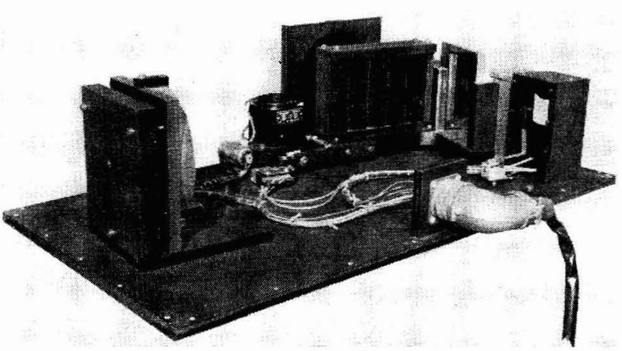

Figure 3. Optical system

METHODOLOGY

This method is based on the optical absorption characteristics of ozone in the ultraviolet spectrum. Although ozone has several intense absorption bands at various wave lengths within the ultraviolet, visible, and infrared regions of the spectrum, the strongest is the Hartley band centered between 250 and 260 mμ. The ozone absorption data as reported by Vigroux (*33*) are shown in Table I.

Table I. Ozone Decadic Absorption Coefficients

Wave Length, Mμ	Km.$^{-1}$, P.P.H.M.$^{-1}$
265	0.125
280	0.0543
302	0.0038
313	0.00087

The essential experimental data are the intensities of the various radiations as transmitted through the approximately 300-foot sample of air. Attention was focused on the lines at 265, 280, and 313 mμ. Conventionally, the absorption of a sample is determined as the ratio of the transmitted to the incident radiation. In this problem, the frequent measurement of the incident radiation is made experimentally difficult by the very great thickness of the sample and the requirement for continuous recording. Therefore, following the method of Regener (*23*), the measurement of ozone concentrations was based on the ratios of energies measured at the three wave lengths. The degree to which this method can distinguish between ozone and other attenuants is discussed.

From the well-known laws of absorption in homogeneous media, the equation for any one wave length takes the form

$$I_\lambda = I_{0\lambda}\, 10^{-s\alpha_\lambda}\, c^{-s\sigma_\lambda} \qquad (1)$$

where I_λ = transmitted radiation at wave length λ
$I_{0\lambda}$ = incident radiation at wave length λ
s = optical path length
α_λ = ozone decadic absorption coefficient
c = concentration of ozone
σ_λ = decadic absorption coefficient of all other pollutants, Rayleigh scattering, and other attenuants

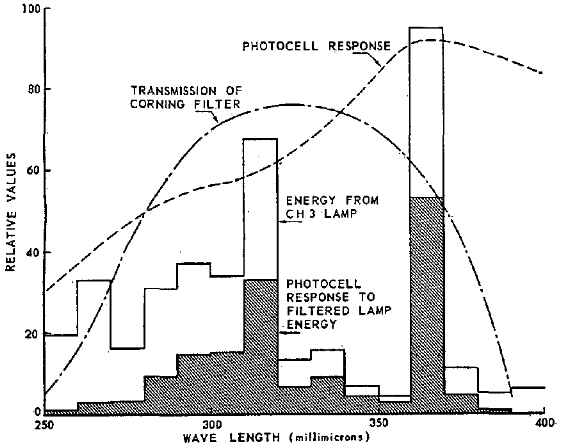

Figure 4. Spectral response of components of spectrometer

In this case the transmitted radiation is measured at three wave lengths and at several levels of ozone concentration. For a pair of wave lengths at time t

$$\frac{I_{\lambda_1 t}}{I_{0\lambda_1}} = 10^{-s\alpha_{\lambda_1}}\, C_t^{-s\sigma_{\lambda_1}} \qquad (2)$$

$$\frac{I_{\lambda_2 t}}{I_{0\lambda_2}} = 10^{-s\alpha_{\lambda_2}}\, C_t^{-s\sigma_{\lambda_2}} \qquad (3)$$

Under the same experimental conditions, but at a different ozone concentration

$$\frac{I_{\lambda_1 t'}}{I_{0\lambda_1}} = 10^{-s\alpha_{\lambda_1}}\, C_{t}'^{-s\sigma_{\lambda_1}'} \qquad (4)$$

$$\frac{I_{\lambda_2 t'}}{I_{0\lambda_2}} = 10^{-s\alpha_{\lambda_2}}\, C_{t}'^{-s\sigma_{\lambda_2}'} \qquad (5)$$

where

λ_1 = 265 mμ
λ_2 = 313 mμ
C_t' = ozone concentration at time t'

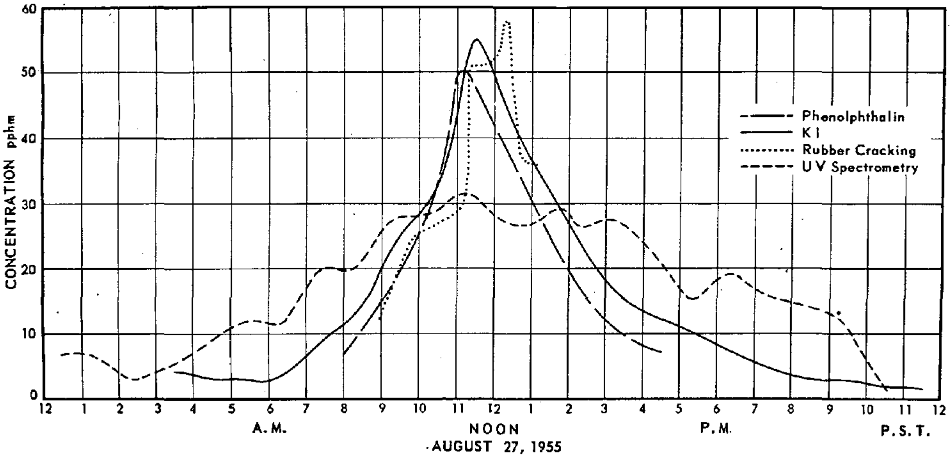

Figure 5. Diurnal variation of oxidants and ozone in Pasadena

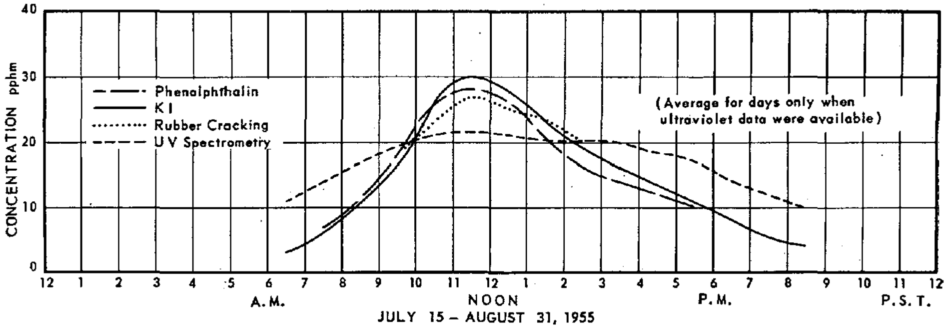

Figure 6. Diurnal variation of oxidants and ozone in Pasadena

Average of approximately 50 days

C_t = ozone concentration at time t
$\alpha_{\lambda_1} = 0.123$
$\alpha_{\lambda_2} = 0.00087$

Taking ratios and simplifying,

$$\frac{I_{\lambda_1 t}}{I_{\lambda_2 t}} \Big/ \frac{I_{\lambda_1 t'}}{I_{\lambda_2 t'}} = 10^{-s[(\alpha_{\lambda_2} - \alpha_{\lambda_1})(C_t' - C_t) + (\sigma_{\lambda_2}' - \sigma_{\lambda_1}') - (\sigma_{\lambda_2} - \sigma_{\lambda_1})]} \quad (6)$$

The unusual reference condition exists in the Los Angeles atmosphere wherein the ozone concentration becomes approximately zero each night (usually between 12 and 4 A.M.). Thus, C_t is set equal to 2 p.p.h.m. Except for the effect of the σ's, C_t' is determined at any other time of the day by observing the ratio of the intensities and substituting them in Equation 6.

The terms in σ represent pollutant absorptions and aerosol scattering other than ozone. Generally, σ will vary independently of C. However, work by Baum and Dunkelman (*1*, *2*) provided attenuation data over a wide range of visual range values in Pasadena, measured over long atmospheric paths during which times there were undoubtedly appreciable concentrations of some gaseous pollutants which absorb radiation in this region as well as aerosol scattering of the radiation. These attenuation data are shown in Table II.

It can be seen from these data that $\sigma_{\lambda_2} - \sigma_{\lambda_1}$ may vary from −0.43 to −0.31. Since the σ terms represent the comparison of two separate atmospheric conditions, the summation, $(\sigma_{\lambda_2}' - \sigma_{\lambda_1}') - (\sigma_{\lambda_2} - \sigma_{\lambda_1})$, may have any value between +0.12 and −0.12. By comparison the term, $(\alpha_{\lambda_2} - \alpha_{\lambda_1})(C_t' - C_t)$, has the value 0.12 $(C_t' - C_t)$. Thus, the influence of other attenuants may introduce an error of ±1 p.p.h.m. in the ozone determination. At low concentrations this is a large

Table II. Decadic Coefficients of Attenuation[a]
(Standard path = 1 km.)

Visual Range, Miles	σ_1 265 Mμ,	σ_2, 302 Mμ	(Exclusive of Ozone) $\sigma_2 - \sigma_1$
0.37	4.60	4.17	−0.43
1.24	1.69	1.22	−0.47
1.56	1.30	0.87	−0.43
3.10	1.19	0.76	−0.43
5.00	0.95	0.61	−0.34
6.80	0.80	0.39	−0.41
12.4	0.74	0.43	−0.31
62.1	0.43	0.21	−0.22

[a] Computed from data by Baum and Dunkelman (*2*).

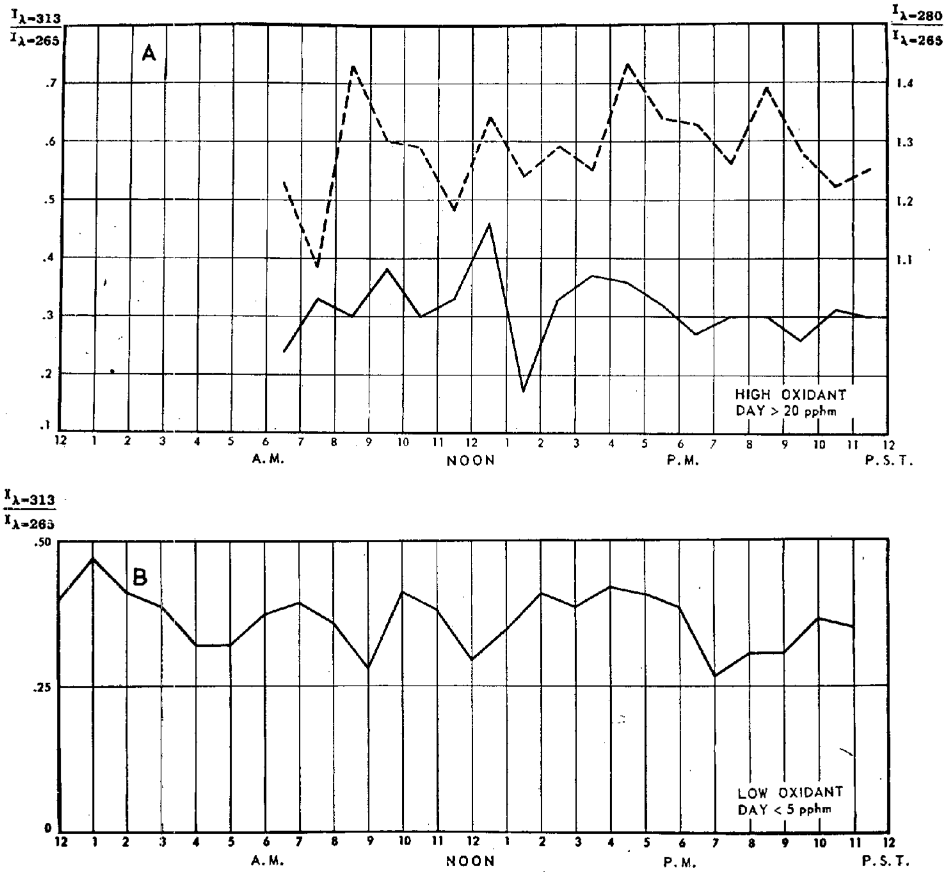

Figure 7. Diurnal behavior of intensity ratios

A. Nov. 10, 1955 B. Nov. 12, 1955

Read dotted line with scale on right; read solid line with scale on left fraction of the determined value, but at concentrations above 10 p.p.h.m. this error is 10% or less. A method for reducing this error is to make simultaneous determinations of visual range and apply a suitable correction based on Baum's data.

Therefore, in presenting the ozone data in this paper, the equation

$$(C_t' - C_t) = \frac{\log\left(\frac{I_{\lambda_1 t}}{I_{\lambda_2 t}} \cdot \frac{I_{\lambda_2 t'}}{I_{\lambda_1 t'}}\right)}{S\,(\alpha_{\lambda_1} - \alpha_{\lambda_2})}$$

is used, wherein it has been assumed that the σ terms add up to zero and

C_t = 2 p.p.h.m.
S = 269 feet for early data
S = 325 feet for later data

Two values of ozone concentrations were available from the intensity ratios, $\frac{I_{280}}{I_{265}}$ and $\frac{I_{265}}{I_{313}}$, for each sweep of the spectrum. Two sweeps 1 minute apart were made every 15 minutes throughout each 24-hour period.

OZONE CONCENTRATIONS IN THE ATMOSPHERE

Figure 5 shows the behavior of oxidant and ozone concentrations on a typically bad smog day in Pasadena. The characteristic sharp rise in the morning, peaking in the middle of the day, and gradually diminishing in the late afternoon, are well demonstrated. This graph also shows the responses of various chemical systems to the smog atmosphere which were recorded simultaneously as part of an intensive program of atmospheric monitoring carried out in 1955 (*26*). The ultraviolet determinations of ozone lie below the oxidant measurements. This finding is repeated consistently throughout the approximately 50 diurnal curves which were averaged (Figure 6).

A hypothesis which can be advanced to explain this behavior is as follows. Ozone is formed photochemically and until a sufficient quantity is available, say 20 p.p.h.m., the chemical systems which are subject to interferences of reducing agents lag behind until the middle of the day when the highest concentration of other oxidants, in addition to ozone, are formed. Then the oxidant values exceed the ozone, the difference becoming greater with higher ozone concentrations.

DISCUSSION

In order to get some insight on the reliability of the instrumental factors, the equipment was run under three sets of experimental conditions. One set of ozone data was obtained over an optical path of 269 feet, two thirds of which was about 4 feet above a roof of a building. There was, obviously, considerable atmospheric turbulence from local heating. For comparison, a second set of data was obtained with 325 feet of optical path which was approximately 50 feet over the terrain. There appeared to be no significant feature of the data which could be attributed to the local turbulence. A third set of data was obtained with the receiver only 40 feet from the projector on two types of days: low oxidant *vs.* high oxidant. Figure 7 shows the behavior of the ratios for Nov. 10 and 12, 1955. These variations are somewhat higher on the high oxidant day, but no systematic error seems to be apparent from an instrumental point of view. However, it would be desirable to monitor the intensity ratios at the source simultaneously with the received intensities. It would seem that more data of these kind should be obtained. It was difficult to do so in this experimental setup because the projector was on the roof of one building and the receiver on another 300 feet away.

One other experiment was run in which a measure of the short-time (1 minute) variability of air mass over the 300-foot optical path was obtained. Figure 8 shows a plot of ozone concentration *vs.* time over a 45-minute period. Experimentally an ozone determination was made every minute of this period. Arithmetically, 5-minute averages were

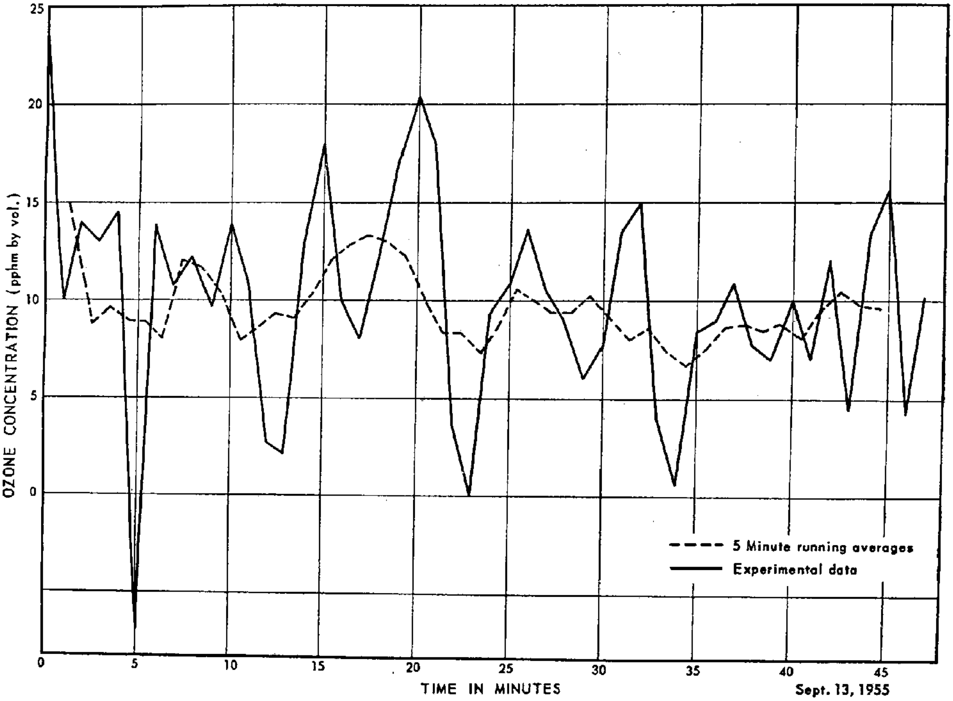

Figure 8. Ozone concentrations in Pasadena

obtained. Obviously the sample was a very inhomogeneous one. These data further indicate the desirability of having the instrument perform the integrations by performing slower sweeps of the wave length spectrum—say up to 15 minutes per sweep.

Previously the effect of aerosol scattering on the ozone measurement was discussed. It was shown that if Baum's nighttime data was assumed to apply to daytime conditions, errors of 1 to 2 p.p.h.m. in ozone concentrations were incurred. Baum's data also suggest that gaseous pollutants which absorb in this region are also included in the error estimate. To strengthen the conclusion in this regard, sulfur dioxide, one pollutant known to be present, was analyzed to determine its effect on these ozone determinations.

For sulfur dioxide

$$\begin{aligned}\alpha_{265} &= 0.0195 \text{ km.}^{-1} \text{ p.p.h.m.}^{-1}\\ \alpha_{230} &= 0.031 \text{ km.}^{-1} \text{ p.p.h.m.}^{-1}\\ \alpha_{313} &= 0.007 \text{ km.}^{-1} \text{ p.p.h.m.}^{-1}\end{aligned}$$

The pair of α's for ozone and sulfur dioxide give

$$\begin{aligned}(\alpha_{265} - \alpha_{230})_{SO_2} &= -0.11\\ (\alpha_{265} - \alpha_{230})_{O_3} &= +0.069\end{aligned}$$

Therefore, 10 p.p.h.m. of sulfur dioxide would give an error of about 2 p.p.h.m. in ozone. Thomas Autometer sulfur dioxide data for Los Angeles indicate sulfur dioxide concentration averages about 10 p.p.h.m. during the middle of high oxidant or ozone days.

If the other pair of lines are used, one obtains

$$\begin{aligned}(\alpha_{265} - \alpha_{313})_{SO_2} &= +0.0126\\ (\alpha_{265} - \alpha_{313})_{O_3} &= +0.122\end{aligned}$$

Thus, 10 p.p.h.m. of sulfur dioxide would be read as 1 p.p.h.m. of ozone. It should be noted that these effects are in opposite directions. Therefore, averages of ozone values determined from both ratios would essentially eliminate the sulfur dioxide effect at these wave lengths and at these low concentrations.

The use of this instrument on the smog studies in Pasadena has indicated the desirability of making similar ozone measurements in other parts of the Los Angeles Basin. Toward this end, as well as meeting the objective of making ozone measurements automatically for its large-scale air monitoring program, the Air Pollution Control District has had two additional instruments built and is currently evaluating their performance in the field.

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Qualitative Microdetermination of Organic Phosphorus Compounds

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▶ Phosphorus-containing organic compounds are of great importance in biological systems, insecticides, and war gases. Methods are proposed for the sampling, degradation, and detection of minute amounts of such materials. A newly discovered phosphorus reagent has been adapted for use in detecting as little as 0.2 γ of combined phosphorus. The proposed procedures are applicable to acids, esters, acyl halides, and anhydrides together with their thio analogs.

The wide occurrence of organic phosphorus compounds in biological systems, as well as their frequent use in insecticides and chemical warfare agents, makes their determination a problem of great importance in many fields. The most generally applicable approach to the microdetection of these compounds is their conversion to inorganic phosphate, for which sensitive tests now exist. Only in rare cases do phosphorus-containing functional groups possess characteristic chemical properties which would permit their direct detection and positive identification.

Until recently, the principal methods of detecting inorganic phosphates were subject to a number of interferences. The discovery by Robinson and West (*4*) of a more highly selective reagent, *o*-dianisidine molybdate, has made possible the development of correspondingly selective tests for organic phosphorus compounds. Two new procedures are described here and a direct comparison is made with an adaptation of a previous test. Each of the tests exhibits characteristics which would be advantageous under a variety of conditions.

The application of the most general method to the detection of a phosphorus compound in a mixture of gases has also been demonstrated.

EXPERIMENTAL

Sulfuric Acid–Dianisidine Molybdate, Method A. A very general and efficient reagent for degrading organic compounds of phosphorus is refluxing, concentrated sulfuric acid. In a few cases, it is advantageous to add mercury(II) sulfate as a catalyst to speed the degradation of volatile substances which would otherwise escape before decomposing. The catalyst also minimizes carbon formation by organic contaminants in the sample. The brief digestion is followed by neutralization, buffering, and addition of *o*-dianisidine molybdate.

The unknown can be detected as the solid or the liquid. It is often more conveniently handled as the carbon tetrachloride solution or as an adsorbate on silica gel.

Chemicals. The organic phosphorus compounds studied were commercially available materials, except for sarin (isopropyl methylphosphonofluoridate, a nerve gas), and were used without further purification. All were reagent grade with the exception of the phenylphosphonothionic dichloride, which was technical grade, and Malathion, which contained 95% of the insecticide.

Research samples of octylphenyl acid phosphate and trihexyl phosphite were kindly donated by the Virginia-Carolina Chemical Corp., trimethyl phosphite, by the Monsanto Chemical Co., phenylphosphinic acid, phenylphosphonic acid, and phenylphosphonothionic dichloride, by the Victor Chemical Works.

Reagents. Sulfuric acid, 96%.

Sodium carbonate–sodium formate solution. For samples in carbon tetrachloride solution: 21.0% sodium carbonate (anhydrous), 4.10% sodium formate; for samples on silica gel: 14.0% sodium carbonate (anhydrous), 2.75% sodium formate. The carbonate should not contain more than 0.0003% phosphate as an impurity. The formate should not contain more than 0.001% phosphate.

o-Dianisidine molybdate reagent. Dissolve 2.5 grams of sodium molybdate dihydrate in 15 ml. of water and 5 ml. of concentrated hydrochloric acid. Dissolve 0.125 gram of *o*-dianisidine in 2 ml. of glacial acetic acid and add this with stirring to the molybdate solution. Allow the mixture to stand overnight and filter. Store the solution in a glass-stoppered bottle. It is stable for 6 to 12 months if agitation with air is avoided.

The droppers used to deliver the sulfuric acid and sodium carbonate–sodium formate solutions are heated in a flame and their tips drawn to 1 mm. or less in outside diameter. They will then deliver roughly 100 drops of sulfuric acid or 45 drops of carbonate-formate solution per milliliter. This decreases the dilution factor.

Procedure. In the bottom of a Pyrex No. 7740 test tube, $3 \times {}^3/_8$ inches, is placed 1 drop of sulfuric acid. The sample, in 0.01 to 0.50 ml. of carbon tetrachloride or on approximately 0.02 gram of silica gel, is dropped in. The tube is warmed in a flame along most of its length to drive off the solvent without heating the sulfuric acid at the bottom (30 to 40 seconds). Only then is the acid heated. It is refluxed not more than one fourth of the way up the tube for at least 30 seconds or until any carbonaceous matter has dissolved.

The tube is air cooled by being waved vigorously (10 seconds), the bottom half is water cooled (10 seconds), and 3 drops of carbonate-formate solution are added. The liquid is rolled up the inner walls to ensure complete mixing and neutralization. Two drops of *o*-dianisidine molybdate reagent are added.

A reddish-brown precipitate indicates the presence of phosphorus compounds. At microgram concentrations, the cloudiness is easily seen against a black background. The test appears within 30 seconds; the procedure requires 2 minutes.

If the unknown is relatively volatile or if the sample solution contains much organic matter, a pinch of mercury(II) sulfate (about the mass of a wheat grain) may be added as an oxidation catalyst prior to the digestion. The test should then be carried out in a hood, as the mercury salt tends to sublime. Any red precipitate of mercury oxide initially formed on addition of the carbonate-formate solution should redissolve to give a colorless solution after mixing is complete.

The blanks remained clear and colorless, and proved to be unnecessary.

Sensitivity. In Table I are listed the compounds which have been detected in carbon tetrachloride solution by this method. Those compounds which required a catalyst are specifically noted.

Table I. Phosphorus Compounds Detected by Sulfuric Acid–Dianisidine Molybdate Method

Compound	Detection Limit, γ	PO_4 Equiv., γ
Tributyl phosphate	2	0.7
O,O,S-triethyl phosphorodithioate	1	0.4
Tri-*p*-tolyl phosphate	2	0.5
O,O,O-tri-*m*-tolyl phosphorothionate	2	0.5
Malathion[a]	2	0.6
Tetraethyl pyrophosphate	1	0.7
Trimethyl phosphite	1	0.8
Trihexyl phosphite	2	0.6
Triphenyl phosphite	1	0.3
Phenylphosphonic acid	1	0.6
Diethyl ethylphosphonate	3[b]	1.7
Dibutyl butylphosphonate	2	0.8
Bis-(2-ethylhexyl)-2-ethylhexylphosphonate	2	0.5
Phenylphosphinic acid	0.5	0.7
Sarin[c]	15[d]	10

[a] *O,O*-Dimethyl phosphorodithioate of diethyl mercaptosuccinate.

[b] Mercuric sulfate required; sensitivity, 10 to 15 γ with no catalyst.

[c] Isopropyl methylphosphonofluoridate.

[d] Mercuric sulfate required; sensitivity, 30 to 60 γ with no catalyst.

The sensitivity of the *o*-dianisidine molybdate reagent for phosphate ion is known to be 0.3 to 0.5 γ. It is apparent that the majority of the organic phosphorus compounds were efficiently converted to phosphate by the above procedure.

With compounds containing phosphorus bound only to oxygen or sulfur atoms, the volatility of the unknown has little effect on the test sensitivity. Trimethyl phosphite, for example, boils at 111–12° C., or 230° below the reflux temperature of sulfuric acid, and it might have been expected to escape before it could be degraded to less volatile acids. The phosphites, phosphates, and their thio analogs were easily decomposed.

Compounds containing a carbon-to-phosphorus bond were much less reactive, however, and their volatility became a factor in determining test sensitivity. Thus, sarin, which boils at about 150° C., gave tests of rather poor sensitivity, even with mercuric sulfate present. Diethyl ethylphosphonate, boiling point 200° C. (130° less than the reflux temperature of sulfuric acid), gave sensitive tests, but only with the catalyst present. Dibutyl butylphosphonate and other less volatile phosphonates were efficiently decomposed and detected with or without a catalyst.

INTERFERENCES. If the sample contains amounts of extraneous organic matter, heating it with the sulfuric acid will cause excessive carbon formation which obscures the test. Also, the sulfuric acid consumed in oxidizing such excess organic material can be considerable, and this causes a change in the final pH obtained after addition of the carbonate-formate solution. The *o*-dianisidine molybdate reagent cannot be used at a pH much above 7 without giving cloudy, green blanks.

Of the relatively few interferences which West and Robinson encountered in detecting inorganic phosphates, several of the most important are eliminated by the sulfuric acid digestion employed here. For example, inorganic and organic sulfides were completely removed. Silicon compounds yielded an inert, dehydrated film of silica which was invisible in the test tube while wet.

Inorganic nitrites and nitrates interfered by giving a cloudy red color, but 1% isoamyl nitrite in carbon tetrachloride showed no interference. Organic nitrogen compounds containing nitro, azo, or amino groups also were without effect.

The procedure avoids direct heating of the sulfuric acid while carbon tetrachloride is present, as this generates phosgene and consumes acid.

When the test was run on silica gel samples, the moisture contained in the gel caused volatilization of some of the sulfuric acid as the hydrated acid. A less concentrated base-buffer solution was therefore used.

Hydrocarbon solvents cannot be used for the sample, as their vapors are charred by hot, concentrated sulfuric acid. A suitable solvent that can be used in place of carbon tetrachloride is 1,1 - dichloro - 2,2 - difluoroethane.

APPLICATION TO AIR ANALYSIS. It was of interest to demonstrate not only the sensitivity of the test to samples adsorbed on silica gel, but also the efficiency with which silica gel collects vapors of phosphorus compounds from air. Trimethyl phosphite was selected as the substance to be detected because it has a fairly low boiling point (111–12° C.), and also because its vapor pressure is known (*3*) at widely different temperatures.

The silica gel tubes used to collect the samples were 2 mm. in inside diameter and contained an 0.8-cm. column of the fine granular gel (60 mesh).

The synthetic gas mixtures were prepared by bubbling filtered air through carbon tetrachloride solutions of the trimethyl phosphite at room temperature (30° C.), the saturated vapor then being passed through a silica gel tube. After 3 ml. of the original 7 ml. of solution had been vaporized (30 to 45 minutes), the silica gel was transferred to a test tube and the above test was run (without catalyst). Positive tests were obtained with carbon tetrachloride solutions containing as little as 3 γ per ml. of trimethyl phosphite in the original solution. Blanks run on the entire procedure were negative.

The vapor pressure of the ester was estimated to be 37 mm. at 30° C., the known data for it being similar to that for toluene. Assuming the solutions to be ideal, the ratio of phosphite to carbon tetrachloride in the vapor was 0.26 of that in the liquid. The procedure detected 3 γ of trimethyl phosphite in 4.1 liters of air–carbon tetrachloride mixture (19% carbon tetrachloride by volume).

The fact that such small silica gel tubes were able to strip microgram quantities of the phosphite from the gas mixture may indicate that most organic phosphorus compounds can be similarly collected. The difference in boiling point between the phosphite and carbon tetrachloride is only 35° C., and it is possible their adsorption affinities for silica gel do not differ by a large factor. It is remarkable that the gaseous carbon tetrachloride did not elute the trimethyl phosphite from the silica gel. The majority of organic phosphorus compounds are much less volatile than the phosphite, and should be adsorbed even more efficiently.

It is also evident that the detection method is sensitive to phosphorus-containing adsorbates on silica gel.

Sulfuric Acid–Hydrazine Molybdate, Method B. Although West and Robinson found it advantageous to add 85% hydrazine hydrate to the precipitate obtained from *o*-dianisidine molybdate and inorganic phosphate, the blanks obtained in the present tests were unsatisfactory when this was done. However, the reduction of phosphomolybdic acid by hydrazine to give molybdenum blue can be carried out on a separate sample which has been digested with sulfuric acid, and this may serve as a useful confirmatory test.

The heteropoly blue test is well known (*1*), but its application in the following way is novel, and comparison of its characteristics with those of other tests is of interest.

REAGENTS. Sulfuric acid, 96%.

Sodium carbonate–acetic acid–hydrazine solution: 17.0% sodium carbonate (anhydrous), 0.85% hydrazine monohydrate, 2.3% acetic acid, freshly made.

Sodium molybdate solution: 3.00% sodium molybdate dihydrate.

The droppers used to deliver all these reagents are prepared as described before.

PROCEDURE. In the bottom of a Pyrex No. 7740 test tube, 3 × $^3/_8$ inches, is placed 1 drop of sulfuric acid and 1 to 20 drops of the unknown in carbon tetrachloride solution. The solvent evaporation, digestion, and cooling are carried out as before.

Three drops of the carbonate-acetate-hydrazine solution are added, taking the usual care in mixing. Then 1 drop of molybdate solution is added.

The solution turns blue within 1 minute if phosphorus compounds are present. The color is best seen if the liquid is poured onto a white spot plate. The blank remains practically colorless.

SENSITIVITY. Mercuric sulfate cannot be used as a catalyst in the digestion as it gives a gray precipitate with the hydrazine and molybdate. The test, therefore, applies to compounds which do not require a catalyst. The sensitivity to tributyl phosphate, *O,O,S*-triethyl phosphorodithioate, and phenylphosphonic acid was two to four times that of the method using *o*-dianisidine molybdate reagent.

INTERFERENCES. Excessive amounts of organic matter will interfere as mentioned previously.

The heteropoly blue test is considerably less selective than the *o*-dianisidine molybdate reagent. Arsenic compounds give a positive test when in sufficiently high concentration. As much as 100 γ of triphenylarsine can be tolerated, however. No interference occurs from silicon compounds, which are decomposed by the digestion process as mentioned previously.

Sodium Perborate–Dianisidine Molybdate, Method C. FOR ACIDS, ACYL HALIDES, AND ANHYDRIDES CONTAINING PHOSPHORUS. Organic phosphorus compounds may, if desired, be divided into subclasses based on their chemical properties. One such subgroup is composed of acids, alkyl or aryl acid esters, salts, and very readily hydrolyzed acyl derivatives. These are converted by alkaline sodium perborate solution into nonvolatile salts which are readily degraded to sodium phosphate by strong heating with excess perborate. The *o*-dianisidine molybdate reagent can then be added directly without the neutralization and buffering required in the preceding methods.

REAGENTS. Sodium perborate, 1% aqueous, freshly made.

o-Dianisidine molybdate reagent, diluted to half the strength used in Method A.

Droppers of ordinary size are satisfactory, as the dilution factor is small in this method.

PROCEDURE. In the bottom of a Pyrex No. 7740 test tube, 3 × $^3/_8$ inches, is placed 1 drop of perborate solution and 1 to 20 drops of the sample in a volatile solvent such as water, isopropyl alcohol, or carbon tetrachloride.

The tube is warmed along its length to drive off the solvents (45 seconds). The small amount of white residue is heated strongly over a flame until it dis-

Table II. Phosphorus Compounds Detected by Sodium Perborate–Dianisidine Molybdate Method

Compound	Detection Limit, γ	PO_4 Equiv., γ
Sarin	0.5	0.3
Phenylphosphonic acid	1	0.6
Tetraethyl pyrophosphate	1	0.7
Octylphenyl acid phosphate[a]	5	1.4
Phenylphosphonothionic dichloride	1	0.5
Parathion[b]	4	1.3
O,O,S-triethyl phosphorodithioate	80	42.0
Tributyl phosphate	200	72.0

[a] Mixture of mono- and diaryl acid phosphates, approximately equimolar.

[b] *O,O*-Diethyl-*O*-*p*-nitrophenyl phosphorothionate. The liquid mixture should be boiled for 45 seconds before solvents are driven off to ensure complete hydrolysis.

appears (30 seconds). The tube is air-cooled by being waved vigorously (20 seconds), and then the bottom half is water-cooled (10 seconds).

Two drops of dianisidine molybdate reagent are added. A reddish-brown precipitate indicates the presence of phosphorus compounds. At microgram concentrations it can be viewed as a light cloudiness against a black background. The test appears within 30 seconds.

SENSITIVITY. The compounds studied by this method are listed in Table II.

In the detection of sarin, a nerve gas which is more volatile than most of the compounds studied, this method was far superior to Methods A and B. With other members of this subgroup, the sensitivity equaled that of Method A. With difficultly hydrolyzed compounds such as esters, it was ineffective. Requiring only two reagents, it is the most convenient method where applicable.

INTERFERENCES. The method does not permit the presence of a large excess of organic matter which is likely to be carbonized and obscure the test. Most of the interferences observed by West and Robinson in detecting inorganic phosphate are observed here. The test tolerated as much as 250 γ of sodium metasilicate; more than this gave a positive reaction.

The use of dianisidine molybdate reagent at full strength caused cloudiness in the blanks. Apparently this was due to a reaction with sodium borate.

DISCUSSION

The best test for organic phosphorus compounds that has been previously described appears to be that of Feigl (*2*), in which the unknown is ignited with calcium oxide at red heat, and the resulting calcium phosphate is detected by the benzidine molybdate method. The procedure requires five reagents, a considerable amount of time, and is said to apply to nonvolatile compounds only. Where it is applicable, its sensitivity approximately equals that of the tests which utilize *o*-dianisidine molybdate.

Calcium oxide as a degradative reagent is relatively ineffective because it is not an oxidant or even a strong base. The Feigl test relies on conversion of the phosphorus compound to a salt before the unknown escapes through volatilization. The salt can then be ignited strongly and air-oxidized to calcium phosphate. The types of compounds that will give salts in this way are about the same as those to which Method C is applicable: acids, acyl halides, and anhydrides. It is unlikely that trialkyl phosphates, dialkyl alkylphosphonates, or many of their thio analogs would respond.

Method A appears to be the most general one now available for organic compounds of phosphorus, and is also the most selective with respect to other hetero-elements (*4*). Method B is most sensitive, while Method C is the most convenient and selective for acids and easily hydrolyzed acyl derivatives. All three methods are much more nearly independent of the volatility of the unknown than previously described procedures.

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Detection of Nerve Gases by Chemiluminescence

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▶ Nerve gases can be detected by the chemiluminescence produced in the presence of a solution containing 5-amino-2,3-dihydro-1,4-phthalazinedione (luminol) and sodium perborate; 0.5 γ of nerve gas can be readily detected. A plot reasonably close to a straight line was obtained when the amounts of nerve gas were plotted against the maximum luminosity values, indicating that the reaction may also be used for quantitative purposes. The most promising potential use indicated for the reaction is the application to continuous automatic sampling of the atmosphere.

DESCRIPTIONS have been given of specific colorimetric (*2*) and fluorescence (*3*) reactions suitable for the detection and determination of the nerve gases which are organic pentavalent phosphorus compounds having structures either of the type $R(R'O)(PO)F$ or $(R_2N)(R'O)(PO)CN$ (*4*, *8*) with very reactive P—F or P—CN linkages. These reactions are outlined in Table I. A paper indicator test described in a German report (*10*) has come to be known as the Schönemann reaction. It was based on the oxidation of *o*-tolidine to a colored substance by alkaline peroxide in the presence of the nerve gas. A greatly improved reaction based on the use of *o*-dianisidine was developed by Gehauf and others (*2*). It had the desired specificity and a sensitivity comparable to the best colorimetric methods, but it was realized that a new order of sensitivity would be needed to meet some of the problems imposed by the high toxicity and rapid

Table I. Reactions for Assay of Nerve Gases

Reaction	Reactants	Assay Method	Approx. Minimum Sensitivity, γ
Schönemann (*10*)	*o*-Tolidine, alkaline peroxide, nerve gas	Colorimetric (yellow)	. . .
Gehauf and others (*2*)	*o*-Dianisidine, alkaline peroxide, nerve gas	Colorimetric (orange-red)	0.5
Gehauf and Goldenson (*3*)	Indole, alkaline peroxide, nerve gas	Fluorescent (blue-green)	0.03
This paper	Luminol, alkaline peroxide, nerve gas	Chemiluminescent (blue-green)	0.5

Table II. Nerve Gas Concentration Related to Luminescence

Concn. of Nerve Gas in Reagent Mixture, γ/Ml.	Microphotometer Reading, μa., at Indicated Time in Minutes[a]					
	0.25	0.5	0.75	1	1.5	2
0	0.01	0.01	0.01	0.01	0.01	0.01
31	0.73	0.60	0.40	0.25	0.15	0.10
16	0.35	0.36	0.24	0.17	0.10	0.07
6.2	0.15	0.17	0.10	0.08	0.06	0.04
3.1	0.06	0.06	0.055	0.05	0.04	
0.62	0.02	0.02	0.015	0.01	0.01	
6.2	0.15	0.18	0.12	0.08	0.06	0.04

[a] Following addition of nerve gas.

physiological action of the nerve gases. This led to the development of the more sensitive fluorescent reaction mentioned in the table.

Later the colorimetric and fluorescence reactions were used in devices for continuous monitoring of the atmosphere (*1, 11*). For this purpose, the colorimetric and fluorescence reactions have the disadvantage that sources of visible or ultraviolet light are required to illuminate the sample solution. When the chemiluminescence reaction described here was discovered, its use for detection purposes was studied further because it did not require such sources of light.

In the commonly used luminol reaction (*5*), chemiluminescence is produced by treatment of a dilute aqueous alkaline solution of luminol with hydrogen peroxide and potassium ferricyanide. The light produced is normally a greenish-blue color, but may be intensified and/or changed in color by addition of accelerators and fluorescent dyes (*5–7*). Nerve gases such as sarin give the chemiluminescence in place of the potassium ferricyanide. It is possible that the Fe—CN linkage acts in this reaction as postulated previously (*2*) for the P—CN and P—F linkages in the nerve gases. The addition of fluorescein (0.002 gram per 100 ml.) to the reagents does not appreciably increase the luminosity upon addition of the nerve gas.

EXPERIMENTAL

Roberts (*9*) investigated the sensitivity of the luminol reaction in order to determine the possibility of using it in an automatic alarm. He found an approximate minimum sensitivity of about 0.5 γ of nerve gas. For this sensitivity test, a luminol-perborate reagent was prepared having the following composition: 0.05 gram of luminol (Eastman White Label); 0.01 gram of sodium perborate (c.p.); 0.1 gram of trisodium phosphate (12 H_2O) in 100 ml. of distilled chlorine-free water.

As the luminol is insoluble in water and only slightly soluble in alcohol, ether, and benzene, it is necessary to dissolve it in an alkaline, aqueous medium. It is soluble in a perborate solution, but the addition of trisodium phosphate makes it easily soluble. The luminol is somewhat soluble in acetone. However, the addition of 4% acetone by volume to the reagent quenches the luminescence obtained from addition of nerve gas to the reagent.

The reagent blank luminosity is somewhat larger when the solution is fresh. After standing 1 to 2 hours, it drops to a value which remains constant for at least 1 day. The reagent used in this work was allowed to age for 3 hours prior to use.

The chlorine in tap water interferred with the reaction by giving a transient blue flash of light of much greater intensity than large amounts of nerve gas. The addition of ordinary distilled water yields some luminescence measurable with a photomultiplier tube. However, the addition of a small amount of thiosulfate to the water eliminated this interference. The sensitivity of the reagent to chlorine is of the order of 0.001 γ per ml.

An Aminco microphotometer was set up as follows to measure the chemiluminescence of the reaction. The cover was removed from the 931-A photomultiplier tube to expose the entire area of the light-sensitive surface. A cell (19 × 4 × 65 mm.) was constructed to fit the filter holder nearest to the phototube. The calibration was set at 100 and the phototube voltage was set at the maximum.

Portions of 0.5 ml. of known nerve gas solutions in isopropyl alcohol were added to 2.5 ml. of the luminol-perborate reagent in the specially constructed cell. A transient blue-green luminescence was formed which reached peak intensity in 15 seconds and persisted for about 2 minutes. The photometer readings obtained are given in Table II. The maximum readings were plotted against nerve gas concentration. The points were reasonably close to a straight line, indicating that the reaction may also be used for quantitative purposes.

DISCUSSION

In regard to the practical application of the chemiluminescence test, the preliminary work indicates that its use for a visual test would be limited because it must be observed in the dark. However, Huntress has carried out the reaction on a moist towel, and there is a possibility that the reaction might be adapted to a paper detector for special uses. The most promising potential use indicated for the reaction is the application to continuous automatic sampling of the atmosphere. The colorimetric and fluorescence reactions have the disadvantage that sources of visible or ultraviolet light are required to illuminate the sample solution. By use of the chemiluminescence reaction, such sources of light would be unnecessary. Also, by use of a barrier-type photocell and a spring-operated pump for obtaining the air sample, a device not requiring a power supply could probably be designed.

Some difficulty might be experienced in application of this reaction to quantitative assessment, because the rate of generation and complete conversion of the available "fuel" to chemiluminescence would require careful control. For some applications, a device to integrate the total chemiluminescent energy produced may be satisfactory.

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Fluorometric Method for Estimation of Cyanide

Application to Estimation of Free Hydrogen Cyanide in Ethyl Dimethylphosphoramidocyanidate Vapor

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▶ Appreciable quantities of free hydrogen cyanide were found as an impurity in vapor streams of tabun (ethyl dimethylphosphoramidocyanidate). As existing procedures for estimating microquantities of cyanide were unsatisfactory, nicotinamide as a reagent for cyanide in the von Braun reaction was investigated. The free hydrogen cyanide is separated from the tabun vapor and determined by the nicotinamide–chloramine-T procedure. This involves conversion of cyanide to cyanogen chloride by chloramine-T. The cyanogen chloride cleaves the pyridine ring of nicotinamide, giving a product which has a strong blue fluorescence in alkaline medium. A plot of fluorescence intensity vs. cyanide concentration approximately follows the Bouguer-Beer law. Tabun concentration is determined by the Schönemann reaction. The analytical procedure is confirmed by a total cyanide determination—i.e., free hydrogen cyanide plus cyanide obtained upon hydrolysis of tabun. The method is more rapid and sensitive than procedures previously described.

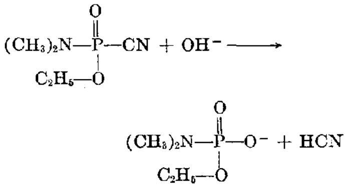
Determination of cyanide by conversion to cyanogen chloride and the subsequent action of the cyanogen chloride on pyridine compounds [von Braun reaction (*9*)] yielding yellow glutaconic aldehydes, which may condense with aromatic amines [König reaction (*12, 13*)] or compounds having active methylene groups to form intensely colored products, have been reported by Aldridge (*1*) and Gehauf, Falkof, and Witten (*6, 7*). The latter suggested the possibility of using a quantitative colorimetric cyanide method with 3-methyl-1-phenyl-5-pyrazolone to condense with the glutaconic aldehyde, yielding an intense blue color. Procedures for estimation of microgram quantities of cyanide and tabun (GA) by this pyridine-pyrazolone method were developed by Epstein (*4, 5, 10*).

In attempts to use the pyridine-pyrazolone procedure for the measurement of tabun–hydrogen cyanide ratios in tabun vapor, several difficulties were noted; lack of reproducibility, length of time required for color development, variation of color intensity with active chlorine concentration, and instability of the reagents. Although Gehauf, Falkof, and Witten (*7*) tested nicotinamide as a chromogenic reagent in this reaction, they did not mention the appearance of a fluorescence. As nicotinamide has been estimated fluorometrically using cyanogen bromide (*3, 14*) as a reagent, it was studied as a reagent for the fluorometric estimation of cyanide and tabun by the von Braun reaction.

EXPERIMENTAL

Effect of Cyanogen Chloride on Nicotinamide. Initially, a yellow color was produced by the action of cyanogen chloride on nicotinamide in buffered solutions at pH 7, and a plot of intensity *vs.* cyanogen chloride concentration approximately followed Beer's law. When viewed under ultraviolet radiation, the yellow solutions had a weak greenish fluorescence. Upon addition of alkali they became colorless under visible light but intensely fluorescent with a bluish hue when viewed under ultraviolet radiation. The intensity of fluorescence was proportional to the intensity of the yellow color present before the addition of alkali.

Determination of cyanide in strongly alkaline medium is desirable for two reasons: Alkaline solutions are more efficient for the collection of hydrogen cyanide and they promote rapid hydrolysis of the tabun:



$$(CH_3)_2N-\underset{\underset{\textstyle C_2H_5-O}{|}}{\overset{\overset{\textstyle O}{\|}}{P}}-CN + OH^- \longrightarrow (CH_3)_2N-\underset{\underset{\textstyle C_2H_5-O}{|}}{\overset{\overset{\textstyle O}{\|}}{P}}-O^- + HCN$$

However, neither the yellow color nor the fluorescence was produced when the reagents were added directly to alkaline cyanide solutions. After collection of the tabun and hydrogen cyanide in strong alkali, the pH was reduced and the solution simultaneously buffered by addition of potassium bicarbonate prior to addition of the chloramine-T and nicotinamide.

Effect of pH on Fluorescence. Addition of $6N$ alkali to the sample solution, after addition of the nicotinamide and chloramine-T reagents, was necessary to destroy the yellow color

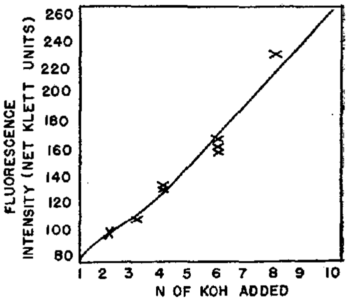


Figure 1. Variation of fluorescence intensity with normality of alkali added after addition of nicotinamide–chloramine-T reagents to solution containing 5 γ of cyanide

which masks the fluorescence. A curve of fluorescence intensity *vs.* normality of the alkali added is shown for a given quantity of cyanide (Figure 1). Six normal potassium hydroxide was chosen as the most alkaline solution which was convenient to use and still maintained a high level of fluorescence. The time necessary to attain maximum fluorescence varied inversely as the normality of the potassium hydroxide solution added; hence, addition of 6*N* alkali also reduced the time for the analysis.

Separation of Hydrogen Cyanide from Tabun. Quantitative removal of tabun from the air stream contaminated with tabun and hydrogen cyanide by use of bubblers containing diethyl phthalate has been reported (*2*). One bubbler of diethyl phthalate absorbed 10 γ of tabun over a 20-minute period before any slippage was observed. Two bubblers in series absorbed all quantities of tabun with which they were tested and passed all amounts of cyanide. Dibutyl phthalate was also used satisfactorily in place of the diethyl ester.

Stability of Reagent Solutions. As the reagents used in the pyridine-pyrazolone procedure are stable for only 90 minutes, storage tests were performed on the chloramine-T and nicotinamide solutions. These reagents were stable for approximately 3 days if stored in a dark bottle in a refrigerator when not in use. The decrease in sensitivity when the stored solutions are used is shown in Table I.

Table I. Effect of Storage on Nicotinamide – Chloramine - T Reagent Solutions

Time after Preparation, Days	Cyanide Taken, γ	Cyanide Found, γ
0	1.5	1.55
1	1.5	1.48
2	1.5	1.50
3	1.5	1.48
4	1.5	1.35
0	6	6.05
1	6	6.1
2	6	5.9
3	6	5.65
4	6	5.25

Variation in Fluorescence Intensity with Chloramine-T Concentration. The effect on fluorescence intensity of varying the amount of chloramine-T reagent was not fully explored and further work is needed. Preliminary studies indicated that the intensity of fluorescence is dependent on the concentration of chloramine-T (Figure 2). Experience of the authors has been that small variations in chloramine-T concentration are not so serious with respect to precision in this method as in the pyridine-pyrazolone procedure.

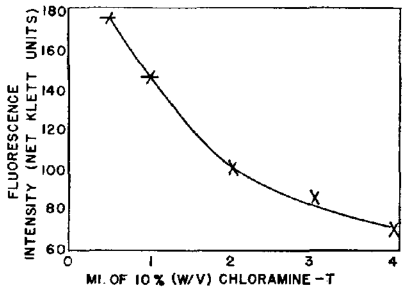


Figure 2. Effect of increasing concentration of chloramine-T on fluorescence intensity

REAGENTS AND APPARATUS

Standard Cyanide Solution. Reagent-grade potassium cyanide was analyzed argentimetrically (*11*) and the value obtained was used as cyanide content.

Potassium cyanide equivalent to 1 gram of cyanide ion was dissolved in 1 liter of distilled water. One milliliter of this solution was equivalent to 1000 γ of cyanide ion. The appropriate dilutions were made with distilled water.

Nicotinamide, U.S.P., 25% w./v. in water

Chloramine-T, U.S.P., 10% w./v. in water

Potassium hydroxide, c.p., 0.5*N*

Potassium hydroxide, c.p., 6*N*

Potassium bicarbonate, c.p., 2*N*

Diethyl or dibutyl phthalate

Klett fluorometer with Rubicon galvanometer

Primary filter, Corning No. 5970 (5.0 mm. thick)

Secondary filters, Corning Nos. 4308, 3389 (each 2.55 mm. thick)

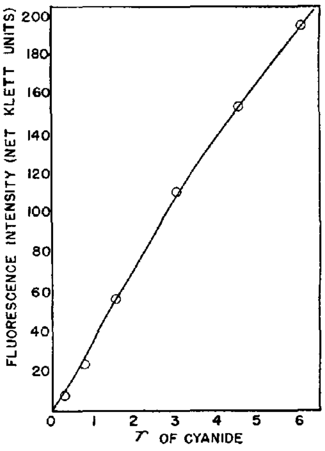


Figure 3. Standard curve for estimation of cyanide by nicotinamide–chloramine-T procedure

PROCEDURE

Standardization of Fluorometer. Before each series of readings the slit width of the fluorometer was adjusted so that a standard fluorescent glass read 150 fluorometer scale units. The fluorescence of the glass corresponded to the fluorescence of a solution containing 0.08 γ of quinine sulfate per milliliter.

Preparation of Standard Cyanide Curve. A standard curve (Figure 3) is prepared by using known concentrations of the standard cyanide solution in the range from 0.3 to 6.0 γ of cyanide ion per milliliter of solution. To 1 ml. of sample solution of desired cyanide concentration in a 25-ml. graduated cylinder are introduced 4 ml. of 0.5*N* potassium hydroxide, 4 ml. of 2*N* potassium bicarbonate, 2 ml. of nicotinamide solution, and 1 ml. of chloramine-T solution. The stop watch is started. Contents of the graduated cylinder are diluted to 20 ml. with distilled water and emptied into the Klett cell. Three minutes after the stop watch is started, 4 ml. of 6*N* potassium hydroxide are added and the reading is taken by following the fluorescence increase on the galvanometer until maximum fluorescence is reached—usually within 45 seconds after addition of the 6*N* potassium hydroxide. The window of the Klett fluorometer must be closed during the 3 minutes after addition of the chloramine-T to keep ultraviolet radiation away from the solution.

A blank determination is made and net Klett values are obtained by subtracting the blank value from the observed Klett value.

Determination of Unknowns. A sample of air is drawn through four bubblers connected in series at a flow rate of approximately 0.5 liter per minute. The first two bubblers contain 10 ml. each of diethyl phthalate, and the remaining two contain 2 ml. each of 0.5*N* potassium hydroxide After sampling (time of sampling depends upon expected cyanide concentration), the contents of the potassium hydroxide bubblers are emptied into a 25-ml. graduated cylinder and each bubbler is rinsed with 1 ml. of water. The rinsings are added to the graduated cylinder, bicarbonate, nicotinamide, and chloramine-T solutions are added, and the procedure is followed as for known samples. The cyanide concentration in

Table II. Estimation of Free Hydrogen Cyanide in Tabun Using Nicotinamide–Chloramine-T Procedure

Tabun by Indole-Perborate, γ	Cyanide Due to Hydrolysis of Tabun,[a] γ	Free Cyanide, γ	Total Cyanide, γ
0.63	0.10	0.05	0.14
0.62	0.10	0.05	0.15
0.45	0.07	0.05	0.11
0.91	0.15	0.23	0.37
1.16	0.19	0.28	0.47
1.55	0.25	0.40	0.63
1.23	0.20	0.73	1.00
15.91	2.55	0.72	3.18
1.00	0.16	0.95	1.16
5.04	0.81	0.90	1.60
1.13	0.18	0.77	0.93
1.90	0.31	0.15	0.47
1.50	0.24	0.56	0.82
2.10	0.34	0.08	0.44

[a] Calculated value obtained by dividing result of indole-perborate determination by 6.23.

micrograms is obtained from the calibration curve.

Checking the Analysis. The analysis may be checked (and the tabun–hydrogen cyanide ratio determined simultaneously) by the following procedure.

Total cyanide is determined as in the procedure for free hydrogen cyanide, except that diethyl phthalate bubblers are not used. Tabun is then determined by the indole-perborate method (*8*).

A satisfactory check on the procedure results when the total cyanide value obtained is equal to the sum of the free cyanide value plus the calculated cyanide due to the hydrolysis of tabun. Typical results obtained by this procedure are shown in Table II.

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Chromatographic Detection of Mixed Halide Ions in 10^{-10}-Gram Particles

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▶ Mixed soluble chlorides, bromides, and iodides in a single microscopic crystal can be determined by precipitating the mixed halide crystals on a transparent gel film in which colloidal silver dichromate is dispersed. The particle containing the mixed halides is dissolved by water vapor and diffuses into the film, where the halide ions precipitate as silver halide. Because of solubility product differences, the ions precipitate preferentially, forming concentric bands which are developed to distinctive colors by sun lamp, ammonia vapor, and water vapor at elevated temperatures. The area covered by each concentric band is semiquantitatively related to the amount of halide ion present. The limit of detection is of the order of 5 × 10^{-11} gram of sodium chloride, bromide, or iodide. Heterogeneous collections of airborne particles may be analyzed without individual particle handling.

HERETOFORE, chromatographic separation of ions has not been seriously applied to individual small airborne particles. Although such ionic separations have been observed by Seely (*5*) using his gelatin reagent film on collections of meteorological dusts, no attempt has been made to quantify such micro separations. Several chromatographic procedures are available whereby the chloride group ions can be separated from each other (*3, 4, 6*). In each instance the qualitative methods are designed for quantities much larger than those that are encountered in individual airborne particles. The method described here applies variations of these chromatographic techniques to small particle analysis in such a manner as semiquantitatively to detect and separate mixtures of chloride, bromide, and iodide ions contained in a single soluble particle.

PRINCIPLE

This method utilizes the photosensitivities and solubility product differences of the chloride group salts. Soluble particles containing the three ions are collected on a special reagent film, which is described in detail elsewhere (*1, 2*). This film is made from a commercial gelatin film, K-509, type F 408 (Eastman Kodak Co., Rochester, N. Y.), by precipitating colloidal silver dichromate in the gel structure. When moisturized by water vapor, the soluble particles on the film dissolve and diffuse into the gelatin. The chloride group ions immediately react with the silver dichromate and precipitate as silver halide. As silver iodide is least soluble of the three silver halides, it precipitates first in a circular area about the point where the particle is dissolving. The ions diffuse through the film in ever-widening circles. When

Table I. Chromatogram Calibration Data

Sodium Chloride		Sodium Bromide		Sodium Iodide	
Reaction area $\times 10^{-7}$ sq. cm.	Weight $\times 10^{-12}$ gram	Reaction area $\times 10^{-7}$ sq. cm.	Weight $\times 10^{-12}$ gram	Reaction area $\times 10^{-7}$ sq. cm.	Weight $\times 10^{-12}$ gram
47	74	21	91	152	1062
10	20	95	393	152	1142
53	143	76	280	9.5	51
129	330	64	251	166	1100
55	150	192	1162	274	1690
53	148	160	791	78	384
144	590	128	520	32	126
80	297	156	520	230	1510
133	390	110	523	103	382
159	795	75	344	57	167
630	1680	64	175	62	255
10	22	860	5900	160	1430
445	1230	26	78	5.1	19
36	111	659	4350	126	1050
77	217	15	24	23	69
16	33	10	29	5	14
22	61	24	54	7.8	26

the iodide has completely precipitated as the silver salt, the next most insoluble salt, silver bromide, begins to precipitate. The diffusion and precipitation continue until all bromide has reacted. At this point, silver chloride precipitates. Hence, three distinct concentric areas occur; the three chloride group ions are effectively separated.

The areas of precipitation are related to the quantity of each ion present because of the stoichiometric reaction of silver dichromate with the chloride group ions.

DEVELOPMENT OF CHROMATOGRAM

The soluble mixed halide particles are dissolved on the film by placing the film in a closed container which has a water-saturated atmosphere maintained at about 70° C. After 15 minutes in this environment, the ions have completely diffused and precipitated as the silver salts. The central circular area of silver iodide is lemon yellow, the concentric rings of silver bromide and chloride are colorless. The film is exposed several inches from a sun lamp for about 5 minutes. The silver halide salts are partially reduced. The silver iodide area is orange-yellow, the silver bromide area is lavender, and the silver chloride area is pink. In many cases it is difficult to distinguish the chloride area from the bromide. Exposure for 30 to 60 seconds in hot ammonia vapor turns the chloride area lemon yellow, at the same time decolorizing the bromide and iodide areas. Several minutes in the hot water vapor and additional sun lamp exposure restore the distinctive colors and complete the development of the chromatogram. Three brightly colored, sharply separated concentric bands are visible microscopically (Figure 1). The central spot area of silver iodide is orange and is darker at the boundary than in the center. The next band of silver bromide is blue-violet, and the outer band of silver chloride is lemon yellow.

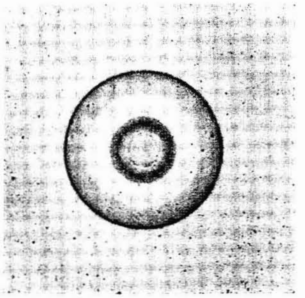

Figure 1. Separation of single particle composed of sodium chloride, sodium bromide, and sodium iodide

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The development chambers may be any small covered jars in which the film can be suspended to react with the vapors from the liquid in the bottom. The ammonia vapors are handily generated by placing a few milliliters of 30% ammonia water in a jar heated to 70° C. just before inserting the film.

CALIBRATION OF REAGENT FILM

A number of salt solutions were prepared, each containing measured molar percentages of sodium chloride, sodium bromide, and sodium iodide. These solutions were aspirated to a fine fog, the water was dried from the droplets, and the crystals were impacted on the reagent film. The chromatograms were developed and micrometer eyepiece measurements made to determine the diameters of the total particle reaction areas.

The number of moles of sodium halide in each particle reaction area was determined by plotting the diameter measurements on a previously constructed calibration curve (*1*). Because the relative percentage of sodium chloride, bromide, and iodide was known, it was a simple matter to calculate the weight of each constituent present. Each particle reaction area is composed of the three concentric bands of halide precipitations. The individual area of each band was measured and tabulated with the weight of halide ion each represented (Table I). The area covered by each of the three ion bands is plotted on log-log paper *vs.* the weight of each halide. For each halide measured a linear relationship exists when plotted in this manner. The weight of each sodium halide is a function of the surface area of its reaction and not of the diameter, because the distance of subsequent reactions from the central reaction area is variable depending on the quantity of the first halides precipitating.

ERRORS AND LIMITATIONS

Each datum point on the three calibration curves deviates considerably from the centrally drawn straight line. The mean of all such deviations is about 15% and represents the cumulation of measurement errors and errors inherent in the method. The limit of detection of any single ion in a mixture of the three is about 5×10^{-11} gram. If any one of the three halides in a single crystal is less than 10% of the total weight, its presence may not be detected by the method. The technique is limited to the analysis of soluble particles composed of mixtures of the chloride group ions and to slurrylike crystalline masses of these salts. Liquid droplets containing these solutes do not diffuse sufficiently to permit a separation of the halide bands.

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Quantitative Determination of Chloride Ion in 10^{-6}- to 10^{-12}-Gram Particles

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▶ A quantitative technique is described which permits an accurate measure of chloride ion content in water-soluble particles of 10^{-6} to 10^{-12} gram. The method employs a transparent gelatin reagent film containing colloidally dispersed red silver dichromate. When soluble chlorides are dissolved on the film, they diffuse into the gelatin layer and react with the silver salt; chloride ion preferentially precipitates as silver chloride. Microscopic examination reveals a clear, colorless circular area on the red film where this reaction occurs. The diameter of the circular area is a function of the quantity of chloride ion involved in the reaction. This method permits analysis of micron-sized particles in a heterogeneous collection without individual particle handling.

For many years investigators have been analyzing masses of particles from the upper atmosphere and coastal air masses for soluble chlorides and other ions (*5, 11*). The analytical methods of Crozier and Seely (*2*) and later work by Seely (*9, 10*) introduced new qualitative techniques whereby individual particles in heterogeneous collections could be identified. Others have extended and applied these methods to various small particle investigations (*1, 4, 6, 7*). Methods have been developed whereby water-insoluble reagents have been colloidally dispersed in commercial gelatin films (*3*), then used to identify various ions in liquid aerosol droplets. Most of these techniques are qualitative in their applications.

One of the more recent attempts at quantitative methods of particle identification was made by Sano (*8*). He extended the methods of Seely (*9*) to give a measure of the particle size distribution of sodium chloride aerosols. His method, however, is subject to certain technical difficulties which Pidgeon (*7*) showed were also inherent in the Seely method. The need for more positive quantitative methods of small particle determination led to the method described here.

MECHANISMS OF TECHNIQUE

The reagent film manufacturing technique is essentially the method employed previously by the author to make a salt water droplet-sensitive film (*3*). The gelatin film used is a commercial one designated type K-509 (Eastman Kodak Co., Rochester, N. Y.), having a cellulose acetate buterate base coated on both sides with a gelatin layer 20 microns thick. One gel surface is masked with tape so that the red silver dichromate is precipitated on only one side of the film. The film is dipped for 15 seconds in a solution consisting of 2% poly(vinyl alcohol) by weight (Elvanol 51-05, Du Pont) and 0.25% hydrated sodium dichromate in distilled water. The poly(vinyl alcohol) is essential to prevent large particle precipitation on the surface of the film in the second bath. The film is drained vertically for 15 seconds and then immersed for 15 seconds in a second bath which consists of 5% silver nitrate by weight in distilled water. The film is vigorously washed in distilled water for 30 seconds to remove the unreacted reagents, the tape removed, and the finished film dried for 10 minutes at 70° C. Reagent grade chemicals should be used. The temperatures of the dip baths are not critical. As the silver salts in the gelatin are photosensitive, the dried film must be stored in the dark until ready for use.

After the particles are collected on the film (Figure 1, *a*), they are dissolved by placing the film in a heated, water-saturated atmosphere for 30 minutes. A covered jar maintained at 70° C. with water in the bottom is an adequate reaction vessel in which to suspend the film. After the specified time the film is removed, dried by room air for several minutes, and microscopically examined for the clear spots (Figure 1, *b*).

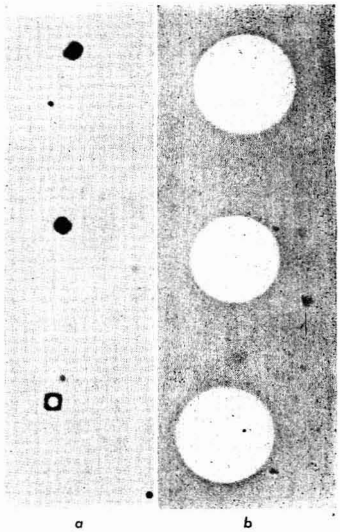

Figure 1. Sodium chloride crystals and developed spots on reagent film

a. Sodium chloride crystals on film
b. Sodium reaction areas in same field of view

CALIBRATION OF REAGENT FILM

Two approaches were used in the film calibration. The first involved the construction of a theoretical curve based on concentration of silver dichromate in the gelatin film. The second involved the measurement of sodium chloride crystals of various sizes, their reaction diameters on the film, and the plotting of these data as an empirical curve.

In the first method it was assumed that the reaction volumes in the reagent film were small cylinders, the base of which was the observed circular spot and the altitude was the 20-micron gel depth. The silver dichromate concentration in the gel film was determined by reacting six salt crystals of similar size on the reagent film and measuring the reaction volumes. Knowing the size of the sodium chloride crystals, the reaction volumes, and the chemical reaction equation, the arithmetic mean quantity of silver dichromate per unit volume of gelatin was computed. For the film manufacturing process described above, the silver dichromate concentration is 0.0747 ± 0.0018 gram per cc., which is a probable error of the mean of 2.4%. Using this value, theoretical reaction diameters of other sizes of sodium chloride crystals were computed and plotted as a theoretical linear curve on log-log paper. The discussion below shows that the basic assumption made is essentially true only for crystals larger than 20 microns.

In the second method a large number of measured sodium chloride crystals were reacted on the film and the spots were measured (Table I). A direct plot was made on log-log paper of spot diameter *vs.* the size of one face of the cubic sodium chloride crystal. The resulting curve almost coincided with the theoretical curve down to a crystal size of 20 microns. For cubic crystals having a face width less than this value, the curve deviates sharply from the theoretical.

The theoretical curve presumes the reaction volume is a perfect cylinder, but this is not true. A cross section cut from the spot, laid sideways and viewed microscopically, reveals that the reaction volumes have rounded edges, saucerlike, at the interface of gelatin and acetate backing. For large sodium chloride particles, where the reaction diameters are large compared to the 20-micron depth, these rounded edge deviations are insignificant; for small particles, the deviation becomes large. Hence, the empirical curve deviates significantly from the theoretical in this region. The empirical formula for the straight line portion of the empirical curve for crystal sizes of not less than 20 microns is

$$w = 0.54d^{2/3}$$

where w is the width of one crystal face of a cubic sodium chloride particle and d is the diameter of the reaction spot on the film. The average deviation of each plotted point from this curve is 2.7%. No empirical equation has been computed for crystal sizes of less than 20 microns. The average deviation of each point from a centrally drawn curve through these points is 5.7%.

Table I. Chloride Reagent Film Calibration Data

Face Widths of Cubic Sodium Chloride Crystal, Microns	Spot Diameter on Reagent Film, Microns	Face Widths of Cubic Sodium Chloride Crystal, Microns	Spot Diameter on Reagent Film, Microns
70.6	1608	11.9	116
63.3	1338	18.8	199
64.6	1409	6.00	53.6
65.0	1362	7.80	68.2
70.6	1547	9.40	97.2
46.9	625	19.1	218
42.8	753	19.2	228
46.8	887	2.61	16.0
38.6	671	2.09	12.0
39.2	680	1.78	10.3
32.0	511	1.78	10.5
44.2	846	1.34	8.19
31.1	511	1.05	7.56
39.0	681	1.36	8.19
42.8	793	2.20	12.4
49.1	942	2.41	15.3
41.3	723	1.68	10.7
53.6	1016	1.25	9.45
55.5	1116	1.36	8.82
28.8	409	1.15	8.19

PREPARATION AND MEASUREMENT OF SODIUM CHLORIDE CRYSTALS

Sodium chloride crystals having face widths greater than 10 microns were made by cooling hot, saturated solutions of pure salt. The crystals which precipitated were filtered, washed with absolute alcohol, and resuspended in acetone; the smaller crystals were separated by decantation. Several drops of acetone containing the suspended crystals were spread on a microscope slide and heat dried. Crystals of appropriate size were selected by using a wide-field stereoscopic microscope. The selected crystals were transferred to the reagent film by a fine needle. The crystals produced by the precipitation method were rectangular but not necessarily cubic. Therefore, three faces of each crystal were measured to determine the size and volume of the particle. A 10× or 43× objective and a 10× micrometer eyepiece were used in measuring the face widths. Calibration measurements of Table I are based on the volumes of crystals measured in this manner. However, for ease in plotting, these volumes have been reduced to a single face length value of a cube of equivalent volume.

A more controlled method of manufacture was needed for sodium chloride crystals having face widths less than 5 microns. It is difficult to select and transfer particles of this size by hand and impossible to turn a crystal for measurement of its third plane. A simple apparatus devised to produce cubic sodium chloride crystals of less than 5 micron consists of an aspirator for producing a salt water aerosol and a long, heated drying tube for evaporating the water in each droplet. The crystals issuing from the end of the tube were impacted on the film and measured under the microscope (Table I).

DISCUSSION

Additional experiments showed that chlorides mixed with soluble material such as sodium nitrate are quantitatively measured just as are individual pure crystals of sodium chloride. Water droplets are also quantitatively measured for chloride content provided they have certain limiting percentages of chloride ion. These vary from about 11% by weight in 5-micron diameter droplets to about 3% in 50-micron diameter droplets to about 0.5% in 500-micron droplets. Reaction areas were observed on the film around insoluble particles which contained soluble chlorides. The efficiency of the soluble chloride leaching process from such insoluble particles has not been investigated.

The sodium chloride crystals used in the calibration were not absolutely rectangular. Small chipped areas and irregularities were present in almost all the calibration crystals. Because the volumes and weights of the crystals were computed from measurements of three sides of the crystals, such irregularities led to significant errors.

The linear portion of the calibration curve follows the theoretical curve. No empirical equation appears to fit the lower portion of the calibration curve. The concentration of silver dichromate in the gelatin varies slightly for different runs using the production method outlined above. This error averages about 1%.

The method is limited to the quantitative analysis of water-soluble halides as particulates, as components in other soluble crystal masses, or as solutes in small water droplets. Quantities of sodium chloride less than 10^{-12} gram are not measurable by this technique unless thinner gelatin films become available.

Some of the advantages of this method over previous ones are: permanence of reaction areas, ease of manufacture to yield a uniform concentration of reagent in a known gel thickness, and greater color contrast between reaction areas and background.

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Sensitive Detector Crayons for Phosgene, Hydrogen Cyanide, Cyanogen Chloride, and Lewisite

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▶ Methods of preparation are described for crayons capable of detecting cyanogen chloride, cyanogen bromide, hydrogen cyanide, phosgene, lewisite, and ethyl dichloroarsine in low concentrations. Semiquantitative detection levels are discussed.

A simple means for detecting and semiquantitatively estimating the amount of trace quantities of gases in the atmosphere or in an enclosed space is frequently desired. One of the easiest ways of doing this is to use detector crayons, which are made by mixing detector reagents with suitable inert fillers and binders and forming the resulting mixture into crayons. These detector crayons can write on many surfaces such as paper, wood, painted surfaces, and the like, to give sensitive marks which change color in contact with the appropriate gas or liquid.

In many cases reagent systems are known which are capable of detecting the desired compound with the requisite sensitivity by a color change. These systems may often be used as the detector reagents which are incorporated into crayons. Detector papers can also be used for various gases. However, crayons are usually much more stable than the papers in storage because of their much smaller surface area which reduces the tendency of the active ingredients to volatilize and/or oxidize.

There are several ways in which detector reagents can be incorporated into crayons. One method is to mix the detector reagents with blanc fixe (precipitated barium sulfate) or other fillers, add a suitable amount of wax-in-water emulsion for a binder, form crayons by extrusion, molding, or casting, and then dry the mixture (*4, 5*). These crayons may suffer from decreased sensitivity, probably because the wax partially protects the active ingredients from the gases.

Another method is to mix the detector reagents with blanc fixe or other suitable fillers and binders and then compress the mixture to make a crayon in a manner similar to making tablets. On a small scale this method is fairly easy, and was used in making most of the crayons described here. Perhaps the simplest method of making detector crayons is to dissolve the active ingredients in a suitable solvent, absorb this solution into molded plain white blackboard chalk crayons, and then dry the chalks. However, by this method it is hard to control the amount of active ingredients incorporated into the crayon. These soaked crayons often deteriorate more rapidly in storage than other types, presumably because of their lower content of active ingredients. In many cases the detector reagents can probably be mixed with the usual commercial crayon ingredients and extruded, molded, or compressed into crayons in the ordinary fashion.

The sensitivity of the crayon marks to a gas can be expressed as a Ct value, where C is the concentration of the gas and t is the time necessary for the crayon mark to respond to concentration C.

If the crayon marks are exposed to similar environments of air turbulence, temperature, humidity, etc., the length of time necessary to cause a color change is, to a first approximation, inversely proportional to the concentration of reactive gas. Thus, the Ct value is approximately constant and is a measure of the sensitivity of the crayon mark. Although detector crayons are primarily qualitative, use of Ct values gives a rough estimate of concentration. For example, it can be calculated that the phosgene detector crayon described below ($Ct = 0.03$ mg. minute per cubic meter) will turn red in 1 minute when suspended at 90° F. in a turbulent atmosphere containing 7.5 p.p.b. of phosgene (0.03 mg. per cubic meter). The sensitivities of several of the crayons described herein (Table I) were determined under controlled laboratory conditions in hot weather. It is possible that under ordinary field conditions these crayons might be as much as 10 times less sensitive than that observed under controlled laboratory conditions. Thus, the effective Ct values under ordinary field conditions might be about 10 times as high as given in Table I for a turbulent gas environment.

An extensive study of the specificity of and interferences to these crayons has not been made. They appear to be fairly specific and not too susceptible to interference by other gases. However, high concentrations of chlorine will interfere with most of these tests.

The incorporation of detector reagents into crayons is illustrated in the examples below. No attempt was made to find the optimum composition and proportions of ingredients in these crayons; however, those described here are sensitive, stable in storage, and write well. It may be possible to improve the sensitivity and other characteristics of these crayons further by using different proportions of active ingredients. Also, other inert fillers and binders and different crayon making methods may be used.

PREPARATION OF CRAYONS

For Cyanogen Chloride. Rudner and coworkers have reported (*6*) that a mixture of 4-benzylpyridine and barbituric acid can be used to detect cyanogen chloride.

Ingredients. 4-Benzylpyridine (Reilly Tar & Chemical Corp.), 10%.

Barbituric acid (Eastman Organic Chemicals Dept., D.P.I.), 4%.

Blanc fixe, neutral, amorphous, dry (Barium Reduction Corp., South Charleston, W. Va.), 86%.

Procedure. The ingredients were thoroughly mixed with a mortar and pestle. The liquid benzylpyridine was fully absorbed by the other dry ingredients. Approximately 15-gram portions of this mixture were then pressed into crayons by placing them in a $^5/_8$-inch diameter cylinder. With a Carver laboratory hydraulic press, a force of approximately 2000 pounds was applied to a $^5/_8$-inch diameter piston which compressed the crayon. The pressure applied to the crayon was approximately 6000 pounds per square inch; this pressure was also used for the other crayon preparations. The piston and cylinder were lubricated before use with a thin film of silicone stopcock grease.

Table I. Sensitivity of Crayons for Detection of Gases[a,b]

Gas Detected	*Ct* Value, Mg. Min./Cu. Meter		Relative Humidity, %	Gas Environment
	Gas Concn., Mg./Cu. Meter			
Cyanogen chloride	0.369	1.045		
	1.2	1.3	19.5	Turbulent
	1.0	0.7	69	Turbulent
	2.2	2.1	19.5	Static
	Gas Concn., Mg./Cu. Meter			
Hydrogen cyanide[c]	2.5	120		
	6	8	20	Turbulent
	3	4	70	Turbulent
	8	15	20	Static
	Gas Concn., Mg./Cu. Meter			
Phosgene	0.064	0.611		
	0.02	0.02	19.5	Turbulent
	0.6[d]	0.03	70	Turbulent
	2.6[d]	0.04	19.5	Static

[a] Determined by Battelle Memorial Institute.

[b] Crayon marks were on paper exposed to gas at 32° C.; *Ct* values obtained at least twice with several observers.

[c] Results obtained using crayon containing Chloramine T. Crayon containing Dibromantin appeared to have *Ct* value of about 23 mg. minute per cubic meter.

[d] High value probably due to hydrolysis of phosgene on glass walls of dilution apparatus. Actual concentration of phosgene was probably much less than 0.064 mg. per cubic meter.

The white marks from this crayon first turn red and then blue in the presence of cyanogen chloride or cyanogen bromide. The *Ct* of 1 mg. minute per cubic meter (Table I) is equivalent to detecting 0.4 p.p.m. (1.0 mg. per cubic meter) of cyanogen chloride in 1 minute. These crayons are stable for at least 3 years when stored at room temperature.

For Hydrogen Cyanide. Hydrogen cyanide can be readily converted to cyanogen chloride by means of chlorinating agents. The cyanogen chloride formed can then be detected by means of the cyanogen chloride detector crayon (*3*).

Ingredients. Chloramine T, N.F. (Mallinckrodt), 14%.

Blanc fixe, neutral, amorphous, dry, 86%.

Procedure. The ingredients were mixed with a mortar and pestle, and the mixture was then pressed into crayons.

This crayon makes white marks upon which were superimposed cyanogen chloride detector crayon marks. This mixed mark turns red-blue in the presence of hydrogen cyanide. The *Ct* of about 5 mg. minute per cubic meter (Table I) is equivalent to detecting 5 p.p.m. (5 mg. per cubic meter) in 1 minute.

The chloramine T crayon is stable for at least 3 years at room temperature but is unstable at 65° C. If a crayon stable at 65° C. is desired, Dibromantin (1,3-dibromo-5,5-dimethylhydantoin, Arapahoe Chemicals, Boulder, Colo.) can be substituted for the Chloramine T.

For Phosgene. Brown, Wilzbach, and Ballweber have reported the preparation of a sensitive phosgene detector paper (*2*) containing 4-(*p*-nitrobenzyl)pyridine, *N*-phenylbenzylamine, and sodium carbonate.

Ingredients. 4-(*p*-nitrobenzyl)-pyridine, 2%.

N-phenylbenzylamine, 5%.

Sodium carbonate, c.p., 5%.

Blanc fixe, neutral, amorphous, dry, 88%.

Procedure. A benzene solution of the nitrobenzylpyridine and phenylbenzylamine was absorbed in the blanc fixe. A sufficient quantity of benzene was used so that the solution was completely absorbed by the blanc fixe and yet the blanc fixe was completely wetted. The benzene was allowed to evaporate overnight. The purpose of this impregnation step was to mix the blanc fixe intimately with the active ingredients. This mixture was impregnated with a water solution containing the sodium carbonate. A sufficient quantity of water was used so that the solution was completely absorbed by the solid, and yet the entire mass was completely wetted. The mixture was kept cool while being mixed to prevent melting of the *N*-phenylbenzylamine. After the mixture was dry, it was reduced to a powder with a mortar and pestle. This mixture was then pressed into crayons as before.

The light yellow marks from this crayon turn red in the presence of phosgene. This is the phosgene detector crayon referred to in Table I. This crayon cannot be used in an atmosphere containing high concentrations of hydrogen chloride because the hydrogen chloride destroys the sodium carbonate present in the crayon mark. Low concentrations of hydrogen chloride do not interfere with the test. These crayons are stable for over 1 year at room temperature. The *Ct* of 0.03 mg. minute per cubic meter (Table I) is equivalent to detecting 8 p.p.b. in 1 minute. In very high concentrations of phosgene the red color of the crayon mark tends to fade. Removal of the crayon mark to fresh air causes the color to return. The lewisite detector crayon described below can be used to indicate high concentrations of phosgene.

Witten and associates have reported the use of a mixture of 2-amino-Michler's ketone, Michler's ketone, and *N*-phenyl-1-naphthylamine to detect phosgene (*7*).

Ingredients. 2-amino-4,4′-bis(dimethylamino)benzophenone (2-amino-Michler's ketone), 1 gram.

4,4′-Bis(dimethylamino)benzophenone (Michler's ketone), 0.5 gram.

N-phenyl-1-naphthylamine, 5 grams.

Acetone, 80 ml.

Molded plain white chalk crayons.

Procedure. The three active ingredients were dissolved in the acetone. The crayons were completely immersed in the solution and allowed to stand for 24 hours, after which they were removed and allowed to dry in the air at room temperature. These crayons were about one half as sensitive to phosgene as the crayons described above.

For Lewisite. Brown and Denkewalter reported (*1*) that 4,4′-bis(dimethylamino)thiobenzophenone (thio-Michler's ketone) reacts with lewisite (dichloro(2-chlorovinyl)arsine) to give a green color.

Ingredients. 4,4′-Bis(dimethylamino)thiobenzophenone, 5%.

Blanc fixe, neutral, amorphous, dry, 95%.

Procedure. A benzene-chloroform solution of the 4,4′-bis(dimethylamino)-thiobenzophenone was completely absorbed by the blanc fixe. The solvent was removed first by letting it evaporate overnight and then by application of vacuum for 12 hours. The dry mixture was reduced to a powder and pressed into crayons.

The light tan marks from this crayon turned an intense green-blue on contact with lewisite liquid or vapor. These crayon marks also turn green-blue in the presence of ethyldichloroarsine, and purple in high concentrations of phosgene. This crayon might be useful in locating phosgene leaks. Chlorine and cyanogen bromide vapors cause the marks to become grayish in color.

ACKNOWLEDGMENT

The *Ct* values of these crayons were determined by Battelle Memorial Institute, Columbus, Ohio.

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Determination of Fluorides in Plant Tissue, Air, and Water

Apparatus and Procedures

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► Special equipment was developed and analytical procedures were adapted for determination of fluorides in vegetation, air, and water, in order to study the effect of volatile fluorides on vegetation. The equipment includes a steam-distilling apparatus with a complete electric heating system, two types of absorbers for air analyses, one of which also functions as a steam-distilling flask, and a photoelectric filter photometer for titration of fluorides with thorium nitrate. The main advantages are low blanks, fast distillation, quantitative recovery, safe operation, and convenient and efficient washing. Consideration was given to sampling of plant material and effect of silica on the determination of fluorides in vegetation. Results of a cooperative analytical project involving 15 different laboratories are included.

REAGENTS

For Air, Water, and Plant Tissue Analysis

- Sodium hydroxide solution, 1*N*, 0.1*N*, 0.01*N*
- Hydrochloric acid solution, 1*N*, 0.1*N*, 0.01*N*
- Perchloric acid, 70 to 72%
- Silver perchlorate solution, 25%
- Thorium nitrate solution, 0.20 gram $Th(NO_3)_4.4H_2O$/liter or 0.00145*N*
- Sodium fluoride standard solution, 10 γ F/ml.
- Sodium alizarinsulfonate, 0.01 and 0.035%
- Distilled water, fluorine-free (purified by demineralizer column)

For Plant Tissue Analysis

- Calcium oxide, special fluorine-free, Fisher Scientific Co. (Catalog No. C-116/1)
- Sodium hydroxide pellets
- Phenolphthalein indicator
- Thorium nitrate solution, 0.01*N*
- Sodium fluoride standard solution, 100 γ F/ml.

A PROJECT involving the effects of fluorides on vegetation necessitated determination of fluorides in the air and in plant tissue. The method used is based on the procedure of Willard and Winter (*9*). To adapt the general method to the specific needs of the project, modifications have been made, equipment has been improved, and new techniques have been developed, based on several thousand determinations and help from two cooperative projects with 15 laboratories. Earlier work has been reviewed by Busch, Carter, and McKenna (*1*), McKenna (*3*), and Elving, Horton, and Willard (*2*).

PRINCIPLE OF METHOD

Steps involved in the determination of fluorine in plant material include conversion of the insoluble fluorine compound into soluble fluoride ion, separation of the fluoride ion from substances interfering in the final determination, and measurement of the fluoride ion.

Fresh or dried plant material is ashed in the presence of an alkaline fixative—e.g., fluorine-free calcium oxide—in a muffle furnace at 600° C. The resulting ash is fused with a fivefold amount of sodium hydroxide, releasing completely the bound fluorine in the form of soluble fluoride ion. The latter is separated from interfering substances by a perchloric acid steam distillation of the caustic melt at 135° ± 2° C. in the presence of silica and silver ions. The fluorine is separated as fluosilicic acid and practically all interferences, such as aluminum, boron, nitrates, nitrites, chlorides, sulfur dioxide, hydrogen sulfide, phosphate, and sulfates, are eliminated. The fluoride ion is determined by the thorium nitrate direct or back-titration method in the presence of sodium alizarinsulfonate at pH 3.0. For determination of the end point, visual or photometric techniques are applied.

Determination of fluorine in air and water is usually limited to the separation from interferences by perchloric acid distillation and measurement of the fluoride ion by thorium nitrate titration. In the presence of fluorine-containing organic substances, ashing and perhaps even fusion may be necessary.

APPARATUS

Steam Distillation Apparatus. A new type of steam-distilling apparatus for the distillation of fluorine as fluosilicic acid (Figures 1 and 2) (Yonkers Laboratory Supply Co., Yonkers, N. Y., to specifications) has been described (*5*). This apparatus ensures a short distillation time for the collection of 500 ml. of distillate (75 minutes), low-distilling blanks (2 γ of fluorine), good recovery (98 to 101%), and automatic, efficient washing. The electric heating system provides safe operation and maintains a temperature of 135° ± 2° C. in the distilling flask.

Air Absorbers. A closed - type conical-shaped borosilicate glass absorber of 500-ml. capacity was specially designed for absorbing volatile fluorides from the air (*4*) (made by the Yonkers Laboratory Supply Co., Yonkers, N. Y., to specifications). This absorber (Figure 3, left) has a small surface and closed system, minimizing losses and contamination. It is efficient for air speeds up to 70 cu. feet per hour, using only 40 to 70 ml. of absorbing solution, is easy to operate, and gives low blanks.

A smaller absorber (300-ml. capacity) of similar design (Figure 3, right) operates with 40 ml. of absorbing solution and can be converted into a new type of steam-distilling unit by connecting to a condenser above and to a steam generator below (Figure 4).

Photoelectric Filter Photometer. The instrument (Figure 5, upper) developed and used for the photoelectric end point determination in the titration of fluorides with thorium nitrate has been described (*6*) (made by Meyer Opticraft, Inc., New York, N. Y., to specifications). A new model (Figure 5, lower) is basically similar, but it is more compact and rugged, and can be more easily operated by inexperienced personnel (made by Marley Products Co., New Hyde Park, N. Y., to specifications).

ANALYTICAL PROCEDURES

Determination of Fluorine in Plant Tissue. FRESH PLANT MATERIAL. The fresh sample of plant material, cut into fine pieces, is transferred to a tared Mason jar, to which 2 to 3 grams of fluorine-free calcium oxide have been added (representing approximately 10% of the dry sample weight). The jar is closed tightly and reweighed. Moisture is determined at the time of sampling. The fresh sample fixed with lime can be analyzed immediately or stored indefinitely in a cold room (below 0° C.). The content of the jar is then transferred quantitatively to a 500- or 750-ml. tared porcelain casserole and mixed thoroughly with enough distilled water to cover the sample. The alkaline reaction of the suspension is checked with phenolphthalein.

DRIED PLANT MATERIAL. The plant material may be dried in an oven (70° to 80° C.) to reduce the moisture to approximately 5%. The entire sample is then powdered in the Wiley cutting mill (mesh 20 to 40). A 1- to 5-gram sample is usually taken for analysis, depending on the expected fluorine content. Moisture is determined at the same time on 1 to 2 grams of the material. The sample is weighed in a tared nickel evaporating dish or crucible, and approximately 0.3 gram of calcium oxide (usually representing 10% of the sample weight) is added. Enough distilled water is added to cover the sample, and after thorough mixing the suspension is checked for alkalinity with phenolphthalein.

EVAPORATION AND ASHING. The water is evaporated and the sample charred by placing it under the infrared lamp for about 4 hours, then ashed in the electric muffle furnace at 600° C. for approximately 2 hours.

FUSION. The ash is fused in the same nickel dish or crucible in which the procedure was started, by adding 5 grams of sodium hydroxide pellets. The amount of sodium hydroxide is related to the weight of the ash, the ratio used being 5 to 1. The content of the crucible is fused in the electric furnace at 600° C. for 10 minutes. When the melt is cool, it is dissolved in a minimum of water and transferred quantitatively to the steam-distilling apparatus, and approximately 0.5 gram of glass wool is added to the distilling flask. The total volume of water used should not exceed 75 ml. Fifty milliliters of 70% perchloric acid are then added, providing an excess over the portion neutralized by the fusion mixture. In addition, 1 to 2 ml. of the 25% solution of silver perchlorate are added to prevent carry-over of halides other than fluorides. The final volume of the solution in the distilling flask should not exceed 150 ml., at which time the mixture is ready for distillation.

In the analysis of fresh plant material, when the total ash exceeds 1 gram, it is necessary to take an aliquot

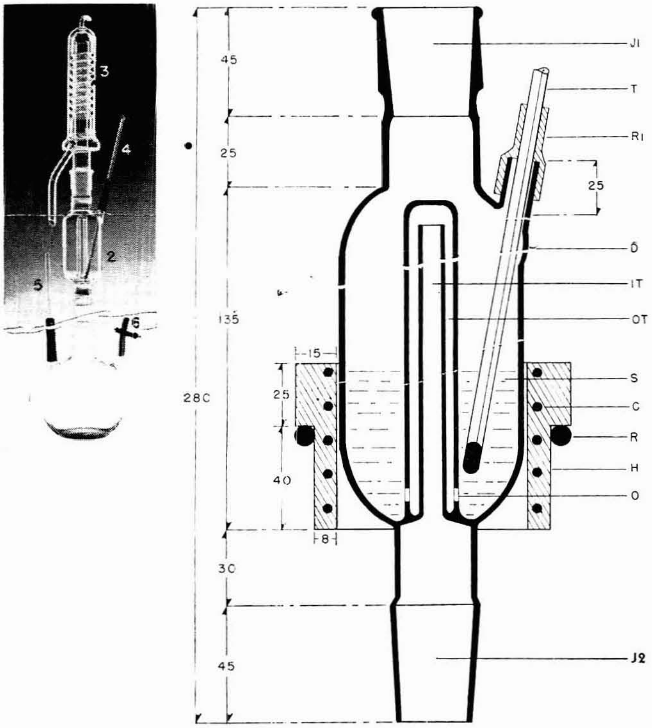


Figure 1. Apparatus

Left. Steam-distilling unit of borosilicate glass
1. Flat-bottomed flask, 2000 ml.
2. Distilling flask
3. Friedrich condenser
4. Thermometer, 150° C.
5. Safety tube
6. Steam outlet which can be closed by Hoffman clamp

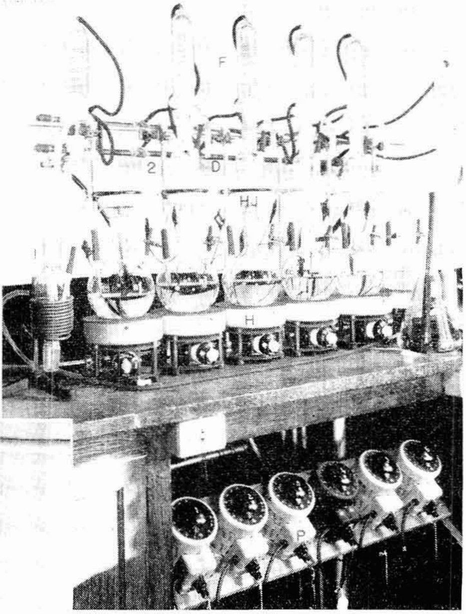
Right. Distilling flask section (dimensions in millimeters)
C. Nichrome wire spiral
D. Distilling flask
H. Heating jacket
IT. Inlet tube for steam
J1, *J2*. Ground-glass joints ₸
O. Outlet for steam
OT. Exit tube for steam
R. Metal ring
R1. Rubber connection
S. Solution
T. Thermometer, 150° C.

Figure 2. Distilling set of six units, shown in various positions

1. Loading operation, distilling flask placed in water-cooled Cu spiral
2. Unit ready for steam distillation
3. Washing of still. Friedrich condenser and distilling flask placed in ground-glass joint support connected to water pump. Outlet tube of condenser fitted with rubber tube dipping into washing solution

D. Distilling flask
F. Friedrich condenser
H. Hot plate
HJ. Heating jacket
P. Powerstat

Distillate collected in 500-ml. polyethylene containers placed on stand under condensers outlet (not shown)



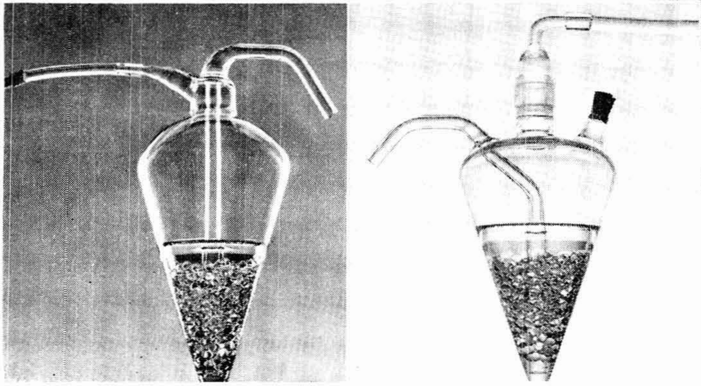


Figure 3. Absorber

Left. Closed-type, conical 500-ml. absorber of borosilicate glass, containing glass beads 6 mm. in diameter to increase efficiency of absorption. Air to be analyzed enters through tube on right, vacuum being applied to tube on left

Right. 300-ml. absorber having three outlets but otherwise similar to absorber at left. By connecting outlet in center to condenser, tube on left to steam generator, and introducing thermometer in place of rubber stopper, absorber may be converted to steam-distilling flask (Figure 4)

for fusion and distillation. In this case, after determining the weight of the total ash and homogenizing it with a spatula, a 1-gram aliquot is fused with 5 grams of sodium hydroxide in a nickel crucible and the melt is transferred to the still.

DISTILLATION. The distillation is started by turning on the hot plate switch to position "high" and the Powerstat dial to division 100 (Figure 2). Usually the distillation starts at approximately 110° C. When the temperature reaches about 130° C., the steam is admitted from the steam generator by closing the Hoffman clamp (Figure 1, left) and the Powerstat dial turned to division 65. The temperature is maintained at 135° ± 2° C. by turning off the Powerstat temporarily if the temperature exceeds 137° and turning it on again when the temperature drops to 135° C. This is done three to five times during distillation. A volume of 450 to 500 ml. of distillate is collected, the distillation being completed in about 75 minutes. The distillate collected in polyethylene bottles is adjusted by weighing to 500 ml. and is ready for titration. Under these conditions the material can be stored, preferably in a cold room, for several days.

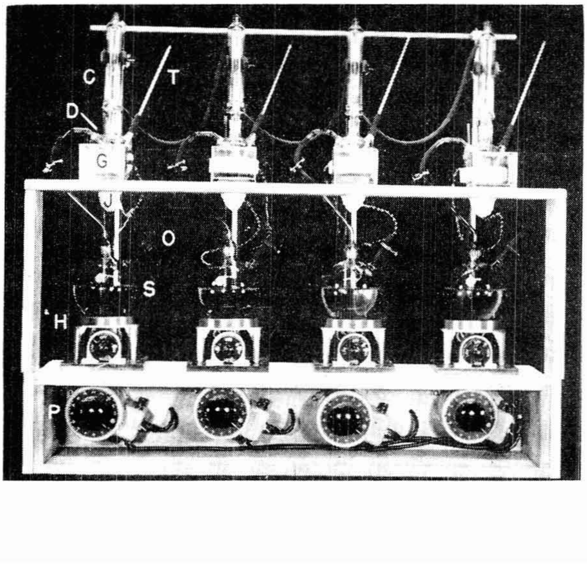


Figure 4. Steam-distilling apparatus of four units

C. Condenser
D. Absorbing-distilling flask, same as in Figure 3, right
G. 250-ml. receiver for distillate, used also as titration cell in photoelectric filter photometer (see Figure 5)
H. Electric hot plate
J. Electric heating jacket
O. Outlet for steam
P. Powerstat
S. Steam generator
T. Thermometer, 150° C.

TITRATION. Procedures used are the visual back-titration technique and direct titration with photoelectric end point determination. The visual back-titration technique has been described (*4*).

For direct titration with photoelectric end point determination, a blank is prepared by adding to the left cell of the filter photometer (Figure 5) 250 ml. of fluorine-free distilled water adjusted to pH 3.0 ± 0.05 and 2 ml. of sodium alizarinsulfonate indicator. An equal volume of distillate is placed in the right cell and adjusted to pH 3.0 ± 0.05 and the same amount of indicator is added. A magnetic stirring rod covered with polyethylene is placed in the sample cell. At this step the solutions in both cells are light green. The light source and the magnetic stirrer, adjusted to a convenient speed, are turned on, the galvanometer is connected, and the optical system is balanced by means of the iris diaphragms until the galvanometer spot is placed in the middle of the scale. The Ayrton shunt is then switched to the desired sensitivity, depending upon the range of titrated fluoride [for a fluorine content up to 100 γ to position "x1" (maximum sensitivity); for concentrations up to 1000 γ to position "x10"]. The fluorine-containing solution is now titrated dropwise with a standard thorium nitrate solution using a microburet, the tip of which is introduced through an opening in the top of the instrument (Figure 5). The reaction is completed when the galvanometer spot is deflected from its initial position to a scale reading of 25 divisions arbitrarily chosen. In the absence of fluorine, a small volume of the thorium nitrate solution is required to produce this deflection, and this volume is always deducted from the results obtained in the analyses. The amount of fluoride corresponding to the volume of thorium nitrate used is obtained from calibration curves relating known concentrations of fluorine in micrograms and milliliters of standard thorium nitrate solution (Figure 6).

Determination of Volatile Fluorides in Air. A volume of 40 to 70 ml. of fluorine-free distilled water, obtained by passing distilled water through a demineralizing column, is added to the absorber by applying a slight vacuum on the left tube (Figure 3, left) or right tube (Figure 3, right). The absorber can be emptied by applying a slight pressure to the same tube. After the absorber has been placed in the area to be tested, it is connected through an air meter to a vacuum source. Maximum speeds of 70 cu. feet of air per hour can be used with the absorber in Figure 3, left, and up to 40 cu. feet per hour with the absorber in Figure 3, right. When the absorption is completed, the absorbing solution from the absorber (Figure 3, left) is transferred quantitatively into the titration cell of the photoelectric titrator. The volume is brought up to 250 ml. and adjusted to pH 3.0 ± 0.05.

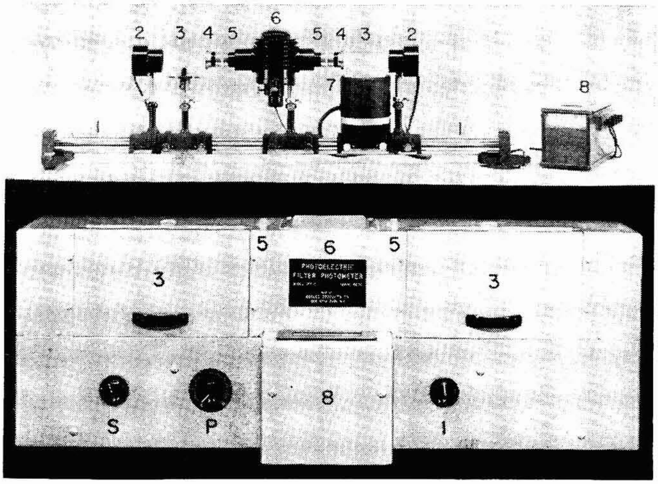


Figure 5. Photoelectric filter photometer

Upper. First model

1. Optical bench
2. Weston Photronic photocells, Model 594
3. Cells for solution with plane parallel glass plates, 250-ml. capacity and 10 cm. long
4. Green gelatin filters having maximum transmittance at 520 mμ
5. Meyer Trioplan lenses, 3 inches, *f* 2.8, provided with adjustable iris diaphragms
6. Lamp housing containing 6-volt and 4-ampere bulb supplied through transformer directly from 115-volt line
7. Magnetic stirrer
8. Leeds & Northrup mirror galvanometer with internal reflection. Sensitivity 56 divisions per microampere, resistance 1120 ohms, period 3.1 seconds. Parts described are placed on optical bench on convenient riders, adjustable in position and height; vertical columns are provided with locking collars

Lower. New model

3. Cell compartments closed by removable covers
5. Lenses, diaphragms, and filters
6. Lamp housing
8. Galvanometer, provided with Ayrton shunt, controlling sensitivity, not shown

I. Galvanometer switch
P. Potentiometer regulating speed of magnetic stirrers
S. Switch acting on main lamp and lamp of galvanometer

Table I. Fluorine Content of Dried and Fresh Leaves Fixed with Calcium Oxide

(Average parts per million on dry weight basis)

Species	Range of F Content, P.P.M.	No. of Samples Analyzed	F, P.P.M. Dried	F, P.P.M. Fresh
Gladiolus	<20	4	12	13
	20–100	20	38	33
	>100	10	270	260
Corn	<20	8	14	15
	20–100	28	38	37
	>100	16	160	145
Forage	<20	34	7	7
Tomato	<20	2	4	4
	>100	6	232	229
Pome fruit	<20	10	14	10
Rose	<20	2	17	13
	>100	4	949	980
Camellia	>100	6	1540	1515
Dogwood	20–100	2	36	39
Oak	>100	4	128	139
Pine	>100	2	385	405
Sweet gum	20–100	2	33	31

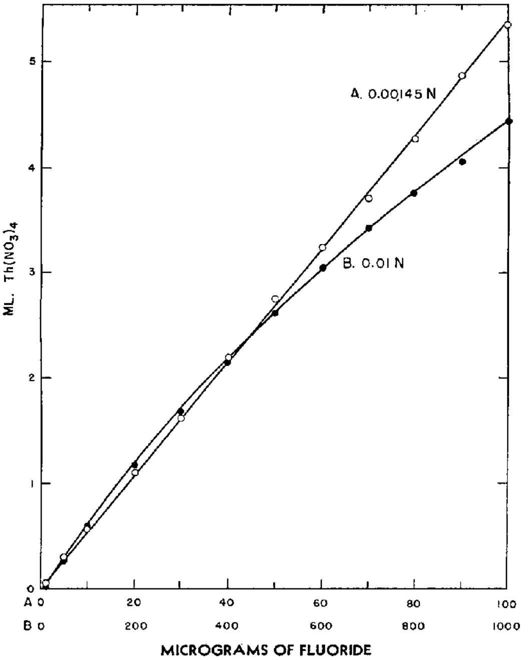


Figure 6. Calibration curves for titration of fluorides with thorium nitrate

A,B. Linearity for up to about 300 γ F and falling off with higher amounts

The titration is carried out according to the procedure described above.

If visual back-titration is used, the solution from the absorber is transferred quantitatively to a polyethylene beaker and adjusted to pH 3.0 ± 0.05 and the titration is carried out in Nessler tubes.

When the steam distillation from perchloric acid solution is required, the absorber (Figure 3, right) is used. After the absorption is completed, 25 ml. of perchloric acid are added, and the absorber is converted to a distilling flask by connecting it to a condenser above and a steam generator below, a thermometer being placed in the side opening (as shown in Figure 4). The distillation is carried out as described above, a volume of 250 ml. of distillate being collected directly in the titration cell of the photoelectric titrator. If visual back-titration is used, the distillate is collected in the polyethylene containers.

When the steam-distilling apparatus shown in Figures 1 and 2 is used with the reagents in the procedure described, blanks of 2 to 4 γ of fluorine are usually obtained. When blank determinations are carried out using the equipment described in Figures 3 (right) and 4, a blank of only 1 γ of fluorine is usually obtained. The blank values are always subtracted from the analytical results.

Determination of Fluoride in Water. According to the concentration of fluoride in water, a sample can be either steam distilled directly or concentrated in the presence of a fixative.

In the first case a sample of 50 ml. or less is steam distilled and titrated, using the apparatus and procedure described.

In the second case a convenient volume of water is concentrated to about 5 ml. under the infrared lamp in the presence of calcium oxide and is transferred quantitatively to the distilling apparatus and processed following the procedures given.

RESULTS AND DISCUSSION

The fluorine content of fresh samples of vegetation fixed with calcium oxide was compared with samples of the same material dried before fixing. Table I shows good agreement between the two sampling procedures for a wide range of species. In these experiments the effect of dew, rain, or dust was not considered. In the routine procedure the analysis of dry plant material was preferred because of its convenience.

When 20 to 25 grams of dried leaves were finely ground and thoroughly mixed, sample aliquots of 0.1 to 10 grams gave comparable results for fluorine (Table II).

The steam distillation from the perchloric acid solution eliminates most of the interfering substances. However, the presence of excessive amounts of silica in the sample may reduce the recovery of fluorine during distillation (*7–9*). Table III shows that the amount of fluorine recovered from grass hay decreased with increasing amounts of silica. The sodium hydroxide fusion was not used in analyzing these samples. As the silica content of plants may vary considerably, the caustic fusion of the ash was included in the routine procedure.

The present method for the determination of fluoride in vegetation was tested by 15 different laboratories, using the procedure described, conventional steam-distilling units, and visual thorium nitrate titration. Table IV shows that the coefficient of variation between the 15 laboratories was 9.1%.

In analyzing air for volatile fluorides, fluorine-free distilled water is used as an absorbing medium. This choice was made after comparative analyses showed that distilled water and alkaline-absorbing solutions gave equivalent results for air samples containing less than one to

Table II. Fluorine Content of Dried Leaves

(According to size of sample aliquot)

Sample Analyzed, Grams	F in Dried Leaves, P.P.M.		
	Corn	Apple	Tea
10	79	36	97
5	84	36	94
2.5	83	34	101
1	86	36	93
0.5	85	41	101
0.1	84	38	101
General average	84	36	98

Table III. Effect of Silica on Amount of Fluorine Recovered from Sample of Grass Hay Containing 6.6 % Silica on Dry Weight Basis

Sample Size, Grams	SiO$_2$, Mg.	F on Dry Weight Basis, P.P.M.			Relative % Recovery, Considering 1-G. Sample as 100%
		First 500 ml. of distillate	Second 500 ml. of distillate	Total	
1	0.060	44	..	44	100
2	0.120	41	..	41	93
4	0.240	38	1	39	88
5	0.300	35	2	37	84

several hundred parts per billion of hydrofluoric acid.

When interfering ions are known not to be present, the absorbed fluorine is titrated directly without being distilled. In this case the air sample is collected in the bubbler described in Figure 3, left. However, when sulfur dioxide or other interfering substances are known to be present, the absorbed fluorine is steam distilled from a perchloric acid solution, using the apparatus shown in Figure 4. A minimum of 4 γ of fluorine has to be present in the absorbing solution, to obtain results with an error not exceeding 10%.

Table IV. Results of Fluorine Determinations in 15 Laboratories Supplied with Same Plant Materials

	F in Dried Leaves, P.P.M.		
Collaborators	Corn	Apple	Tea
1	88	39	109
2	75	35	95
3	77	35	101
4	93	35	107
5	81	37	98
6	86	44	107
7	82	39	97
8	72	35	93
9	81	39	99
10	74	41	92
11	72	35	94
12	82	38	102
13	82	40	100
14	87	39	113
15	82	41	103
Average	81	38	101

Insoluble fluorine compounds were converted into soluble fluoride ion in a relatively short time by direct fusion of the plant material with sodium peroxide in a Parr bomb. Preliminary trials with several species of plants have shown good agreement between the sodium peroxide fusion and calcium oxide ashing; the average time required to complete a direct sodium peroxide fusion is 30 minutes, compared with 6 hours for ashing with calcium oxide in the standard procedure. If similar results are obtained with other plant species, the sodium peroxide fusion may be employed in routine analyses.

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[END OF SYMPOSIUM]

Determination of Traces of Boron in Silicon

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▶ Traces of boron in silicon can be determined in the concentration range of 0.001 to 1 p.p.m. The procedure involves a chemical concentration step employing the use of cation permeable membranes and extraction followed by spectrographic analysis in an atmosphere of argon. Simple operations and the minimum use of reagents result in low blanks. The method can be used for the determination of other impurities in silicon and many other materials.

A SENSITIVE METHOD has been needed for the determination of traces of boron in silicon used in semiconductor devices, because boron has a great effect on the electrical properties of silicon. Luke (*1*) developed a colorimetric procedure covering the concentration range of 0.1 to 1 p.p.m. of boron in silicon. The method described here provides for the determination of 0.001 to 1 p.p.m., and is based on a concentration and separation of sodium borate from crystalline silicic acid after the removal of excess sodium ions, followed by spectrographic estimation.

The principal point of interest is the availability of a superior method for the determination of boron at low concentrations, which heretofore could only be conjectured by inference from electrical measurements. These electrical measurements can be ambiguous when compensating impurities are present, which is often the case. The procedure described provides a means for the explicit determination of boron, and hence can be used to evaluate chemical procedures as sources of boron contamination when preparing silicon in bulk and crystal form.

EXPERIMENTAL

Apparatus. Platinum dishes, 50 and 300 ml.

Platinum covers.

Platinum electrodes, 7 × 1 × 0.1 cm.

Platinum spatula.

Quartz centrifuge tubes, 7 ml., homemade.

Quartz stirring rods.

Quartz medicine droppers, 3-ml. capacity made from 9-mm. quartz tubing.

Polyethylene electrolytic cell, consisting of two chambers separated by an Amberplex C-1 cation-permeable membrane (Figure 1). The cell was made by cutting a 16-oz. polyethylene bottle in half and inserting the membrane in the cap in which a 19-mm. diameter hole had been cut. The cells were tested for leakage.

Direct current power supply, rated at 3 amperes at 50 volts.

Bausch & Lomb medium quartz spectrograph, equipped with a logarithmic step sector with a step ratio of 1 to 1.5. A slit width of 10 microns was employed.

Arc discharge chamber, consisting of a Lucite cylinder, 6.3 cm. long and 9 cm. in outside diameter, with a wall thickness of 0.6 cm. One side of the cylinder was fitted with a side tube in line with the optical center of the spectrograph and containing a quartz window. A smaller hole in the chamber end of the side tube was sufficient to accommodate the focal path of the system and to eliminate condensation of sample vapors on the quartz window.

Direct current arc source. A motor generator set rated at 0.625 kw. was differentially compounded to provide a no-load voltage of 180 volts. During arcing the arc voltage was 28 at 21.5 amperes.

Materials. Cation permeable membrane, Amberplex C-1, Rohm & Haas Co., Philadelphia, Pa. The membrane was pretreated by soaking overnight in a solution containing 0.6 gram of sodium hydroxide in 200 ml. of deionized water. It was then cut into 25-mm. disks and rinsed thoroughly with deionized water before mounting in the cells.

Monobed deionization resin, MB-1, Rohm & Haas Co., Philadelphia, Pa.

Polyethylene bottles, Nalgene No. 1204, 16 ounce, Dynalab Corp., Rochester, N. Y. These bottles were used for electrolytic cells and for storage of solutions.

Polyethylene carboy, Nalgene No. 1208, 5 gallon, Dynalab Corp., Rochester, N. Y.

Spectrographic electrodes, United Carbon "no boron," $^1/_4$-inch diameter graphite preformed electrodes: anode —100 L, cathode —100 U.

Spectrographic plates, Eastman Kodak 103-0, 4×10 inches.

Reagents. Deionized water. Distilled water was passed through a polyethylene column (5.4-cm. diameter) containing Amberlite monobed resin (bed depth, 110 cm.) at a rate of 5 ml. per minute. Deionized water was stored in a polyethylene carboy. The first 5 gallons was discarded before collection of effluent. When 500 ml. of the water was evaporated to dryness in a platinum dish with 50 mg. of spectrographically pure graphite, no traces of boron or indium were detected spectrographically.

The column was used intermittently because of the need for single batches of homogeneous water. When putting the column into use again, the first 2 liters of water were discarded.

Sodium hydroxide, electrolytic pellets, Fisher Scientific Co., Catalog No. S-318.

Standard boron solution. Reagent grade boric acid (0.2860 gram) was dissolved in deionized water and diluted to 1 liter. A 5-ml. portion of this solution was diluted to 500 ml. and stored in a polyethylene bottle. The solution contains 5×10^{-7} gram of boron per ml.

Indium internal standard. This was prepared by dissolving 19.5 mg. of indium metal of 99.999% purity (American Smelting & Refining Co., South Plainfield, N. J.) in constant-boiling hydrochloric acid. To this solution in a platinum dish was added 5.0000 grams of spectrographically pure graphite powder (150 mesh) and the mixture was evaporated to dryness. The sample was mixed in a polyethylene bottle by rolling for 3 hours. Spectrographic examination of the internal standard revealed the absence of boron.

Argon, commercial grade.

Washing of Apparatus. All platinum, quartz, and polyethylene ware was cleaned with a dilute hydrofluoric acid solution, rinsed with distilled water, and washed thoroughly with deionized water prior to use.

CHEMICAL PROCEDURE

Place an accurately weighed 1-gram sample of silicon in a 300-ml. platinum dish. Add 2.1 grams of sodium hydroxide and 20 ml. of deionized water. It is possible to dissolve silicon in much less sodium hydroxide than is required stoichiometrically to form the metasilicate. Cover the dish with a platinum cover and warm momentarily on a low temperature hot plate to start dissolution of the sample. Warm gently from time to time to keep the reaction going, but avoid such rapid dissolution that the sample is lost by excessive spraying. To avoid contamination, samples should not be crushed prior to dissolution. A powdered silicon sample requires approximately 45 minutes for dissolution, while large pieces require up to 5 hours. In the latter case replenish the deionized water from time to time, using the same volume of water in the reagent blank.

Transfer the sample solution to the upper chamber of the polyethylene electrolysis cell. By washing with deionized water dilute to a 60-ml. volume. Add 0.6 gram of sodium hydroxide and 200 ml. of deionized water to the lower polyethylene chamber. Place a platinum anode into the upper chamber and a platinum cathode into the lower chamber. Allow the upper cell to dip into the lower cell, avoiding entrapment of air bubbles at the membrane interface, and cover the upper cell with a sheet of polyethylene. Cool the lower cell by placing in an ice water bath.

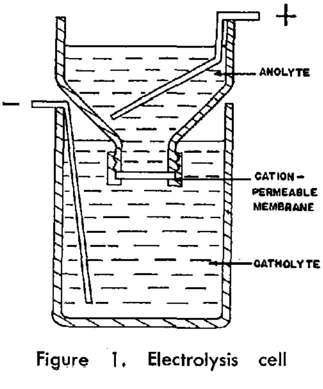

Figure 1. Electrolysis cell

The resistance of the cell is measured using a 0- to 50-volt voltmeter placed in parallel and a milliammeter (0 to 500 ma.) placed in series with the cell. As the resistance of the cell is relatively high, apply maximum voltage throughout the electrolysis. The resistance of the cell will drop, allowing increased flow of current. Continue electrolysis until the resistance again rises to approximately 400 to 500 ohms, resulting from the depletion of sodium ions in the anolyte. Gas bubbles collecting on the membrane interface are removed periodically throughout the course of the electrolysis by momentarily stopping the current flow and reseating the anolyte chamber free of bubbles. A crystalline deposit of silicic acid which may form on the platinum anode during the electrolysis is removed by scraping with a platinum spatula. At the end of the electrolysis (approximately 5 hours), the pH of the anolyte should be 7 to 8.

Transfer the solution in the upper cell to a 300-ml. platinum dish, cover, and evaporate to incipient dryness on a hot plate. Triturate the practically dry residue of silicic acid, using a platinum spatula, and transfer to a quartz centrifuge tube. Using a quartz medicine dropper, add 2 ml. of deionized water to the platinum dish, swirl to wash the sides of the dish, and pour into the tube. Repeat with another 2-ml. portion of water. Stir the suspension in the tube by means of a quartz stirring rod, and remove the rod, which is washed with 0.5 ml. of water. Centrifuge for 5 minutes and decant the clear solution into a tared 50-ml. platinum dish using a second quartz medicine dropper. Repeat the extraction with four successive 2-ml. portions of water, stirring well during each extraction. Combine the aqueous extracts in the platinum dish and evaporate to dryness in an oven at 110° C. Cool and weigh.

Crush the weighed solid residue, transfer it to another tared platinum dish containing 10.0 mg. of indium internal standard mixture, and mix thoroughly. Reweigh the mixture to determine the yield of transfer of the sample.

SPECTROGRAPHIC PROCEDURE

Transfer the mixture to a preburned graphite cup electrode and mount as the anode in the arc discharge chamber containing a mounted, preburned graphite cathode. Adjust the distance between electrodes to 4 mm. Have the logarithmic step sector rotating at constant speed (800 r.p.m.). Sweep the arc chamber with argon for 10 minutes at a moderate rate. Stop the flow of argon, open the shutter of the spectrograph, and ignite the sample at a current of 21.5 amperes for 20 seconds. Close the shutter at the end of this time before interrupting the flow of current.

Develop spectrographic plates for 4 minutes at 20° C. using Eastman Kodak D-19 developer, wash for 30 seconds in Eastman Kodak SB-5 stop bath, and fix for 10 minutes in Eastman Kodak acid hardening fixer. Rinse in running water for 30 minutes and allow the plates to dry at room temperature.

PREPARATION OF WORKING CURVE

Standard silicon samples for preparation of the working curve were prepared by adding aliquots of four different boron concentrations (5×10^{-6} to 5×10^{-9} gram) to 1-gram portions of pure silicon.

These standards were carried through the chemical concentration procedure and a correction factor for sample loss during transfer was determined by weighing before and after transfer to the dish containing the internal standard. Silicon and reagent blanks were also run through the procedure to determine the amount of residual boron present in the silicon used for preparation of the standards, as well as that contributed by the reagents in the course of the procedure. The reagent blanks were run by adding all of the reagents to boron-free silicic acid (10 mg.) and carrying it through the entire procedure. The silicon and reagent blanks contained no traces of indium.

The use of a log-stepped sector placed at the slit during spectrographing of the samples enabled the density of the boron line (2497.7 A.) in the photographed spectra to be determined at several exposure levels. According to the method of Strock (*3*), measurement of the logarithm of relative exposure time (log RET) of the boron line relative to the internal standard line (In 2560.2 A.) was made at a constant exposure level (20% transmittance) and resulted in the value, Δ log RET, which was plotted against the logarithm of the concentration of boron to obtain the necessary analytical working curve.

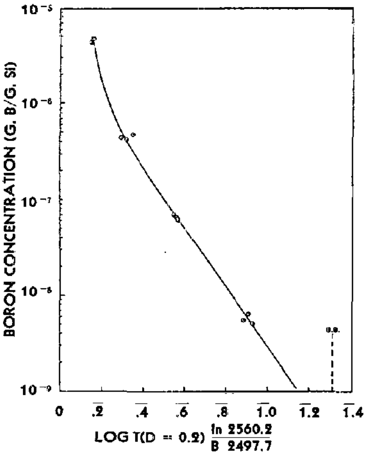

Figure 2. Concentration calibration curve for B 2497.7 A. line in silicon samples

The concentrations used in the plot were obtained from the boron added in the standards after correcting for loss during transfer. The boron concentrations for the silicon and reagent blanks were read from this curve and divided by the per cent transfer to give the corrected boron content of the blanks.

The original concentration values were then corrected by adding the boron concentration of the silicon and reagent blank to the amount of boron initially added and multiplying these figures by the per cent transfer. These corrected concentration values more closely approach the amount of boron present in the measured samples and were plotted against Δ log RET to obtain the final working curve (Figure 2).

Table I. Determination of Boron in Standard Silicon Samples

Concn., G.B/ G.Si	Sample Av., $\bar{x} = \frac{x}{N}$	Sample Std. Dev.[a]
4.4×10^{-6}		
4.7×10^{-6}	4.55×10^{-6}	0.21×10^{-6}
3.2×10^{-7}		
4.2×10^{-7}		
5.4×10^{-7}	4.27×10^{-7}	1.10×10^{-7}
6.2×10^{-8}		
6.5×10^{-8}		
7.0×10^{-8}	6.57×10^{-8}	0.41×10^{-8}
4.8×10^{-9}		
5.6×10^{-9}		
6.5×10^{-9}	5.63×10^{-9}	0.85×10^{-9}

[a] $S = \sqrt{\frac{\Sigma x^2 - \frac{(\Sigma x)^2}{N}}{N - 1}}$

In view of the good results obtained in a study of the recovery of boron during the chemical procedure, a more rapid method of preparation of a working curve is possible, based on the preparation of a boron-free silicic acid matrix. Thus, a less pure grade of silicon can be carried through the chemical procedure and boron completely removed from the silicic acid residue by extraction. The pure residue can then be extracted five times as in the regular procedure and a known amount of boron added to the combined extracts to provide a silicon standard of known boron concentration. This method greatly reduces the silicon and reagent blank of the starting material.

RESULTS AND DISCUSSION

Dissolution of metallic silicon is accomplished with concentrated sodium hydroxide solution to prevent loss of boron by volatilization. Although this process is slow, complete dissolution of the sample is possible with no loss of boron. The tendency of boron to accompany silicon makes analytical chemical separation of these two elements difficult, particularly when trace amounts of boron are involved. If, however, excess sodium ions from the sodium hydroxide used to dissolve the silicon sample are removed from the sample solution by electrolysis through a cation-permeable membrane, it is possible on evaporation to obtain a crystalline deposit of silicic acid from which small amounts of sodium borate are easily and completely removed by extraction with water. Because the pH of the solutions during the chemical procedure is always on the alkaline side, the boron is present as sodium borate and is not lost by volatilization during evaporation of the solutions. Diffusion of borate ion through the cation-permeable membrane is negligible within the precision of the method.

The extraction of the silicic acid residue results in a solution containing the boron and small amounts of silicic acid, which are soluble in water. Thus, a concentration of the boron from a 1-gram sample of silicon to approximately 10 mg. of silicic acid is effected. Of the various convenient methods for estimation of trace elements, spectrographic analysis provides the most sensitivity for boron, and, when performed in an atmosphere of argon, interference from the small amount of silicon present in the arced sample is surpressed. The high sensitivity of this method, therefore, is due to the combination of chemical concentration with spectrographic analysis in an atmosphere of argon.

The reagent blanks in the procedure are remarkably low (approximately 2×10^{-9} gram of boron) and may be attributed to the fact that the only reagents employed in the procedure are sodium hydroxide and deionized water, thereby greatly minimizing the possibility of contamination. Also, all heating operations are performed in platinum ware, and polyethylene and quartz are the only other materials to come in contact with the samples.

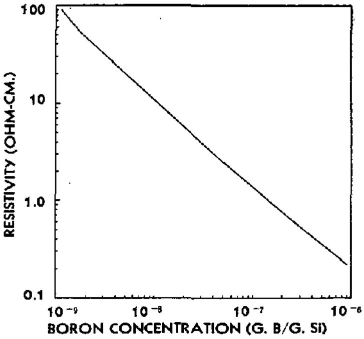

Figure 3. Resistivity vs. boron concentration

Drawn from data of Prince (*2*) assuming boron as the only impurity present

The precision was determined by running duplicate or triplicate analyses at four different concentrations over the range of 5×10^{-6} to 5×10^{-9} gram of boron per gram of silicon (Table I). Each analysis was made at different times and in a completely random order. The over-all precision is 26%, which is satisfactory for quantitative spectrographic methods for trace amounts of elements.

In order to determine the loss of boron during the chemical concentration procedure, samples of the original silicon were carried through the proce-

Table II. Determination of Boron in Polycrystalline Silicon Samples

Sample	Description	G.B/G.Si[a]
1	Densified	1.2×10^{-8}
2	Densified	$<1.0 \times 10^{-9}$
3	Needles and clumps	3.6×10^{-9}
4	Needles and clumps	$<1.0 \times 10^{-9}$
5	99.85% Si	4.5×10^{-7}

[a] Average of duplicate determinations.

dure and known amounts of boron were added just prior to the spectrographic step, thereby eliminating the possibility of loss. The values of Δ log RET for these samples of known added amounts of boron were then used to obtain the concentrations from the working curve. Since the working curve was obtained experimentally with samples where known amounts of boron were added at the beginning of the procedure, a comparison of these concentrations with those added after the chemical procedure gave the loss due to the chemical steps. The recovery of boron was quantitative within the limits of precision of the method.

Table III. Determination of Boron in Single Crystals of Silicon

Sample[a]	Resistivity Type	Measured Resistivity, Ohm-Cm.	G.B/G.Si	Resistivity of Uncompensated Silicon, Ohm-Cm.
1	*n*	57.2	1.5×10^{-8}	7.5
2	*p*	446	6.6×10^{-7}	0.3
3	*p*	46	$<1.0 \times 10^{-9}$[b]	>100
6	*p*	10 and up	2.5×10^{-9}	38
7[c]	*p*	0.02	5.0×10^{-6}	0.02
8[c]	*p*	0.06	9.8×10^{-7}	0.09

[a] Numbers correspond to numbers of polycrystalline material in Table II from which crystals were grown.
[b] Average of triplicate determinations.
[c] Boron-doped samples.

ANALYSIS OF SILICON SAMPLES

A number of samples of polycrystalline silicon from a variety of commercial sources for use as a raw material to grow single crystals were analyzed for boron, and the results of some of these analyses are presented in Table II.

Table III gives some of the results of analyses of single crystals of silicon obtained from various laboratories. The measured electrical resistivities are given, as well as the resistivities of uncompensated silicon equivalent to the amount of boron detected in the samples. These values were obtained from Figure 3, based on the work of Prince (*2*). By comparing the observed and calculated values of resistivity one can ascertain the contribution of boron to the measured resistivity of the crystal.

In the case of sample 1, the boron content of the crystal is almost the same as that of the starting material. An examination of the resistivities indicates the presence of a high concentration of *n*-type impurities. In sample 2 there is a large pickup of boron during the growing of the crystal, which was purposely doped with arsenic and antimony. This is an example of a crystal containing a large amount of boron which is highly compensated with a resultant high resistivity. There is a slight loss of boron in the growing of crystal 3. Assuming no compensation, the resistivity of the crystal (46 ohm-cm.) is equivalent to 1.8×10^{-9} gram of boron per gram of silicon. Because less than 1.0×10^{-9} gram of boron per gram of silicon was found, it appears that small amounts of other *p*-type impurities are present. Sample 6 also indicates some compensation by small amounts of other *p*-type impurities. To show more dramatically the correlation of resistivity and boron concentration, crystals 7 and 8 were doped with large amounts of boron, and it can be seen that in these samples the resistivity is determined primarily by the boron.

CONCLUSIONS

This method is capable of determining very small amounts of boron in silicon. Increased sensitivity could be achieved by further purification of the sodium hydroxide used to dissolve the samples, thereby permitting the determination of down to 0.0001 p.p.m. of boron in silicon, which is the lower limit of detection by the spectrographic method. This could possibly be achieved by repeated electrolysis of sodium hydroxide solutions through the cation-permeable membrane.

The results of the application of this method to actual samples of silicon point out the fact that boron is just one of many impurities for which trace concentrations must be determined in order to get a better understanding of their effect on the electrical properties of silicon.

While this novel prechemical concentration–spectrographic technique has been successfully applied to the determination of boron in silicon, further research has indicated its applicability to the determination of numerous impurities in silicon, and to the trace analysis for impurities in many other materials.

ACKNOWLEDGMENT

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Spectrophotometric Determination of Tungsten in Tantalum, Titanium, and Zirconium Using Dithiol

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▶ The increased use of high-purity tantalum, titanium, and zirconium necessitates a method for determining <0.10% tungsten in these materials. The tungsten-dithiol complex can be extracted with amyl acetate without interference and the blue-green color measured spectrophotometrically. A method is described by which it is possible to analyze six samples in 2.5 to 3 hours.

THE PROBLEM of determining small amounts of tungsten in the presence of other readily hydrolyzable metals such as titanium, tantalum, and zirconium has become more acute with the increased use of these metals. Tungsten can be introduced either from the ore or during melting. The method described, originally developed for determination of tungsten in tantalum, has been extended to include determination in titanium and zirconium.

The hydroquinone method for tungsten (*2*) could not be used for determination in tantalum metal because it lacked sufficient sensitivity on a sample size that could be used without having tantalum hydrolyze, and the presence of even small amounts of columbium and titanium interfered with the tungsten complex. The thiocyanate method (*3,4*) was not satisfactory because the tantalum hydrolyzed under the conditions necessary for reduction of tungsten(VI) to tungsten(V), and the color of the tungsten thiocyanate complex was not stable.

Several authors (*1,5–7*) reported use of the organic reagent, 4-methyl-1-2-dimercaptobenzene, commonly called dithiol, for the determination of traces of tungsten in a variety of materials. This reagent seemed to be of sufficient sensitivity and specificity to warrant investigation.

In 1944, Miller (*5*) made a rather complete semiquantitative study of the determination of tungsten with dithiol. Tungsten reacts with dithiol under reducing conditions in 10 to 11*N* hydrochloric acid solution to form a blue-green complex, which is extractable with isoamyl acetate. In her study of 58 cations, six acids, and 17 anions, she found few interferences. Under the conditions necessary for the determination of tungsten, none of the interfering elements was expected to be present in sufficient quantity of proper valence state to cause difficulty, with the exception of molybdenum. As this study progressed, it was found that conditions could be varied sufficiently to give separate quantitative recoveries of tungsten and molybdenum.

APPARATUS AND REAGENTS

All absorbance measurements were made in 1.00-cm. cells with a Beckman Model DU spectrophotometer. Dithiol was obtained from the Eastern Chemical Corp., Newark, N. J., and the British Drug Co., Ltd., Toronto, Canada.

Amyl acetate, from the Fisher Scientific Co., was solvent-purified.

Dithiol. Dissolve 0.5 gram of dithiol in 100 ml. of amyl acetate.

Stannous chloride. Dissolve 20 grams of stannous chloride dihydrate in 50 ml. of hydrochloric acid and dilute to 100 ml. with water.

Standard tungsten solution. Dissolve 1.260 grams of pure tungstic oxide in 100 ml. of 10% sodium hydroxide solution, dilute to 1 liter with water, and store in a caustic-resistant bottle. Determine concentration of tungsten by the conventional cinchonine method.

Tungsten addition solution. Dilute an aliquot of the standard tungsten solution with water to give a tungsten concentration of 0.02 mg. per ml. Use this solution within a few hours after preparing.

Standard molybdenum solution. Dissolve 1.500 grams of pure molybdic oxide in 100 ml. of 10% sodium hydroxide solution and dilute to 1 liter with water. Determine concentration of the molybdenum by the conventional α-benzoinoxime method.

Molybdenum addition solution. Prepared in the same way as the tungsten solution.

PROCEDURE

Dissolution of Sample. TITANIUM. Transfer the sample containing not more than 0.20 mg. of tungsten and weighing not more than 1 gram to a 50-ml. platinum dish. Add 5 ml. of water, then hydrofluoric acid and nitric acid dropwise until a clear solution is obtained. Add 3 ml. of sulfuric acid and evaporate, using moderate heat, to light fumes of sulfuric acid. Cool and add 5 drops of hydrofluoric acid (0.2 ml.).

TANTALUM. Transfer the sample containing not more than 0.20 mg. of tungsten and weighing not more than 1 gram to a 50-ml. platinum dish. Add 5 ml. of hydrofluoric acid and nitric acid dropwise until a clear solution is obtained. Add 3 ml. of sulfuric acid. This next step is critical. Evaporate using moderate heat until a light, white precipitate is visible. If the evaporation is carried too far, excessive precipitation of tantalum occurs, and the sample should be discarded. Cool and add 5 drops of hydrofluoric acid.

ZIRCONIUM. Transfer the sample containing not more than 0.20 mg. of tungsten and weighing not more than 1 gram to a 50-ml. platinum dish. Add 5 ml. of water and hydrofluoric acid dropwise until a clear solution is obtained. Evaporate, using moderate heat, until the first crystals of salts separate. Cool and add 5 drops of hydrofluoric acid.

Development of Color. Transfer the solution obtained in any of the above procedures to a 125-ml. Erlenmeyer flask, using 15 ml. of hydrochloric acid (1 to 2). Cool to 20° C. Add 3 ml. of stannous chloride solution and 10 ml. of dithiol solution. Shake for 10 minutes. Transfer the solution to a separatory funnel, using two 3- to 5-ml. washings of amyl acetate. Keep the organic layer to less than 20 ml. When the layers have separated, draw off the acid layer into the original flask and reserve. Wash the amyl acetate layer with two 2- to 3-ml. portions of hydrochloric acid (1 to 1) and return these washings to the flask.

The acetate layer now contains any molybdenum present. The molybdenum can be determined at this point by diluting to 25 ml. with amyl acetate and measuring the absorbance at 685 mμ. Use a reagent blank carried through all steps of the procedure as the reference solution in the spectrophotometer. Obtain the percentage of molybdenum present by referring to a standard curve prepared by measuring the absorbance of solutions containing known amounts of standard sodium molybdate solution ranging from 0.01 to 0.20 mg. of molybdenum, which have been treated as described.

Add 25 ml. of hydrochloric acid and 0.2 gram of titanium sponge to the reserved solution and heat gently until the solution is a medium purple due to the presence of titanium(III). [If the sample is titanium metal, additional titanium is not required. However, heating until titanium(III) is formed is necessary.] Add 10 ml. of dithiol solution and heat 20 minutes in a water bath at 80° to 90° C., swirling the flask frequently.

Transfer the solution to a separatory funnel, using small washings of amyl acetate, and keeping the volume of the organic layer to less than 20 ml. Draw off and discard the acid layer. Wash the acetate layer twice with 3 to 5 ml. of hydrochloric acid (4 to 1). Transfer the amyl acetate layer to a dry 50-ml. graduated cylinder. If the amyl acetate layer is cloudy, filter through a dry filter paper into the cylinder. Dilute the solution to 25 ml. with amyl acetate. Measure the absorbance at 640 mμ in a 1-cm. cell, using amyl acetate as the reference solution.

Determine the tungsten concentration of the sample by referring to a standard curve prepared by measuring the absorbance of solutions containing known amounts of sodium tungstate solution ranging from 0.01 to 0.20 mg. of tungsten which have been treated as described.

SELECTION OF REDUCTANT

In an attempt to determine the valence of tungsten in the tungstendithiol complex, a known amount of tungsten(VI) was reduced to tungsten(V) by the method of Crouthamel and Johnson (*3*). The reaction of tungsten(V) with dithiol was instantaneous, and with additional heating and shaking, recoveries of 0.095 mg. of tungsten were 0.094 and 0.097 mg. From these results, it would appear that the tungsten in the dithiol complex has a valence of (V).

With this in mind, it was felt that the method of Bagshawe and Truman (*1*) for the determination of tungsten in steel would be adequate. However, several modifications were necessary to prevent tantalum hydrolysis and formation of other insoluble tantalum products. The addition of phosphoric acid was omitted, and the sulfuric acid volume was increased sufficiently to prevent tantalum hydrolysis. Under these conditions, stannous chloride did not completely reduce tungsten, and recoveries were low and erratic.

Short (*7*) found that tungsten(V) could be readily formed by using the titanium(III) formed in solution as the reductant and that stannous chloride was not a strong enough reductant for tungsten but was adequate for molybdenum. As tungsten-free titanium sponge is readily available, it was felt that it would serve as a good reductant for tungsten. However, titanous chloride added as a solution is equally effective. On two samples containing 0.034% tungsten, results of 0.036 and 0.038% were obtained when 0.2 gram of titanium(III) was added in hydrochloric acid (1 to 1) solution. Additional hydrochloric acid was added to bring the solution acid concentration to 9 to 10*N* hydrochloric acid. In the procedure described, addition of 0.2 gram of titanium as sponge was selected because of volume considerations rather than for any chemical advantages.

DISSOLUTION OF SAMPLE

Titanium and zirconium can be dissolved in hydrochloric acid, but tantalum cannot. The dissolution is not rapid in any case; hydrofluoric acid and nitric acid, in combination, will dissolve all these metals rapidly. Unfortunately, nitric acid interferes with the dithiol reaction. Even with careful addition and controlled evaporation to remove the nitric acid, the results were erratic and frequently low. Light fuming prior to extraction with sulfuric acid gave complete recovery of tungsten in tantalum and titanium, but tungsten recoveries were low when zirconium was treated in the same manner. As zirconium will dissolve in dilute hydrofluoric acid, the addition of nitric acid and sulfuric acid was eliminated, and the dilute hydrofluoric acid solution was evaporated to a low volume prior to extraction. This procedure gave complete tungsten recoveries.

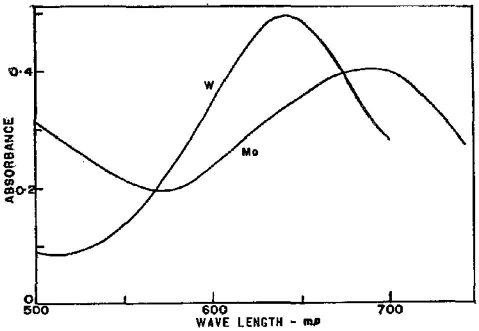

Figure 1. Absorption spectra of tungsten and molybdenum dithiol complexes

EFFECT OF TUNGSTEN CONCENTRATION

The colored compound of tungsten-dithiol exhibits two absorption bands: one centered at 360 mμ and the other at 640 mμ (Figure 1). However, the absorbance at 360 mμ was much too great to be usable in the range of tungsten to be analyzed. The 640 mμ band was selected because of the desirable sensitivity for the amounts under investigation.

Table I. Recovery of Tungsten in Presence of Varying Amounts of Molybdenum

(Matrix, 0.3 gram of tantalum)

Tungsten Present, Mg.	Molybdenum Added, Mg.	Tungsten Recovered, Mg.	Recovery, %
0.099	0.0108	0.102	103.2
0.099	0.0216	0.101	102.1
0.099	0.0324	0.102	103.2
0.099	0.054	0.100	101.1

The green-blue colored system measured at 640 mμ follows Beer's law from 0.01 to 0.20 mg. of tungsten in 25 ml. of amyl acetate when 1-cm. cells are used (absorbance values from 0.050 to 1.0). If the concentration of dithiol solution is increased from 0.5 to 1%, the colored system follows Beer's law from 0.01 to 0.40 mg. of tungsten in 50 ml. of organic solvent, when 1-cm. cells are used. Where more than 0.2 mg. of tungsten is expected, a 1% instead of a 0.5% solution of dithiol can be used. If the measured absorbance is less than 1.0 in a 50-ml. volume, all the tungsten present has reacted.

CARE OF REAGENT

One of the most important causes of erratic results with dithiol is air oxidation of the reagent. It should be stored under refrigeration and if possible in an inert atmosphere. Dithiol, on decomposition, forms a yellow liquid. If the crystalline dithiol contains this yellow liquid, even though stored under refrigeration, it should be discarded. For best results, the reagent solution should be made up just before use.

INTERFERENCES

The possibility of simultaneously reducing, extracting, and determining molybdenum and tungsten with dithiol was studied by Bagshawe and Truman (*1*) and Short (*7*). They found that under conditions necessary to reduce tungsten(VI) to tungsten(V)—9 to

Table II. Recovery of Varying Amounts of Tungsten

Matrix	Sample, G.	Tungsten, Mg. Present in sample	Added	Recovered	Recovery, %
Titanium	0.200	0	0.038	0.035	92.1
			0.057	0.062	108.8
			0.095	0.100	105.3
			0.133	0.128	96.2
Zirconium	0.200	0	0.038	0.042	110.5
			0.057	0.059	103.5
			0.095	0.100	105.3
			0.133	0.128	96.2
Tantalum	0.200	0	0.038	0.038	100
			0.057	0.057	100
			0.095	0.098	103.2
			0.133	0.137	103.0
		0.068	None	0.068	...
			0.038	0.104	94.7
			0.057	0.130	108.8
			0.095	0.161	97.9
Tantalum	1.000	0.013	0.000	0.013	...
			0.019	0.033	105.2
			0.038	0.053	105.2
			0.057	0.071	101.7

Table III. Determination of Tungsten in Watertown Arsenal Titanium Samples

Participating Laboratory	% Tungsten WA22	WA8
1[a]	0.05, 0.05	0.41, 0.41
	0.05, 0.06	0.42, 0.39
2[a]	0.06, 0.06	0.40, 0.41
	0.06, 0.06	0.41, 0.41
3[a]	0.06, 0.06, 0.06	0.42, 0.42, 0.43
	0.06, 0.06, 0.06	0.42, 0.42, 0.41
4[a]	0.05, 0.05	0.40, 0.40, 0.40, 0.36
	0.05, 0.06	0.40, 0.40, 0.40, 0.39, 0.38
Metals Research Laboratories[b]	0.054, 0.055	0.38, 0.38

[a] α-Benzoinoxime precipitation–hydroquinone colorimetric method.
[b] Dithiol method.

11N hydrochloric acid and a strong reductant such as titanium(III)—molybdenum recoveries were low. For quantitative recoveries of molybdenum, more moderate reducing agents and weaker acid solutions, 6N hydrochloric acid or less, were necessary. The supposition by both authors was that under conditions necessary for tungsten reduction, some of the molybdenum was reduced to molybdenum(III), which did not form a colored dithiol complex.

Since sequential extraction of molybdenum and tungsten had been utilized by Bagshawe and Truman (*1*) and Short (*7*), conditions for this type of extraction were investigated. It was found that molybdenum could be reduced and extracted in 4N hydrochloric acid by using 20% stannous chloride in 1 to 1 hydrochloric acid at a temperature of 20° C. (Table I). A small amount of sulfuric acid (not more than 4 ml.) could be present. No tungsten was extracted even after shaking 20 minutes. The acidity was then increased to 9 to 11N hydrochloric acid, titanium(III) used as the reductant, and tungsten extracted.

Hydrofluoric acid in low concentrations did not interfere and served two useful purposes; it prevented tantalum hydrolysis and facilitated dissolution of the added titanium sponge.

RESULTS AND DISCUSSION

As no acceptable metal standards were available, precision and accuracy were checked using synthetic solution standards. Tungsten - bearing metals were used to check precision. All the metals used were first analyzed with dithiol for tungsten. In order to determine reproducibility, five portions of a sample of titanium containing 0.095 mg. of tungsten were analyzed. An average of 0.096 mg. of tungsten was recovered with a maximum difference of 0.003 mg. Varying amounts of tungsten (0.038 to 0.133 mg.) were added to titanium, zirconium, and tantalum. As is shown in Table II, recoveries were satisfactory.

Two titanium samples prepared by the Watertown Arsenal and issued to the panel on methods were submitted to these laboratories for determination by the dithiol method (Table III). Values obtained by other laboratories using an α - benzoinoxime precipitation–hydroquinone colorimetric method are also given in Table III.

The molybdenum extraction, in most cases, may be omitted, as molybdenum is usually present in negligible quantities or not at all. However, the addition of stannous chloride was continued because conversion of titanium (metal) to titanium(III) was more rapid.

The advantages of this method are its sensitivity, specificity, rapidity, and simplicity.

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Spectrographic Determination of Alumina in Lead Borosilicate Glass Frits

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▶ Alumina in lead borosilicate frits can be determined by a spectrographic procedure. The method covers the range from 1.30 to 8.00% alumina with a coefficient of variation of ± 2.3% of the amount present for triplicate determinations. A systematic study of matrix effects showed that the method gives excellent results over relatively wide matrix changes. The procedure is speedy and simple in operation. It has been successfully used as a quality control measure for glass frits.

LEAD BOROSILICATE frits are glasses with relatively low softening points. They are effective sealing compounds and are mainly used to join one glass to another or a metal to a glass. Frits may also be used to impart density to soft porcelain and are sometimes incorporated in glazes to promote fusion to the surface of various ceramics.

The function of alumina in these frits is to reduce attack by atmospheric moisture, particularly in an acidic environment. Alumina also increases the viscosity and raises the softening point of the frit, thereby critically affecting its efficiency as a sealant.

Therefore a rapid and accurate determination of this constituent is necessary as a quality control measure.

The only previously published work specifically on the spectrographic analysis of frits was a semiquantitative procedure (*11*). However, Lounamaa (*7*) has recently developed a quantitative method for lead-making slags (which is a similar matrix). A preliminary fusion with lithium carbonate and boric acid was utilized to obtain a reproducible physical form and to reduce matrix effects.

Other workers (*5, 10, 12*) have employed similar techniques, using a flux containing an element with relatively low ionization potential to suppress any interelement effect. A procedure of this type greatly dilutes the sample by a buffer-flux mixture until the latter becomes the predominant matrix material. Such procedures involve mixing and weighing errors which are attendant upon high dilutions.

A preliminary fusion was not necessary in the work described here because the frits are made from a melt and already have a reproducible physical form. As no elements of very low ionization potential were present in the matrix, an alkali buffer was not employed.

Most of the work described in the literature for preliminary fusion techniques has been done with high voltage spark excitation in conjunction with a pressed pellet, which involves rather expensive equipment such as a briquetting press and spark source. The present procedure involves only one mixing operation, direct loading of electrodes, and an inexpensive direct current arc for excitation.

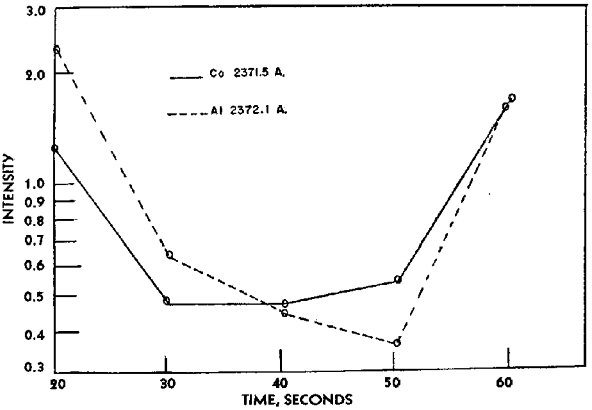

Figure 1. Volatilization rates of aluminum and cobalt at 8.5 amperes direct current

Some general spectrographic methods using a similar approach have been reported (*3, 6, 12*). However, the conditions chosen for these methods usually represent a compromise between the optimum conditions for several individual elements so that all of them may be determined in one operation. The method described here was developed specifically for the determination of alumina in lead borosilicate frits and the conditions chosen were optimum for this constituent only.

DEVELOPMENT OF METHOD

It is almost impossible to reproduce a lead-base frit of predetermined composition because of the volatility of lead oxides and the fact that the frits are made from a melt at elevated temperatures. Accordingly the spectrographic method was designed in such a manner that a relatively large matrix variation would have a minimum effect on the analytical results.

In this connection, it was discovered that an addition of 2 parts of graphite to 1 part of sample was beneficial. First, the arc burn was much improved. Second, the reducing effect of the graphite increased the volatility of the aluminum and prevented the formation of a refractory alumina bead. This increase in volatility was evident even as the lead, silicon, and boric oxide contents of the frit were changed.

When cobalt was added to the graphite as cobaltic oxide, the distillation rate of this internal standard was similar to that of aluminum (Figure 1). Cobalt, like aluminum, exhibits a high volatility in the first 20 seconds, which slackens during the next 30 seconds and then increases sharply in the final 10 seconds. Thus, even though the volatilization rates of aluminum and cobalt are not uniform through the arcing cycle, the same general pattern of distillation is shown by both elements in this matrix.

A study of excitation conditions (Figure 2) showed that higher currents (8.0 to 9.5 amperes) gave the smallest fluctuation of intensity ratio. Accordingly, an arc current of 8.5 amperes was chosen.

A systematic investigation of electrodes disclosed that a narrow diameter, relatively deep, cratered anode was desirable. Such an electrode minimized sample spraying and ejection, and at the same time reduced the well-known tendency of the direct current arc to wander. Detailed specifications of the electrodes are given below. The electrodes have previously been used effectively in silicate analysis by Ahrens and coworkers (*1*).

When the sample was arced in the electrodes under the conditions previously described, all the aluminum volatilized within 70 seconds over a wide range of matrix changes. As any additional time would only increase undesirable spectral background, a 70-second exposure was chosen.

At the relatively high arc current used, self-absorption of all the commonly used aluminum atom lines in the region from 2500 to 3100 A. was exhibited. Accordingly, aluminum 2372.1 A. was chosen for the determination. This line actually consists of two aluminum lines which cannot be resolved with most commercially available spectrographs. These lines, together with the cobalt internal standard line and the excitation potentials (*8*, *9*) are as follows:

Wave Length, A.	Intensity	Excitation Potential, Volts Low	High
Al I 2372.084	3	0.00	5.20
Al I 2372.115	10	3.60	8.80
Co I 2371.458	12	2.13	7.33

It is evident from these data that aluminum 2372.084 A. originates from the ground state and is therefore subject to self-absorption. However, its intensity rating is low (lower transition probability) in comparison to aluminum 2372.115 A., which originates from a much higher energy level. The predominant effect is therefore due to the latter line, which is much less subject to self-absorption. This has been confirmed empirically by running the analytical curve many times and observing that a linear relation exists between the logarithms of intensity ratio and concentration up to 8.00% alumina.

Cobalt 2371.458 A. was chosen as the internal standard line because its excitation characteristics so closely approximate those of the aluminum line. The above table shows that the difference in energy levels is exactly the same for the cobalt lines chosen as for aluminum (5.20 volts). Also, the close wave length proximity of the internal standard and analysis lines obviates the need for background correction and nullifies any differences due to variable spectral response of the photographic emulsion.

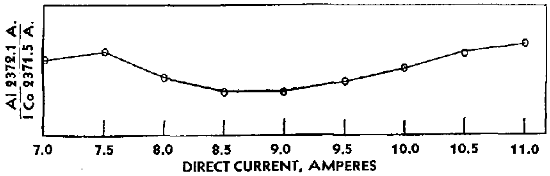

Figure 2. Effect of direct current arc on intensity ratio of Al 2372.1 A./Co 2371.5 A.

Table I. Cobalt Lines[a] Used for Emulsion Calibration[b]

Wave Length, A.	Excitation Potential, Volts Low	High
2339.550	0.51	5.79
2347.657	0.10	5.36
2360.789	1.04	6.27
2371.458	2.13	7.33
2371.845	0.17	5.38
2372.862	0.22	5.42
2377.215	0.63	5.82
2380.483	0.10	5.29
2380.696	0.17	5.36
2357.507	0.92	6.15

[a] From Moore (*9*).

[b] Following lines listed by Harrison (*4*) were also used; no excitation potentials were given: 2360.509, 2361.14, 2381.752, 2385.816, 2382.335, 2351.978.

PROCEDURE

A summary of electrode specifications, apparatus, and operating conditions is as follows.

Electrodes. Anode. $1^{1}/_{2}$-inch graphite rod, $^{1}/_{8}$-inch diameter with $^{1}/_{16}$-inch diameter cup, $^{3}/_{16}$ inch deep.

Cathode. $1^{1}/_{2}$-inch graphite rod, $^{1}/_{8}$-inch diameter with pointed tip.

Spectrographic Equipment and Optics. A Bausch & Lomb large prism spectrograph, with a focal length of 1.8 meters, quartz optics, and Littrow mounting was used. The spectrum from 2300 to 3000 A. was photographed on one 10-inch plate. The reciprocal linear dispersion was 2.0 A. per mm. at 2370 A. A slit width of 20 microns and slit height of 3 mm. were employed. The analytical gap was maintained at 4 mm. throughout the exposure. The distance from source to slit was 23 inches. An image of the electrodes was focused on the collimator by a condensing lens placed at the slit. Half of this lens was coated with aluminum to transmit approximately 65% of the incident light. A special diaphragm with a rectangular aperture $^{3}/_{8}$ inch high was placed at the collimator to mask out the incandescent electrode tips.

Method. The sample was prepared by grinding the frit to a fine powder (200 mesh) in an agate mortar. The internal standard, cobalt, was introduced as 4.00% cobaltic oxide by weight into high purity graphite powder. The sample, 50 ± 0.5 mg., was added to 100 ± 0.5 mg. of the graphite–cobaltic oxide mixture. This composite was thoroughly mixed for 1 minute in a vibrating-type mixer such as the Wig-L-Bug dental amalgamator. A direct-reading, constant sensitivity balance of the Gram-atic type was particularly well suited to the weighing operations.

Part of the above mixture was transferred to the cup of a graphite electrode. Sufficient sample was added to fill the cup after tamping compactly with a Lucite rod. The electrodes should be kept in an oven at approximately 110° C. from the time they are loaded until they are ready to be run. Exposure to the air results in moisture pickup which may affect the results.

Excitation Conditions. A direct-current arc, 220 ± 0.3 volts open circuit voltage, was used with Stabiline electronic regulator on an alternating current input with full wave rectification. The current was set at 8.5 amperes on initiation of the arc. A 70-second exposure was used with no preburn.

Photographic Conditions. Eastman process emulsion was used with Kodak D-19 developer. Tank development was carried out in a thermostatically controlled plate processor kept at 21° ± 0.5° C. Developing time was $2^{1}/_{2}$ minutes.

Photometry. The transmittances of aluminum 2372.1 A. and cobalt 2371.5 A. were measured on a nonrecording, projection-type densitometer. Any of the standard commercially available units can be used for this purpose.

The transmittance values were then converted to intensity ratios by means of a special photographic calibration curve made for the region from 2300 to 2400 A. A calculating board greatly facilitates this operation.

Emulsion Calibration. The spectral response in the region from 2300 to 2400 A. for a process emulsion produced a lower contrast than the region from 2600 to 3000 A. commonly used. Accordingly, a special calibration procedure was developed.

Table II. Composition of Synthetic Frit Standards

	% Al_2O_3	% SiO_2	% B_2O_3	% PbO
1	8.00	11.00	11.00	70.00
2	6.00	12.00	12.00	70.00
4	3.60	13.20	13.20	70.00
5	2.16	13.92	13.92	70.00
6	1.30	14.35	14.35	70.00

A variation of the two-step method first described by Churchill (*2*) was used. Transmittance readings of triplicate exposures of a frit control standard were taken on selected cobalt lines photographed on a two-step aluminized filter. These lines are listed in Table I.

The conditions used were the same as for the analysis. Because the control standard is run on each plate routinely, a check on the plate calibration may be made at any time without sacrificing plate space or running any additional exposures.

A new calibration was necessary only for a new emulsion batch. Variations between plates of the same batch are compensated for by the two control standards which are run on each plate.

The aluminized filter used in this method transmits approximately 65% of the light passing through the unfiltered lens. Transmittance readings from triplicate exposures of the filtered and then the unfiltered portions were averaged for each line listed in Table I. A preliminary curve and then an emulsion calibration curve were derived from these data.

Preparation of Standards. Standards were prepared by melting calculated amounts of boric acid, alumina and silica at 600° C. overnight. The resulting hard "clinker" was then weighed; in all cases the loss in weight corresponded to the theoretical loss of water from the boric acid to form boric oxide. This sintering process yielded a glasslike material which was ground to a fine powder and then dry mixed with litharge to give standards of the composition shown in Table II.

Immediately after mixing operations were completed, the standards were placed in tightly capped vials and stored in a desiccator. This was necessary because of the hygroscopic nature of the frits (due mainly to their borate content). If this is not done, a pronounced shift in the working curve will be exhibited.

RESULTS

The analytical curve obtained from triplicate exposures of these standards is linear from 1.30 to 8.00% alumina. The slope of this line is 49° when the log concentration of alumina is plotted as the ordinate and the log intensity ratio of the analytical line pair is plotted as the abscissa. A background correction is not necessary for this alumina concentration range. This simplifies and speeds up the calculation of analytical results.

PRECISION AND ACCURACY

The statistical precision of this method was found by running a commercial frit sample 15 times. The precision, expressed as coefficient of variation, is ± 2.3% of the amount present for triplicate determinations.

The accuracy of the method cannot be precisely determined. However, a close estimate may be obtained by a comparison with wet analytical results. Values obtained independently on eight commercial samples are listed in Table III.

MATRIX EFFECTS

The complete chemical compositions of the eight frits are also given in Table III. The values listed were all determined by wet chemical analysis. Even though these samples represent a wide matrix variation, the difference between spectrographic and wet chemical results is, in almost all cases, less than the statistical variability of the spectrographic method itself.

The excellent agreement between the two methods indicates that the spectrographic procedure is accurate in samples of somewhat different composition. However, it was also necessary to determine the exact limits of matrix variation within which the method would be applicable. In this connection, a more thorough study of matrix changes was made.

The first step in this investigation was to prepare a series of synthetic frits whose composition was systematically changed over a wide range. This was done by adding synthetic mixtures to NBS Sample 93, a high boron, siliceous glass. The synthetic blends contained various proportions of alumina, lead monoxide, and boric acid which were fused at 600° C. for 2 hours and then dry mixed with the NBS glass to give samples of the compositions shown in Table IV.

Only in the case of Sample 93-3 was a detrimental matrix effect observed. This sample had the lowest boric oxide content and highest lead monoxide content. However, Sample 93-6 also had the same high lead monoxide content and gave accurate results. Accordingly, the matrix effect should be attributed mainly to the low boric oxide content. This method is valid, therefore, within the following ranges of composition:

Constituent	Range, %
Lead monoxide	60 to 75
Sodium oxide	0 to 0.83
Silica	10 to 16
Boric oxide	8 to 20

The homologous nature of the cobalt and aluminum lines chosen is

Table III. Matrix Variation[a] and Comparison of Spectrographic and Wet Chemical Results on Frits

	Matrix			% Al_2O_3		
Sample	% PbO	% SiO_2	% B_2O_3	Spectrographic	Wet chemical[b]	Diff.
1	74.12	12.17	11.40	2.07	2.10	+0.03
2	70.55	15.99	11.19	2.08	2.09	+0.01
3	70.66	12.19	15.04	2.08	2.08	0.00
4	66.80	16.02	15.11	2.05	2.11	+0.06
5	70.44	12.19	10.99	6.18	6.19	+0.01
6	66.53	16.15	11.13	6.17	6.05	−0.12
7	66.68	12.33	14.56	6.20	6.30	+0.10
8	63.00	16.13	14.56	5.92	6.06	+0.14

[a] Frit was dissolved in nitric-hydrofluoric acid mixture and the lead precipitated as lead sulfate from 1 to 1 alcohol-water mixture. Silica was determined on separate sample by double dehydration from hydrochloric acid and treatment with hydrofluoric acid. Boron from separate sample was titrated by Chapin's method with glycerol solution.

[b] After separation of lead, R_2O_3 was precipitated from filtrate. Titanium oxide, zirconium oxide, and lead were determined in R_2O_3; remainder was reported as Al_2O_3.

Table IV. Effect of Change in Matrix on Accuracy of Spectrographic Alumina Determination

	Analysis after Additions, %				% Al_2O_3			
Sample	PbO	Na_2O	SiO_2	B_2O_3	Spectrographic	Calcd.	Diff.	Relative % Dev.
93-2	67.66	0.69	13.43	12.13	6.05	6.00	0.05	0.83
93-2A	64.95	0.83	16.12	12.15	5.80	5.84	0.04	0.69
93-3	75.00	0.69	13.43	4.79	5.00	6.00	1.00	17
93-4	59.78	0.69	13.43	20.00	6.20	6.00	0.20	3.3
93-5	73.39	0.42	8.06	12.03	5.80	6.00	0.20	3.3
93-6	74.20	0.56	10.75	8.43	5.95	6.00	0.05	0.83

probably largely responsible for the relatively small influence of matrix variations on the analytical results.

It is also probable that the direct current arc promotes fusion of the sample–internal standard mixture, thereby incorporating the cobaltic oxide into a new glasslike structure of similar physical form for all samples. This is a great aid in improving the efficiency of the internal standard.

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Determination of Zirconium in Steel

Direct Spectrophotometric Method

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▶ A direct spectrophotometric method for the determination of small amounts of zirconium in steels is described. After removing interfering ions by electrolysis with a mercury cathode, the zirconium is determined by measuring the absorbance of its chloranilate complex at 550 or 330 mμ. Results by this method compare favorably with those by the p-dimethylaminoazobenzenearsonic acid and mandelic acid methods.

Colorimetric methods for zirconium usually involve the formation of lakes (*1,2,6*) or rely upon absorbance measurements obtained by dissolving a precipitate (*4,8*). Neither method is entirely satisfactory. Lakes are affected adversely by the presence of impurities. Indirect methods are empirical and results must be obtained by comparison with standard samples of similar composition (*4*).

Thamer and Voigt (*9,10*) showed that zirconium ions in perchloric acid solution form soluble, colored complexes with chloranilic acid and used this as a colorimetric method for the determination of small amounts of zirconium. Absorbance was measured at 330 mμ. Frost-Jones and Yardley (*3*) also studied the chloranilic acid method but measured the absorbance at 525 mμ. The sensitivity was less at this wave length, but larger amounts of zirconium could be determined than by the method of Thamer and Voigt.

As these methods involve the direct measurement of a stable, soluble complex of zirconium, they were investigated for the determination of zirconium in steel. The major obstacle is using the chloranilic acid method for the determination of zirconium in steel is the interference caused by the ferric ion. Ferric ions form a dark-colored complex with chloranilic acid which absorbs strongly in both the visible and ultraviolet regions. Attempts to eliminate this interference by reducing iron(III) to iron(II) were unsuccessful. Complete reduction could not be attained by using hydrazine or hydroxylamine. Sulfites, dithionites, and other sulfur-containing compounds gave low results. Ascorbic acid formed complexes which absorbed. Heterogeneous reductants—for example, zinc metal—were unsuccessful because the solution became reoxidized immediately upon removal of the reductant.

Separation methods were tried. Ether extractions did not remove the iron completely. As electrolysis with a mercury cathode using a Melaven cell gave excellent separations, this was adopted as the method for removing interfering ions. After electrolysis, chloranilic acid was used to determine the zirconium remaining in solution. Very small amounts of zirconium (0.1% or less) could be determined most accurately by measuring the absorbance at 330 mμ, whereas larger amounts gave better results at 525 mμ. Therefore two procedures were devised. If the range of zirconium in the sample is unknown, measurement at 525 mμ is recommended.

PROCEDURE

Reagents. Chloranilic acid (available from Eastman Kodak Co.): 0.1% solution, dissolve 1 gram of

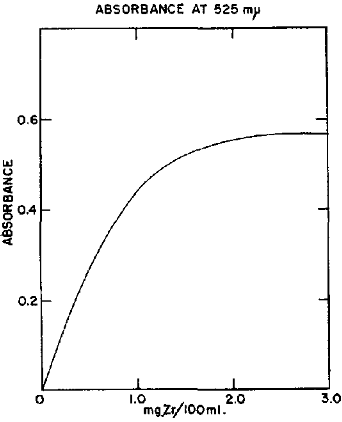

Figure 1. Standard curve for spectrophotometric measurement of absorbance of zirconium at 525 mμ

chloranilic acid in 1 liter of distilled water; $2 \times 10^{-4}M$ solution, dissolve 0.042 gram of chloranilic acid in 1 liter of distilled water.

Perchloric acid, 72%, G. F. Smith Chemical Co.

Method A. Samples Containing 0.1% Zirconium or More. Weigh a 0.2- to 0.5-gram sample of steel and dissolve in about 20 ml. of 6*M* hydrochloric acid. Warm, if necessary. Add 7 ml. of 72% perchloric acid and evaporate until copious fumes of perchloric acid are obtained. Dilute to about 20 ml. with water and electrolyze, using a mercury cathode in a Melaven cell (*7*), with stirring, for 50 minutes using a current of 0.5 ampere. Transfer the solution to a 100-ml. volumetric flask, add 8 ml. of 0.1% chloranilic acid and 5 ml. of 72% perchloric acid, then bring up to volume with distilled water. Measure the absorbance at 525 mμ using a 5-cm. cell. Determine the amount of zirconium from the standard curve (Figure 1).

Method B. Samples Containing Less than 0.1% Zirconium. Weigh a 1.0- to 5.0-gram sample of the steel and dissolve in 25 to 50 ml. of 6*M* hydrochloric acid, heating if necessary. Add 46 ml. of 72% perchloric acid and evaporate to copious fumes of perchloric acid. Transfer to a 500-ml. volumetric flask and dilute to volume with distilled water. Take a 25-ml. aliquot and electrolyze as directed in Procedure A. Transfer the resulting solution to a 100-ml. volumetric flask, add 10 ml. of 72% perchloric acid and 13 ml. of $2 \times 10^{-4}M$ chloranilic acid, then dilute to volume with distilled water. Measure the absorbance at 330 mμ using a 1-cm. quartz cell. Determine the amount of zirconium from the standard curve (Figure 2).

DISCUSSION

The method was tested first on "synthetic" steels obtained by adding known amounts of standard zirconium perchlorate solution to a solution of ferric perchlorate. These solutions were electrolyzed and the zirconium content was determined. Quantitative recovery of the zirconium was obtained in all experiments.

The interference of various ions was studied. Varying amounts of foreign ions were added to solutions containing known amounts of zirconium and determinations were made, without electrolysis, at both 525 and 330 mμ. Interferences were the same at both wave lengths (Table I). The effect of various other foreign ions is given by Thamer and Voigt (*9*). The effect of varying the concentration of perchloric acid was studied. Quantitative results were obtained in solutions 1.5 to 2.5*M* in perchloric acid. Acid concentrations lower than 1.5*M* gave high results for zirconium, whereas concentrations greater than 2.5*M* gave low results.

The method was tested also using nickel-chromium steels whose zirconium content had been determined by the method of Hayes and Jones (*4*) (Table II).

Table I. Effect of Diverse Ions

Ion	Amount Tolerated, Mg./100 Ml.[a]	Times Greater than Zirconium Concn.
SO_4^{--}	20	200
Cl^-	500	5000
Ti^{+4}	10	100
Fe^{+++}	0.5	5
Nb^{+5}	1.0	10
WO_4^{--}	0.5	5
F^-	0.1	1

[a] Amount that causes an error of 3% in determination of zirconium.

Table II. Zirconium in Nickel-Chromium Steels

(Per cent zirconium)

Steel No.	Chloranilic Acid, Method B (Absorbance Read at 330 Mμ) Sample 1	Sample 2	Sample 3	Av.	Hayes and Jones Method
307-4	0.028	0.033	0.035	0.032	0.02
307-5	0.036	0.045	0.053	0.045	0.03
307-6	0.042	0.040	0.037	0.040	0.05
T-1755	0.0073	0.0043	0.0074	0.006	0.003

Table III. Zirconium in Simple Carbon Steels

Steel No.	Per Cent Zirconium Colorimetric, 330 mμ	Colorimetric, 525 mμ	Mandelic acid	Phosphate method
1	0.008	0.008	No ppt.	0.025
2	0.090	0.108	0.110	0.20
3	0.160	0.221	0.220	0.34
TL72802	0.022	0.018	0.025	0.05

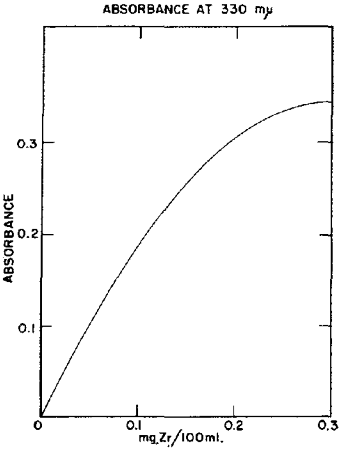

Figure 2. Standard curve for spectrophotometric measurement of absorbance of zirconium at 330 mμ

The zirconium content of simple carbon steels was determined by the chloranilic acid method using Procedures A and B. These determinations compared with results obtained from the mandelic acid method (*5*) and the phosphate method are given in Table III.

These data indicate substantial agreement between both chloranilic acid methods and the mandelic acid method. Results from the phosphate method are high. As mandelic acid is a more specific precipitant for zirconium than the phosphate ion, the high results in the phosphate method are caused by coprecipitation of impurities.

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Infrared Absorption Spectra of Methylenedioxy and Aryl Ether Groups

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▶ Methylenedioxy, methoxy, and ethoxy groups attached to the aromatic nucleus exhibit 12, 10, and nine major bands associated with these respective groups. Most of them are common to all three groups. The analytical value of the bands for the detection of the groups is discussed.

Following the original observation by one of the authors (*9*, *12*) that compounds containing methylenedioxy groups exhibit characteristic maxima at about 1040 to 1020 and 943 to 935 cm.$^{-1}$ in their infrared spectra, a more detailed examination of the spectrum of this group has been made on 100 compounds. The ability to recognize this group by infrared spectroscopy would be of value because the chemical test for this group sometimes fails through an intense coloration produced by some other part of the molecule (*6*). For comparison, an examination was made on a number of analogous *o*-dimethoxy compounds and other methoxy compounds. Spectra were also studied for a limited number of aromatic ethoxy compounds.

EXPERIMENTAL

Infrared absorption spectra from 5000 to 700 cm.$^{-1}$ were obtained with either a Beckman Model IR-2 or Perkin-Elmer Model 21 spectrophotometer, both equipped with sodium chloride optics. Measurements in the 3000-cm.$^{-1}$ region were obtained with the former instrument equipped with a lithium fluoride prism or with a Beckman Model IR-3 spectrophotometer equipped with sodium chloride optics. The solvent notations are given in Table I.

METHYLENEDIOXY COMPOUNDS

The spectrum of liquid methylenedioxybenzene, determined with a sodium chloride prism in the region from 3330 to 700 cm.$^{-1}$ and with a lithium fluoride prism in the region from 5000 to 2500 cm.$^{-1}$, and that of veratrole are illustrated in Figure 1. From a comparison of these spectra and those of 99 other methylenedioxy compounds (Table I) it may be concluded that the methylenedioxy group attached to the aromatic ring exhibits 12 major bands associated with this group—viz., very strong bands at about 1480, 1250, 1040, and 926 cm.$^{-1}$; strong bands at about 3010, 2960, 2910, 2780, 1360, and 1130 cm.$^{-1}$; a medium band at about 1400 cm.$^{-1}$; and a weak band at about 719 cm.$^{-1}$

The 3300- to 2500-Cm.$^{-1}$ Region. The methylene fragment of the methylenedioxy group would be expected to give rise to a doublet due to resonance interaction between the two C—H bonds, not far removed from that of a normal C—CH$_2$—C group, the members of which occur at 2924 and 2857 cm.$^{-1}$ (*4*). Two bands which occur in the region from 3000 to 2700 cm.$^{-1}$ are assigned to this mode of vibration. The strong band at 2778 cm.$^{-1}$ in the methylenedioxybenzene spectrum, which occurs in all other methylenedioxy compounds within the range from 2801 to 2770 cm.$^{-1}$, is considered to be the upper band of this doublet. When compounds are measured in the liquid state, in carbon tetrachloride solution, or in potassium bromide, this is a very sharp band; it is replaced by a broad band at 2817 to 2770 cm.$^{-1}$ in hexachlorobutadiene mulls. It occurs beyond the normal range of C—H stretching vibrations and therefore is diagnostic for the methylenedioxy group. Absorption due to the —CH$_2$N or —CHO groups, if present in the molecule, may obscure this band.

The strong band at 2890 cm.$^{-1}$ in the methylenedioxybenzene spectrum is probably the lower member of the doublet. A band within the limits from 2941 to 2890 cm.$^{-1}$ occurs in all methylenedioxy compounds, but is of no diagnostic value alone as it occurs within the normal range of aliphatic C—H stretching vibrations. Difficulty may be experienced in detecting these bands with a sodium chloride prism in some instruments, but this is obviated by the use of a lithium fluoride prism.

Bands also occur at 3012 and 2985 cm.$^{-1}$ in the methylenedioxybenzene spectrum, beyond the range expected for aromatic C—H frequencies. Usually, but not invariably, these two bands also occur in other methylenedioxy compounds at about 3000 and 2960 cm.$^{-1}$, similar in position to the bands of methoxy compounds (discussed below).

The 1600- to 1100-Cm.$^{-1}$ Region. The very strong band at 1477 cm.$^{-1}$ in the methylenedioxybenzene spectrum occurs in all methylenedioxy compounds and may be assigned to aliphatic C—H bending. A medium band due to C—H bending of normal methylene compounds that occurs in the same region renders this band of little analytical value for detecting the presence of the methylenedioxy group.

The medium band at 1401 cm.$^{-1}$ in the methylenedioxybenzene spectrum occurs in many other methylenedioxy compounds within the range from 1427 to 1391 cm.$^{-1}$. The band, however, is weak in many cases and absent in others. Because normal methylene groups also give rise to a band in this region, it is of little diagnostic value.

A sharply defined, strong band occurs in the spectrum of methylenedioxybenzene at 1361 cm.$^{-1}$, and in the spectra of many other methylenedioxy compounds within the range from 1376 to 1350 cm.$^{-1}$ The band is of varying intensity, from weak to strong, and is absent in five compounds. It may occur in other compounds containing a normal C—CH$_2$—C group but is absent in methoxy compounds and, for this reason, may be analytically important.

The presence of the aromatic C—O linkage in aromatic methylenedioxy compounds would be expected to give a band due to the stretching vibration in the same region as that of aromatic and unsaturated ethers at about 1250 cm.$^{-1}$ (*3*). In fact, every methylenedioxy compound exhibits a very strong band in the region from 1266 to 1227 cm.$^{-1}$, assignable to this vibration. In some cases the single peak may appear as a strong doublet. Where both methylenedioxy and aromatic ether groups occur in the same molecule,

Table I. Methylenedioxy Compounds

Compound[a]	State[b]	Band Frequency, Cm.$^{-1}$ [c]													
Methylenedioxybenzene	L	3012	2985	2890		2778	1477	1401	1361	1236		1130	1043	937	718
1-Methoxy-2,3-methylenedioxybenzene*	T	3012	2959 2941	2890	2849	2778									
	C						1493 1460	a	1350	1250	1176	a	1053 1031	924	
Piperonyl alcohol															
lithium fluoride prism	T	3012	a	2915 2882		2770									
Sodium chloride prism	T		2950w	2890		2778									
	N						m	m	m	1247		1121	1032	920	m
6-Bromopiperonyl alcohol	T	3021	2967	2933 2899		2778									
	N						m	1406	m	1236		a	1036	927	m
	C						1475	1404	1372	m		a	1036	931	m
6-Phenylpiperonyl alcohol	C						1477	a	1362	m		1124	1036	931	m
Piperonyl bromide	T						1490	a	1361	1242		1121	1042	930	m
6-Bromopiperonyl bromide	T	3021	2994	2915		2778									
	C						1477	1403	1351	1242		1117	1036	935	m
6-Bromopiperonyl *tert*-butyl ether	L						1481	1393	1362	1241		a	1040	935	719
Piperonal	T	3012	2959	2899		2778									
	N						m		m	1255		1122	1034	925	m
	C						1488	1399	1357	m		1117			
Piperonal	S						m	m	m	1253		1125	1040	934	721
6-Nitropiperonal	N						m	1418	m	1236		1122	1028	920	725
6-Bromopiperonal dimethyl acetal*	T				2841	2778									
	C									1235			1031	930	m
1,2-Dibromo-4,5-methylenedioxybenzene	T			2899		2793									
Piperonylic acid	N						m	1408	m	1256 1242		1114	1034	930	723
	K		2985	2924		2786	1449	1410	1366	1258 1244		1115	1036	933	723
6-Bromopiperonylic acid	N						m	1408	1351	1242		a	1031	922	m
Myristicinic acid*	H			2915	2841	2801									
	N						m	m	m	a		1117	1042	939 919	m
Piperonylamine	T						1481	a	1379w 1357w	1238		1121	1040	939	m
Piperonylamine hydrochloride	N						m	a	m	1242		1126	1041	935	m
N,*N*-Dimethyl-6-phenylpiperonylamine	C						1477	1410w	m	m		1124	1036	934	m
Homopiperonyl cyanide	N						m	1414	m	1245		1121	1034	925	725
β-3,4-methylenedioxyphenylpropionic acid	K		2976	2924 2899		2786	1441	1418	1357	1236		1122	1034	934 923	720
Safrole	T			2907		2786									
	L						1437	1395	1357	1244		1121	1041	929	717
Isosafrole	T		2976	2924 2899		2786									
	L						1439	a	1353	1242		1122	1041	937	719
Isomyristicin*	T	3012	2959 2941	2915 2882	2857	2778									
	N						m	a	1351	1233	1193	1133	1045	930	m
	K	3012	2959	2915 2899	2849	2793	1427	a	1353	1233	1198	1135	1045	929	716
	S						m	m	1357	1232	1198	1138	1049	939	717
3,4-Methylenedioxy-β-nitrostyrene	N						m	a	1362	1264 1242		1129	1031	921	m
	C						1481	a	1355	m		1121	1031	930	m
2-(3′,4′-methylenedioxyphenyl)cyclohexanol	C						1486	a	1370 1350	1244		1126	1040	938	m
2-(3′,4′-methylenedioxyphenyl)cyclohexanone	C						1484	a	1361	1245		m	1036	935	m
	T	2976	2954	2941 2882		2793									
5-(3′,4′-methylenedioxyphenyl)-4-nitrocyclohexene	N						m	1399w	m	1248 1238		1120	1035	930	m
	C						1481	a	1362	1238		1120	1038	935	m
4-(3′,4′-methylenedioxyphenyl)-5-nitro-1,2-cyclohexanediol	N						m	a	m	1264 1241		a	1040	930	m
4-Amino-5-(3′,4′-methylenedioxyphenyl)-1,2-cyclohexanediol	N						m	a	m	1247		a	1040	930	m
N-(6-amino-3,4-methylenedioxybenzoyl)-*p*-methylaminophenyl benzoate	N						m	1397	1361	1263 1248		a	1044	943	m
N-(6-benzalamino-3,4-methylenedioxybenzoyl)-*p*-methylaminophenyl benzoate	N						m	1397	1361	1263 1248		a	1044	943	m

[a] Compounds marked * contain methylenedioxy and methoxy groups.

[b] L, liquid film; K, potassium bromide; C, chloroform; T, carbon tetrachloride; S, carbon disulfide; N, Nujol; H, hexachlorobutadiene.

[c] b, broad; w, weak; s, strong; a, absent; m, masked.

(*Continued on page 906*)

Table I. Methylenedioxy Compounds (*Continued from page 905*)

Compound[a]	State[b]	Band Frequency, Cm.$^{-1}$[c]													
N-(4,5-methylenedioxy-2-nitrobenzoyl)-*p*-methylaminophenol	N						m	a	m	1258		a	1035	930	m
	H					2817									
Methyl α-methyl-3,4-methylenedioxycinnamate*	C												1044	941 923	m
α-Methyl-3,4-methylenedioxycinnamyl acetate	C												1042	930	m
2,3,6,7-Bis(methylenedioxy)-9,10-dihydroanthracene	H					2786									
	N						m	a	m	1256 1235		a	1036	939	m
	K	2994	a	2907		2770	1479	1416	1370	1239		1120	1038	919	716
5-Ethyl-1-hydroxy-8,9-methylenedioxy-6-phenanthridone	N						m	a	1361	1266		1130	1042	941	m
5-Ethyl-1-keto-8,9-methylenedioxy-1,2,3,4-tetrahydro-6-phenanthridone	N						m	a	1350	1242		1129	1028	930	m
1-Keto-8,9-methylenedioxy-1,2,3,4-tetrahydrodibenzo[*b,d*]-6-pyrone	N						m	1408 1397	m	1259 1242		1134	1026	941	m
1-(3′,4′-methylenedioxybenzoyl)-indole	T						1486	a	1376 1351	1253		1122	1042	935	m
1-(3′,4′-methylenedioxybenzoyl)-2,3-dihydroindole	H					2809									
	C						1484	a	1361	1248		1121	1040	936	m
1-(3′,4′-methylenedioxy-6′-nitrobenzoyl)-2,3-dihydroindole	C						1484	1401	1361	1263		1121	1036	935	m
1-(2′-amino-4′,5′-methylenedioxybenzoyl)-2,3-dihydroindole	H					2778									
1-(2′-amino-4′,5′-methylenedioxybenzoyl)-2,3-dihydroindole	C						1477	1399	1370	1258		1117	1040	936	m
4,5-Dihydro-9,10-methylenedioxy-7-oxo-7*H*-dibenzo[*f,hi*]pyrrocoline	C						1490 1468	1389	1355	1263 1238		1136	1038	938	m
4,5-Dihydro-9,10-methylenedioxy-7-oxo-7*H*-dibenzo [*f,hi*] pyrrocoline	N						m	1393	1351	1258 1242		1124	1036	937	m
4,5-Dihydro-9,10-methylenedioxy-dibenzo[*f,hi*]pyrrocolinium chloride	N						m	1401	1364	1259		1126	1029	923	m
5-Hydroxy-3,7-dimethoxy-3′,4′-methylenedioxyflavone*	K	2994	a	2924	2857	2801	1439	a	1364	1258 1238	1175	1110	1034	926	714
5,7-Dihydroxy-3-methoxy-3′,4′-methylenedioxyflavone*	K	a	2976	2924	2857	2786	1447	1393	1362	1241	1172	1125	1041	935	719
Ambelline*	N						m	1408	1353	1230		1133	1041	935	m
Berberine hydrochloride*	K	3003	2950	2924	2848	2793	1477	1420 1387	1364	1272 1233	1178	a	1036	933	712
Caranine	C						1479	1427	1351	1250		1122	1031	923	m
Acetyl caranine	N						m	1418	1351	1235		1129	1030	934	m
	C						1486	1427	1370	m		1129	1040	938	m
Coccinine*	N						m	a	1357	1264 1277		1135	1026	919	m
Crinamine*	N						m	1404	m	1247		a	1035	928	m
	C						1488	1401	1370	m		a	1038	940	m
Crinamine acetate*	N						m	1401	m	1242		1119	1033	930	m
	C						1481	1390	1374	1241		a	1035	939	m
Crinamine perchlorate*	N						m	a	m	1263 1239		1129	1029	928	m
Dihydrocrinamine*	N						m	a	m	1266 1236		1133 1117	1032	929	m
	C						1481	a	1370	m		a	1036	935	m
Crinine	N						m	a	1359	1259 1244		a	1028	928	m
	C						1493	1404	1368	1256 1236		1116	1042	938	m
Acetyl crinine	N						m	1401w	m	1245		a	1036	936	m
Dihydrocrinine	N						m	a	m	1235		1131	1042	941	m
	C						1481	a	1362	m		1133	1041	938	m
Croweacin aldehyde*	T	3012	2950	2899	2857	2778									
	C						1475	1391	a	1238		1131	1042	943 927	m
Falcatine*	N						m	a	1359	1259 1244		1125	1047	926	m
	C						1471	1420	1357	1263		1124	1047	935	m
Dihydrofalcatine*	T	3030	2959	2907	2849	2786									
Falcatine acetate*	N						m	a	1357	1266 1250		1129	1046	930	m
Falcatine hydrochloride*	N						m	1393	1357	1258 1245		1121	1026	930	m
Galbacin	K	3012	2950	2924		2778	1439	a	1374	1253		1129	1041	940	717
Galcatin*	L	3003	2959	2924 2890	2833	2786	1481	1418	1372	1248 1232	1195	1125	1030	935	719

[a] Compounds marked * contain methylenedioxy and methoxy groups.

[b] L, liquid film; K, potassium bromide; C, chloroform; T, carbon tetrachloride; S, carbon disulfide; N, Nujol; H, hexachlorobutadiene.

[c] b, broad; w, weak; s, strong; a, absent; m, masked.

(*Continued on page 907*)

Table I. Methylenedioxy Compounds (*Continued from page 906*)

Compound[a]	State[b]	Band Frequency, Cm.$^{-1}$[c]													
Hydrastine*	K	3021w	2967 2941	2899	2851 2841	2809	1477	1420	1357	1253	a	1117	1034	935	715
Hydrastinine	T					2809									
	N						m	1416w	m	1235		1131 1119	1031	935	m
	C						1481	a	m	1238		1117	1037	935	m
Hydrohydrastinine	T					2793									
	N						m	a	m	1259 1238		1138 1121	1040	930	m
	C						1477	a	1379 1368	1258 1235		1136	1035	942	m
Hydrohydrastinine hydrochloride	N						m	a	1361	1244		1129	1031	937	m
Norhydrohydrastinine	N						m	a	1361	1244		a	1031	922	m
	C						1481	a	1359	1263		1124	1037	930	m
Oxyhydrastinine	N						m	1418w	m	1258 1242		1117	1037	923	m
Oxyhydrastinine	C						1471	1414w	1368	m		1117	1031	934	m
Lycorine	N						m	1403	1357	1261 1242		1131	1041	939	m
Lycorine α-methiodide	N						m	a	1351	1263 1242		1129	1031	926	m
Lycorine β-methiodide	N						m	a	a	1258		1117	1031	930	m
Lycorine hydrochloride	N						m	a	m	1258 1242		1131	1031	929	m
Lycorine perchlorate	N						m	a	a	1250		m	1031	927	m
Diacetyllycorine	T						1484	a	1355	1263		1134	1032	943	m
Dihydrolycorine	N						m	a	1361	1256 1239		1136w	1040 1031	925	m
Dihydrolycorine diacetate	T					2793									
Manthine*	C						1473	a	1362	m		1129 1119	1031	935	m
Manthidine*	N						m	a	m	1227		1136 1124	1034	935	m
	C						1479	a	1361	m		a	1036	935	m
Montanine*	N						m	a	m	1227		1133	1032	935	m
	C						1488	a	1374	m		1136	1040	939	m
Narceine hydrochloride*	K	3003	2950		2857	2770	1456	1418 1397	1376	1252	1192	a	1047	922	719
Narcotine*	K	2994	2950	2890	2849	2801	1477	1427	1362	1276 1264		1120	1036	935	721
Natalensine*	N						m	1399w	m	1227		1121	1025	922	m
	C						1479	1399	1362	m		1117	1032	935	m
Natalensine methiodide*	N						m	1397w	m	1242		1121	1031	922	m
Natalensine *m*-nitrobenzoate*	N						m	1393w	m	1250		1129	1033	935	m
Dihydronatalensine*	N						m	a	m	1232		1122	1033	930	m
	C						1477	a	1361	m		1124	1035	937	m
Piperine	C						1486	a	1361	1248		1135	1038	930	m
	K	3012	a	2933		2801	1443	1406	1366	1252		1136	1031	928	719
Podophyllotoxin*	K	3003	2950	2933 2899	2841	2778	1481	1418	1374	1236	1185	1126	1042	935	720
Savinin	C									1250			1042	930	
(−)-Hinokinin	C												1036	930	
(+)-Isohinokinin	C												1042	935	
Tazettine*	H	3049	2985	2950 2883	2841	2809									
	N						m	a	m	1250		1124	1035	937	m
	C						1477	a	1377w	1239		a	1036	935	m
Methylal*	T	3012	2959	2915	2849	2755				a					
	C												1036	922	
	L						1471	a	a	a		1133	1064	922	a
Ethylal	T	2985	2941	2890	2817w 2770w 2747w										
Propylal	T	2967	2941	2882	2817w 2778w										

[a] Compounds marked * contain methylenedioxy and methoxy groups.

[b] L, liquid film; K, potassium bromide; C, chloroform; T, carbon tetrachloride; S, carbon disulfide; N, Nujol; H, hexachlorobutadiene.

[c] w, weak; s, strong; a, absent; m, masked.

these may give rise to separate bands in the same region (5-hydroxy-3,7-dimethoxy-3′,4′-methylenedioxyflavone, berberine hydrochloride, galcatin, narcotine), but in most cases only a single peak appears. Epoxy compounds, acids, and esters also possess an absorption band at approximately 1250 cm.$^{-1}$ For these reasons, the very strong band in this region cannot be taken as analytically diagnostic for the methylenedioxy group. Aliphatic ethers exhibit their C—O stretching vibration at longer wave lengths, 1150 to 1060 cm.$^{-1}$ (*2*); a suggested reassignment of this band is discussed below. In support of the views above, the 1250-cm.$^{-1}$ band is absent in methylal and ethylal and weak and broad in *n*-propylal which contain only aliphatic C—O linkages. Occasionally a very weak overtone band occurs at about 2500 cm.$^{-1}$

In the spectrum of methylenedioxy-

Table II. Methoxy Compounds

Compound	State[a]	Band Frequency, Cm.$^{-1}$[b]									
Anisole	T	3003	2959	2915	2841						
	L	3003	2950	2907	2841	1458	1335	1247	1176	1079	1042
Guaiacol	L	3003	2959	2933	2841	1456	1361	1261	1175	1112	1022
Veratrole	T	3003	2959	2915	2841						
	L	3003	2950	2915	2833	1458	1332	1253	1176	1125	1028
1,2,3-Trimethoxybenzene	T	2994	2959	2907	2833						
	K					1471	a	1256	1176	1112	1031
Vanillin	T	3012	2967	2924	2849						
	K					1464	a	1271	a	1127	1032
Veratraldehyde	T	3021	2976 2950	2924	2849						
	T	3003	2959	2915	2833						
	N					m	m	1242	a	1138	1019
Veratric acid	K	3003	2967	2924	2841	1460	1348	1264	1183	1135	1024
2,3,6,7-tetramethoxy-9,10-dihydro-anthracene	K	2994	2950	2915	2849	1458	1342	1261	1192	1148 1088	1032
Galbulin	K	2994	2959	2915	2841	1453	1353	1259	1192	1143	1020
Galgravin	K	3003	2959	2915	2841	1456	1328	1260	1183	1148	1026
Isoeugenol	T	3012	2967 2950	2915 2890	2849						
Mescaline	C					1456	1333	a	1176	1125	1000
p-Dimethoxybenzene	T	3003	2959	2915	2841						
3,4-Dimethoxybenzyl alcohol	T	3012	2967 2950	2924 2882	2849						
2-Bromo-4,5-dimethoxybenzyl alcohol	T	3012	2967 2950	2924	2849						
2-Bromo-4,5-dimethoxybenzyl bromide	T	3012	2967 2950	2924	2857						
p-Methoxybiphenyl	T	3012	2959 2950	2915	2841						
p-Methoxybenzonitrile	T	3012	2976 2941	2924	2849						
3-(2′,3′-dimethoxyphenyl)-propanol	T	3012	2959 2950	2924 2890	2849						
Methyl *p*-methoxybenzoate	T	3012	2959	2915	2849						
1,2-Dimethoxyethane	T	3003	2941	2899	2833						
Dimethyl acetal	T	3003	2950	2915	2849						
Methyl acetate	T	3012	2967	2915	2857						
Methyl benzoate	T	3012	2967	2915	2857						
Methyl *m*-bromobenzoate	T	3012	2959	2915	2849						
Methyl carbonate	T	3012	2967	2915	2857						
Methyl oxalate	T	3012	2959	2915	2857						
Ethyl-2-methoxyethyl carbonate	T		2959w	2933 2899	2833						
2-Methoxybutyric acid	T		2941	2915w	2841						
2-Methoxyethanol	T	3003	2959	2899	2841						
Methoxyacetic acid	T		2941	2915	2841						
2-Methoxyethyl vinyl ether	T	3003	2941	2899	2841						

[a] See [b], Table I.
[b] See [c], Table I.

benzene a strong band appears at 1130 cm.$^{-1}$ and in many other methylenedioxy compounds within the range from 1136 to 1115 cm.$^{-1}$ This is within the region (1150 to 1060 cm.$^{-1}$) assigned by Lecomte (*8*) and Tschamler and Leutner (*11*) to the O—C (aliphatic) stretching vibration of aryl ethers. A band was observed in the same region in methoxy and ethoxy compounds (Tables II and III). The band is of varying intensity from weak to strong, but is absent in about one fourth of the compounds. Although the band in this region has been assigned to an O—C (aliphatic) stretching vibration, it is more likely that the very strong band at about 1040 cm.$^{-1}$ should be assigned to this vibrational mode. The present band may be due to some other vibration of the aromatic ether linkage.

The 1100- to 700-Cm.$^{-1}$ Region. A very strong band appears in the spectrum of methylenedioxybenzene at 1043 cm.$^{-1}$, and a readily identified band of similar intensity appears in the range from 1047 to 1025 cm.$^{-1}$ in all other methylenedioxy compounds. A band in the same region also appears in the spectra of methylal, ethylal, *n*-propylal, all aromatic methoxy compounds (Table II) except mescaline and its sulfate, and all aromatic ethoxy compounds (Table III). Where both methylenedioxy and methoxy groups occur in the same molecule (Table I, marked by asterisk), only a single peak appears in this region. That the absence of the band in mescaline is not due to the presence of three vicinal methoxy groups is shown by the fact that the band does appear in the spectra of pyrogallol trimethyl and triethyl ethers. This strong band common to methylenedioxy, methoxy, and ethoxy groups appears to be due to the O—C (aliphatic) stretching vibrations of aryl alkyl ethers. As the band at about 1136 to 1115 cm.$^{-1}$ varies from strong to weak and is absent in about one fourth of the compounds, while the band at 1040 cm.$^{-1}$ is constant and of strong intensity throughout, the O—C (aliphatic) stretching vibration should be assigned to the latter and not to the former band. A weak overtone of this band usually appears at about 2080 cm.$^{-1}$

An intense band at 937 cm.$^{-1}$ appears in the spectrum of methylenedioxybenzene, and a band of similar intensity occurs in all other methylenedioxy compounds within the range from 938 to 919 cm.$^{-1}$ In the majority of the spectra this is distinct from neighboring bands and may be regarded as the most characteristic band of the methylenedioxy group. With a few exceptions aromatic methoxy and ethoxy compounds do not exhibit absorption bands in this region, and when they do, they are generally of lower intensity. It should be noted that a strong band at

Table III. Ethoxy Compounds

Compound	State[a]	Band Frequency, Cm.$^{-1}$ [b]								
Phenetole	T	2994	2941 2915	2890						
	L	2976	2933	2882	1473	1389	1242	1156	1117	1048
3,5-Diethoxy-4-methoxyphenol	K	2976	2933	2899	1462	1387	1258	1156	1122	1024
1,2,3-Triethoxybenzene	L	2976	2924	2890	1464	1387	1248	1156	1120	1038
o-Diethoxybenzene	T	2994	2941 2915	2899						
Diethylene glycol diethyl ether	T	2985	2950	2874						
Hydroquinone diethyl ether	T	2994	2941 2915	2882						
Ethyl acetate	T	3003	2950 2915	2890						
Ethyl benzoate	T	2994	2950 2915	2882						
Ethyl oxalate	T	2985	2941 2915	2890						

[a] See [b], Table I.
[b] See [c], Table I.

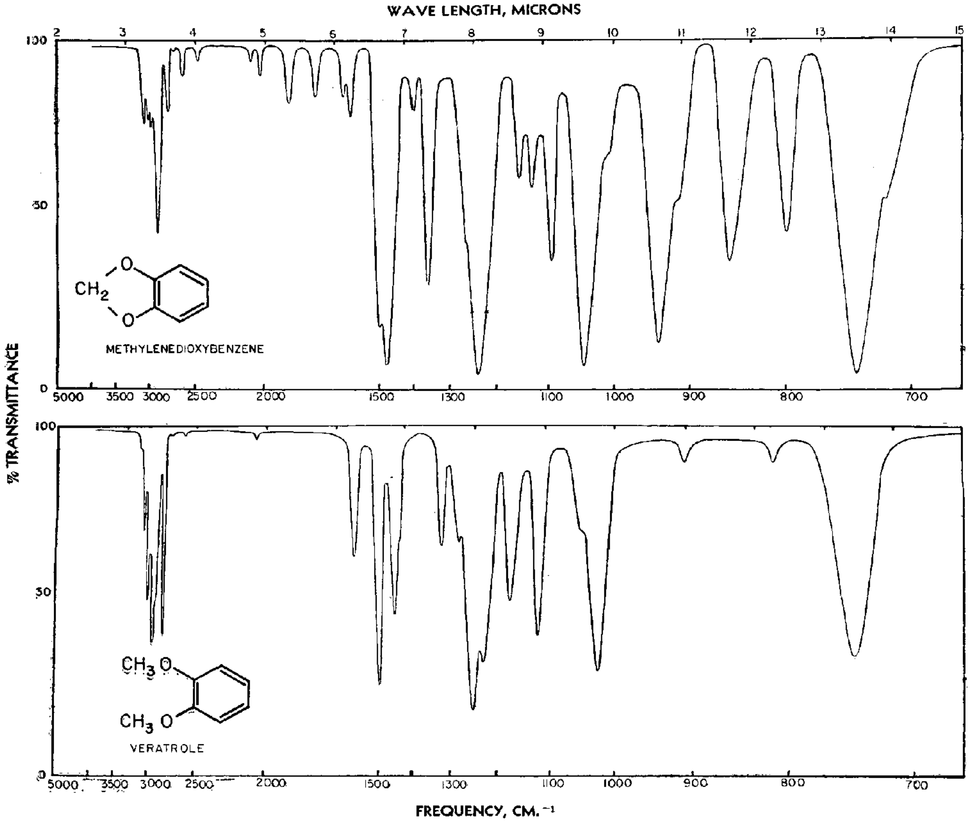

Figure 1. Infrared absorption spectrum of methylenedioxybenzene and veratrole

Samples were liquid films of capillary thickness

922 cm.$^{-1}$ also appears in the spectrum of methylal but is weak in propylal and absent in ethylal. A weak overtone of this band usually appears at about 1850 cm.$^{-1}$

Finally, a distinct shoulder appears at 718 cm.$^{-1}$ on the side of the very intense 740-cm.$^{-1}$ band in the spectrum of methylenedioxybenzene. This latter band probably is due to the aryl C—H bending vibrations of four adjacent hydrogens (*1*). A weak but distinct band occurs in the spectra (potassium bromide disks) of all other methylenedioxy compounds within the range from 725 to 712 cm.$^{-1}$

In conclusion, for the identification of the methylenedioxy group by infrared spectroscopy, 12 bands may be detected at about 3010, 2950, 2910, 2780, 1480, 1400, 1360, 1250, 1130, 1040, 926, and

719 cm.$^{-1}$ Those at about 2950, 1400, 1360, and 1130 cm.$^{-1}$ may be absent or weak. All but the bands at 2780, 926, and 719 cm.$^{-1}$ are produced by either methylene or methyl (including methoxy) groups; therefore, these bands, particularly that at 926 cm.$^{-1}$, are diagnostic for the methylenedioxy group.

METHOXY COMPOUNDS

From a comparison of the spectra of veratrole (Figure 1) and a number of other methoxy compounds (Table II), it may be concluded that 10 major bands are associated with methoxy groups attached to the aromatic nucleus—viz., a group of four bands in the 3000-cm.$^{-1}$ region at about 3003, 2950, 2915, and 2850 cm.$^{-1}$, and six strong bands at about 1460, 1342, 1250, 1179, 1124, and 1028 cm.$^{-1}$

The 3300- to 2500-Cm.$^{-1}$ Region. A normal methyl group exhibits two strong bands at 2960 and 2874 cm.$^{-1}$ corresponding to asymmetrical and symmetrical C—H stretching vibrations (*4, 5*). In methoxy compounds two distinct bands occur at about 2950 and 2850 cm.$^{-1}$, which may be assigned respectively to the same types of vibrations.

The 2850-cm.$^{-1}$ band invariably is present in the spectra of methoxy compounds and usually is well separated from the other bands. It lies beyond the range of those derived from normal methyl groups and may be detected in their presence. It also is distinct from the characteristic 2778-cm.$^{-1}$ band of methylenedioxy groups and may be detected when both methoxy and methylenedioxy groups are present. Ethoxy compounds contain no bands in this region. For these reasons the 2850-cm.$^{-1}$ band may be taken as diagnostic for the methoxy group. A weak infrared band near 2820 cm.$^{-1}$, which appears to be associated with the presence of an aliphatic methoxyl group, has been reported in the spectra of a number of alkaloids (*7*).

The invariant band at 2950 cm.$^{-1}$ occurs in the same position as that of normal methyl groups and is of little value alone. In methoxy compounds, however, it usually is flanked by two further invariant bands at 3003 ± 9 cm.$^{-1}$ and 2915 ± 9 cm.$^{-1}$, and the triplet of bands may be analytically important.

The 1460-Cm.$^{-1}$ Band. In almost all methoxy compounds a strong band occurs at about 1460 cm.$^{-1}$; it may be assigned to the asymmetrical C—H bending vibration of the methyl group. As this is the position for the same vibration of C—Me groups, it is of little analytical value.

The 1340-Cm.$^{-1}$ Band. A strong band in this region occurs in nearly all methoxy compounds and may be assigned to the symmetrical C—H bending of the methyl group. Again it occurs in a similar position to that of a C—Me group and is of little value alone.

The 1250-Cm.$^{-1}$ Band. A strong band at about 1250 cm.$^{-1}$ occurs in all aromatic methoxy compounds and has already been assigned (*3*) to the aryl C—O stretching vibration. It also occurs in methylenedioxy compounds, vinyl ethers, phenols, acids, and esters and thus is of limited analytical value.

The 1180-Cm.$^{-1}$ Band. In the spectra of almost all methoxy compounds a band, usually strong, has been observed within a normal range of 1192 to 1175 cm.$^{-1}$

The 1125-Cm.$^{-1}$ Band. In all the spectra of methoxy compounds examined, the presence of a band at about 1125 cm.$^{-1}$ has been confirmed. Although this band has been assigned by Lecomte (*8*), Tschamler and Leutner (*11*), and Bellamy (*3*) to the O—C (aliphatic) stretching vibration, the authors prefer to assign this mode of vibration to the 1028-cm.$^{-1}$ band (discussed below) and the present band to some other vibration of the aromatic ether linkage, because it may also occur in methylenedioxy and ethoxy compounds. Although a weak band occurs at 1115 cm.$^{-1}$ in the spectrum of anisole, it is more likely that the strong band at 1079 cm.$^{-1}$ should be reassigned to this aryl ether linkage and not, as suggested by Tschamler and Leutner (*11*), to the O—C (aliphatic) stretching vibration.

The 1028-Cm.$^{-1}$ Band. A strong common band within the range of 1042 to 1019 cm.$^{-1}$ occurs in the spectra of all the methoxy compounds (except mescaline) examined so far, and should be assigned to the O—C (aliphatic) stretching vibration for reasons discussed in the section on methylenedioxy compounds.

An attempt was made to calculate integrated intensity coefficients employing half-intensity band widths by the method of Ramsay (*10*). For the 2850-cm.$^{-1}$ band, simple monomethoxybenzenes had *A* values of about 240 while dimethoxybenzenes exhibited values between 500 and 600. Monomethyl esters had values of approximately 85. The presence of other C—O linkages in the molecule gave exceptionally high and variable *A* values. Several monomethylenedioxy compounds showed *A* values between 175 and 230 for the 2780-cm.$^{-1}$ band, while one dimethylenedioxy compound, galbacin, had an *A* value of 478.

ETHOXY COMPOUNDS

From a detailed examination of the spectra of phenetole, *o*-diethoxybenzene, and a restricted number of other ethoxy compounds (Table III), it may be concluded that ethoxy groups attached to the aromatic nucleus exhibit nine major bands associated with this group—viz., a triplet of bands at about 2940, and six strong bands at about 1470, 1390, 1250, 1156, 1120, and 1035 cm.$^{-1}$, respectively. Without exception all of these bands occur in compounds containing either methyl (including methoxy) or methylene groups, so they are of little analytical value for the detection of this group.

The asymmetrical and symmetical C—H stretching vibrations at about 2980 cm.$^{-1}$ and 2890 cm.$^{-1}$, with an intermediate band at 2930 cm.$^{-1}$, lie in the approximate range of those of normal —C—CH$_3$ and —C—CH$_2$—C— groups. The bands at about 1470 and 1390 cm.$^{-1}$ occur in the same positions as those of methyl and methylene groups assigned to asymmetrical and symmetrical C—H bending vibrations, respectively. The band at 1250 cm.$^{-1}$ is assigned to the aromatic C—O stretching vibration common to aromatic methylenedioxy and methoxy groups. The band at 1156 cm.$^{-1}$, occurring in all the aromatic ethoxy compounds examined and in most of the aromatic methoxy compounds, has already been discussed.

For reasons given above, the band at about 1120 cm.$^{-1}$ is due to a vibration of the aromatic ether group. Finally, the band at about 1035 cm.$^{-1}$ is assigned to the O—C (aliphatic) stretching vibrations common to methylenedioxy and methoxy groups.

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Alteration of Infrared Spectra of Steroids in Potassium Bromide

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▶ Some factors that influence the quality and reproducibility of the spectra of steroids in potassium bromide disks have been investigated. This communication compares the spectral differences that arise when potassium bromide disks of polyhydroxy steroids are prepared by simple hand grinding and by vigorous mechanical vibrations. The effect of brief heating of the disks after dispersion in a vibrator is noted.

WHERE solubility conditions permit, it is preferable to measure infrared spectra in solution, so that intermolecular interactions are reduced to a minimum and correlations between structure and spectra can be based on the individual molecule rather than the unit cell of the crystal. Nevertheless, solubility limitations often necessitate the use of solid phase spectra and increasing use has been made of the alkali halide pressed disk technique, following the initial work of Schiedt and Rheinwein (*8*, *9*) and Stimson and O'Donnell (*10*). The advantages and limitations of the use of physical states in determining infrared spectra have been documented (*5*, *7*).

When the potassium bromide disk technique is employed, it is important that the spectra so obtained be reproducible by other investigators using identical methods of sample preparation. Before the experiments were undertaken, it was expected that increased sample dispersion would lead to more reproducible intensity measurements (*4*). Subsequently Kirkland (*6*) obtained reproducible quantitative spectra by means of a mechanical agitator. In connection with preparation of a second volume of an atlas of steroid spectra (*2*) the authors have investigated the influence of the following factors on the reproducibility and quality of steroid spectra in potassium bromide disks.

Method of mixing steroid with salt.
Duration of mixing and state of subdivision of the compounds under investigation.
Dilution of the compound in potassium bromide.
Stability of the physical state of the substance dispersed in the disk of potassium bromide as a function of time and temperature.

FACTORS INVESTIGATED

Preparation of Mixture of Salt and Organic Compounds. The major variable is the dispersion of the compound in potassium bromide. In the work reported the organic compound was mixed in a mullite mortar with a pestle by hand operation (hand grinding), or by vibration in an agate ball mill at 60 cycles per second (vibrated). The effect of these methods of sample preparation are illustrated by the spectra of cortol (pregnane-3α,11β,17α,20α,21-pentol), Figure 1.

There are considerable differences in these spectra. The O—H stretching bands near 3400 cm.$^{-1}$ are sharper and less intense when the sample is hand ground than when it is vibrated. The bands in the region 1500 to 650 cm.$^{-1}$ (fingerprint) are very much sharper. After vibration, nearly all the fine structure in the disk prepared from the hand-ground mixture has been replaced by a broad envelope of absorption. These two spectra represent extreme conditions, but some deterioration was observed in the spectrum of most polyhydroxysteroids when the vibration was used for more than 2 or 3 minutes or after prolonged hand grinding (approximately 15 minutes).

The related compound cortolone (3α,17α,20α,21 - tetrahydroxy - pregnan-11-one) shows a similar spectral change (Figure 2,*A* and *B*) when the mixture is vibrated. The O—H stretching band at 3400 cm.$^{-1}$ exhibits the characteristic changes associated with the use of the vibrator or prolonged hand grinding—increase in intensity and loss of detail. A parallel series of changes was observed in the carbonyl band at 1690 cm.$^{-1}$ After 1-minute hand grinding a low intensity shoulder appeared at 1702 cm.$^{-1}$, and with continued hand grinding or vibration this shoulder increased in intensity at the expense of the main 1690-cm.$^{-1}$ band. Full vibration with the agate balls led to considerable loss in detail of the 1500 to 650-cm.$^{-1}$ region (Figure 2,*B*).

A third example is provided by the spectrum of pregnane,3α,20α-diol (Figure 3). In this case the spectrum was independent of the length of time of hand grinding within the limits of 1 and 20 minutes. The spectrum was identical with that obtained from a Nujol mull or when the compound without grinding was pressed between two potassium bromide disks. The spectrum in the range 1500 to 650 cm.$^{-1}$ exhibited a number of sharp bands and is described as the "crystalline" spectrum. However, when the mixture of pregnane-3α,20α-diol and potassium bromide was vibrated, the spectrum deteriorated as in the cases considered above. The degree of change was in large measure dependent on the time of vibration, and was discernible after about 3 minutes. After approximately 15 minutes the spectrum was essentially unaltered by further treatment. This prolonged vibration resulted in a smoothed-out spectrum with a diminution in intensity or disappearance of a number of prominent bands of the hand-ground disk, such as those at 1425, 1370, 1301, and 1086 cm.$^{-1}$ From 1075 to 800 cm.$^{-1}$ the spectral changes were negligible, the broad band at 700 cm.$^{-1}$ of the hand-ground disk was lost in an unresolved absorption.

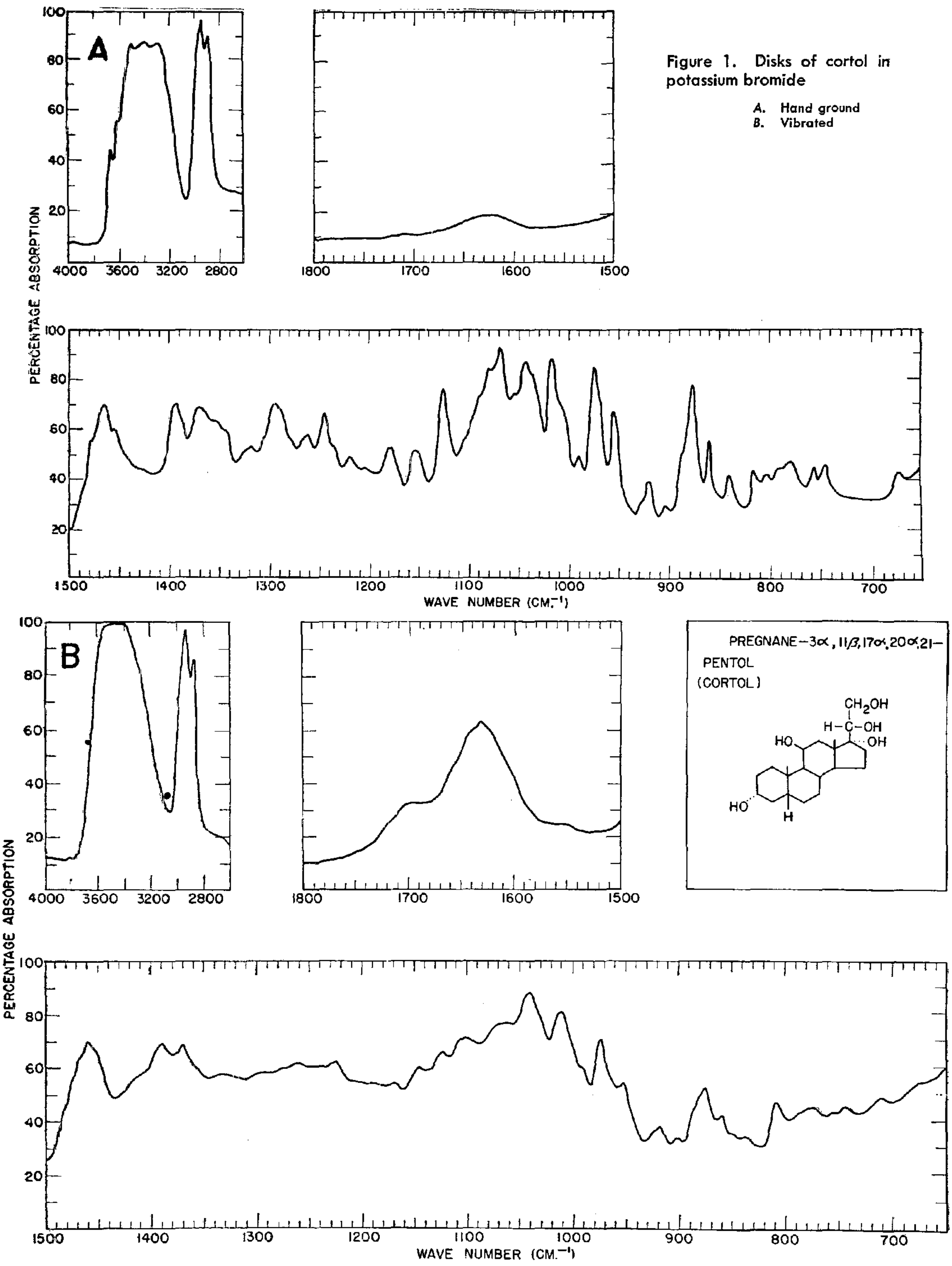
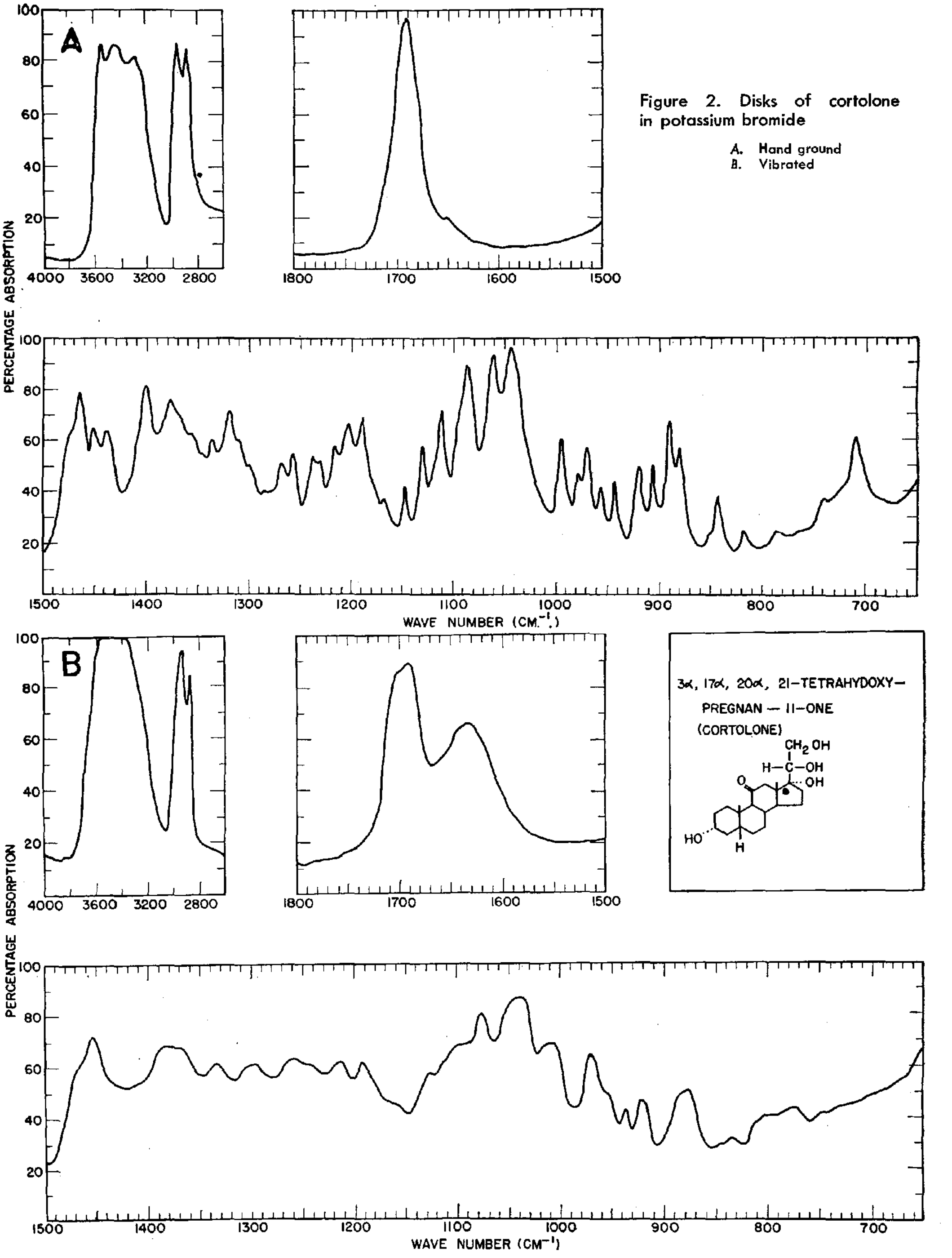


Figure 1. Disks of cortol in potassium bromide

A. Hand ground
B. Vibrated

Figure 2. Disks of cortolone in potassium bromide

A. Hand ground
B. Vibrated



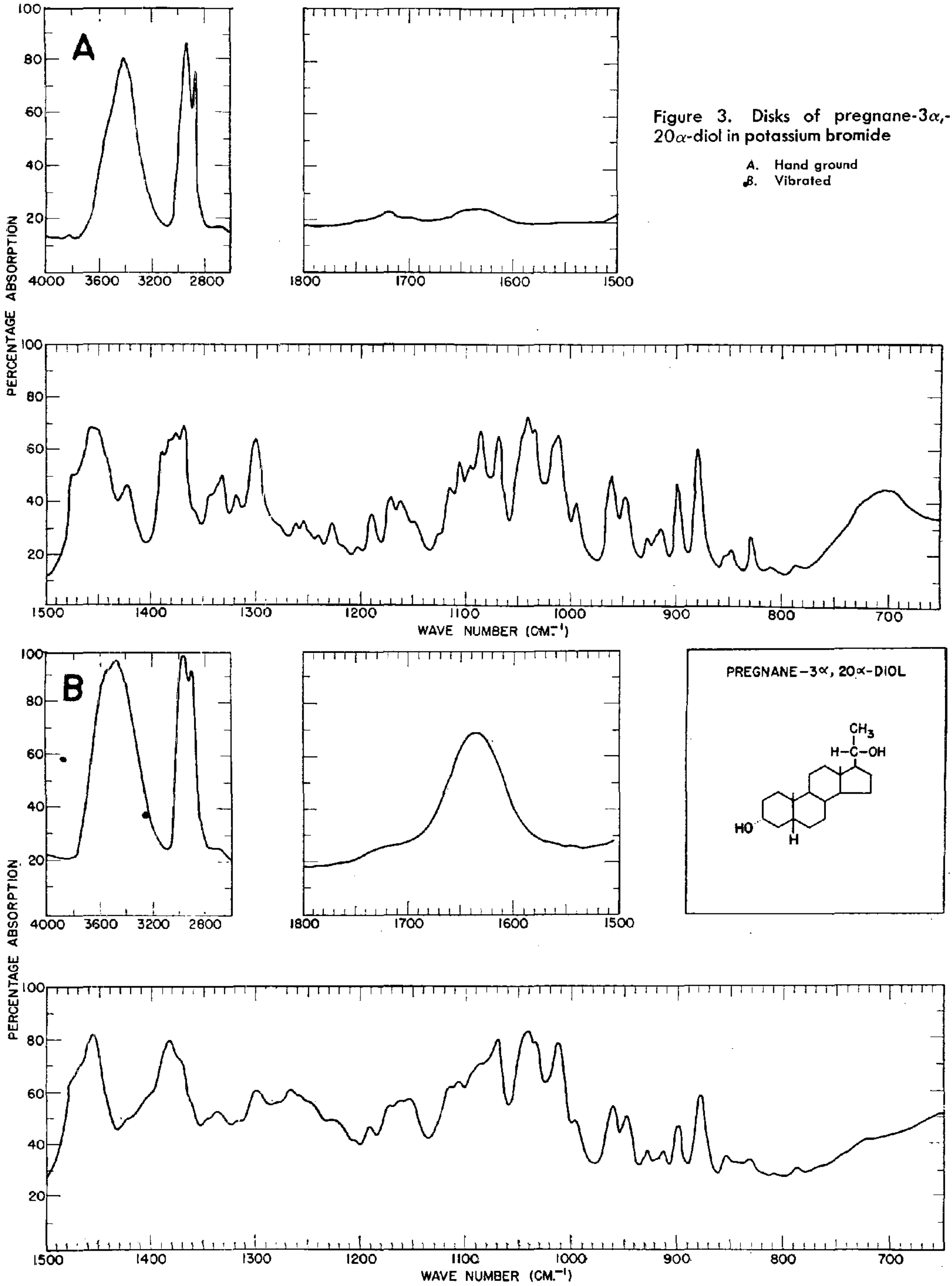


Figure 3. Disks of pregnane-3α,-20α-diol in potassium bromide

A. Hand ground
B. Vibrated

Dilution of Compound in Potassium Bromide. The ratio of compound to potassium bromide affects the nature of the spectrum, particularly for vibrated samples. When the spectrum of a hand-ground sample of pregnane-3α,20α-diol was compared with two concentrations (0.25 and 0.5%) vibrated under identical conditions, the spectrum of the more dilute sample showed greater deterioration than the more concentrated. More concentrated mixtures, such as 2%, exhibited no deterioration in the spectra after strong mechanical vibration.

Stability of Disks. Disks made by prolonged vibration (15 minutes) of the sample and salt were heated at 100° to 110° C. up to 5 minutes and the spectra were redetermined after the disk was powdered as in the hand grinding procedure and again pressed. A disk of pregnane-3α,20α-diol, which before heating exhibited a deteriorated spectrum, after heating showed a complete reversion to the original hand-ground spectrum. The change was pronounced after about 2 minutes' heating at 100° to 110° C. and reversion of the spectrum was complete after 5 minutes at this temperature. The most marked deviation from the hand-ground spectra after vibration as well as the most pronounced reversion of heating was found with such highly oxygenated compounds as pregnane-3α,17α,20α-triol, cortolone, cortol, cortisone, androstan-3β,17β-diol, and 17aα-methyl-3β,17aβ-dihydroxy-D-homoandrostan-17-one.

Disks prepared by prolonged vibration, which exhibit a deteriorated spectrum, become opaque when heated at 100° to 110° C. for 5 minutes. Such a disk, if powdered and repressed, will give a spectrum identical with that of the original hand-ground disk. The opacity is intimately bound with the spectral changes that take place and might be described in terms of microfractures inside the disk as a strain is released on heating. Thermal expansion of air or water vapor is unlikely; were this the explanation, the same phenomenon should be observed with all disks, whether hand ground or vibrated. This is not the case and in the author's experience the production of opacity has been limited to preparations that have exhibited a deteriorated spectrum after vibration. The spectra of some of the hand-ground disks have been redetermined after storage for as long as a year without measurable changes. A disk of pregnane-3α,20α-diol with a deteriorated spectrum, after storage at room temperature for 2 months, had reverted partially to the hand-ground or "crystalline" spectrum. Other compounds such as pregnane-3α,17α,20α-triol, 11β,17α,21-trihydroxy-Δ^4-pregnene-3,20-dione, and pregnane-3α,11β,17α,20α,21-pentol, have not as yet changed on storage. Furthermore, a deteriorated spectrum from a vibrated disk is unaltered by simple grinding and repressing without prior heat treatment.

Disks of potassium bromide, with and without the addition of steroid, made with the use of the vibrator invariably show pronounced bands at 3500 and 1635 cm.$^{-1}$ These bands are considerably more intense than those observed after hand grinding. Their behavior requires some explanation. A disk pressed from damp potassium bromide does not exhibit these bands to any great extent and they will not become prominent until the powder is sufficiently dry to flow freely in the vibrator. Potassium bromide dried at 100° C. under high vacuum for 6 hours shows these bands after vibration, but they are less intense than when a steroid is also present. They are probably due to water and become significant only when the water is absorbed on the potassium bromide in a particular manner through the medium of strong mechanical vibration. With the polyhydroxy ketonic steroids, heating the vibrated disks diminishes and in some cases completely removes these bands. At the same time the deteriorated spectrum is restored to one resembling the hand-ground spectrum. From a practical viewpoint then, these bands do not seriously interfere with the spectrum, because they can so readily be diminished or eliminated. The conditions under which these vibrated disks are heated cannot be described as a drying procedure and the tentative conclusion can be drawn that heat treatment results in desorption of the small amount of water present in potassium bromide.

EXPERIMENTAL

The spectra in potassium bromide were determined with a Perkin-Elmer Model 21 double-beam spectrometer with sodium chloride optics. The disks were pressed in a Perkin-Elmer evacuable die, giving disks of 13-mm. diameter. For each disk 400 mg. of potassium bromide containing about 2 mg. of steroid were used. The compounds were mixed with potassium bromide in a mullite mortar and pestle or in a vibration mill fitted with an agate capsule and two agate balls supplied by the Research and Industrial Instrument Co., 12 Marlborough Yard, London N. 19. This mill operates at 110 volts 60 cycles. The potassium bromide was Harshaw Chemical Co., infrared quality. Some of the disks were made without further drying of the potassium bromide and some after drying at 100° under high vacuum for 6 to 7 hours. No difference was observed in the spectra of potassium bromide in either sample.

DISCUSSION

The sensitivity of the spectrum to the conditions of potassium bromide disk preparation was observed by Farmer (*3*) for benzoic acid and by Barker and associates (*1*) for carbohydrates. These show a superficial resemblance to the effects noted for polyhydroxysteroids, but differ in several important details. According to Farmer, pressed potassium bromide disks of benzoic acid exhibit "deteriorated" spectra after vibration, but, contrary to observations on steroids, the effect is enhanced and not reversed by subsequent heat treatment. Farmer heated the powder before pressing, the author preferred to heat disks after pressing, but the latter has demonstrated that heating potassium bromide-steroid powders prior to pressing brings about some reversion to a crystalline type of spectrum. Heating the disk is more effective, possibly because of better heat conduction.

Barker and associates noted irreversible changes in the spectra of potassium bromide disks prepared from certain carbohydrates, and in the specific case of β-D-glucose, transformation to α-D-glucose monohydrate was demonstrated. The reversible phenomenon observed with hydroxysteroids cannot be explained simply on the basis of hydrate formation; thus in the case of pregnane-3α,20α-diol the "deterioration" is in no way enhanced by addition of aqueous methanol to the diol prior to grinding and pressing. A full explanation of this phenomenon must await a detailed study of the kinetics of the grinding and pressing processes. It may be assumed, however, that the organic material will normally be much softer than the potassium bromide and vigorous grinding will lead to a preferential breakup of the organic particles. Thin crystalline layers of organic matter sandwiched between colliding potassium bromide crystals will be subject to frictional forces which may cause local temperatures to rise above the melting point of the organic compound. Cooling will occur very rapidly after the collision and there may be insufficient time to permit the full reestablishment of the crystalline lattice. Thus the "deteriorated" spectrum might be associated with an amorphous or partly disorganized crystalline lattice. Although the temperature of 105° C. attained during the heat treatment is normally well below the melting point of the organic compound, it may provide the necessary kinetic energy for relaxation of the disorganized lattice structure and re-establishment of the crystalline spectrum.

The spectra of hydroxysteroids in potassium bromide disks at elevated temperatures are being investigated in the neighborhood of the melting point of the steroid, in the hope of providing additional information on the nature of the phenomenon.

SUMMARIZING REMARKS

Because deteriorated spectra are seldom observed with hand-ground preparations, it might seem preferable to forego the practical convenience of the mechanical vibrator and resort to hand grinding in the routine preparation of potassium bromide disks. However, there is the problem of polymorphism to consider, and frequently, though not invariably, the vibrator technique helps to eliminate ambiguities arising from this cause. With this in mind, the authors adopted the following routine procedure for the preparation of potassium bromide disks of steroids.

The steroid (2 mg.) and potassium bromide (400 mg.) are weighed successively into the capsule of the vibrator and vibrated with an agate ball for 15 minutes. The material is then transferred to the die, which is evacuated and the powder is pressed at 7 tons per sq. inch for a minimum of 3 minutes, after which the pressure and vacuum are released and the pellet is removed. The pellet is next heated at 105° for a minimum of 5 minutes. If it remains clear, its spectrum is determined. If it becomes opaque during the heat treatment, the disk is reground by hand, using a mortar and pestle, the resultant powder is repressed and the spectrum of the new disk is accepted for characterization of the compound.

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Infrared Spectra of Organic Azides

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▶ The infrared spectra of a series of ten organic azides, the substituents of which covered the gamut of electropositive to electronegative, were studied to determine the range of frequencies where the strong asymmetric vibration of the azido group was likely to occur. The data show the N_3 asymmetric vibration to be in the region of 2114 to 2083 cm.$^{-1}$ and confirm the constancy of this frequency, practically independent of the environmental structure. It appears that this absorption can normally be expected within the range of 2170 to 2080 cm.$^{-1}$ This corresponds to approximately 0.2 micron in wave length. It is therefore still sufficiently characteristic to make it important for recognition of this group.

THE azido group, —N_3, can be identified by the strong $N\equiv N$ asymmetric stretching absorption which occurs with great consistency close to 2130 cm.$^{-1}$ The corresponding symmetric stretching is at considerably lower frequency and is not only much weaker, but also appears to be more variable in position. Accordingly, it appears to be of relatively little value for analytical use.

The spectrum of hydrazoic acid has been examined by Eyster (*9*), who assigned the band at 2141 cm.$^{-1}$ to the $N\equiv N$ asymmetric vibration and that at 1269 cm.$^{-1}$ to the corresponding symmetric mode. Methyl azide has been studied (*10*); the corresponding bands in this case are at 2141 and 1351 cm.$^{-1}$ Azides as a group have been systematically studied by Sheinker and Syrkin (*18*) who examined the Raman spectra of sodium azide and the infrared spectra of 12 azides. They found a strong band in all cases in the range 2167 to 2080 cm.$^{-1}$ and a second weaker one in the range 1343 to 1177 cm.$^{-1}$ In accordance with the earlier work, these were assigned to the asymmetric and symmetric vibrations, respectively. Confirmation of this was obtained by Boyer (*2*) and Lieber, Levering, and Patterson (*12*), the latter repeating earlier work on sodium azide (*17*) and examining five other organic azides not previously studied. They reported a relatively strong band in all cases in the range of 2151 to 2128 cm.$^{-1}$, with a second weaker and more variable band near 1282 cm.$^{-1}$ Accordingly, it seemed probable that Sheinker and Syrkin (*18*) had quoted a wider range for the asymmetrical vibration than is likely to be found in normal practice. In order to re-evaluate this latter point, the infrared spectra of a series of alkyl, alicyclic, and aromatic azides were studied.

COMPOUNDS USED IN STUDY

Table I lists the compounds used in this study, their physical properties, and the methods used. In a search of the literature on the preparation of organic azides, it was found that, in some cases, different values for the physical constants were given. The situation for benzyl azide is summarized in Table II. A plot of log p *vs.* $1/T$ showed that the value for the boiling point obtained for benzyl azide in this research agrees fairly well with those given by most other investigators,

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Table I. Organic Azides

RN_3, R =	B.P., ° C./ Mm. Hg	M.P., ° C.	n_D^{20}	Reference
n-Butyl	71/225	..	1.4192	(*4, 11*)
n-Decyl	67/0.65	..	1.4425	(*11*)
Benzyl	78–78.5/12	..	1.5373	(*14*)
Cyclopentyl	72/77	..	1.4616	(*3, 11*)
Phenyl	41–42/5	..	1.5598	(*13*)
p-Tolyl	55–56/4.5	..	1.5521	(*8*)
p-Bromophenyl	69/2.1	20	1.6127	(*8*)
p-Nitrophenyl	...	74	...	(*15*)
m-Chlorophenyl	49–50/1.2	..	1.5806	(*8*)
o-Chlorophenyl	45/0.85	..	1.5878	(*8*)

Table II. Boiling Points Reported for Benzyl Azide

B.P., ° C.	Mm. Hg	Reference
108	23	(*20*)
74	11	(*5*)
82.5	16.5	(*6*)
71–71.5	13	(*14*)
72	8	(*16*)
64	3	(*16*)
78–78.5	12	This research

whereas the value given by Moulin (*14*) does not. The refractive index agrees with that of Moulin (*14*), n_D^{19} 1.5380, and of Philip (*16*), n_D^{24} 1.5341, assuming a straight-line relationship between temperature and refractive index over that range. In the case of chlorophenyl azides, the comparison of physical properties obtained in this research with that reported (*19*) is summarized in Table III. In view of the situation summarized in Table III, the purities of *o*- and *m*-chlorophenyl azides obtained for this research were established by elemental analysis.

Table III. Properties of *o*- and *m*-Chlorophenyl Azides

	Spauschus and Scott		This Research	
ArN_3, Ar =	B.p., °C./Mm. Hg	n_D^{25}	B.p., ° C./Mm. Hg	n_D^{20}
o-Chlorophenyl	58–60/1.2	1.5855	45/0.085	1.5878
m-Chlorophenyl	49–51/0.7	1.5787	49–50/1.2	1.5806

Calcd. for $C_6H_4ClN_3$: C, 46.92; H, 2.62; Cl, 23.09; N, 27.39. Found: for *o*-chlorophenyl azide, C, 47.03; H, 2.61; Cl, 23.00; N, 27.43; for *m*-chlorophenyl azide, C, 46.97; H, 2.69; Cl, 23.01; N, 27.47.

Dimroth and Pfister (*7*) have reported 105° at 10 mm. and 20° as the boiling and melting points of *p*-bromophenyl azide, while Spauschus and Scott (*19*) have reported 50° to 60° at 0.9 mm., and 1.6106 for the boiling point and n_D^{25} for the same compound. As the boiling point of the *p*-bromophenyl azide prepared for this research was determined at a different pressure, its purity was established by elemental analysis. The data obtained are summarized below:

Calcd. for $C_6H_4BrN_3$: C, 36.40; H, 2.02; Br, 40.36. Found: C, 36.35; H, 2.27; Br, 40.51.

The properties of the other organic azides used in this research and summarized in Table I are in agreement with the values previously reported in the literature.

INFRARED SPECTROSCOPY

The infrared absorption spectra were obtained on a Perkin-Elmer spectrometer Model 21, which was calibrated with polystyrene as a standard. Repetition of the infrared spectrum of sodium azide gave bands at approximately the wave length previously reported (*12*). The infrared spectra of the series of organic azides are summarized in Table IV. Each measurement reported in Table IV was repeated at least twice.

Table IV. Infrared Spectra of Organic Azides

RN_3, R =	N_3 Asymmetric, $Cm.^{-1}$	N_3 Symmetric, $Cm.^{-1}$
n-Butyl	2083	1256
n-Decyl	2092	1256
Benzyl	2088	1256
Cyclopentyl	2083	1256
Phenyl	2114	1287
p-Tolyl	2092	1261
p-Bromophenyl	2110	1287
p-Nitrophenyl	2114	1285
m-Chlorophenyl	2096	1288
o-Chlorophenyl	2088	1297

DISCUSSION

Bellamy (*1*) in discussing the work of Sheinker and Syrkin (*18*) felt that these investigators quoted a wider range, 2167 to 2080 cm.$^{-1}$, for the asymmetric vibration than was likely to be found in normal practice, basing this assumption upon the work of Lieber, Levering, and Patterson (*12*). However, a careful study of Sheinker and Syrkin's work (*18*) in comparison with that of Lieber, Levering, and Patterson (*12*), will show that this assumption is not valid. Although Lieber, Levering, and Patterson (*12*) showed only a range of 31 wave numbers for the five azides studied, the environmental structures associated with the azido group were very nearly the same; the investigations of Sheinker and Syrkin (*18*), for 12 organic azides, covered a more representative range of electropositive and electronegative environmental groups, for which they obtained a difference of 87 wave numbers. Accordingly, the present study was an effort to obtain an additional answer to the question raised by Bellamy (*1*).

Table IV shows that for a good spread of electropositive and electronegative environmental groups the range in this research for the N_3 asymmetric band was only 31 wave numbers—namely, from 2114 to 2083 cm.$^{-1}$ This does not entirely vitiate the observations of Sheinker and Syrkin (*18*); however, it supports the assertion of Bellamy (*1*) and confirms the rather astonishing and interesting fact that the strong N_3 asymmetric band is fairly constant regardless of its environmental situation. The widest range thus far reported is that of Sheinker and Syrkin (*18*), but this still represents a difference of only approximately 0.2-micron wave length. This insensitivity of the N_3 asymmetric frequency is well documented by all investigators who have studied this problem, as well as the present research summarized in Table IV. On the other hand, the present study appears to be in disagreement regarding the variability of the N_3 symmetric band. Table IV shows a rather interesting constancy, the range being only 41 wave numbers in contrast to 166 wave numbers reported by Sheinker and Syrkin for approximately the same range of environmental changes. To the structural diagnostician this latter point is probably not too important, because reliance is placed upon the asymmetric band for the recognition of the azido group. Accordingly, if the range of 2170 to 2080 cm.$^{-1}$ be accepted for the N_3 asymmetric vibration likely to be found in normal practice, it is still sufficiently characteristic and intense to be important in recognition of this group.

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Versatile Gas-Liquid Partition Chromatography Apparatus

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▶ In building the chromatographic apparatus described, an attempt was made to remove as many as possible of the instrumental limitations of the technique and to devise equipment capable of incorporating future developments with a minimum of modification. The instrument comprises one recorder unit which is connected as required to one of several column-furnace units maintained in a stand-by condition. Provision was made for rapidly changing columns and column temperatures. To permit the extension of the range of the gas-liquid partition chromatography method to higher molecular weights, a hot wire thermal conductivity detector was constructed entirely from refractory materials. It is capable of reliable operation at temperatures upward of 300° C.

WHILE THE PRINCIPLE of gas-liquid partition chromatography was clearly enunciated by Martin and Synge (*4*) as early as 1941, the importance of their suggestion was not generally recognized at that time. Since 1952, however, when the first account of the use of the method appeared in James and Martin's classic paper (*3*) describing the isolation and microestimation of the volatile fatty acids, progress in applying it has been extremely rapid.

Gas-liquid partition chromatography is too new for any preferred form of equipment to have established itself. In consequence, the range of choice open to the designer of apparatus for carrying out the procedure is at present unusually wide. In these circumstances it is to be expected that the various forms taken by the equipment will strongly reflect the differing requirements each was designed to meet. This paper gives an account of the line of development that has been taken at Shell's Thornton Research Centre.

Work on gas-liquid partition chromatography started early in 1953, but within a few months the urgent need to build a special-purpose chromatograph for the nearby Shell chemical plant diverted much of the effort that would have been available for instrument development. During the construction of this apparatus, assistance to the analysts was virtually confined to providing them with a series of thermal conductivity detector cells and they were forced to work with makeshift equipment.

While this situation was embarrassing at the time, two important benefits followed from it. In the first place, the construction and testing of the chemical plant's apparatus familiarized the instrument development team with the technique and gave them a realistic appreciation of the problems likely to be encountered in designing future equipment. Secondly, and even more important, the hiatus gave the analysts time to accumulate useful working experience with gas-liquid partition chromatography and enabled them to provide a reasonably accurate forecast of the way they would use the custom-built apparatus they were later to be provided with.

Thornton Research Centre carries out applicational research for the Shell group outside the U.S.A. and Canada. Its problems concern the manifold

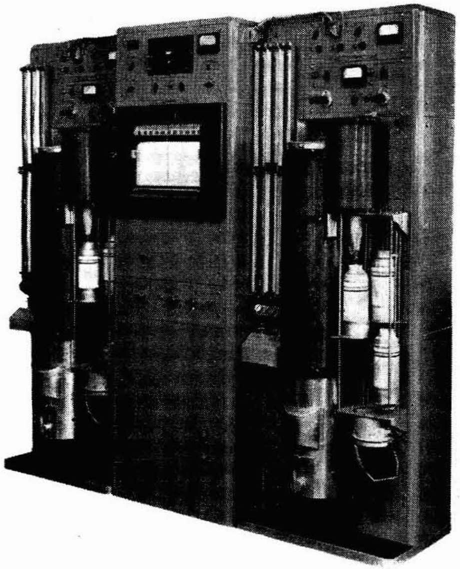


Figure 1. General assembly of gas-liquid partition chromatography apparatus

uses of oil products and are of a varied nature. Consequently, the analytical section handles a great variety of work and gas-liquid partition chromatography is used as one of a whole armory of analytical tools. It has found application in problems such as:

Solvent analysis, particularly the estimation of traces of aromatics in mixtures of saturated hydrocarbons (*5*).

Oil constitution studies in which gas-liquid partition chromatography is used to prepare cuts, obtained by fractional distillation, for detailed analysis by mass spectroscopy (*6*).

The analysis of reaction products.

The characterization of distillation cuts.

By the spring of 1954, when the chemical plant's chromatograph went into service, it was evident that the analysts required a gas-liquid partition chromatography apparatus which would provide conveniently for:

Analyzing a great variety of liquid samples which arrive in almost random order of volatility.

Investigating combinations of stationary liquids and column operating conditions for their ability to resolve given mixtures (*1*).

Preparing small quantities of substances, isolated by gas-liquid partition chromatography, for further analysis and identification.

There was thus a clear need for apparatus which would make feasible the application of this powerful new separating technique to the widest possible range of investigations. Hence, the design objectives were to remove the instrumental limitations of the method and to devise an apparatus capable of incorporating future developments with as little modification as possible.

APPARATUS

Separation of the functions of the various parts of the equipment appeared to be the only way in which a provision for change could be built into the design. The apparatus, therefore, takes the form of a number of units, the design of each of which can be drastically modified if need be, without requiring any significant alteration of the remainder. It was also realized that the degree of flexibility demanded of the apparatus was so great that it would not be possible to carry out all analyses in the same column-furnace combination. Frequent changes of stationary phase— i.e., columns—and column conditions (temperature, carrier gas flow rate, etc.) would be called for, and would have to be made without undue loss of working time.

These considerations underlie the conception of the apparatus, which comprises one recording unit which may be connected to either of two column-furnace units as required, as shown in Figure 1. In order to effect the change-over rapidly—i.e., by the trans-

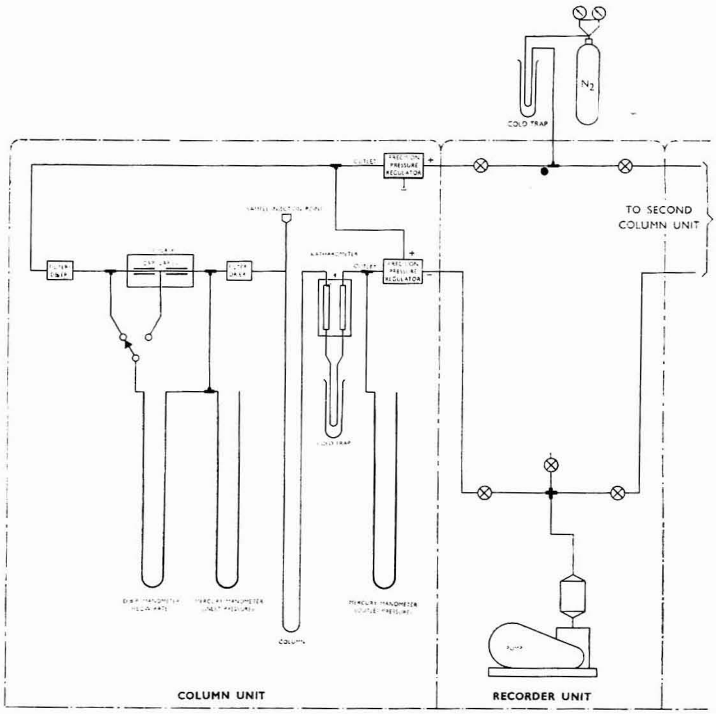


Figure 2. Gas flow system

for all electrical connections only—each column-furnace unit is provided with its own detector and gas flow system and thus comprises mainly the carrier gas flow system, comprising pressure regulators, manometers, and flowmeter; a single column within a furnace provided with automatic temperature control; and a detector with automatic temperature control and cold trap.

The recording unit embodies mainly these features: recorder; multipoint temperature indicator; input selector, range change, base line, and bridge current controls; stabilized bridge current supply; and vacuum pump and control valves.

Column-Furnace Units. The recorder unit calls for no particular comment, but the column-furnace units present some interesting design problems which justify a more detailed description. The carrier gas flow system, shown in Figure 2, provides for operating the katharometer (the preferred type of detector) at reduced pressure in order to enhance the sensitivity of the apparatus. Particular care has been taken to monitor the column-operating parameters with adequate accuracy. Inlet and outlet pressures are measured on mercury manometers with respect to atmosphere. An ice flask, which also houses the cold junctions of thermocouples used for temperature measurement, contains the capillaries of a dual range flowmeter, the pressure drop across which is displayed on a dibutyl phthalate manometer. The filter-driers adjacent to these capillaries guard them from contamination when the system is open to atmosphere, as when changing columns. The vacuum pump can handle the flow of carrier gas from several columns, which are normally kept continuously purged so that heavy ends from preceding analyses do not accumulate in them.

Obviously, the flexibility demanded of the apparatus has a strong influence on the design of the furnace, which is required to have unusual characteristics. Not only must it keep the whole of the column at the same predetermined temperature, but in order to deal promptly with samples of different boiling ranges, it must be capable of attaining that temperature rapidly. Moreover, the analysis of wide-cut materials in a single run would be made possible if the column temperature could be changed in a substantially stepwise manner during the course of an analysis. These considerations point to a furnace with a low heat capacity, a high rate of heat transfer, and low heat losses.

In an endeavor to meet these requirements, an unconventional furnace with forced air circulation was built within a glass vacuum jacket of the maximum dimensions it was possible to accommodate on the available glass-blowing lathe. The column was located within a vertical tube, $1^{5}/_{8}$ inches in diameter and 3 feet 3 inches long, down which air was drawn at about 50 feet per second by means of a high-speed radial fan (Figure 3). The air issuing from the fan flowed past a non-inductively wound heater coil concentric with it and well clear of the bottom of the vacuum jacket. The designed maximum temperature of the working space was 350° C.

This furnace has a water equivalent of rather less than 1 kg., and the heat transfer achieved by the rapid turbulent air flow is such that the thermal time constant at the center of a 6-mm. diameter glass column packed with powdered alumina is about 35 seconds.

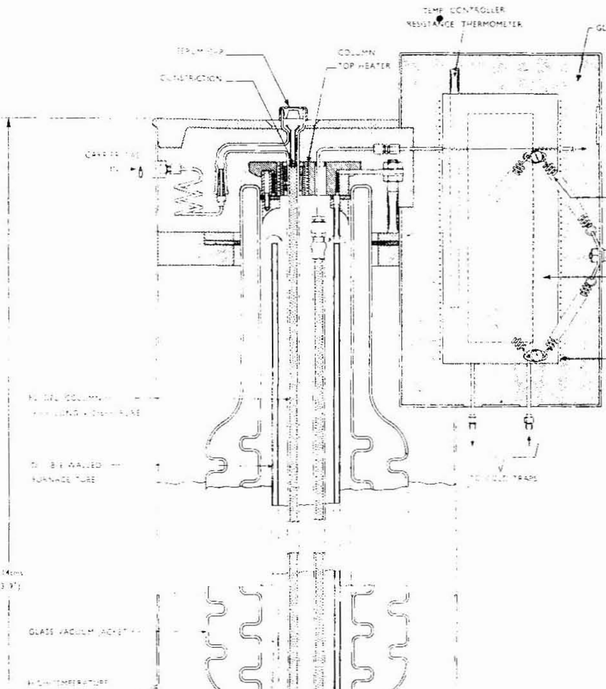


Figure 3. Furnace and column assembly

Starting from cold the furnace will reach 200° C. in 10 minutes with a power input of 1500 watts, while its steady loss at this temperature is 250 watts rising to 400 watts at 300° C. The uniformity of temperature within the working space is within ±1° at 300° C. and somewhat better at lower temperatures.

In view of its extremely rapid response to changes in heater power, it was not possible to control the temperature of this furnace with a commercial proportional temperature controller, as all such instruments on the United Kingdom market employ a variable duty ratio on/off system with a cycle time exceeding 30 seconds. Therefore, the experimental work was carried out using a modified Brown amplifier to bias the grid of a large thyratron, which was caused to conduct for a proportion of each cycle of mains voltage according to the error signal present during that cycle. Figure 4, which is a plot of the temperature at the center of the packed column as a function of time, shows the almost stepwise response achieved by this combination of furnace and controller. The temperature of each of the furnaces incorporated in the complete gas-liquid partition chromatography apparatus is regulated by a proportional temperature controller incorporating a platinum resistance thermometer and a thyratron output stage, while a bimetal thermostat protects the windings and vacuum jacket should the controller or the fan drive fail. A port has been provided through which hot air can be released from the furnace when it is required to cool a column rapidly.

The furnaces have been mounted well forward of the other items comprising the column-furnace units in order to facilitate changing columns and to provide some flexibility in design. While the furnaces in use now are no larger than that on which the development work was carried out, each is mounted within a cylindrical cover big enough to house a larger unit of similar design providing a working space about $4^1/_4$ inches in diameter and 3 feet 3 inches high. This feature of the apparatus will permit the future use of either very long coiled columns or a number of U-shaped columns in series.

Particular attention has been paid to simplifying the operations of changing and packing columns, which take the form of precision bore, borosilicate glass U-tubes 6 feet long and 6 mm. in diameter. The carrier gas enters by a cone joint at the (cool) end of a side arm and is then sucked through a restriction, passes over the heated packing on which the sample is vaporized, and enters the separating portion of the column. The sample is introduced through a natural rubber serum cap by means of a hypodermic syringe. The needle extends beyond the constriction, which both locates it and provides a high local gas velocity to prevent the sample vapors diffusing back and condensing on the cooler parts of the column entry. The column efflux leaves via a graded joint, a glass-to-metal seal, and a readily demountable metal-to-metal vacuumtight seal. Connections to both inlet and outlet stainless steel tubes (which have a bore of 1.25 mm.) are made by robustly supported seals of the latter type and the transfer line to the detector is heated to prevent condensation of the sample components.

Detector. The high resolving power of gas-liquid partition chromatography is accompanied by concentrations of components in the column efflux which change quickly and reach relatively high peak values. Instruments to detect these components must, therefore, respond rapidly and must be operated at temperatures high enough to prevent condensation. Moreover, there is always a need for maximum sensitivity and consequently for an extremely high degree of stability. The katharometer or differential thermal conductivity cell can be designed to possess these attributes, combined with the further advantages of simplicity and generality of application. It was selected as the detector in the present apparatus, whose form of construction will, of course, permit the use of alternative sensing means (such as beta-ray ionization) if required.

Extension of the gas-liquid partition chromatography method to high molecular weights necessarily involves running the detector at higher temperatures. However, existing designs of katharometer include in their construction materials which deteriorate with continued use at temperatures much above about 150° C. Any attempt to widen the scope of the method thus entails a reconsideration of katharometer design. This development, described elsewhere (*2*), has been undertaken and has resulted in the production of a katharometer constructed entirely from refractory materials. It has been extensively tested at 300° C. and there is nothing in its design that would preclude its working at even higher temperatures.

The choice of this temperature as the design target was the result of the interplay of a number of factors. Three conditions favored a high temperature; these were an increasing number of requests for analyses of high molecular weight materials; the need to produce a design which would not quickly be rendered obsolete by the rapid advances to be expected in a new technique; and the need to avoid condensation in the detector when investigating the properties of liquids used as stationary phases at elevated temperatures.

On the other hand. counseling caution, was the probability that the development of an appropriate form of construction would present a very intractable problem if the design temperature were set too high, and a suspicion that, at some unknown temperature, limitations of the thermal conductivity method itself might be encountered—perhaps as a result of chemical or physical changes taking place at the unusually hot surface of the wire. The availability of an oven convenient for testing the proposed elements of the design finally dictated the precise figure of 300° C.

Figure 5, *a* is an assembly drawing of the high-temperature katharometer. To achieve the maximum rapidity of response, each of its two thermal

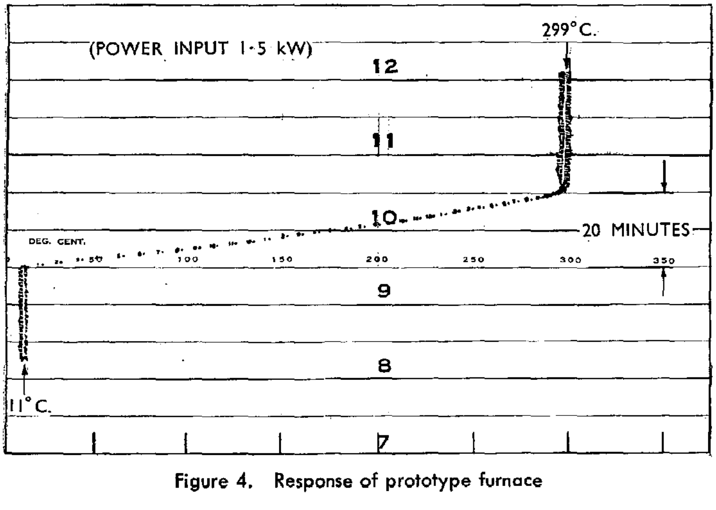
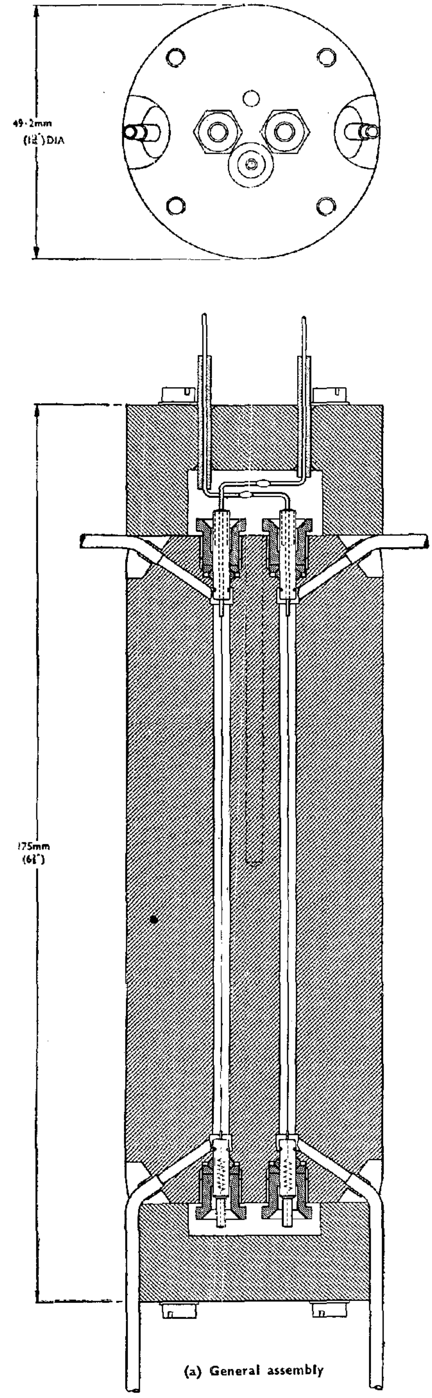
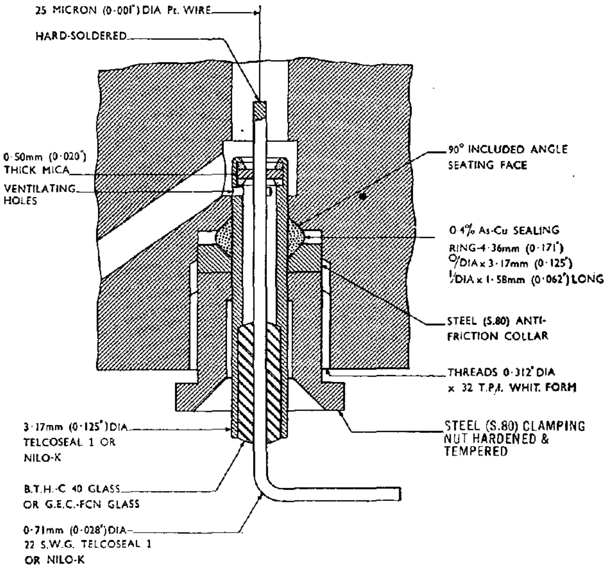


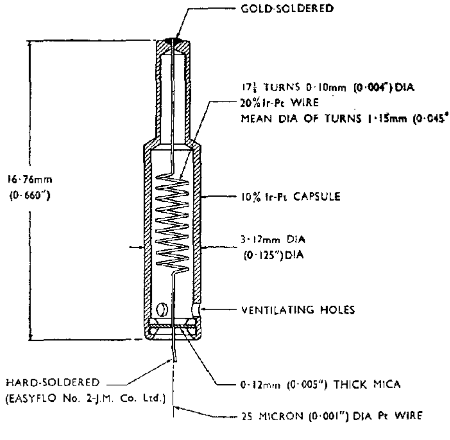
Figure 4. Response of prototype furnace



(a) General assembly



(b) Insulated wire anchorage



(c) Resilient wire anchorage

Figure 5. High-temperature katharometer

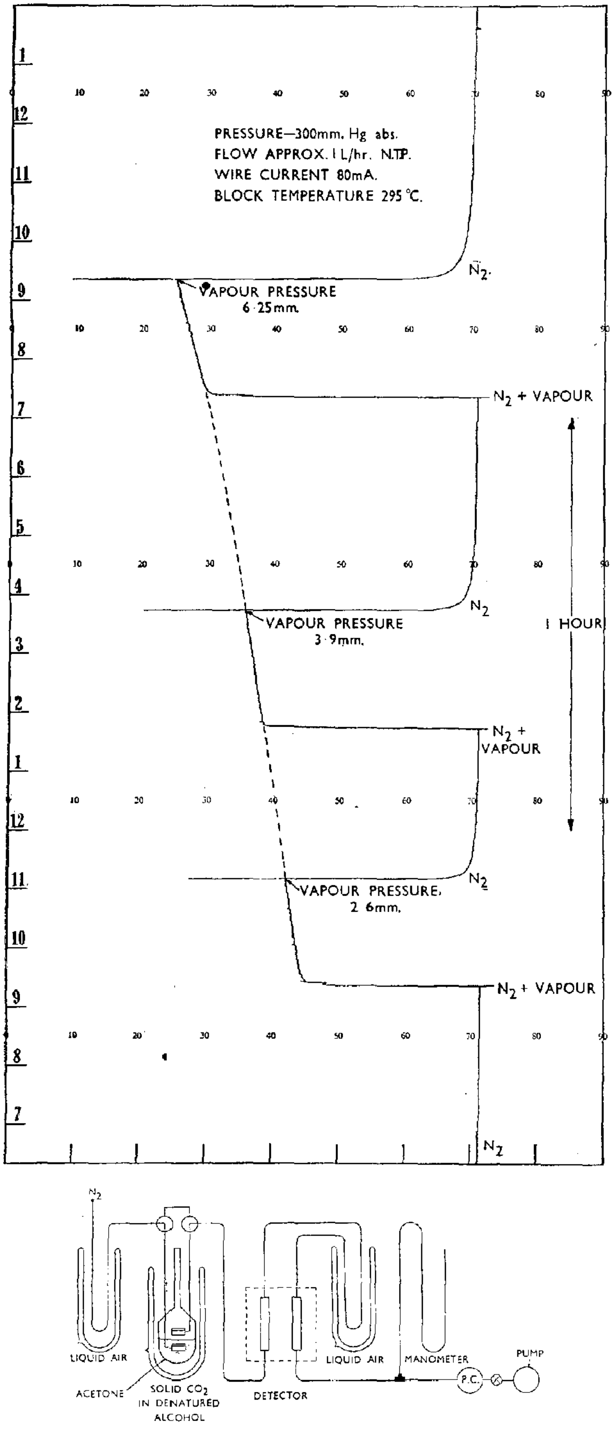


Figure 6. Stability and sensitivity of katharometer operating at 300° C.

conductivity cells has a straight hot wire suspended along the axis of a narrow bore through which the gas sample flows. Pure platinum wires 25 microns in diameter and 100 mm. long are used in 3-mm. diameter bores. These dimensions result in a sample residence time of only a fraction of a second for a carrier gas flow rate of 1 liter per hour (NTP). The column efflux passes through one of the cells to a low-impedance liquid air trap which removes any sample components present, and then to the second identical cell; the two hot wires form arms of a Wheatstone bridge in the conventional manner to compensate for changes in their temperature other than those caused by variations of the composition of the gas in the first cell. At low gas pressures this compensation is inefficient unless both cells share substantially the same pressure.

The problems of constructing katharometers to withstand high temperatures were found to be largely those of choosing suitable materials, particularly for electrical insulation and gas seals. For simplicity, demountable seals are avoided where possible by hard-soldering the gas connections at joints which can be made without heating the katharometer block as a whole.

Small glass-to-metal seals provide the insulated anchorages for the hot wires in the manner shown in Figure 5, *b*. The essential feature of this demountable seal design is the use of a 0.4% arsenical copper sealing ring; this does not anneal at the maximum working temperature, whereas leaks invariably develop from this cause with unalloyed copper. Care was taken to support the central wire with a mica washer in order to permit accurate location of the fine platinum wire in its bore.

The output of the Wheatstone bridge is very sensitive to variations of tension in the hot wires. As these have to operate at high temperatures, it is important to stress them as lightly as is consistent with avoiding sag and microphony. The earthy ends of the wires are, therefore, resiliently mounted by the use of laterally supported and encapsuled springs (Figure 5, *c*). There are practical difficulties in achieving a very weak spring of this convenient form and it is advantageous to match the expansion coefficient of the katharometer block to that of the platinum wires. Partly for this reason and partly for its ability to resist corrosion and to provide adequately hard sealing faces, the block is made of stainless steel (S. 80). Gold-soldering of the springs to their capsules is adopted to ensure reliability and in particular to avoid the use of flux, as this joint is the last to be made when assembling the katharometer and can be inspected only from the outside. The wire tensions may be checked after assembly, however, by determining their resonant frequencies to transverse vibration (approximately 150 c.p.s. with the present design).

As the katharometer is required to operate at subatmospheric pressures and the carrier gas may be hydrogen, it is sensitive to traces of air. Therefore, it should be leak-free almost in the high-vacuum sense. A number of cells incorporating seals of the type just described have been made which have had aggregate leaks, when hot and cold, consistently below 0.01 liter-micron per second, and showing no tendency to increase after as many as 10 cycles between 50° and 300° C.

The katharometer is mounted within a thick Dural cylinder carrying a heater winding by which it is maintained at the desired working temperature. It is essential to keep transient thermal gradients from the katharometer; to this end the temperature of its enclosure is regulated by a controller identical to those used with the furnaces, and a thermal barrier in the form of a $^1/_{32}$-inch air space is provided between the katharometer block and the Dural sheath. In consequence, the detector takes several hours to reach its steady working condition; it is left continuously at a temperature somewhat above the highest column temperature normally used. The hot wires are fed with constant current from electronically regulated power supplies stable to better than 0.05% per hour. Each katharometer-heater assembly is resiliently mounted adjacent to its furnace top, with a single liquid air trap immediately underneath it. The preparative function of the equipment is not at present provided for, but panel space has been left for installation of a manifold and additional liquid air traps to permit recovery of separated components.

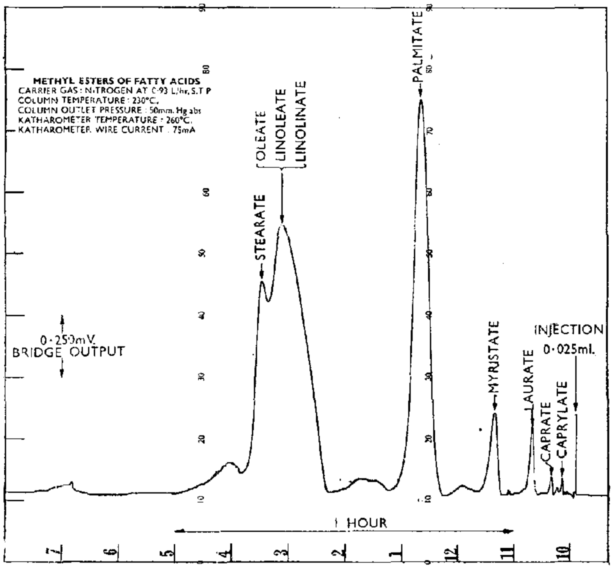


Figure 7. Chromatogram at high temperature and low pressure

APPLICATIONS

The high temperature katharometer has been extensively tested both hot and cold. The record shown in Figure 6 was obtained at 295° C. using pure nitrogen as the carrier gas and saturating it with the vapor of refrigerated acetone wherever it was desired to simulate the presence of a sample component. The record follows the slowly rising temperature of the acetone and returns to the base line when the saturator is bypassed. This has proved a useful method of sensitivity measurement. In contrast with its effect at room temperatures, the presence of acetone vapor reduces the hot wire temperature. The satisfactory return to the base line

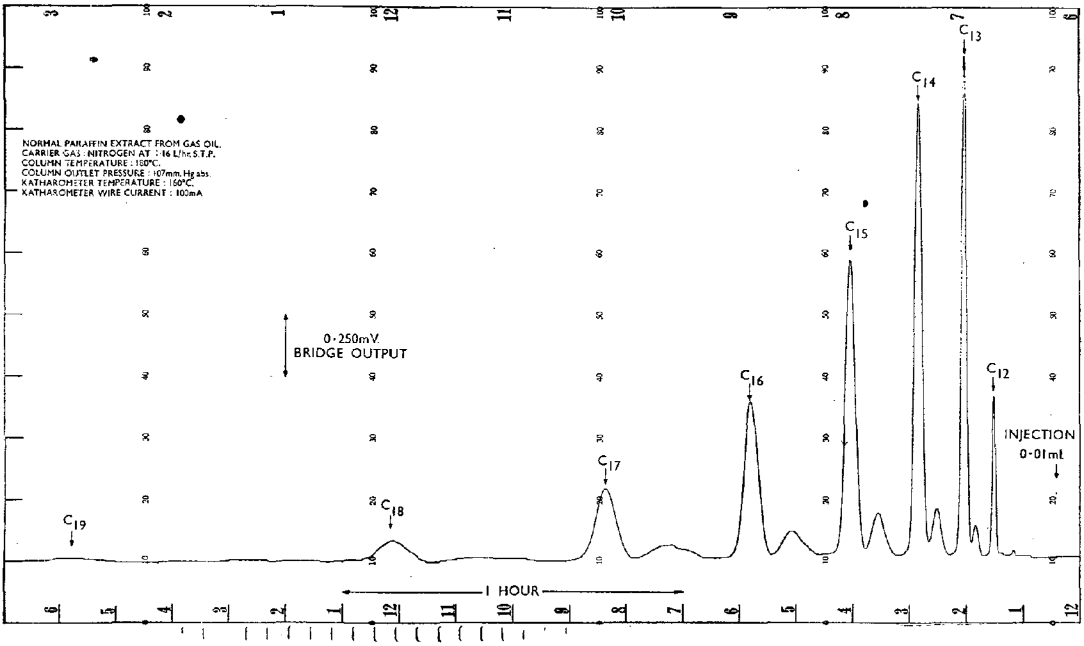


Figure 8. Chromatogram with constant column temperature

indicates that no serious irreversible change of the wire surface has occurred.

Figure 7 is a typical record from the complete apparatus illustrating its performance at a katharometer temperature of 260° C. and column outlet pressure of 50 mm. of mercury absolute. The possibilities of changing column temperature in the course of a chromatogram are indicated by comparing Figures 8 and 9. Figure 8 was obtained with column temperature constant at 180° C.; the C_{19} peak emerging about 3 hours after injection is just recognizable. Figure 9 was obtained under conditions differing only in that, after emergence of the C_{15} peak, the column temperature controller was reset to 215° C. The sharpening and heightening of subsequent peaks are evident, and the C_{19} component, now appearing about 0.5 hour after injection, is clearly defined. The usefulness of the record is not drastically impaired by the slight base-line shift occurring at the change of column temperature; such shifts are observed to depend upon the previous history of the column.

Considerable experience with the equipment gives grounds for confidence that it will enable the extension of gas-liquid partition chromatography into the range of higher molecular weights to proceed against a now very extensive background of experience with thermal conductivity detectors, and relieve the analyst from many problems of instrumentation.

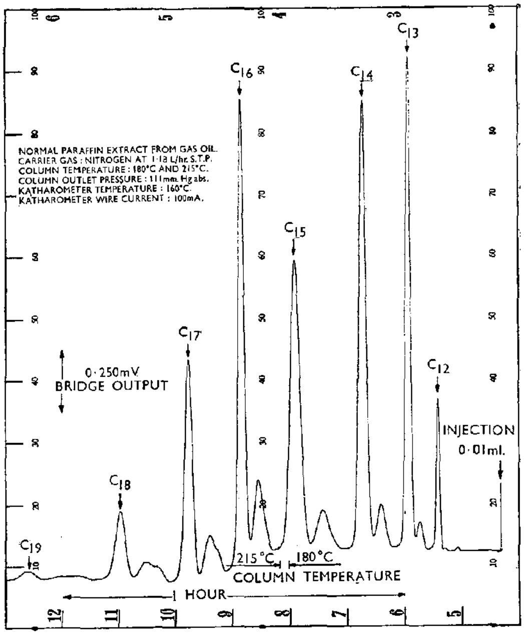


Figure 9. Chromatogram with stepped column temperature

ACKNOWLEDGMENT

Thanks are due to the Directors of Shell Research, Ltd., for permission to publish this paper.

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Analysis of Volatile Organic Sulfur Compounds by Gas Partition Chromatography

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▶ A method is described for the analysis by gas partition chromatography of a sample containing hydrogen sulfide, methyl, ethyl, and propyl mercaptans, dimethyl and diethyl sulfides, dimethyl disulfide, and thiophene. The sulfur compounds have also been separated from light hydrocarbons and from methanol and ethanol. Benzene and thiophene were also separated. A method is outlined for determining the sensitivities of the instrument to vapor samples containing air. The relationship among retention volume, polarity of the column liquid, and polarizability of the gases being analyzed is discussed.

Analytical methods for the quantitative determination of hydrogen sulfide, mercaptans, and alkyl sulfides and disulfides in the presence of each other are of considerable importance in industrial laboratories and in fundamental investigations. Because of similarities in chemical behavior of these compounds, chemical procedures (*1–6*) are usually difficult and the results may be unreliable. The success achieved by gas chromatography as an analytical tool has suggested the application of this technique, based on physical rather than chemical differences, to the analysis of sulfur compounds. Hydrocarbons virtually identical in their properties have been separated by this means, and it was felt that separation of sulfur compounds, which differ greatly in volatility, should be possible.

The system chosen for investigation was one that had been encountered in work on the pyrolysis of dimethyl disulfide (*5*). It contained hydrogen sulfide, methyl, ethyl, and propyl mercaptans, dimethyl and diethyl sulfides, dimethyl disulfide, and thiophene.

EXPERIMENTAL

The hydrogen sulfide was prepared in the laboratory. The other compounds were standard grade, obtained from Eastman Kodak Co., Rochester, N. Y.

The choice of a suitable chromatographic system was governed by experience gained in this laboratory in hydrocarbon analysis (*11*) and by the nature of the compounds studied. Adsorption methods using activated alumina or silica gel columns were avoided, as the acidic nature of some of the sulfur compounds might lead to irreversible adsorptions. A preliminary investigation showed that suitable separations could be accomplished by using a partition-elution column with tricresyl phosphate as the liquid phase on a Celite column.

The apparatus is illustrated in Figure 1.

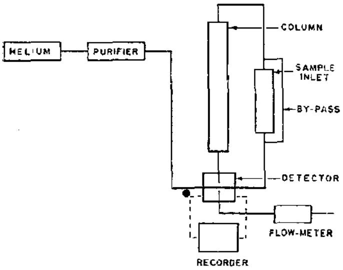

Figure 1. Schematic outline of chromatography apparatus

Helium was used as the carrier gas because of its low viscosity and the large difference between its thermal conductivity and those of the compounds being analyzed. The sample inlet system was designed for admission of vapor samples by the convenient syringe and serum-cap technique. The less volatile components of the mixture were admitted at partial pressures not exceeding their vapor pressures at room temperature, to avoid condensation in the apparatus. Air was also present in the vapor samples of these compounds. The column was a 4-foot borosilicate glass U-tube of 5-mm. internal diameter, mounted in a heating jacket by means of which the column temperature could be increased rapidly. The column was filled with a mixture of tricresyl phosphate (Eastman Kodak technical grade) and Celite 545 (Johns Manville) in the proportions 30 to 70 by weight, according to the method described by James and Martin (*9*).

The thermal conductivity cell (*14*) contained detecting and compensating filaments, mounted in channels drilled in a brass block. The cell gave excellent temperature compensation and much better flow-rate compensation than some commercially available cells in which the compensating filament is not placed in the gas stream but sits in a diffusion cavity. The fact that the cell was made from brass did not in any way affect the determination. Its sensitivity remained unaltered during the investigation and no reaction with the sulfur compounds was observed.

The two filaments of the cell were mounted in the usual manner in opposing arms of a bridge circuit and carried a current of approximately 200 ma. Any imbalance in the bridge circuit caused by the appearance of a substance other than the carrier gas in the detecting channel of the cell was displayed on a Leeds & Northrup Speedomax recorder of adjustable sensitivity (1 to 20 mv. full scale).

The time required for elution of a group of compounds differing greatly in boiling points can be reduced sharply by gradual increase of column temperature during the analysis. This procedure has been used successfully by other workers (*7*). Lower boiling components of a mixture, which move through the column with relatively high velocities, can be resolved at or near room temperature. The rate at which the higher boiling compounds pass through the columns is greatly increased at elevated temperatures (*8*). An exactly reproducible heating rate was used in all analyses.

Owing to the increase in gas viscosity with rising temperature, the flow rate through the columns decreases markedly. In order to maintain the carrier gas flow at the initial rate, the pressure differential should be increased with the temperature. However, such an increase would affect only the compensating filament in the conductivity cell, causing it to operate like a Pirani gage, with resulting deviations in the base line of the recorder. Hence, it is necessary to keep the pressure differential constant and accept the considerable change in flow rate. For example, at a pressure differential of 3 pounds per square inch, the flow rate changed from 50 ml. per minute at 19° C. to 33.5 ml. per minute at 112° C. The reproducibility of these figures suggests that the change in flow rate is a better measure of the true column temperature than that indicated by a thermometer placed inside the heated column jacket.

RESULTS AND DISCUSSION

A chromatogram, showing the separation of the components of a mixture containing hydrogen sulfide, methyl mercaptan (methanethiol), ethyl mercaptan (ethanethiol), methyl sulfide, propyl mercaptan (propanethiol), ethyl sulfide, thiophene, and dimethyl disulfide, is presented in Figure 2. *n*-Pentane and isopentane were added to the mixture to relate the relative retention volumes of hydrocarbons to those of the sulfur compounds. The compounds were identified by their retention volumes and by reinforcing the peaks with the pure substances.

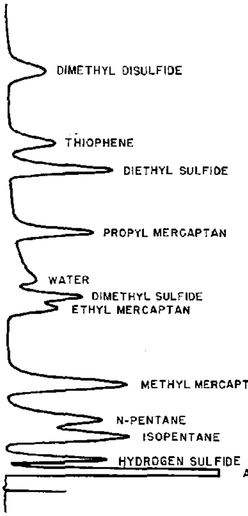

Figure 2. Separation of volatile sulfur compounds plus pentanes with tricresyl phosphate column

Satisfactory separation of the hydrogen sulfide from the air present in the syringe and of the pentanes and methyl mercaptan was obtained with a reasonable elution rate at room temperature. After methyl mercaptan appeared, the temperature of the column was raised to speed up elution of the remaining compounds. Lower temperatures result in sharper separations but greatly increase the retention volumes for substances of relatively low volatility (*7, 10, 16*). Ethyl mercaptan and dimethyl sulfide were separated at approximately 70° C. and the column temperature was allowed to rise to approximately 120° C. to accelerate the elution of dimethyl disulfide.

Water vapor, introduced with the sample, appeared as a peak between dimethyl sulfide and propyl mercaptan. It could be eliminated by placing a drying agent like sodium sulfate between the inlet point and the column. The air peak could also be eliminated by using sample collecting and admission systems in which air is excluded. In the syringe technique, the sharp peaks due to the pressure differential during the insertion of the sample served as a convenient reference point from which to determine retention volumes.

Figure 3 further demonstrates the separation of a hydrocarbon and a related sulfur compound and the effect of column temperature on the separation. Thiophene and benzene could not be completely resolved at 115° C. but were satisfactorily separated at 77° C.

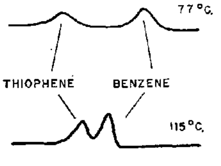

Figure 3. Effect of temperature on separation of thiophene and benzene with tricresyl phosphate column

To show the separation of mercaptans and the corresponding alcohols, a mixture containing methanol, ethanol, and methyl and ethyl mercaptans was passed through the column, while the column temperature was increased gradually to approximately 100° C. The resulting chromatogram is shown in Figure 4. *n*-Pentane was again added to show the relative position of the hydrocarbons.

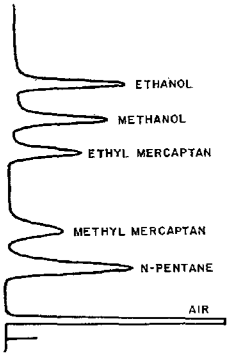

Figure 4. Elution order for mercaptans, alcohols, and hydrocarbon with tricresyl column

In quantitative analysis by gas chromatography, peak areas are customarily used as a measure of the amount of substance placed on the column (*13*). Measurements of this type depend on experimental parameters such as carrier gas flow rate, sensitivity of the thermal conductivity cell to the compound at a particular cell temperature, and recorder sensitivity and chart speed. However, the method is capable of a high degree of accuracy if experimental conditions are standardized carefully. In the present study the peak areas were directly proportional to the amounts of the substances placed on the column.

In dealing with compounds like alkyl sulfides and mercaptans, it is difficult to admit micromole quantities of the pure substances into the apparatus to determine sensitivities, an operation that should be repeated with each analysis. A method was devised which permits rapid determination of the sensitivity of the apparatus to a particular compound by means of a calibration involving a mixture of the compound and air. The method is illustrated with ethyl mercaptan (boiling point 34.7° C.) and is applicable to all volatile substances having a reasonably high vapor pressure.

A few drops of the mercaptan are placed in a polyethylene bag fitted with a serum cap. A volume, V_1, of the air-mercaptan vapor mixture is withdrawn with a syringe and injected into the apparatus. Peak areas, A_1 for the mercaptan and A_2 for air, are measured. In a second experiment, the same amount of air-mercaptan vapor is withdrawn from the bag and an additional volume, V_2, of air is then drawn into the syringe. Injected into the apparatus, this yields the same peak area for the mercaptan—i.e., A_1—and a larger peak, A_3, for air. Assuming that the ideal gas laws are applicable, the unknown volume of mercaptan V_x in V_1 is

$$V_x = V_1 - \left(\frac{A_2}{A_3 - A_2}\right) V_2$$

With a column temperature of 78° C. and a helium flow rate of 50 ml. per minute, the elution time for the mercaptan was 2.5 minutes. It was therefore possible to obtain a reliable average value within a reasonable period. By using the same syringe for admitting both standards and samples for analysis, errors in syringe calibration are largely eliminated. The method becomes inaccurate if V_1 and V_2 are very dissimilar or if the vapor pressure of the substance being analyzed is low. It is important to saturate the syringe lubricant with the compound, to avoid errors due to adsorption. This can be done by purging the syringe several times with the vapor.

The volume, V_x, is then converted to micromoles and the sensitivity of the apparatus is calculated in square centimeters of peak area per micromole. In an experiment with ethyl mercaptan, V_1 was 0.60 ml., and V_2 was 0.30 ml. The sensitivity of the apparatus to this compound was 1.44 sq. cm. per micromole at a chart speed of 1 inch per minute. A 0.03-sq. cm. peak, the limit of quantitative estimation in the present work, therefore, corresponded to 2×10^{-8} mole of ethyl mercaptan.

A logarithmic relationship between the peak retention volume of a substance and its vapor pressure at a given elution temperature has been reported by several investigators (*8*, *12*). In the present work the situation is complicated by the temperature increase during the analysis, but the elution order for the organic sulfur compounds in Figure 2 agrees qualitatively with the general relationship.

The influence of the polarity of the compound on its retention volume can be seen in the relative positions of the hydrocarbons and the mercaptans. The pentanes, with boiling points of 28° to 36° C. and a molecular weight of 72, have a smaller retention volume than has methyl mercaptan with a boiling point of 7.6° C. and a molecular weight of 48. The dipole moments of *n*-pentane and methyl mercaptan are 0 and 1.26, respectively (*15*). The more polar mercaptan presumably interacts more strongly with the highly polar tricresyl phosphate phase on the column than does the nonpolar hydrocarbons.

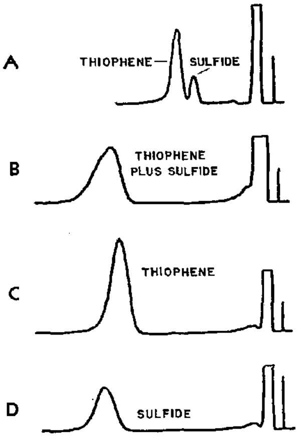

Figure 5. Effect of nature of column liquid on order of elution of thiophene and diethyl sulfide

- A. TCP
- B. Paraffin
- C. Thiophene only with paraffin column
- D. Diethyl sulfide only with paraffin

The elution order for thiophene and benzene conforms to the usual pattern; the less volatile, more polar thiophene has the larger retention volume.

However, the elution order for thiophene and diethyl sulfide (Figure 2) is different from that predicted by boiling points or dipole moments. The sulfide [boiling point 92° C., dipole moment 1.51 (15)] has a smaller retention volume than thiophene [boiling point 84° C., dipole moment 0.6 (16)]. The observed reversal of elution order is presumably due to an electron interaction effect. Thiophene, because of its aromatic character, is strongly polarized by the polar tricresyl phosphate, causing an induced dipole-dipole interaction which is greater than that for the less polarizable diethyl sulfide. The thiophene is therefore retained to a greater extent on the column. Evidence to support this contention is presented in Figure 5. The top chromatogram shows again the elution order with a tricresyl phosphate column. The remaining chromatograms are for a thiophene–diethyl disulfide mixture and for thiophene and the sulfide separately, all done with a column in which paraffin oil replaced tricresyl phosphate as the liquid phase. With a nonpolar liquid on the column, the more volatile thiophene has the smaller retention volume.

These results provide an additional illustration of the technique of separating two compounds which on one column appear together, by altering the nature of the column liquid. Furthermore, they indicate that gas partition chromatography may be a useful tool for investigation of dipole-dipole interactions between molecules.

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Vapor Phase Chromatography and the Telegrapher's Equation

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▶ A review is made of the mathematical relationship between the electrical transmission line and the vapor phase chromatography column, when linearity and the absence of diffusion within the mobile phase of the column are assumed, and it is shown that the sample concentration within the mobile or static phase is the analog, not of voltage or current in the transmission line, but of a linear combination of these. The basic chromatographic solution is simpler than the transmission line solution, and may be extended easily and with good approximation to include diffusion within the mobile phase. Several conclusions, such as the existence of an optimum carrier gas flow rate, are derived from the simple theory established.

The purpose of any useful theoretical discussion of the kinetics of gas chromatography should be the prediction of the cause and effect relationship among the parameters at the experimenter's disposal, such as column length, density of packing, and flow rate on the one hand, and the experimental results of interest, such as components separation, on the other.

The characteristic feature of chromatography, which must be taken into account in any theory of this process, is a constant departure, a constant upsetting of equilibrium conditions. The assumptions made to establish a simple theory are the essential assumption of linearity, and the further assumption that a sufficient approximation is obtained by treating separately the effect of diffusion between the mobile and the static phase at any point along the column, and the effect of diffusion within the mobile phase along the length of the column. The theory discussed here refers to the kinetics of the chromatographic process at a given temperature, and the more physical-chemical problem of the effect of temperatures intervenes only to the extent that the several characteristics of the sample and of the column, such as pressure, capacity, and diffusion, which are treated as constant parameters, can be strongly dependent upon the temperature at which the column operates. It must be recognized that the use of relatively large pressures at the column entrance constitutes a departure from linearity, for the treatment of which the discussion presented here should be elaborated.

With the assumption of linearity, the kinematical problem of gas chromatography, in which a small amount of a volatile compound is injected in a carrier gas at the column entrance, is mathematically similar to the problem presented by the older form of chromatography, when a steady stream of sample was inserted in the column, and the delayed and separate arrivals of the several components were observed as a succession of fronts, at the column exit. It is similar also to the problem of heat exchange between a flowing medium and a stationary medium, or, for that matter, to a whole family of countercurrent problems.

There is a certain amount of literature available on this subject (*2–4*, *7*), from which the results shown here could have been derived, but the preferred method used here was to derive these results directly from the well-known treatment of the telegrapher's equation, which has been masterfully handled by Reimann (*6*) and by Carson (*1*), to mention two names only, and which constitutes one of the great classics of communication theory.

DISCUSSION

The assumption of linearity makes it possible to represent a fractionating column by the electrical analog shown in Figure 1. The volume entrained by the mobile phase is represented by the upper row of continuously distributed capacitances, C, which travels from left to right at velocity v. The resistance, R, represents the resistance to the static diffusion which would take place along the column even when v is zero; this resistance will be assumed infinite at first, in order not to introduce a higher order term in the differential equation.

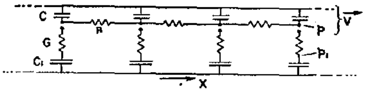

Figure 1. Electrical analog of fractionating column

p, p_1. Mobile and static partial pressures
G. Diffusion between phases
v. Flow rate

The equivalent free volume of the static phase is represented by the lower row of continuously distributed capacitances, C_1, which are connected in turn through the leakance paths, G, to the successive capacitances of the mobile phase. In the case of gas chromatography, these capacitances represent the ability of the carrier gas and of the packing material of the column to hold a certain concentration of the several components of the sample. This concentration can be represented for the mobile phase by the product Cp, in which p designates the partial pressure of a given component in the mobile phase. Likewise, the concentration of the static phase can be represented by the product C_1p_1, in which p_1 represents the partial pressure with which the static phase is in equilibrium.

Two equations can be obtained immediately by means of this model. The first is the conservation equation, which states that the rate of change with time of the integrated concentration to the right of any given abscissa x is equal to the rate of flow, Cvp, of this component across the abscissa, x. The second equation states that the rate of increase of the concentration in the static phase is proportional to the differential pressure, $p - p_1$, and to the leakance, G. These two equations are:

$$\frac{\partial}{\partial t}\left(C\int_x^\infty p\,dx + C_1\int_x^\infty p_1\,dx\right) = Cvp \tag{1}$$

$$G(p - p_1) = C_1\frac{\partial p_1}{\partial t} \tag{2}$$

Differentiation of Equation 1 with respect to x yields:

$$C\frac{\partial p}{\partial t} + C_1\frac{\partial p_1}{\partial t} + Cv\frac{\partial p}{\partial x} = 0 \tag{3}$$

Combining 2 and 3, we obtain a single differential equation, which is valid for both p and p_1:

$$\left[\frac{\partial^2}{\partial t^2} + G\left(\frac{1}{C} + \frac{1}{C_1}\right)\frac{\partial}{\partial t} + \frac{Gv}{C_1}\frac{\partial}{\partial x} + v\frac{\partial^2}{\partial x\partial t}\right](p, p_1) = 0 \tag{4}$$

New independent variables, u and z, are introduced:

$$u = \frac{1}{v}\left(\sqrt{\frac{C_1}{C}} + \sqrt{\frac{C}{C_1}}\right)x - \sqrt{\frac{C}{C_1}}\,t \tag{5}$$

$$z = \frac{1}{v}\left(\sqrt{\frac{C_1}{C}} - \sqrt{\frac{C}{C_1}}\right)x + \sqrt{\frac{C}{C_1}}\,t \tag{6}$$

Their substitution in 4 transforms the latter into a simplified form of the telegrapher's equation:

$$\left(\frac{\partial^2}{\partial z^2} + 2\alpha\frac{\partial}{\partial z} - \frac{\partial^2}{\partial u^2}\right)(p, p_1) = 0 \tag{7}$$

where

$$\alpha = \frac{G}{\sqrt{C_1C}} \tag{8}$$

With the new independent variables, u and z, p and p_1 are related by the two equations:

$$p = p_1 + \frac{1}{\alpha}\left(-\frac{\partial p_1}{\partial u} + \frac{\partial p_1}{\partial z}\right) \tag{9}$$

$$p_1 = p + \frac{1}{\alpha}\left(\frac{\partial p}{\partial u} + \frac{\partial p}{\partial z}\right) \tag{10}$$

The telegrapher's equation (7) without the α term has the solution:

$$p, p_1 = f(u \pm z) \tag{11}$$

which represents waves propagating with velocity unity to the right or to the left, and the term in $\partial/\partial z$ imposes the condition that any wave front propagated with velocity unity to the right or to the left decreases exponentially with time, while leaving a diffused trail behind.

The physical meaning of the change of variable introduced by Equations 5 and 6 is that the real column has been replaced by a virtual column in which the mobile phase travels with velocity unity to the right, the formerly immobile static phase travels with velocity unity to the left, and any inserted sample would remain immobile between the two phases if α were infinite, would travel to the right with velocity unity if injected in the mobile phase and if α were zero, and diffuses about the abscissa of injection when α has a finite value.

It is important to note that Relations 9 and 10 are not the relations which exist between current I and voltage V in a transmission line, but are instead the relations which would exist between $V + I$ and $V - I$ in a transmission line of surge impedance unity with series resistance but without shunt leakance, for p and p_1 are analogous to the two quantities just written.

The standard solutions for the telegrapher's equation are usually written for the application of a constant voltage at the beginning of a semiinfinite line at time zero. Differentiation with respect to time of this standard solution and the application of symmetry consideration give immediately the solution for the voltage and current when a half unit charge is applied at $u = 0$ and $z = 0$ on an infinite line. They are:

$$V_1 = \frac{1}{4}e^{-\alpha z}\left[\frac{z}{\sqrt{z^2 - u^2}}I_1(\alpha\sqrt{z^2 - u^2}) + I_0(\alpha\sqrt{z^2 - u^2}) + \delta(u - z) + \delta(u + z)\right] \tag{12}$$

$$I_1 = \frac{1}{4}e^{-\alpha z}\left[\frac{u}{\sqrt{z^2 - u^2}}I_1(\alpha\sqrt{z^2 - u^2}) + \delta(u - z) - \delta(u + z)\right] \tag{13}$$

for $|u| < z$ and zero beyond. (I_0 and I_1 are the Bessel functions of an imaginary argument of order 0 and 1, and δ is defined by $\int_{-\epsilon}^{+\epsilon}\delta(x)dx = 1$ for a vanishingly small ϵ.) When a half unit charge is caused to travel from left to right at $u = 0$ and $z = 0$, the resulting voltage and current along the line are obtained similarly and are:

$$V_2 = \frac{1}{4}e^{-\alpha z}\left[\frac{u}{\sqrt{z^2 - u^2}}I_1(\alpha\sqrt{z^2 - u^2}) + \delta(u - z) + \delta(u + z)\right] \tag{14}$$

$$I_2 = \frac{1}{4}e^{-\alpha z}\left[\frac{z}{\sqrt{z^2 - u^2}}I_1(\alpha\sqrt{{}^2 - u^2}) - I_0(\alpha\sqrt{z^2 - u^2}) + \delta(u - z) + \delta(u + z)\right] \tag{15}$$

Since p is analogous to $V + I$, the insertion of a unit p charge in the mobile phase, and of no charge in the static phase, is equivalent to the insertion of a half charge of voltage and a half charge of current in the transmission line, and the resulting expressions for p and p_1 are obtained as indicated below:

$$p = V_1 + I_1 + V_2 + I_2 = e^{-\alpha z}\left[\frac{\alpha(z+u)}{2\sqrt{z^2-u^2}} I_1\left(\alpha\sqrt{z^2-u^2}\right) + \delta(z-u)\right] \quad (16)$$

$$p_1 = V_1 - I_1 + V_2 - I_2 = \frac{\alpha}{2} e^{-\alpha z} I_0\left(\alpha\sqrt{z^2-u^2}\right) \quad (17)$$

$$\text{for } |u|<z,\ p = p_1 = 0 \text{ for } |u|>z$$

It can be verified immediately that the solutions given by Equations 16 and 17 satisfy 9 and 10 and hence the differential Equation 7. (The δ function in Equation 16 takes care of the discontinuous character of 17 when forming p with 9, and cancels itself out in the right member of 10.) Furthermore, these solutions satisfy the initial conditions of insertion of a unit charge in the mobile phase, and none in the static phase, and it is remarkable that these solutions are actually simpler than the corresponding solutions for the electrical problem.

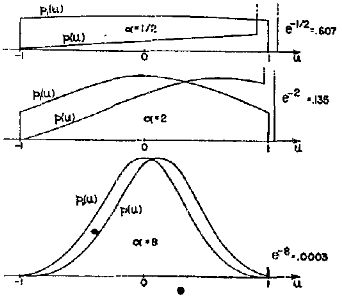

Figure 2. Plots of $p(u)$ and $p_1(u)$ at $z = 1$

Figure 2 plots Equations 16 and 17 as functions of u for $z = 1$ and $\alpha = \frac{1}{2}$, 2, and 8, respectively. This is mathematically equivalent to plotting these functions for the same value of α and increasing values of the virtual time z and changing the scale of u to keep the curves within the confines of the margins. These plots thus give an insight into the diffusion process as time increases.

In Figure 2 (upper), the larger fraction of the initial charge is still contained within the large spike at the right, which represents the δ function. In its progress along the static phase, this charge has left a trail on the static phase, shown by the nearly horizontal p_1 curve. The mobile phase has, in its turn, received a small charge from the static phase, as indicated by the nearly uniformly rising p curve.

In Figure 2 (center), most of the original charge has already diffused, and the p and p_1 curves are beginning to exhibit the shape of an error curve, which is fully developed in Figure 2 (lower), where the undiffused portion has dwindled to 0.03% of the original charge. This last figure underlines the difference of interests of the communication engineer, who amplifies the small information carrying spike at the right and sends it along in the next transmission line section, and of the chemical engineer, who is interested solely in the diffused component exhibited by the error curve, because different values of C_1 cause the different components to separate more and more from each other.

When the initial charge has diffused, use can be made of the first term of the asymptotic expansion of I_1:

$$I_1(x) \cong \frac{e^x}{\sqrt{2\pi x}} \quad (18)$$

and Equation 17 can be transformed into a sufficiently approximate expression for p:

$$p \cong \frac{1}{2}\sqrt{\frac{\alpha}{2\pi z}}\, e^{-\frac{\alpha u^2}{2z}} \quad (19)$$

The expression Equation 19 is symmetrical in u about the origin 1 because it refers to the virtual column used so far for the sake of mathematical simplicity. It would be also symmetrical in x for a column in which $C_1 = C$. In actual columns we have, in general, $C_1 >> C$; for a study of the general character of our solution in terms of real column length and real time we may neglect the term containing $\sqrt{\frac{C}{C_1}}\, x$ in Equations 5 and 6 and with a simple change of scale in x and t, we may write:

$$u = \xi - \tau \quad (20)$$

$$z = \xi + \tau \quad (21)$$

Substitution in Equation 19 yields:

$$p = \frac{1}{2}\sqrt{\frac{\alpha}{2\pi(\xi+\tau)}}\, e^{-\frac{\alpha(\xi-\tau)^2}{2(\xi+\tau)}} \quad (22)$$

This expression gives the same plot in ξ for a given τ and in τ for a given ξ, and this plot is characterized by a steeper ascent than descent for increasing ξ or τ. This is as expected for ξ, because a large static capacity causes the pressure curve to trail off more in the direction of flow. For this reason, we might expect a slow rise and a faster decay of the elution curve, p, as a function of τ at a given column length ξ. The explanation of the seeming paradox, that the opposite is the case, is given by the circumstance that diffusion continues to take place during elution, so that the descent of p with time at the column exit is actually less steep than the ascent.

The theoretical finding that elution curves have a steeper ascent than descent agrees qualitatively with the elution curves obtained for the more volatile components, which are the first to appear at the column exit. The circumstance that the opposite occurs sometimes for the less volatile components may be interpreted as a departure from linearity for the latter.

Actually, the value of α in Equation 22 is so large in most practical cases that little departure from symmetry should be expected for the elution curves, and large departures in either direction suggest departures from linearity.

One of the most important parameters in gas chromatography is the relative "band width" of the several components—i.e., the ratio of the time of passage of a component to the time interval between adjacent components.

A measure for the band width of a component can be obtained from the δu interval at both ends of which the exponent of Equation 19 is unity:

$$\delta u = 2\sqrt{\frac{2z}{\alpha}} \quad (23)$$

The band width can be obtained in real time by making the change of variables defined by Equations 5 and 6, and substituting for α its value given by 8:

$$\delta t = 4C_1\sqrt{\frac{x_0}{CvG}} \quad (24)$$

where x_0 designates the length of the column.

The flow speed of any component is obtained by setting $u = 0$ in Equation 5 and is:

$$v_s = \left(\frac{x}{t}\right)_{u=0} = \frac{Cv}{C + C_1} \quad (25)$$

and the excess of the transport time, t, of any component over the transport time, t_a, of a component without affinity for the fixed phase is given by:

$$t - t_a = \frac{C_1 x_0}{Cv} \quad (26)$$

(The theory developed here is based on the assumption of linearity, and the effects of gas compressibility are not taken into account.)

The ratio $\frac{\delta\tau}{t - t_a}$ may thus be considered as a measure of the relative band width due to dynamic diffusion alone, under the assumption made so far that R is infinite, as otherwise we would have been led to a third-order differential equation. A sufficiently good approximation can be obtained for the effect of a finite R by computing the spreading due to R alone within a column in which the flow rate is assumed to be zero, and then computing the elution time of the component thus spread. The differential equation for this case is the simpler telegraph cable equation:

$$(C + C_1)R\,\frac{\partial p}{\partial t} = \frac{\partial^2 p}{\partial x^2} \qquad (27)$$

for the establishment of which it is permitted to assume G to be infinite, because a small value of G will demand a correspondingly small value of the optimum flow rate, as will be seen shortly. The solution of Equation 27 for a sample of value unity injected at time $t = 0$ is:

$$p = \sqrt{\frac{R(C + C_1)}{4\pi t}}\; e^{-\frac{R(C + C_1)x^2}{4t}} \qquad (28)$$

A measure for the column length over which the sample has diffused statically after a time interval t can be obtained as the x interval at the ends of which the exponent in Equation 28 is unity:

$$\delta x = 4\sqrt{\frac{t}{R(C + C_1)}} \qquad (29)$$

We substitute now for t the time of travel of the component in the column, $\frac{x_0\,(C + C_2)}{VC}$ and obtain the band width δt_s, due to the static diffusion alone, by dividing δx by the flow rate of this component:

$$\delta t_s = 4\,\frac{C + C_1}{V^{3/2}C^{3/2}}\sqrt{\frac{x_0}{R}} \qquad (30)$$

The combined effect of the kinetic and static diffusions can be obtained by making the convolution of the elution curves which would be obtained for each individual effect alone. As the convolution of two error functions of area unity each is an error function, the second moment (moment of inertia) of which is the sum of the second moments of the two generating error functions, we obtain the combined kinetic and static diffusion time as $\sqrt{\delta t^2 + \delta t_s^2}$. The relative band width:

$$\delta B = \frac{\sqrt{\delta t^2 + \delta t_s^2}}{\frac{C_1 x_0}{Cv}} \qquad (31)$$

has a minimum value which occurs when the flow rate has the optimum value:

$$v_{\text{opt.}} = \frac{C + C_1}{CC_1}\sqrt{\frac{G}{R}} \qquad (32)$$

for which case we have:

$$\delta B_{\text{opt.}} = 4\sqrt{\frac{2(C + C_1)}{C_1 x_0}}\left(\frac{1}{RG}\right)^{1/4} \qquad (33)$$

The concept of the height of the equivalent theoretical plate (HETP), h, and the associated concept of the number of theoretical plates in a column of length x_0, $\frac{x_0}{h}$, are intimately connected with the equivalent transmission line parameters utilized in this discussion.

Consider first the linear extent, within the column, of the "band" corresponding to one component. After its travel through the column, the square of this linear extent, Δx^2, measured between the e^{-1} points of the band, will be given by the square of the band width measured in seconds, $\delta t^2 + \delta t_s^2$, multiplied by the square of the component velocity, $Cv^2/(C + C_1)$. Setting v_{opt} for v, we obtain from Equations 24, 30, and 32:

$$\Delta x^2 = (\delta t^2 + \delta t_s^2)\left(\frac{C}{C + C_1}\,v_{\text{opt}}\right)^2 = 32\,\frac{C}{C + C_1}\,\frac{x_0}{\sqrt{RG}} \qquad (34)$$

Consider next a partition column similar to that illustrated by Figure 1, but differing from it in two important respects:

1. R and G are both infinite.
2. C and C_1 are no longer continuously distributed; instead they are lumped every interval h along the column.

As the mobile phase moves, or rather skips along the fixed phase, at the rate of v/h condensers per second, any unit charge inserted at any epoch of time on one of the $C - C_1$ pairs will be redistributed, after n skips, in accordance with the terms of the binomial expansion of:

$$\left(\frac{C_1}{C + C_1} + \frac{C}{C + C_1}\right)^n \qquad (35)$$

The largest term of this expansion will be the $\frac{C}{C + C_1}\,n - th$ one, and the term y terms distant from this largest term will have a value which can be easily obtained by an application of Sterling's formula $\left(a! \cong \left(\frac{a}{e}\right)^a\sqrt{2\pi a}\right)$:

$$\frac{C + C_1}{\sqrt{2\pi n\,CC_1}}\; e^{-\frac{1}{2}\frac{(C + C_1)^2 y^2}{nCC_1}} \qquad (36)$$

The number Δy of terms clustered around the central maximum term, and greater than e^{-1} times that central term, will be given by:

$$\Delta y^2 = \frac{8n\,CC_1}{(C + C_1)^2} \qquad (37)$$

The width in real length of the band thus developed after n skips will be simply:

$$\Delta x = \Delta y . h \qquad (38)$$

The number n of skips required for the band maximum to travel the length of the column, x_0—i.e., to travel along $\frac{x_0}{h}$ condensers of the fixed phase—is:

$$n = \frac{C + C_1}{C}\,\frac{x_0}{h} \qquad (39)$$

The last three equations yield:

$$\Delta x^2 = \Delta y^2 h^2 = 8\,\frac{C_1}{C + C_1}\,x_0 h \qquad (40)$$

Comparison of Equations 34 and 40 gives immediately the HETP of the column:

$$h = \frac{4}{\sqrt{RG}} \qquad (41)$$

The number of theoretical plates, n_0, can be expressed as follows by means of Equations 33 and 41:

$$n_0 = \frac{x_0}{h} = \frac{x_0\sqrt{RG}}{h} = 8\,\frac{C + C_1}{C}\,\frac{1}{(\delta B_{\text{opt}})^2} \qquad (42)$$

In terms of observable quantities, δB_{opt} can be expressed as the ratio of the band width between the e^{-1} points, over the time $t - t_a$, and the ratio $\frac{C + C_1}{C_1}$ is simply the ratio $\frac{t}{t - t_a}$. In practice, it is more convenient to measure the bandwidth at half height, δt_0, which is $\sqrt{lge^2}$ smaller than the band width between e^{-1} points, and Equation 42 may be written entirely in terms of conveniently measured quantities:

$$n_0 = 8lge^2\,\frac{t(t - ta)}{\delta t_0^2} = 5.54\,\frac{t(t - t_0)}{\delta t_0^2} \qquad (43)$$

If $t - t_a$ were replaced by t in Equation 43, that expression would then be equivalent to the formula given by Phillips (*5*).

CONCLUSIONS

The flow rate of any component is proportional to the flow rate of the carrier gas (Equation 25.)

When the condition of linearity is met, the elution curves in gas chromatography have nearly the symmetrical shape of error functions.

There is an optimum flow rate for maximum band separation, and the maximum band separation obtained with the optimum flow rate is nearly independent of the mobile and static capacities, C and C_1, when $C_1 >> C$—i.e., when $t >> t_a$.

The maximum band separation is proportional to the square root of the column's length and to the fourth root of the diffusion parameters, G and R.

For a given component, the number of theoretical plates of a column is proportional to the product of the transport time of that component times the time interval between the elution of an inert component and that component, and inversely proportional to the square of the band width of that component.

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Titration of Isomeric Substituted 5-Amino-1,2,3-triazoles in Nonaqueous Media

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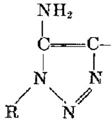
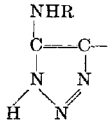
▶ Nonaqueous titration techniques with isomeric substituted 5-amino-1,2,3-triazoles have been compared with the usual aqueous methods. Anhydrous dimethylformamide solvent and sodium methoxide titrant with azo violet as visual indicator provide an accurate method for the determination of the acidic isomer, while glacial acetic acid solvent and perchloric acid titrant provide a method for the basic isomer.

During an investigation (*4*) on the synthesis and isomerization of 4-phenyl-5-amino-1,2,3-triazoles substituted in the 1- and 5-(amino)-positions (I and II, respectively)

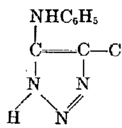


I



II

it became evident that estimation of the acidic isomer (II) by the method originally proposed by Dimroth (*1*), for ethyl 5-anilino-1,2,3-triazole-4-carboxylate (III)



III

by titration with alcoholic potassium hydroxide with phenolphthalein indicator, could not be used for Type II compounds because of weaker acidic properties and lower solubility in aqueous alcoholic solvents. Titrations in nonaqueous media have been found to be applicable in a large number of cases to weak acids and bases (*2*, *3*). The present study relates to a determination of the applicability of nonaqueous titration techniques to compounds of Types I and II and their mixtures.

REAGENTS

Dimethylformamide, technical grade, dried over calcium hydride.

Ethylenediamine, 95 to 100% technical grade.

Sodium methoxide, dissolved in methanol, diluted with benzene, and standardized against benzoic acid.

Azo violet indicator, saturated solution of *p*-nitrobenzeneazoresorcinol in benzene.

o-Nitroaniline indicator, 0.15 gram of *o*-nitroaniline in 100 ml. of benzene.

Glacial acetic acid, commercial grade.

Methyl violet indicator, 0.2 gram of methyl violet in 100 ml. of chlorobenzene.

Perchloric acid, 0.1N in acetic acid, prepared by procedure of Fritz (*2*).

PROCEDURE AND RESULTS

COMPARATIVE METHODS FOR ACIDIC ISOMER (II). Five different procedures for the estimation of the acidic isomer (II) were carried out on an analytically pure sample (*4*) of 4-phenyl-5-anilino-1,2,3-triazole (II, R = C_6H_5—). The results are summarized in Table I.

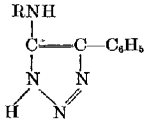
ESTIMATION OF A SERIES OF ACIDIC TYPE ISOMERS (II). Method 4 (Table I), using dimethylformamide solvent and sodium methoxide titrant with potentiometric indicator, was tested on a series of acidic isomers (II), which had given acceptable elementary analyses (*4*) for carbon, hydrogen, nitrogen, and chlorine or bromine. The results are summarized in Table II.

Table I. Titration of 4-Phenyl-5-anilino-1,2,3-triazole

Method	Solvent	Titrant	Indicator	% Recovery
1	Ethyl alcohol[a]	NaOH[b]	Phenolphthalein	98.12[c]
2	Dimethylformamide	NaOMe	Azo violet[d]	100.12
3	Ethylenediamine	NaOMe	*o*-Nitraniline	100.53
4	Dimethylformamide	NaOMe	Potentiometric[e]	100.04
5	Ethylenediamine	NaOMe	Potentiometric	98.38

[a] Diluted 50% with water.
[b] 0.1N aqueous solution.
[c] It is necessary to standardize on shade of pink or red.
[d] Sharp end point was obtained.
[e] Equipment described in (*2*). Sharp end point break.

Table II. Estimation of 5-(substituted phenyl)amino-4-phenyl-1,2,3-triazoles



R =	% Recovery
C_6H_5—	100.05
$C_6H_5CH_2$—	100.02
4-$NO_2C_6H_4$—	100.10
3-ClC_6H_4—	100.03
β-$C_{10}H_7$—	100.00
4-$CH_3C_6H_4$—	100.01
4-$CH_3OC_6H_4$—	100.02
4-ClC_6H_4—	99.99
4-BrC_6H_4—	100.03

ESTIMATION OF A MIXTURE OF ISOMERS (I and II). An impure sample of the basic isomer, 1,4-diphenyl-5-amino-1,2,3-triazole (I, R = C_6H_5—), containing only a small amount of the acidic isomer (II, R = C_6H_5—) and having a melting point of 168.5° to 169° C. was analysed by two procedures. The basic isomer was estimated by titration using glacial acetic acid as solvent and perchloric acid in acetic acid as titrant, with methyl violet indicator. The first appearance of a blue color was taken as the end point. In the second procedure the small proportion of acidic isomer present in the mixture was determined by method 2 (Table I) using dimethylformamide solvent and sodium methoxide titrant with azo violet indicator. Both titrations were carried out in a 40-ml. centrifuge tube. The results for both procedures are summarized in Table III.

Table III. Titration of Mixture of 1,4-Diphenyl-5-amino-1,2,3-triazole and 4-Phenyl-5-anilino-1,2,3-triazole

Estimation of Basic Isomer in Acetic Acid Solvent[a]

Sample, gram	Basic isomer, gram	% basic isomer
0.2443	0.2338	95.69
0.1932	0.1843	95.40

Estimation of Acidic Isomer in Dimethylformamide Solvent[b]

Sample, gram	Acid isomer, gram	% Basic isomer[c]
0.2684	0.0121	95.50
0.1758	0.0079	95.49
	Av.	95.52

[a] Perchloric acid in acetic acid as titrant, methyl violet as indicator.

[b] $NaOCH_3$ as titrant, azo violet as indicator.

[c] By difference.

DISCUSSION

A comparison of nonaqueous titration techniques to titration in aqueous medium shows that the most accurate method is that of potentiometric indicator in dimethylformamide, method 4. However, the greater convenience of a visual indicator in the same solvent more than offsets the slight decrease in accuracy which method 2 entails. Method 4 was further tested on a series of analytically pure 5-(substituted phenyl)amino-4-phenyl-1,2,3-triazoles; results indicate that the method is essentially stoichiometric. Hence, it is recommended in estimations involving compounds of Type II and has been used for further research in this field (*4*).

The importance of having available an accurate nonaqueous titration technique for the estimation of either the basic or acidic component in a mixture of these isomers is illustrated by Table III. Lieber, Chao, and Rao (*4*) have demonstrated that isomers I and II can form a true equilibrium system in which the equilibrium can be approached from either isomer. Synthetically, I is usually made first and II is produced from it by an irreversible thermal isomerization. In attempts to purify I or II, care must be taken that the purification, usually involving recrystallization from a suitable solvent, does not again induce isomerization. This would result in an impure isomer. The elementary analysis does not reveal this and frequently the melting point is misleading. As exact composition–melting point diagrams are unavailable for such systems, nonaqueous titration techniques offer valuable aid in following the purity of the preparation.

ACKNOWLEDGMENT

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Anodic Stripping Polarography

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▶ Anodic stripping polarography is a method of analysis by which a metal is deposited on an electrode and anodically removed under controlled conditions. Using this procedure it was possible to detect metallic ions at concentrations as low as 10^{-4} γ per ml. and to determine lead and cadmium in spectrographically pure zinc. In contrast to other electrodes, no pretreatment was necessary for a small mercury electrode and no change in calibration values was observed over a period of 8 months. Half-peak potentials are independent of concentration and agree closely with the half-wave potentials obtained at a dropping mercury electrode. Analyses were carried out on solutions of copper(II), lead(II), cadmium(II), and thallium(I) from 2×10^{-4} to 2×10^{-8} M. The method is applicable only to metals which can be deposited in mercury and anodically removed.

THE controlled anodic dissolution of metals which have been plated onto an electrode has been studied as a method of analysis. Zakhar'evskii (*10*) deposited metals into a mercury cathode and coulometrically removed them at constant current. Lord, O'Neill, and Rogers (*6*) plated metals onto a rotating platinum electrode, removed them anodically, and integrated the area under the current-time curve. This area was proportional to the amount of metallic ion in solution. Later Gardiner and Rogers (*3*) coated a stationary platinum electrode with a layer of mercury in order to minimize surface effects, and were able to determine cadmium and zinc in dilute solutions.

Procedures of this general type offer an advantage over conventional polarographic methods for the analysis of dilute solutions. If the cathodic deposition current is too small to be readily detected, the metal can be accumulated on the electrode for a relatively long time and then removed suddenly, resulting in a more easily measurable current.

Initially, it appeared that the best electrode would be an inert metal such as platinum, so that the deposited metal could be accumulated in a thin layer at the electrode-solution interface. A relatively large surge of current would be obtained on the anodic cycle (*6*). The method offered a high sensitivity but when applied to dilute solutions the results were erratic and frequent recalibration was necessary. Surface oxide films and absorbed oxygen and hydrogen accounted for some of these difficulties (*5*). A gold wire electrode was also tried but no significant increase in reproducibility was noted.

To minimize the difficulties associated with solid surfaces, a rotating silver wire electrode was coated with mercury. A high sensitivity was obtained, but surface conditioning and reproducibility was again a problem. Gardiner and Rogers had better success in obtaining long-term reproducibility by using the stationary mercury-plated platinum electrode (*3*).

Platinum, gold, amalgamated silver, and mercury-coated platinum electrodes required a surface preconditioning procedure so that reliable results could be obtained. Serious difficulties were encountered when any of these electrodes was used in the analysis of solutions containing more than one reducible ion. When two metals were plated from solutions, interaction between the two caused difficulty on the stripping cycle.

A mercury pool electrode about 3 sq. cm. was successfully applied to cathodic polarographic depositions (*7*). The solution above the electrode was agitated by a glass stirrer to increase the rate of deposition and accumulate more metal for the stripping cycle. When the deposited metals were anodically removed from this large mercury electrode, the rate of electro-oxidation was low. The resultant current-time curves exhibited broad peaks; sensitivity was poor compared to other electrodes. The stirring action distributed the metal uniformly throughout the mercury and little concentration occurred at the surface of the electrodes. The anodic current was, therefore, limited by the rate of diffusion of the metal through the amalgam to the surface of the electrode. If the solution was not stirred, more time was required to deposit equivalent amounts of metals and appreciable diffusion into the mercury was again evident.

To decrease the diffusion of metal into the amalgam, a much smaller electrode (about 0.05 sq. cm.) was devised in which the mercury was confined in a capillary as illustrated in Figure 1. This electrode had significant advantages over others studied. The solution above the electrode could be stirred rapidly to increase the amount of metal accumulated on the cathodic cycle. However, because the mercury was confined to the capillary, little agitation occurred in the mercury phase. A large percentage of the metal remained near the surface of the electrode and was available for rapid anodic dissolution. The purpose of this investigation was to evaluate the possible analytical applications of this electrode for the anodic dissolution of metals deposited from dilute solutions.

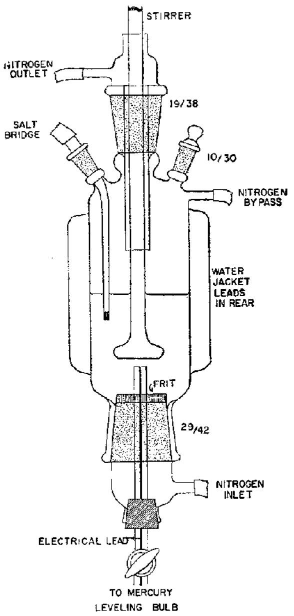

Figure 1. Cell

APPARATUS AND GENERAL PROCEDURE

The electrolysis cell (volume about 25 ml.) is illustrated in Figure 1. A constant temperature of 25° C. was maintained by circulation of thermostated water through the external jacket of the apparatus. Oxygen was removed from the solutions by forcing nitrogen through a sintered glass disk. Seaford grade nitrogen was saturated by passing through water, and used without further purification. The stirrer (Scientific Glass Apparatus Co., Inc. Precision bore stirrer No. J-2170-1) was driven by a synchronous motor at a speed of 600 r.p.m. A conventional, motor-driven polarizing unit was used as a source of voltage. Currents were recorded by measuring the voltage drop across a set of precision resistances by means of a Leeds & Northrup Speedomax recorder (sensitivity, 1 mv.; time response, 1 second full scale).

The electrode consisted of the exposed area of a mercury thread contained in a capillary tube. The surface could be renewed and its area easily repro-

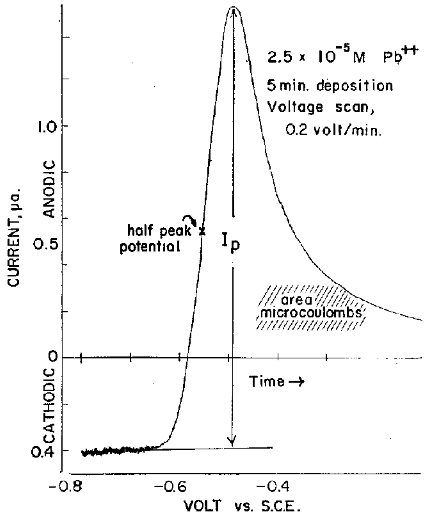

Figure 2. Dissolution curve

duced by ejecting a drop of mercury from the capillary, releveling by means of an external reservoir. This reservoir was constructed of a length of 5-mm. diameter glass tubing which could be raised and lowered with a screw knob adjustment. This electrode is similar to that proposed by Arthur (*1*) for polarographic measurements.

In making a run, a solution of metal plus supporting electrolyte was placed in the cell and nitrogen was passed through the sintered-glass disk for 10 to 15 minutes and then bypassed through a water trap to maintain positive pressure and prevent back-diffusion of air into the cell. A small amount of mercury was then forced out of the capillary to renew the surface, the mercury level adjusted, the stirrer turned on, and the cathodic deposition voltage applied. The potassium nitrate used as a supporting electrolyte was purified by extraction of metal dithiozonates into chloroform followed by recrystallization. Generally, 0.1M solutions were used as supporting electrolytes. Stock solutions of the metal ions were analyzed by conventional techniques.

Three methods of applying anodic stripping procedures were evaluated using the small mercury electrode. In the first procedure the metal was deposited by applying a voltage to the electrode which corresponded to a point in the plateau region of the voltage-current curve. After a specific time, the voltage was scanned to a value which would electrolytically oxidize the metal from the amalgam. This voltage was then maintained constant and the current-time curve was recorded. The area under the curve was integrated with a planimeter and correlated with the amount of metallic ion in the original solution. About 30 minutes were necessary to recover 99% of the available metal anodically. Precision was poor.

The second method was similar to the first, except that the anodic process was allowed to proceed for 10 minutes rather than attempting to integrate the entire curve. There was no appreciable increase in precision. Difficulties were experienced at low concentrations because of the residual current associated with the electrode. The zero current line could not be used as one of the boundaries of the area to be measured and the choice of this line was arbitrary.

The third method involved the usual deposition procedure followed by scanning of the voltage toward a positive value. Rather than determining the area, the peak height was measured as illustrated in Figure 2. This procedure was sensitive and had better reproducibility. Peak heights were proportional to concentration and half-peak potentials could be used to identify the metal. Further research effort was concentrated on a study of this method.

Table I. Half-Peak Potentials of Various Metals[a]

	Volts *vs.* S.C.E.				
Concn., M	Tl^+	Cu^{++}	Pb^{++b}	Cd^{++}	Zn^{++}
1×10^{-4}	0.47	0.01	0.53	0.55	−1.07
5×10^{-5}	0.48	0.02	0.57	0.57	
1×10^{-5}	0.51	0.03	0.57	0.60	
5×10^{-6}	0.51	0.03	0.59	0.60	
1×10^{-6}	0.52	0.03	0.58	0.60	−1.07
5×10^{-7}	0.52	0.03	0.60	0.60	
2×10^{-7}	0.52	0.03	0.60	0.60	
	0.46[c]	0.02[c]	0.58[b,c]	0.58[c]	−1.00[c]

[a] Supporting electrolyte, 0.1M KNO_3.
[b] Supporting electrolyte, 0.1M potassium sodium tartrate.
[c] Potential obtained at dropping mercury electrode.

Table II. Peak Currents Obtained at Various Concentrations[a]

	Microamperes × 10^4/Mole/Liter			
Concn., M	Tl^+	Cu^{++b}	Pb^{++}	Cd^{++}
2.5×10^{-5}	...	8.03	...	6.99
1.0×10^{-5}	6.70	8.25	8.19	7.52
5×10^{-6}	...	8.07	8.62	7.43
2.5×10^{-6}	6.67	8.10	...	7.27
1.0×10^{-6}	6.60	...	8.40	...
5×10^{-7}	6.80	7.90	8.00	7.77
2×10^{-7}	6.50	8.47	8.40	7.78
	Av. 6.65 ± 0.08	8.14 ± 0.16	8.32 ± 0.48	7.46 ± 0.29

[a] Plating time, 300 seconds; voltage scanning rate, 0.2 volt per minute.
[b] Plating time, 105 seconds.

PEAK POTENTIALS

Half-Peak Potential. As the concentration of metallic ion varied, the potential at which the anodic peak appeared was found to change. However, the voltage corresponding to a current value of one half the maximum current, or half-peak potential (Figure 2), was independent of concentration as shown in Table I. The half-peak potentials agreed closely with the value of the half-wave potential obtained at a dropping mercury electrode, and were independent of the length of plating time as well as the rate of anodic voltage scanning.

In the runs involving copper it was necessary to exclude chloride ion from the solution, the potassium nitrate was substituted for the saturated potassium chloride in the salt bridge. The presence of chloride ion reduced the anodic potential at which mercury was oxidized and the oxidation of the copper metal was obscured.

Linearity of Peak Height *vs.* Concentration. The relationship between the height of the anodic peak and the concentration of the ion in solution approached linearity when all other parameters were kept constant. A summary of the data is shown in Table II.

Influence of Voltage Scanning Rate. In a previous study (*9*) in which cathodic polarograms were recorded at a quiet mercury pool electrode, the cathodic current peaks obtained were similar to the anodic peak shown in Figure 2. The cathodic peak heights increased at higher voltage scanning rates in accordance with the Sevcik equation which was derived for oscillographic polarography (*8*):

$$i_{\max.} = 217\ A n^{3/2} v^{1/2} D^{1/2} C$$

where

A = electrode area, square centimeters
n = number of electrons involved
v = rate of voltage scanning in volts per second
D = diffusion coefficient of ion, square centimeters per second
C = concentration in moles per liter

The variation of the anodic current peak with this parameter was studied and the same relationship was found as indicated by the data plotted in Figure 3. It was hoped that the entire Sevcik relationship could be applied to the peaks obtained on the anodic cycle but the experiment was complicated by the nonuniform concentration of metal in the amalgam.

Voltage scanning rates of 1.2 volts per minute allowed analyses to be run on solutions as dilute as $2 \times 10^{-8}M$. The peak heights increased still further at higher scanning rates, but the response time of the recorder was too slow for accurate measurements under these conditions. An oscillographic recorder might possibly increase the sensitivity.

Reproducibility of Peak Currents. Sets of about five runs were made at ten different concentrations for each of the following ions: thallium(I), copper(II), lead(II), and cadmium(II). The conditions of plating time and rate of voltage scanning are recorded in Table II. The average deviation from the mean for each set was then averaged for each metal. The values obtained were 4.1% for thallium, 2.7% for copper, 3.2% for lead, and 3.3% for cadmium.

The deposition and stripping of zinc ion in 0.1*M* potassium nitrate presented difficulties. The extrapolation of the base line in measuring anodic peak heights was not as precise as other metals because of the closeness of the hydrogen discharge potential. Occasionally abnormally high peaks were obtained for zinc solutions which were apparently run under the same conditions. This difficulty was probably caused by changes of the electrode surface upon the application of high negative potentials (*4*).

The precision obtained with lead ions was poor when 0.1*M* potassium nitrate was used as supporting electrolyte. When 0.1*M* sodium potassium tartrate was used, reasonable precision was found. This same phenomena was noted in cathodic polarograms at low concentration levels (*7*).

There was no significant change in the calibration values for two sets of analyses run 8 months apart on a $10^{-5}M$ solution of lead ion.

DURATION OF PLATING CYCLE

One of the important variables affecting the anodic peak heights was the amount of metal deposited, or the duration of the plating cycle. To a certain extent the peaks increased with increasing deposition times. However, some metal is always lost into the mercury and is not available for the stripping cycle. Prolonging the duration of plating beyond a certain time will not cause further increase in peak heights. Beyond this point available metal is lost by diffusion into the amalgam at the same rate it is deposited from solution. This is shown by the curve in Figure 4.

At concentrations greater than $10^{-5}M$ plating times were kept short to reduce the amount of metal deposited, and a cathodic cycle of 25 seconds was convenient. Table III shows the reproducibility and linearity obtained in this concentration region. A plating time of 5 minutes was used for concentrations between 10^{-5} and $10^{-6}M$. A longer cathodic cycle, consistent with sensitivity and convenience, is recommended with more dilute solutions. These time cycles are not critical and are so chosen to give peak heights of reasonable magnitudes. In general better precision was obtained for shorter plating times.

Table III. Peak Current Values of Cadmium Solutions Plated for 25 Seconds

Concn., *M*	Microamperes × 10^4/Mole/Liter
10^{-5}	3.31
5×10^{-5}	3.30
10^{-4}	3.35
2×10^{-4}	3.30
5×10^{-4}	3.28
	Av. 3.31 ± 0.02

EFFECT OF CELL GEOMETRY ON SENSITIVITY

A comparison was made of three electrodes of different areas to study the effect of size on sensitivity. Glass tubing of bore diameters 0.503, 0.171, and 0.071 cm. contained the mercury. The approximate areas of the two smaller electrodes were calculated on the assumption they were hemispheres, while the area of the large electrode was calculated as a plane surface 0.503 cm. in diameter. An anodic peak was recorded with the three electrodes for a solution of $10^{-5}M$ thallous ion in 0.1*M* potassium nitrate.

Table IV. Effect of Electrode Area on Peak Heights

Estimated Electrode Area, Sq. Cm.	Peak Current, μ a.	Peak Current Density, μ a./Sq. Cm.
0.0078	0.102	13.1
0.042	0.94	22.2
0.79	4.3	5.4

Table IV shows that a considerably higher anodic peak current density was observed with the 0.042 electrode even though the cathodic current densities of the 0.042 and 0.79 sq. cm. electrodes were about the same. The anodic curves obtained with the 0.79 sq. cm. electrode exhibited broad plateaus rather than current peaks. This would make it difficult to determine mixtures of metals, since the anodic waves would merge together rather than exhibit individual peaks. When such a large electrode is used, the mercury is stirred by the motion of the solution and an appreciable quantity of deposited metal is removed from the

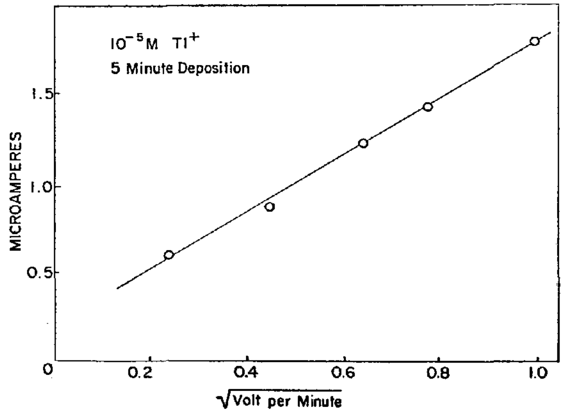

Figure 3. Peak height vs. $\sqrt{\text{rate of voltage scanning}}$

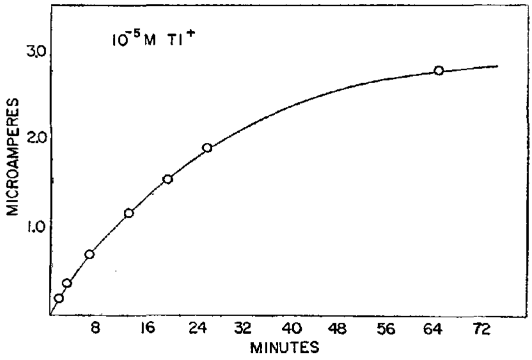

Figure 4. Peak height vs. deposition time

surface and is not therefore readily available for rapid anodic removal. When the 0.0078- and the 0.0432- sq. cm. electrodes were compared, the latter exhibited a higher current density on the stripping cycle. Such variations of current densities with area are not unexpected with small electrodes in stirred solutions (*2*). Electrodes of diameter less than 0.05 cm. were difficult to level.

The effect of the stirrer-electrode distance on the peak values was investigated. The data are summarized in Figure 5. In contrast with work on larger electrodes (*7*), the currents increased with increasing stirrer-electrode distance because the electrode was small compared to the size of the stirrer blades and a shielding effect came into play at short distances. The electrode was centered below the stirrer, and as the distance between the two became smaller, the solution at the electrode surface was stirred only by the slower moving center portion of the propeller. As the distance became larger, more rapid movement of the solution at the interface occurred. The smaller anodic peaks at short stirrer-electrode distances were the direct effect of a smaller amount of metal being deposited on the cathodic cycle. Beyond a distance of about 3 mm. the separation was no longer critical; the stirrer was permanently fixed at a distance of 4 to 5 mm. from the electrode.

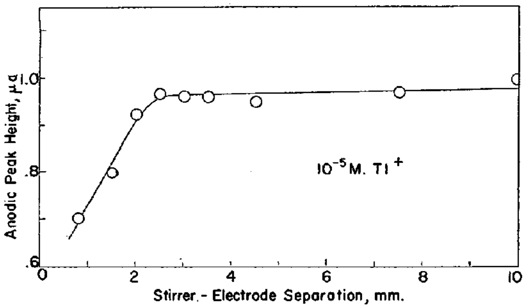

Figure 5. Effect of stirrer-electrode distance on peak values

APPLICATION TO DILUTE SOLUTIONS

A series of analyses was run on lead and cadmium solutions in the range 10^{-6} to $2 \times 10^{-8}M$. A plating time of 35 minutes and a voltage scanning rate of 1.2 volts per minute were used. One of these anodic polarograms for a solution of $5 \times 10^{-8}M$ cadmium(II) is shown in Figure 6. Currents above the zero line are anodic and those below are cathodic. An appreciable signal was obtained even at these high dilutions. The linearity and reproducibility of the data in this concentration range is summarized in Table V.

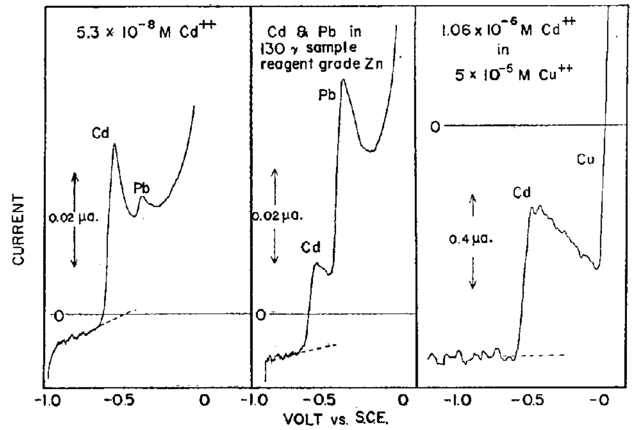

Figure 6. Anodic polarograms

Table V. Peak Current Values Obtained at Low Concentrations of Cadmium and Lead Solutions[a]

Concn., *M*	Microamperes × 10^4/ Mole/Liter	
	Pb^{++}	Cd^{++}
10^{-6}	25.1	59.1
5×10^{-7}	27.1	55.7
2×10^{-7}	26.0	
10^{-7}	24.0	58.7
5×10^{-8}	30.0	57.5
2×10^{-8}		58.5
Av.	26.4±0.17	57.4±0.11

[a] Plating time, 35 minutes; applied potential scanned at 1.2 volts per minute. Supporting electrolyte used, 0.1*M* KNO_3 for Cd^{++} soln., 0.01$NaKC_4H_4O_6 \cdot 4H_2O$ for Pb^{++} soln.

RESOLUTION AND ANALYSIS OF MIXTURES

A series of experiments evaluated the applicability of the mercury electrode to mixtures of reducible metals. In some situations selectivity can be attained by choosing an appropriate value for the deposition potential. For example, small amounts of lead and cadmium were determined in a zinc solution by carrying out the deposition at a potential of −0.9 volt versus the standard calomel electrode. Only the lead and cadmium were deposited and the presence of large amounts of zinc caused no interference. Figure 6 shows an anodic polarogram of the cadmium and zinc present in a 130-γ sample of reagent grade zinc metal. Even though the amount of the sample is small, the lead and cadmium can be readily determined. The percentages found were 0.02% for cadmium and 0.04% for lead. The procedure was checked by standard addition of known amounts of the two ions. It was also possible by using a highly concentrated zinc solution (0.1*M*) to detect the presence of cadmium and lead in highly purified zinc (Johnson Matthey & Co., Inc., spectrographically pure grade). The percentages were 0.00003% cadmium and 0.00006% lead.

Studies were carried out on the determination of cadmium in the presence of an excess of copper. The supporting electrolyte was 0.01*N* potassium nitrate and the copper was deposited along with the cadmium. It was found possible to determine cadmium in a hundredfold excess of copper. There was no apparent change in anodic peak heights for the dissolution of cadmium, even though appreciable quantities of deposited copper were present in the mercury. The maximum ratio which could be tolerated was limited by the fluctuations in the cathodic current for the deposition of copper in the region where the cadmium was being oxidized. This situation is illustrated in Figure 6 in which a cadmium polarogram is recorded in a 50-fold excess of copper. Although the concentration of copper was relatively high, this current-voltage curve was recorded at a high current sensitivity. Consequently, a reasonably high peak for the dissolution of cadmium was obtained. However, the current fluctuations for the cathodic process were magnified and decreased the precision of the peak measurements. At molarity ratios of 100 to one the standard deviation was about 5%. At smaller ratios the precision was higher.

Further studies were carried out to evaluate the method for mixtures of metals which have half-peak potentials close together. Cadmium and thallium in 0.1M potassium nitrate have half-peak potentials of −0.58 and −0.51 volt, respectively, and mixtures of these ions were prepared in various concentrations and ratios. The effect of the presence of thallium on the anodic peak height of cadmium can be evaluated from the data in Table VI.

When the concentrations of the two ions were about equal, the cadmium was readily determined. If there was five times as much thallium as cadmium, the two waves merged together and the analysis was no longer possible at this separation of half-peak potentials. If it is desired to determine the thallium, a deposition potential could be chosen so that only the thallium would be deposited.

As the difference between the half-peak potentials increases, the allowable ratio which can be tolerated also increases. This was illustrated by mixtures of cadmium and thallium in a 0.05M ammonium hydroxide–0.05M ammonium chloride supporting electrolyte. Anodic polarograms of such mixtures are shown in Figure 7. The separation of potentials was 0.26 volt, the cadmium being −0.77 volt, and the thallium −0.51 volt. As shown in Table VI, much larger quantities of thallium could be tolerated under these circumstances. One hundred times as much thallium as cadmium caused no significant difficulty. This sharp resolution is possible because of the large slope of the anodic peaks which minimize overlapping of the waves of individual metals.

DISCUSSION

When a solid electrode is used for the deposition of an ion, the metal can be anodically recovered with 100% efficiency. With a mercury electrode some of the deposited metal is always lost by diffusion away from the surface into the mercury. To evaluate the magnitude of the loss a study was made by integrating cathodic and anodic current-time curves to determine the relative amounts of metal deposited and reoxidized. After deposition of the metal, the voltage was scanned to a value sufficiently positive to produce oxidation and the current recorded until its value was essentially zero. When the amount of metal deposited was below 10 microcoulombs it was found that about 50% of the deposited metal was recovered. At higher concentrations, and/or at longer plating times the percentage of metal lost by diffusion decreases sharply as shown in Figure 8. Below 10 microcoulombs the amount of metal lost is proportional to the amount plated. Above this point the quantity lost is constant and independent of the amount of deposited metal. No explanation has been found for this unexpected behavior.

Even though the proposed method offers a high sensitivity, only a small percentage of the available sample is actually used in the analysis. In 5 minutes' plating time only 0.25% of the metallic ion present in the 25 ml. of solution was deposited on the electrode and only one half of this was recovered on the anodic cycle. One way this waste of sample could be avoided would be to decrease the sample volume so a higher percentage of the desired ion could be deposited from solution. Twenty-five milliliters was chosen as a convenient volume but much smaller cells could be designed by using a vibrating glass rod for agitation rather than

Table VI. Errors Introduced in Anodic Peak Heights of Cadmium by Presence of Thallium

Concentrations, M		Accuracy, %	
Cd^{++}	Tl^{+}	0.07-volt separation	0.26-volt separation
10^{-5}	10^{-5}	2	1
10^{-6}	10^{-6}	2	3
2×10^{-7}	2×10^{-7}	. . .	5
10^{-5}	10^{-6}	1	1
10^{-6}	5×10^{-6}	Not resolvable	. .
10^{-6}	10^{-5}	Not resolvable	0

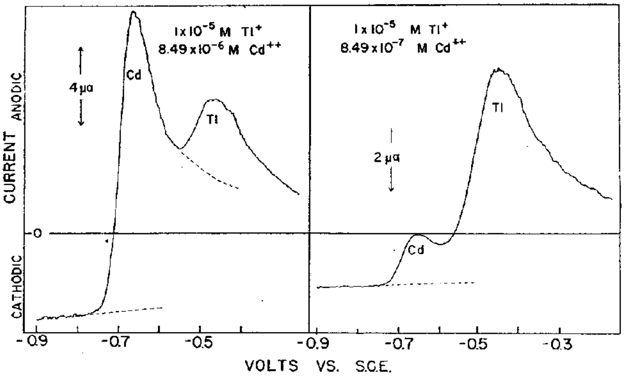

Figure 7. Anodic polarograms, mixtures of two ions

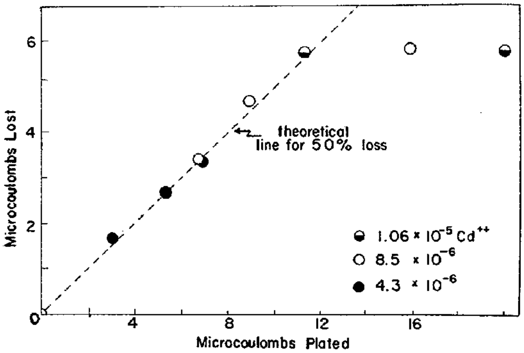

Figure 8. Recovery efficiency

a stirrer. The absolute sample size could then be reduced.

SUMMARY

The electrode is easily reproducible, no pretreatment of any kind is necessary, and calibration values can be maintained over a long period of time. In contrast to other systems, interaction between mixtures of deposited metals is minimized and resolutions of mixtures can be accomplished which are not possible by conventional polarography. The sensitivity of the method is high and solutions as dilute as 0.001 γ per ml. can be analyzed. On the other hand, the precision of the method is only about 3 to 4%, but this is normally adequate at such low concentrations.

ACKNOWLEDGMENT

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Determination of Traces of Potassium in Reagent Chemicals by Sodium Tetraphenylboron and Sodium Cobaltinitrite

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▶ Determination of traces of potassium by turbidimetric sodium cobaltinitrite and gravimetric sodium tetraphenylboron methods was investigated as well as the influence of excess sodium on accuracy. The recoverability and reproducibility of each method were evaluated when applied to reagent grade sodium salts and sodium hydroxide. Results were compared with flame photometric values.

THE increasing demand for chemicals of higher purity emphasizes a need for more accurate methods for determination of trace metals. This paper is primarily concerned with the comparison of the turbidimetric sodium cobaltinitrite (*1*) and gravimetric sodium tetraphenylboron methods for determination of trace amounts of potassium in reagent grade chemicals. The sodium cobaltinitrite gravimetric method is included only to show a direct comparison between two gravimetric procedures. Gravimetric and volumetric methods using sodium tetraphenylboron have been described extensively in the literature (*3*). The authors chose the gravimetric method for simplicity and accuracy.

Solutions containing known amounts of potassium were prepared and the potassium content was determined gravimetrically with sodium cobaltinitrite and sodium tetraphenylboron. A turbidimetric determination of potassium was also made with sodium cobaltinitrite and read on an electrophotometer for greater accuracy. A known amount of sodium ion was added to the solution and the potassium content again determined to show the marked influence of excess sodium on the turbidimetric determination.

Seven sodium salts and sodium hydroxide conforming to ACS specifications (*1*), which require a potassium determination, were analyzed for potassium turbidimetrically with sodium cobaltinitrite and gravimetrically with sodium tetraphenylboron. The results were compared with flame photometric values (Table I). Potassium in sodium acetate was determined by the first two of these methods. Known amounts of potassium were added in order to determine the recoverability of potassium by both methods, in the presence of the large amount of sodium ion in the salt.

APPARATUS AND REAGENTS

ELECTROPHOTOMETER, Fisher Scientific Co. AC Model, equipped with a 650-mμ filter.

SPECTROPHOTOMETER, Beckman Model DU with flame attachment.

SODIUM COBALTINITRITE TEST SOLUTION. Dissolve 25 grams of sodium nitrite ($NaNO_2$) in 50 ml. of water, add 5 ml. of glacial acetic acid and 3 grams

Table I. Per Cent Potassium in Reagent Grade Chemicals

	Method			
	ACS specification[a]	Sodium cobaltinitrite	Sodium tetraphenylboron	Flame photometer
Sodium acetate ($NaC_2H_3O_2.3H_2O$)	335	0.005	0.004	0.005
Sodium bicarbonate ($NaCHO_3$)	338	0.005	0.002	0.002
Sodium carbonate, anhydrate (Na_2CO_3)	346	0.005	0.0009	0.002
Sodium carbonate, monohydrate ($Na_2CO_3.H_2O$)	350	0.003	0.003	0.004
Sodium chloride ($NaCl$)	354	0.001	0.0008	0.001
Sodium hydroxide ($NaOH$)	364	0.01	0.001	0.002
Sodium nitrite ($NaNO_2$)	369	0.002	0.0008	0.001
Sodium oxalate ($Na_2C_2O_4$)	372	0.005	0.001	0.002

[a] No. refers to page (*1*).

of cobalt nitrate [$Co(NO_3)_2.6H_2O$] dissolved in 15 ml. of water, and dilute to 100 ml. Make a fresh solution for each set of tests (*2*).

Sodium Tetraphenylboron Test Solution. Dissolve 1.2 grams of sodium tetraphenylboron in 100 ml. of water and shake with 0.5 gram of alkali free aluminum oxide (Al_2O_3) for 5 minutes. Filter; refilter the initial portions if they are turbid (*6*).

Potassium Solution A. Dissolve exactly 5.000 grams of 99.95% reagent grade potassium biphthalate in a minimum amount of water and dilute to exactly 250 ml. Each 10-ml. aliquot contains 38.2 mg. of potassium ion.

Potassium Solution B. Dissolve 0.5224 gram of 99.95% reagent grade potassium biphthalate in a minimum of water and dilute to 1 liter. One milliliter contains 0.1 mg. of potassium ion.

Sodium Tetraphenylboron Wash Solution. Dilute 10 ml. of sodium tetraphenylboron test solution to 100 ml.

Sodium Solution. Dissolve 35.676 grams of reagent grade anhydrous sodium acetate in a minimum amount of water and dilute to 100 ml. One milliliter of the solution contains 100 mg. of sodium.

EXPERIMENTAL

Gravimetric Sodium Cobaltinitrite Procedure. Exactly 10 ml. of potassium solution A was diluted to 100 ml. with water, 25 ml. of sodium cobaltinitrite test solution was added, and the solution was warmed to 70° C. It was cooled and filtered through a tared Gooch crucible. The precipitate was washed with water, dried at 100° C. for 2 hours, cooled, and weighed. This same procedure was repeated, adding 5-ml. aliquots of sodium solution to each 10 ml. of potassium solution A. The results are shown in Table II.

Gravimetric Sodium Tetraphenylboron Procedure. Exactly 10 ml. of potassium solution A was diluted to 100 ml. with water; 2 ml. of 1 to 1 acetic acid and 25 ml. of sodium tetraphenylboron test solution were added with stirring. The solution was allowed to stand for 1 hour, filtered through a tared Gooch crucible, and washed with three 5-ml. portions of sodium tetraphenylboron wash solution. The precipitate was dried for 2 hours at 110° C., cooled, and weighed as potassium tetraphenylboron. This same procedure was repeated adding 5 ml. of sodium solution to each 10 ml. of potassium solution A. The results are shown in Table II.

Turbidimetric Sodium Cobaltinitrite Procedure. A series of standards was prepared containing 5 to 20 p.p.m. (*7*) of potassium solution B. The standards were diluted to 20 ml. with water, and 5 ml. of sodium cobaltinitrite test solution was added.

The solutions were diluted to exactly 50 ml. with ethyl alcohol with stirring and read with an electrophotometer using a 650-mμ filter. This same procedure was repeated, adding 5 ml. of sodium solution to each standard. The results are plotted in Figure 1.

Table II. Effect of Sodium on Gravimetric Methods

Mg. K Found[a]		Mg. K Found in Presence of 500 Mg. of Na[a]	
Sodium cobaltinitrite	Sodium tetraphenylboron	Sodium cobaltinitrite	Sodium tetraphenylboron
37.9	38.2	40.3	38.2
38.2	38.1	40.5	38.1
38.3	38.1	40.4	38.2

[a] K calcd., 38.2 mg.

Procedures for Sodium Salts and Sodium Hydroxide. The salts analyzed are listed in Table I.

Turbidimetric, Sodium Cobaltinitrite. The sodium compounds were checked for potassium content by ACS specifications (*1*).

Gravimetric, Sodium Tetraphenylboron Determinations. All of the compounds, except sodium chloride, were converted to the chlorides by dissolving 10 grams in a minimum amount of water, adding 10 ml. of hydrochloric acid, and evaporating to dryness. (The conversion to the chlorides was essential for three of the salts and sodium hydroxide whose alkaline solutions will precipitate sodium tetraphenylboron. Sodium nitrite may interfere by breaking down the phenyl group of tetraphenylboron.) The residue was dissolved in 10 ml. of 1 to 1 hydrochloric acid, re-evaporated to dryness, and dissolved in 25 ml. of water. The potassium content was determined gravimetrically with sodium tetraphenylboron. The results are shown in Table I.

Flame Photometric. Ten grams each of the salts and sodium hydroxide were converted to the chlorides. The final residue was diluted to exactly 100 ml. The potassium content was determined by the flame photometer at a wave length of 769 mμ with the slit set at 0.3 mm. and the selector switch at 0.1 mm. Standards were prepared at 2.0, 1.5, 1.0, and 0.5 p.p.m., and a graph was prepared from results obtained from these standards.

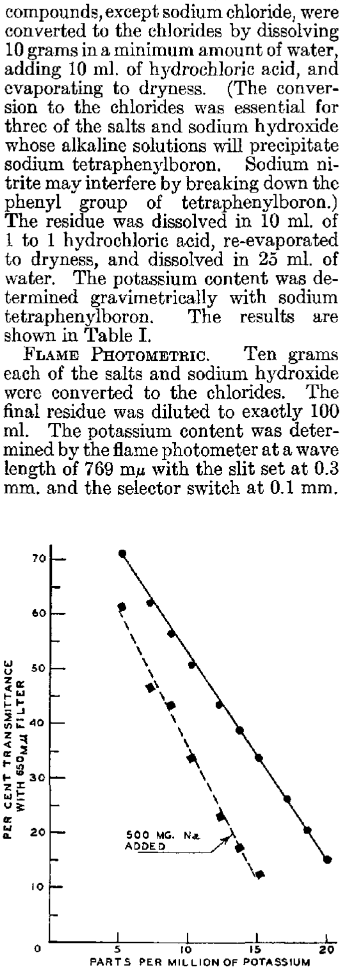

Figure 1. Interference of sodium in determination of potassium by sodium cobaltinitrite method

Table III. Potassium Recoverability in Sodium Acetate

Mg. K added	Mg. K recovered	Difference
Sodium Cobaltinitrite[a]		
0	0.02	..
0.01	0.02	−0.01
0.05	0.07	0
0.10	0.10	−0.02
Sodium Tetraphenylboron[b]		
0	0.02	..
0.01	0.03	0
0.05	0.07	0
0.10	0.11	−0.01

[a] Sensitivity = 0.02 mg. per gram.
[b] Sensitivity = 0.01 mg. per gram.

Potassium Recoverability with Sodium Cobaltinitrite. One gram of sodium acetate was dissolved in 5 ml. of water. Five milliliters of sodium cobaltinitrite and 10 ml. of ethyl alcohol were added with constant stirring. The turbidity of the sample was compared with 0.01-, 0.05-, and 0.10-mg. standards. Known amounts of potassium solution B were added to the sample, the above procedure was repeated, and the turbidity was again compared with the standards. The results are shown in Table III.

Potassium Recoverability with Sodium Tetraphenylboron. Ten grams of sodium acetate was run according to the above gravimetric sodium tetraphenylboron procedure. Known amounts of potassium were added and the procedure was repeated. The results are shown in Table III.

RESULTS AND DISCUSSION

The sodium cobaltinitrite method for the determination of potassium produces results that vary in the presence of certain cations, such as sodium. The marked influence of sodium ion can readily be seen in Table II and Figure 1. The graph shows the effect of sodium ion on the size and amount of the cobaltinitrite precipitate. Transmittance decreases in respect to the increased concentration of the potassium ion more rapidly in the presence of the added sodium ion. Since the sodium cobaltinitrite method for potassium provides no correction for the sodium ion, the results are inaccurate. The influence of sodium on the potassium determination with sodium tetraphenylboron shows little or no effect (Table II). Other ions that also interfere with the sodium cobaltinitrite method are iron, aluminum, calcium, magnesium, and copper (*4*). However, these elements as well as manganese, cobalt, nickel, sulfate, and phosphate do not interfere with the sodium tetraphenylboron method (*6*).

The determination of potassium in the sodium salts and sodium hydroxide by the sodium tetraphenylboron method gives results in closer agreement with the flame photometric findings than results obtained with the turbidimetric sodium cobaltinitrite method. In general, the variation in the two methods is greatest when the sodium ion concentration of the reagent is over 40%. Thus, good agreement was realized by each method for sodium carbonate monohydrate having a sodium content of 37%, whereas the anhydrous salt having a sodium content of 43.4% gave poor agreement. Sodium hydroxide, with a sodium content of 57.5%, showed the greatest variance.

The potassium recoverability of the sodium cobaltinitrite method is only half as sensitive as the sodium tetraphenylboron method and is limited in range from 10 to 20 p.p.m., as shown in Table III.

The salts of the sodium tetraphenylboron complex are well defined, the potassium salt corresponding exactly to the formula $KB(C_6H_5)_4$. The cobaltinitrite precipitate is usually a mixture of monopotassium disodium cobaltinitrite and dipotassium monosodium cobaltinitrite (*7*).

CONCLUSION

The recoverability of potassium and reproducibility of the sodium tetraphenylboron method demonstrate the suitability of this reagent as a replacement for sodium cobaltinitrite. Good filtering characteristics, extremely low solubility of its potassium salt (2.25×10^{-8}) (*5*), and the simplicity of the gravimetric method make sodium tetraphenylboron an excellent reagent for determination of traces of potassium in reagent chemicals.

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Separation and Determination of Neptunium by Liquid-Liquid Extraction

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▶ A rapid and quantitative radiochemical method for the determination of neptunium-237 or neptunium-239 tracer is based on the liquid-liquid extraction of neptunium(IV) into 0.5*M* 2 - thenoyltrifluoroacetone – xylene. Neptunium is separated free from interferences, both radioactive and nonradioactive. The technique may be adapted readily to remote control, and is very effective in the purification of neptunium tracer.

Operation of nuclear reactors of increased neutron flux has stimulated interest in the isolation and determination of the long-lived neptunium-237 alpha emitter ($t_{1/2} = 2.2 \times 10^6$ years). A method (*1*) had been developed previously for the determination of the neptunium-239 beta, gamma emitter ($t_{1/2} = 2.3$ days); however, because this method allowed approximately 16% of the plutonium originally present to follow through the procedure, it could not be used for the determination of neptunium-237.

It was necessary to develop a method which would achieve a clean separation of neptunium from fission products, uranium, plutonium, americium, and curium. A carrier-free method was desired to eliminate alpha absorption errors. Experience accumulated in the development of a solvent extraction method for the determination of plutonium (*4*) using the chelating agent, 2-thenoyltrifluoroacetone (TTA), suggested that an effective radiochemical procedure for the determination of neptunium-237 could be devised through the use of this reagent. Magnusson, Hindman, and La Chapelle (*3*) extracted neptunium-237 with 2-thenoyltrifluoroacetone–benzene away from plutonium and uranium under suitable reducing conditions. It was also desirable to use the new method for the isolation and determination of neptunium-239.

Certain substituted, fluorinated betadiketones react with metal ions to form nonionized chelate compounds which are soluble in nonpolar solvents immiscible with water. Many of these ions can be separated from each other because of the strong dependence of the extraction of these chelate compounds in nonpolar solvents on the acid concentration. Thomas and Crandall (*6*) report that very few aqueous ions extract appreciably from 0.5*M* nitric acid. These ions are zirconium(IV), plutonium(IV), neptunium(IV), cerium(IV), uranium (IV), iron(III), and tin(IV).

In the determination of neptunium-237, the most difficult separation is that of neptunium from the plutonium and uranium which are usually present in the solutions to be analyzed. Previous workers (*3*) have shown that under suitable reducing conditions a solution may contain neptunium(IV), plutonium(III), and uranium(VI), and the neptunium(IV) may be extracted with 2-thenoyltrifluoroacetone–benzene. This paper describes the optimum conditions developed for the quantitative recovery of neptunium-237 or -239 and the decontamination from the usual interferences of other radioelements.

REDUCTION OF PLUTONIUM

It was realized that the most difficult separation from alpha emitters would be that of neptunium from plutonium, while radiozirconium would be the most difficult of the beta-gamma emitters to remove. Plutonium had to be reduced quantitatively to the inextractable trivalent state and maintained in this reduced state during the extraction, while neptunium was reduced to the quadrivalent state which was readily extractable into 2-thenoyltrifluoroacetone–xylene from 1*M* hydrochloric acid or 1*M* nitric acid. Hydroxylamine hydrochloride, stannous chloride, potassium iodide, and ferrous chloride were tested for reduction efficiency in preliminary experiments.

Plutonium(IV) tracer was reduced for 5 minutes at room temperature and then the aqueous phase (1*M* nitric acid) was extracted for 10 minutes with an equal volume of 0.5*M* 2-thenoyltrifluoroacetone–xylene. Hydroxylamine hydrochloride was the least effective of the reagents tested for holding plutonium in the inextractable trivalent state during the extraction. However, by using very high concentrations of hydroxylamine hydrochloride (4.5*M*), it was possible to keep the plutonium approximately 97% in the trivalent state during the 10-minute extraction period. Stannous chloride, potassium iodide, and ferrous chloride were effective reductants. Stannous chloride invariably produced emulsions due to hydrolysis. It was decided to develop the method using potassium iodide or ferrous chloride as the reductant for plutonium and neptunium.

Potassium Iodide Method. Previous workers (*3*) produced a plutonium(III)-neptunium(IV) solution by heating an aqueous solution of 0.1*M* potassium iodide and 5*M* hydrochloric acid at 100° C. for several minutes. Experiments were performed in this laboratory to determine the optimum concentrations of potassium iodide necessary to hold plutonium in the trivalent state at an acid concentration suitable for the extraction of the neptunium(IV)–2-thenoyltrifluoroacetone chelate.

Tracer concentrations of plutonium(IV) were added to aqueous solutions of varying concentrations of hydrochloric acid and potassium iodide. The aqueous phases were extracted at room temperature for 10 minutes with a one-half volume portion of 0.5*M* 2-thenoyltrifluoroacetone–xylene. The organic phases were washed for 3 minutes with an equal volume portion of 1*M* hydrochloric acid and centrifuged for 3 minutes before counting the plutonium alpha radioactivity extracted.

Table I indicates that the use of an aqueous phase 2 to 2.5*M* in potassium iodide and 1*M* in hydrochloric acid effects an excellent separation from plutonium.

Table I. Reduction of Plutonium(IV) Tracer with Potassium Iodide in Hydrochloric acid

Final Aq. Concn.		Plutonium Tracer
HCl, *M*	KI, *M*	Extd., %
0.5	0.15	6.40
	0.30	4.20
	0.60	3.20
1.0	0.15	3.10
	0.30	2.20
	0.60	0.70
	1.00	0.55
	1.50	0.15
	2.00	0.02
	2.50	0.01

The extraction of neptunium(IV) as a function of time was studied in a series of experiments. A high-speed motor stirrer (Palo Laboratory Supplies, New York, N. Y.) with a glass paddle gave excellent mixing of the phases. Aqueous solutions of 1*M* hydrochloric acid and 2*M* potassium iodide containing tracer neptunium-237(IV) were extracted with one-half volume portions of 0.5*M* 2-thenoyltrifluoroacetone–xylene at room temperature for varying periods of time. The organic phases were washed for 3 minutes with an equal portion of 1*M* hydrochloric acid and centrifuged for 3 minutes before counting the neptunium-237 alpha radioactivity.

Table II indicates that a 10-minute extraction period effects essentially quantitative recovery of neptunium.

Table II. Extraction of Neptunium(IV) as a Function of Time

Time, Min.	Neptunium Tracer Extd.,%
2	86.1
5	97.7
8	98.2
10	99.1

The effect of hydrochloric acid concentration on the extraction of neptunium(IV) was studied next. Aqueous solutions of 2*M* potassium iodide and varying concentrations of hydrochloric acid containing tracer neptunium-237-(IV) were extracted for 10 minutes at room temperature with one-half volume portions of 0.5*M* 2-thenoyltrifluoroacetone–xylene. The organic phases were washed as above.

Table III indicates that the extraction of neptunium(IV) is excellent from 1*M* hydrochloric acid but decreases at higher acid concentrations.

Table III. Effect of Hydrochloric Acid Concentration on Extraction of Neptunium(IV)

HCl, *M*	Neptunium Tracer Extd., %
0.5	98.7
1.0	99.1
2.0	97.5
3.0	71.8

Ferrous Chloride Method. When ferrous chloride was substituted for potassium iodide as a reductant, the recovery and decontamination of neptunium were equally efficient. Use of ferrous chloride was particularly advantageous, in that a 5-minute reduction at room temperature with 0.25*M* ferrous chloride effects quantitative reduction of the higher oxidation states of neptunium(V,VI). A 20-minute reduction period at 80° C. was found to be necessary when 2*M* potassium iodide was used. Some free iodine may have been produced. The optimum conditions were as follows:

An aqueous phase containing the neptunium tracer was adjusted to a concentration of 1*M* hydrochloric acid–1*M* hydroxylamine hydrochloride–0.25*M* ferrous chloride. The hydroxylamine hydrochloride reduced oxidants such as potassium dichromate which may have been present. After a 5-minute reduction period at room temperature, a 10-minute extraction with an equal volume of 0.5*M* 2-thenoyltrifluoroacetone–xylene was performed. The recommended procedure given below gave a neptunium recovery of 99 ± 3%.

Reagents. Hydrochloric acid, C.P.

Hydrochloric acid, 1*M*.

Nitric acid, 10*M*.

Hydroxylamine hydrochloride solution, approximately 5*M*. Dissolve 69.5 grams of reagent grade hydroxylamine hydrochloride in 200 ml. of distilled water. Warm to effect solution, if necessary.

Ferrous chloride solution, approximately 2*M*. Dissolve 40 grams of reagent grade ferrous chloride tetrahydrate in 100 ml. of 0.2*M* hydrochloric acid. Store the solution in a dark glass-stoppered bottle. Make fresh solution every 2 weeks.

2 - Thenoyltrifluoroacetone - xylene solution, 0.5*M*. Dissolve 111 grams of 2-thenoyltrifluoroacetone (Graham, Crowley, and Associates, Inc., 5465 West Division St., Chicago 50, Ill.) in 1 liter of reagent grade xylene.

Standard Procedure. A suitable aliquot of the sample solution is pipetted into a separatory funnel or other extraction vessel. The solution is adjusted to a concentration of 1*M* hydrochloric acid–1*M* hydroxylamine hydrochloride–0.25*M* ferrous chloride by the addition of appropriate quantities of these reagents. Potassium iodide may be used as a reductant in place of ferrous chloride. In this case, the aqueous solution is adjusted to 1*M* hydrochloric acid–1*M* hydroxylamine hydrochloride–2*M* potassium iodide, mixed well, heated to approximately 80° C. for 20 minutes, and cooled to room temperature before performing the extraction. Occasionally some free iodine is produced, but this does not interfere with the neptunium recovery. The aqueous phase before the extraction should be approximately 1*M* in total acid, preferably hydrochloric acid. The nitric acid concentration should be kept as low as is practical.

The solution is mixed well and, after a 5-minute reduction period at room temperature, it is extracted for 10 minutes with an equal volume of 0.5*M* 2-thenoyltrifluoroacetone–xylene. When the two phases have disengaged, the aqueous phase is drawn off and discarded. The organic phase is washed by mixing with an equal volume of 1*M* hydrochloric acid for 3 minutes. Wash losses are usually less than 0.1%. After the phases have settled, the aqueous wash solution is discarded, care being taken not to lose any of the organic phase. The neptunium is then stripped from the organic phase by mixing thoroughly for 2 minutes with an equal volume of 10*M* nitric acid. If the aqueous strip solution is too high in gamma radioactivity for alpha measurement, the last traces of radiozirconium and protactinium may be removed readily by performing a 5-minute re-extraction of the 10*M* nitric acid strip solution with an equal volume of 0.5*M* 2-thenoyltrifluoroacetone–xylene.

The small amount of iron extracted (0.04 mg. per ml. of organic phase in a typical experiment) produces a red color and remains in the organic phase when the neptunium is stripped into 10*M* nitric acid, effecting an excellent separation of iron from neptunium. Ordinarily, if an aliquot of the organic phase is evaporated for a neptunium-237 alpha determination, the small amount of iron present causes negligible self-absorption of the alpha particles.

The aqueous strip solution is drawn off into a centrifuge tube and centrifuged for 1 minute. A suitable aliquot of the strip solution is prepared by conventional methods for either alpha counting (*2*) for neptunium-237, or gamma counting (*5*) for neptunium-239.

SEPARATION OF NEPTUNIUM FROM OTHER ELEMENTS

Under the conditions described, an excellent separation of neptunium is effected from aluminum, iron, fission products, thorium, protactinium, uranium, plutonium, americium, and curium. In the determination of neptunium-237, the final stripping step may be omitted and an aliquot of the organic phase counted for alpha radioactivity. The radiozirconium (beta-gamma radioactivity) in the organic phase ordinarily will not interfere with the alpha measurement. Radiozirconium is the only fission product that extracts into the 2-thenoyltrifluoroacetone–xylene. The stripping solution (10*M* nitric acid) removes the neptunium quantitatively from the organic phase. Less than 1% of the radiozirconium is stripped into the 10*M* nitric acid. If necessary, even this small amount of radiozirconium in the final stripping solution may be reduced to a negligible value by performing a 5-minute extraction of the stripping solution with an equal volume of 0.5*M* thenoyltrifluoroacetone–xylene. Neptunium remains quantitatively in the aqueous phase. Protactinium behaves like zirconium in the procedure.

Typical recovery and decontamination values for neptunium are shown in Table IV.

Table IV. Recovery and Decontamination of Neptunium

Element	% Found
Neptunium	99.3
Plutonium	0.02
Americium	0.02
Uranium	0.04
Zirconium	0.5[a]

[a] Re-extraction accounts for negligible value.

INTERFERENCES AND GENERAL APPLICATION OF METHOD

Known interferences are free sulfate, phosphate, fluoride, and oxalate ions. Table V shows the effect of sulfate ion and indicates that free sulfuric acid should be maintained at a concentration of less than 0.1*N*. The standard procedure was employed, with the exception that varying concentrations of sulfuric acid were used in the original aqueous phase. The total acidity was kept 1*N*.

Table V. Effect of Sulfuric Acid on Extraction of Neptunium(IV) with 0.5M 2-Thenoyltrifluoroacetone–Xylene

H_2SO_4, *N*	Neptunium(IV) Tracer Extd., %
0	99.3
0.13	96.6
0.25	93.1
0.38	87.2

Table VI. Effect of Nitric Acid on Extraction of Neptunium Using Standard Method

	Aq. Phase Acidity	Neptunium Tracer Extd., %
1.	0.5*M* HNO_3–0.5*M* HCl	99.5
2.	1*M* HNO_3	99.5
3.	0.2*M* HNO_3–0.8*M* HCl	99.4
4.	1*M* HNO_3	99.2

Neptunium(IV) is unstable in nitric acid (*3*) and previously it has been customary to destroy the nitric acid when preparing neptunium(IV) solutions. However, data in Table VI show that neptunium(IV) tracer can be extracted essentially quantitatively by the procedure given above from nitric acid–hydrochloric acid mixtures or even from nitric acid alone. The neptunium tracer stock solution for experiments 1 and 2 (Table VI) was originally contained in 2*M* nitric acid and probably was chiefly neptunium(V). The standard procedure was used, except that the original aqueous acidity was altered as indicated.

In experiments 3 and 4 (Table VI) the neptunium tracer stock solution was hexavalent neptunium originally contained in 0.1*M* potassium dichromate–1.5*M* nitric acid. The results of these two experiments indicate that neptunium tracer may be recovered essentially quantitatively when introduced into the method as neptunium(VI).

While the extraction of neptunium(IV) tracer from a nitric acid medium appears to be very effective when the standard procedure is used, it is recommended that hydrochloric acid be used whenever possible, as in the preparation of dilutions, because there is some tendency for the formation of extractable ferric ion in the nitric acid system.

When it is not known what interferences are present in solution with the neptunium tracer, the neptunium(IV) tracer can be carried on 0.5 to 1.0 mg. of lanthanum precipitated as the hydroxide. Then the precipitate is dissolved in 1*M* nitric acid, lanthanum fluoride precipitated, and this precipitate dissolved in several drops of 2*M* aluminum nitrate and dilute hydrochloric acid. The aqueous solution may be treated by the standard extraction procedure. Usually only the lanthanum fluoride precipitation is necessary to remove neptunium tracer from many interferences. If it is desirable to use a yield correction for neptunium, which obviously is necessary if much involved chemistry is employed, neptunium-237 is useful for determining the neptunium-239 recovery while neptunium-239 may be used to indicate the neptunium-237 yield.

The liquid-liquid extraction technique described has been applied successfully for several years to the purification and isolation of neptunium-237 and neptunium-239.

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Acid Requirements of the Kjeldahl Digestion

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▶ In studying the acid requirements of a Kjeldahl digestion, acid indices have been calculated from which optimum conditions of digestion may be determined. Data are presented showing that loss of nitrogen occurs as the digest approaches a solid state. Sodium sulfate requires a higher ratio of acid to salt than an equivalent amount of potassium sulfate or potassium sulfate–sodium thiosulfate mixture, thus making this salt unsuitable for use with refractory compounds.

AS A MEANS of determining nitrogen, the Kjeldahl macromethod is a convenient and relatively simple procedure requiring no complicated equipment or technique. However, even after 73 years, comparatively little has been published on the mechanism of the reaction. Hot, concentrated sulfuric acid acts as a weak oxidizing agent. Nevertheless, the condition existing in the boiling acid is favorable to reduction; otherwise, nitrogen would not be recovered as ammonia, but probably would be lost as nitrogen. It is quite likely that the oxidation-reduction range, within which nitrogen is reduced to ammonia, is a narrow one. This may be an explanation of loss of nitrogen which sometimes occurs when oxidizing groups or halogens are present in a compound. Charring generally takes place in the hot acid, and the resulting carbon acts as a reducing agent. Oxidized forms of nitrogen are only partially reduced under these conditions, and are usually subjected to a pretreatment with a suitable reducing agent. Another factor to be considered is the temperature, which at all times should be high enough to induce and ensure pyrolytic decomposition of the sample.

Various factors are involved in the Kjeldahl digestion—e.g., acid required, digestion temperature, boiling rate, salt addition, catalysts, reducing agents, salicylic acid or related compounds, and length of boiling period. The acid requirements are, naturally, based on whatever modification is being used. As an example, in a digestion mixture involving the use of salicylic acid and thiosulfate, the following factors must be considered: conversion of potassium sulfate to the acid sulfate, of sodium thiosulfate to sodium acid sulfate, of salicylic acid to carbon dioxide and water; loss of acid through volatilization during the entire digestion and boiling period; decomposition of the sample; and minimum excess of acid at the end of the determination.

If 10 grams of potassium sulfate are used, the conversion to potassium acid sulfate

$$K_2SO_4 + H_2SO_4 \rightarrow 2KHSO_4$$

requires 5.6 grams of sulfuric acid. When 5 grams of sodium thiosulfate pentahydrate are used as a reducing agent, 3.87 grams of acid are required

$$Na_2S_2O_3 + 2H_2SO_4 \rightarrow \\ 2NaHSO_4 + SO_2 + S + H_2O$$

There is also a secondary reaction which takes place in the hot concentrated acid, converting the sulfur liberated from the thiosulfate into sulfur dioxide:

$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$$

This reaction requires 12.1 grams of sulfuric acid. Salicylic acid, as such, is converted into carbon dioxide and water

$$C_6H_4(OH)COOH + 14H_2SO_4 \rightarrow \\ 7CO_2 + 17H_2O + 14SO_2$$

and 1 gram of salicylic acid consumes 10 grams of sulfuric acid.

The loss of acid during digestion and the boiling period is dependent upon the boiling rate and the total digestion time. With an over-all boiling time of 90 minutes—representing a 30-minute clearing time and 1 hour's additional boil—an average loss for several runs was found to be 3.2 grams, calculated as sulfuric acid, for a mixture of 10 grams of potassium sulfate and 30 ml. of sulfuric acid.

At this point, 31.6 grams of sulfuric acid, or 18 ml. (based on acid strength of 95.5% and a specific gravity of 1.84) have been used for conversion to acid salts and decomposition of salicylic acid. In addition, assuming a total elapsed time of 90 minutes, 3.2 grams of sulfuric acid, or 1.8 ml., are lost through volatilization, bringing the total volume of acid used to 19.8 ml. This, then, leaves 9.2 ml. of acid for excess and for decomposition of the sample. Where the material involved is high in nitrogen and the amount of sample is small—e.g., 0.1 to 0.2 gram—the amount of sulfuric acid used does not present any difficulty, but with materials low in nitrogen (which necessitate large samples), this amount of acid may not be sufficient for either the sample or for maintaining a proper excess.

Both Self (*8*) and Carpiaux (*3*) have reported loss of nitrogen when the final digest was solid. Self further recommended that at least 15 grams of acid be present at the end of the digestion. In a series of determinations, the minimum amount of acid necessary to avoid loss of nitrogen was found to be actually less than 15 grams. Two typical digestion mixtures were used:

A. 10 grams of potassium sulfate and sulfuric acid;

B. 10 grams of potassium sulfate, 5 grams of sodium thiosulfate pentahydrate, and sulfuric acid. An equivalent amount of sodium sulfate (2.86 grams) was substituted for the thiosulfate. This is representative of the condition existing after the thiosulfate has been oxidized to sodium sulfate.

The amounts of acid necessary for conversion of the sulfates to the acid sulfates are 5.6 grams for mixture A and 7.6 grams for mixture B. In each case, the volume of sulfuric acid was varied from 5.00 ml. to 12.5 ml. All determi-

Table I. Recovery of Ammonium Sulfate

Ml. H_2SO_4 Present at Start of Boil Period	Digestion Mixture A: State of digest cold	Digestion Mixture A: $(NH_4)_2SO_4$, Grams Added	Digestion Mixture A: $(NH_4)_2SO_4$, Grams Recovered	Digestion Mixture A: % Recovered	Digestion Mixture B: State of digest cold	Digestion Mixture B: $(NH_4)_2SO_4$, Grams Added	Digestion Mixture B: $(NH_4)_2SO_4$, Grams Recovered	Digestion Mixture B: % Recovered
5.00	Solid	0.1006	0.0962	95.67	Solid	0.1000	0.0965	95.50
	Solid	0.1004	0.0964	96.02	Solid	0.1005	0.0967	96.17
7.50	Solid	0.1006	0.0976	97.04	Solid	0.1007	0.0982	97.53
	Solid	0.1000	0.0970	97.00	Solid	0.1002	0.0975	97.32
10.00	Pasty	0.1002	0.1000	99.80	Fluid	0.1008	0.1008	100.00
	Pasty	0.1002	0.1001	99.90	Fluid	0.1003	0.1004	100.10
12.50	Liquid	0.1005	0.1006	100.10	Fluid	0.1001	0.1001	100.00
	Liquid	0.1000	0.1000	100.00	Fluid	0.1003	0.1003	100.00

Table II. Sulfuric Acid Necessary for Digestion of Various Substances

Sample	Total Grams H_2SO_4 Used	Digestion Time, Min.	Net Grams H_2SO_4/Gram of Sample	Grams H_2SO_4 Calcd.
Sulfuric acid	3.20[a]	90	...	...
Salicylic acid	13.11	75	10.04	10.0
Benzoic acid	15.03	75	12.37	12.05
Sucrose	11.73	95	8.36	6.88
Anthranilic acid	19.57	80	13.92	10.73
Aminosalicylic acid	12.87	75	10.22	8.92
Acetanilide	18.08	80	15.24	13.79
Oleic acid	23.42	100	19.87	17.72
Stearic acid	22.23	95	18.86	17.94
Crepe rubber	22.82	100	19.27	...
Buna rubber	19.24	95	15.87	...
Light lube oil	15.11	100	11.56	...
Heavy lube oil	15.65	105	11.92	...
Leather (chrome tan)	13.75	95	10.38	...
Wool (flannel)	11.49	95	8.12	...
Hemoglobin	12.21	100	8.66	...
Egg albumin	12.09	95	8.72	...
Blood albumin	11.73	95	8.36	...
Gelatin	19.94	90	16.74	...
Casein	13.04	95	9.67	...
Corn meal	9.82	100	6.27	...
Dextrine	10.66	95	7.29	...

[a] Loss over 90-minute boil period; all results calculated on prorated loss.

Table III. Recovery of Ammonium Sulfate Using Sodium Sulfate

Ml. H_2SO_4 Present at Start of Boil Period	State of Digest Cold	$(NH_4)_2SO_4$, Grams Added	$(NH_4)_2SO_4$, Grams Recovered	% Recovered
5.00	Solid	0.1083	0	0
	Solid	0.1001	0	0
7.50	Solid	0.1029	0	0
	Solid	0.1014	0	0
10.00	Solid	0.1001	0.0975	97.45
	Solid	0.1005	0.0977	97.21
12.50	Solid	0.1006	0.0987	98.12
	Solid	0.1000	0.0979	97.90
15.00	Solid	0.1011	0.0979	96.78
	Solid	0.1007	0.0972	97.01
17.50	Pasty	0.1036	0.1018	98.28
	Pasty	0.1028	0.1003	98.37
20.00	Fluid	0.1004	0.1003	99.92
	Fluid	0.1020	0.1009	99.87

nations were given a 60-minute digestion representing the boil period after the clearing of a digestion, and the acid lost during this period was prorated on the basis of a loss of 3.2 grams over a 90-minute period (2.1 grams). Therefore, the basic acid requirements are 7.8 grams (4.4 ml.) for digestion mixture A, and 9.7 grams (5.5 ml.) for digestion mixture B.

The following procedure was used. Digestion mixtures were prepared using 5.00, 7.50, 10.00, and 12.50 ml. of sulfuric acid; 0.1 gram of ammonium sulfate was added to each. All were boiled for 1 hour, cooled, diluted, and distilled in the usual way. Results of a series of duplicate determinations are given in Table I.

It seems apparent that the critical point lies between 7.50 ml. and 10.00 ml. It can be deduced from these results that the amount of sulfuric acid present in the usual digestion mixture is sufficient unless subjected to an unduly long heating period or the necessity of using a large sample. Also, as the digestion mixture approaches the composition of the acid sulfate, loss of nitrogen will occur. The physical appearance of the digest also gives an indication; a loss of nitrogen can be expected if the cooled digest is solid, or nearly so.

The amount of acid necessary to decompose a sample is to some extent dependent upon its structure. The requirements of various types of material (Table II) were obtained by the following procedure.

One-gram samples were digested in a mixture of 10 grams of potassium sulfate and 30 ml. of sulfuric acid (buret), with 0.25 gram of selenium–ferrous sulfate (1 to 1) as a catalyst. After the digestion mixture cleared, boiling was continued for 1 hour. When cool, the digest was diluted with distilled water, transferred to a volumetric flask, and made up to 250 ml. An aliquot was taken and titrated with standard alkali. Blanks were also prepared and boiled for 90 minutes.

Calculations. The acid used was 95.5%, with a specific gravity of 1.84. The total weight of acid at the start is

$$30 \times 0.955 = 52.7 \text{ grams of sulfuric acid} \qquad (1)$$

and at the end

$$0.049 \times N \times \text{ml. of alkali} = \text{grams of sulfuric acid}$$

The difference between Equations 1 and 2 represents the amount of acid used by the sample and lost on boiling. The blank determinations showed an average loss of 3.2 grams of acid during a 90-minute boiling time. Prorating gives a value of 0.036 gram of sulfuric acid lost per minute. Therefore, the amount of acid used by the sample is

$$\text{Eq. 1} - \text{Eq. 2} - (0.036 \times \text{time in minutes}) \qquad (3)$$

Self has stated that carbohydrates require approximately 7.5 grams of acid per gram; proteins, 9.0 grams per gram; and fats, 17.8 grams per gram. Comparison with similar compounds in Table

II shows that these amounts are more or less in agreement.

From time to time the use of other salts has been advocated, particularly sodium sulfate (*1*, *2*, *5*, *6*, *9*). However, where a relatively high temperature is necessary, it is unsatisfactory because solid digests are obtained unless a relatively large excess of sulfuric acid is present. The increase in the acid to salt ratio results in a lower temperature and thus eliminates the use of this sulfate for the more refractory compounds. A series of determinations similar to those made with potassium sulfate was run using 12.8 grams of sodium sulfate (equivalent to 10 grams of potassium sulfate and 5 grams of sodium thiosulfate pentahydrate). The results (Table III) indicate that the same condition exists as with potassium sulfate: When the cooled digest is solid, there is a loss of nitrogen.

The effect of salt addition, naturally, is to elevate the temperature. The importance of the consequent higher temperatures has been pointed out by Lake (*4*) and Perrin (*7*). Figure 1 shows results obtained by progressive addition of potassium sulfate to 30 ml. sulfuric acid and to 30 ml. of sulfuric acid containing sodium sulfate equivalent to 5 grams of sodium thiosulfate pentahydrate. The mixtures were brought to a steady boil, and the temperature was taken with a thermometer enclosed in a thermometer well in the Kjeldahl flask. If these temperatures are plotted against the ratio of acid (volume) to salt (weight), the curves shown in Figure 2 are obtained.

By selection of the proper acid to salt ratio, or acid index, the conditions of digestion can be regulated to obtain optimum temperature. The data in Table I show that, under the conditions stated, certain acid indices exist, beyond which it is unsafe to go. In calculating the ratios after digestion, an arbitrary loss figure of 0.0355 gram per minute calculated as sulfuric acid has been assumed. The value for sulfuric acid lost during the stated boil periods is not exact, and an actual value determined on individual samples would undoubtedly vary from the value used here.

The digestions represent the boiling period after clearing of a digestion, when all organic matter has presumably been destroyed and nitrogen is present as ammonium sulfate. With a 60-minute boil period, the calculated loss will be 60 × 0.0355 or 2.13 grams of sulfuric acid (equivalent to 1.22 ml. of 95.5% acid). At this point in the total digestion period, this will be the only loss. Consequently, the volume of acid at the end of 60 minutes of boiling will be the original volume minus this loss. The calculated values are shown in Table IV. Examination of these data shows that the critical point beyond which nitrogen will be lost is represented by an acid index of 0.88 for digestion mixture A, and 0.68 for digestion mixture B. For optimum conditions the acid index at the end of the digestion should not be lower than these limiting values.

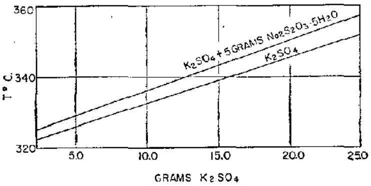

Figure 1. Effect of salt addition on temperature

30 ml. of sulfuric acid

Table IV. Acid Index

Ml. H_2SO_4 before Digestion	Acid Index	Ml. H_2SO_4 after 60-Min. Digestion	Acid Index
Digestion Mixture A			
5.00	0.50	3.78	0.38
7.50	0.75	6.28	0.63
10.00	1.00	8.78	0.88
12.50	1.25	11.28	1.13
Digestion Mixture B			
5.00	0.39	3.78	0.37
7.50	0.58	6.28	0.49
10.00	0.78	8.78	0.68
12.50	0.97	11.28	0.88

The amount of acid necessary for the decomposition of the sample will vary. Table II shows some actual results, and Figures 3 and 4, some calculated values. The total amount of acid will vary depending upon the size of the sample, ease of decomposition, rate of heating, over-all time of digestion, use of salicylic acid or related compounds, and the like. A reasonable estimate of the amount necessary can be made from actual data or calculated values, and an acid index

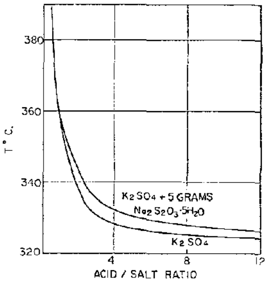

Figure 2. Temperature vs. ratio of acid to salt

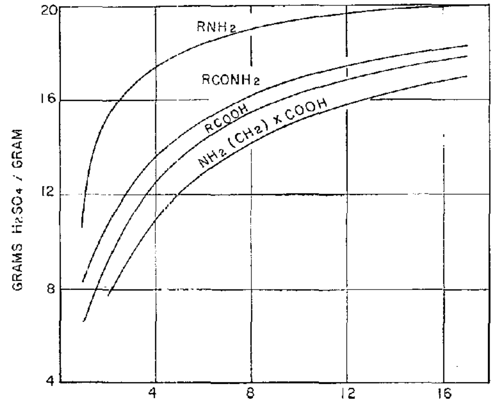

Figure 3. Acid required for decomposition of some amino compounds

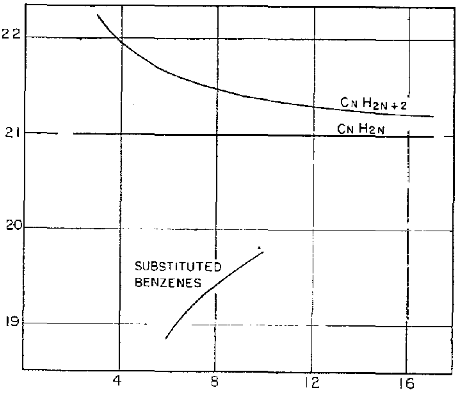

Figure 4. Acid required for decomposition of some hydrocarbons

selected to give optimum conditions throughout the digestion period.

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Tantalum Determination in Presence of Niobium by Precipitation with *N*-Benzoyl-*N*-phenylhydroxylamine

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▶ A quantitative gravimetric determination of tantalum in the presence of niobium, titanium, and zirconium can be made by precipitation with *N*-benzoyl-*N*-phenylhydroxylamine. The sample, containing no more than 50 mg. of tantalum oxide, is dissolved in 200 ml. of solution containing 0.016 to 0.020 mole of hydrofluoric acid acidified with sulfuric acid to pH 1.0 ± 0.1, and the tantalum is precipitated by adding a hot aqueous solution of *N*-benzoyl - *N* - phenylhydroxylamine. The resultant mixture, allowed to stand in a tap water bath, is filtered after 2.5 hours, washed with a saturated solution of the reagent, and ignited at 900° C. One dissolution and reprecipitation are necessary for samples containing less than 10 mg., and two for samples containing more than 10 mg. of niobium pentoxide. The error in the determination is 0.2 mg. of tantalum oxide. Titanium and zirconium show negligible interference compared to niobium.

INCREASED USE of the less familiar metals in special alloys has intensified investigations of the analytical chemistry of the Group IVa, Va, and VIa metals of the periodic system.

The main separative methods employed in the determination of niobium and tantalum minerals were critically reviewed by Atkinson, Steigman, and Hiskey (*2*). The methods of Schoeller (*16*) and Marignac (*13*) and modifications of the Schoeller method are inadequate (*20*). Since the publication of Schoeller's book (*16*) on the determination of these minerals, modifications have shortened the time of analysis and improved the accuracy. Slavin and Pinto (*20*), for example, were able to cut to one third the 15-day Schoeller time. However, the tantalum values must be corrected for residual titanium, and tin must be removed first. According to Fucke and Daubländer (*7*), tantalum can be separated from niobium by precipitation with phenylarsonic acid from a sulfuric acid–hydrogen peroxide solution. The separation is not strictly quantitative, and tin, zirconium, and hafnium interfere.

Dupraw (*5*) used *n*-propylarsonic acid successfully to separate tantalum from niobium, titanium, and tungsten in an oxalic acid–sulfuric acid solution. Titanium interferes above a titanium-tantalum ratio of 1 to 1. When less than 10 mg. of tantalum is present or when titanium is present, tannin must be added to obtain quantitative tantalum precipitation. Zirconium and hafnium interfere (*6*, *8*). Jaboulay (*11*) first separated mixed tantalum-niobium oxides from steel by repeated pyrosulfate fusion and ammonium polysulfide treatment, then applied potassium hydroxide fusion with extraction by aqueous sulfuric acid–hydrogen peroxide solution, and recovered niobium from the filtrate. Stockhausen and Zall (*22*) applied a modified hypophosphite method (*1*) for separating tantalum from the mixed niobium-tantalum oxides recovered in steel analysis. Gillis and coworkers (*9*) separated tantalum from niobium by repeated precipitation with ferroin (*o*-phenanthroline–ferrous sulfate complex) from a hydrofluoric acid solution. This method requires subsequent removal of iron from the tantalum precipitate.

The method proposed here separates tantalum quantitatively and reliably from niobium, titanium, and zirconium by two to three precipitations with *N*-benzoyl-*N*-phenylhydroxylamine (tantalon) from a hydrofluoric acid–sulfuric acid solution at pH 1.0. The operating time is considerably less than that of other methods and the precipitate is uncontaminated by the other metals, thus eliminating the necessity for corrections. *N* - Benzoyl - *N* - phenylhydroxylamine was recommended as an analytical reagent for the precipitation of metals by Bamberger (*3*). It has been used for determination of iron, aluminum, titanium, and copper (*17*), for tin (*15*), and colorimetrically for vanadium (*18*), and recommended as superior to cupferron, when applicable, because it is much more heat- and light-stable. Shome (*19*) points out its pH sensitiveness in gravimetric use. Bamberger (*3*) and Shome (*17*) give detailed methods for its preparation. By these methods, white needles were obtained in a 40 to 50% yield, with a melting point of 120–21° C. crystallized from water. The main by-product is the α,β-dibenzoyl derivative. *N*-Benzoyl-*N*-phenylhydroxylamine on potentiometric titration with perchloric acid shows a basic dissociation constant, pK, of 9.1.

APPARATUS AND REAGENTS

Instrumentation. A Beckman Model G pH meter was used for pH measurements, and a Beckman Model DU spectrophotometer was used in the quantitative determination of contaminants in precipitates. A Nuclear Measurements Corp. PC-1 proportional counter was used for all beta counting.

Tungsten stock solution. Dissolve 5.69 grams of sodium tungstate dihydrate (J. T. Baker Chemical Co.) in water and dilute to 500 ml.; contains 4 mg. of tungstic oxide per ml.

Molybdenum stock solution. Dissolve 4.915 grams of ammonium heptamolybdate (Merck & Co., Inc.) in water and dilute to 500 ml.; contains 4 mg. of molybdic oxide per ml.

Cupferron reagent, 0.2*M*. Dissolve 31 grams of cupferron (G. Frederick Smith Chemical Co.) in water and dilute to 1 liter. Store in the refrigerator.

Cupferron wash solution, 0.02*M*. Dilute 100 ml. of cupferron reagent to 1 liter with ice-cold water.

Ammonium hydroxide wash solution, 5%.

Hydrofluoric acid, 4*M*.

Sulfuric acid, 50% (v./v.).

Tantalum stock solution. Dissolve 1 to 2 grams of tantalum pentoxide (Fisher Scientific Co.) in concentrated hydrofluoric acid in a platinum dish, cool, treat with 10 ml. of concentrated sulfuric acid, and evaporate to evolution of sulfur trioxide fumes. Cool and bring the gellike residue to a clear solution by adding 20 ml. of 4*M* hydrofluoric acid. Dilute with water to a concentration of 4 mg. of tantalum pentoxide per ml. and store in a polyethylene bottle.

Niobium stock solution. Dissolve 1 to 2 grams of niobium metal (Fisher Scientific Co.) in concentrated hydrofluoric acid by addition of small increments of concentrated nitric acid, and treat as in the preparation of the tantalum stock solution.

Titanium stock solution. Fuse 1 to 2 grams of titanium dioxide (J. T. Baker Chemical Co.) with potassium pyrosulfate, dissolve in concentrated sulfuric acid, and dilute with water to a concentration of 4 mg. of titanium dioxide per ml. Store in a glass bottle.

Zirconium stock solution. Dissolve 1 to 2 grams of zirconyl chloride (Fisher Scientific Co.) in 4*M* hydrochloric acid. Dilute to a concentration of 4 mg. of zirconium oxide per ml. and store in a glass bottle.

N-Benzoyl-*N*-phenylhydroxylamine wash solution. Add 0.6 gram of the reagent to 200 ml. of water, boil vigorously to complete solution, and immediately dilute to 1 liter.

PROCEDURE

Solid samples of 0.1 gram or less containing tantalum oxide and one or more of the oxides of niobium, titanium, and zirconium were weighed into platinum crucibles. After 5 ml. of concentrated hydrofluoric acid was added to each crucible, they were placed on the low-temperature hot plate. The crucibles were covered and the covers filled with water to minimize loss of the acid during digestion. The samples dissolved completely in 15 to 30 minutes. The crucibles were cooled, the covers were rinsed into the crucibles with water, and 3 ml. of 50% sulfuric acid was added to each from a graduated pipet or buret. (This quantity of acid gave the required pH of 1.0 ± 0.1 in the final precipitated 300 ml. of solution.) Hydrofluoric acid was then removed by evaporating the solutions on the hot plate until fumes of sulfur trioxide were evolved.

The crucibles were cooled, then the contents of each was treated with 2 ml. of dilute hydrofluoric acid to bring the gellike hydrolysis products into solution. The solution was emptied into a 400-ml. polyethylene beaker containing 185 ml. of water and 2 ml. of 4*M* hydrofluoric acid. The crucible was then policed twice with 0.5-ml. portions of 4*M* hydrofluoric acid and rinsed with water, all being added to the beaker. A total of 5 ml. of 4*M* hydrofluoric acid was used.

A quantity of 0.4 gram of *N*-benzoyl-*N*-phenylhydroxylamine was dissolved in 100 ml. of water in a 250-ml. beaker by vigorous boiling. The hot reagent was then poured at a moderate rate into the sample with reasonably vigorous stirring. Reaction was not rapid. The beakers were then covered and placed in a water bath at room temperature for more rapid cooling. After 2.5 hours the precipitates were filtered on Whatman No. 42 filter paper or its equivalent with gravity or suction filtration, using platinum cones. The precipitate adhering to the beaker required four to five policings for complete recovery. Eight washings with *N*-benzoyl-*N*-phenylhydroxylamine wash solution, including the policings, gave satisfactory results. The precipitates in tared crucibles were then charred over a flame and ignited at 900° C. for 2 hours (preferably in an electric muffle).

Preliminary Removal of Molybdenum and Tungsten. The ice-cold 150 ml. of sample solution (prepared by the above procedure but modified by using 1 ml. of 4*M* hydrofluoric acid to dissolve the gel in the crucible, and emptying it into the beaker of 140 ml. of water containing 0.5 ml. of 4*M* hydrofluoric acid) containing 2.5 ml. of 4*M* hydrofluoric acid is buffered by a solution containing 5 grams of ammonium acetate. The pH is subsequently adjusted to 3 to 4.

The mixed tantalum, niobium, titanium, and zirconium is precipitated with an excess (50 ml. or more) of cold 0.2*M* cupferron added from a buret or pipet with vigorous stirring. After the cupferron addition the mixture must stand for a minimum of 2 hours in an ice bath to ensure complete precipitation. Niobium especially is more slowly precipitated under these conditions. The precipitates were recovered by filtration on Whatman No. 40 filter paper, washed eight times with cupferron wash solution, and then five times with 5% ammonium hydroxide solution to remove the traces of coprecipitated molybdenum and tungsten. The papers containing the precipitates were transferred to tared platinum crucibles, dried, charred, and then ignited at 900° C. for 2 hours in an electric muffle. The ignited precipitates were suitable for dissolution and determination of tantalum by the procedure given above.

STUDY OF VARIABLES

Complexing Agent and Time of Standing. In order to establish the feasibility of the reagent for the quantitative recovery of tantalum from niobium and other metals, the effect of complexing agents was investigated. In the preliminary survey fluoride ion showed much more promise than oxalic acid or hydroxycarboxylic acids in preferentially masking niobium. Mixtures of fluoride and oxalic acid masked the tantalum too strongly.

A hydrofluoric acid concentration as high as 0.016 mole does not prevent quantitative precipitation of tantalum when present alone (Table I). Because the tantalum compound is appreciably soluble at elevated temperatures, the solution must be cooled to room temperature after addition of the hot reagent solution. A minimum of 2.0 hours' standing in a tap water bath gives quantitative precipitation (Table I).

Precipitations of tantalum with *N*-benzoyl-*N*-phenylhydroxylamine in the presence of niobium show increased contamination by the niobium with increased time of standing before filtration. By varying the time of standing from 3 to 86 hours, the quantity of niobium that is coprecipitated with the tantalum increases from 6 to 80%. The slow rate of precipitation of niobium with *N*-benzoyl-*N*-phenylhydroxylamine (yellow precipitate) is evidenced by periodic observation of filtrates which have been allowed to stand.

Acidity. The control of the pH of the solution is important for quantitative precipitation of tantalum in the presence of hydrofluoric acid (Table II). Above pH 1.2 the results become lower as pH increases. This effect was at-

Table I. Effect of Hydrofluoric Acid Concentration and Time of Standing on Tantalum Recovery

(0.0148 gram of tantalum oxide; 0.35 gram of *N*-benzoyl-*N*-phenylhydroxylamine; 300-ml. volume)

HF, Mole	Gram of Ta_2O_5 Found after Standing for				Mg. Ta_2O_5[a] in Filtrate after	
	1.5 hr.	2.0 hr.	2.5 hr.	5.0 hr.	2.5 hr.	5.0 hr.
0.0112	0.0144	0.0148	0.0148	0.0148	None	None
0.0160			0.0148	0.0148	0.01	None
0.0200			0.0146	0.0148	0.11	0.01
0.0240			0.0143	0.0145	0.48	0.31
0.0280			0.0137	0.0141	1.03	0.71
0.0320			0.0135	0.0137	1.22	1.11
0.0360			0.0131	0.0135	1.68	1.29
0.0400			0.0076	0.0131	High	1.71

[a] By radioactive tracer method tantalum in filtrate was determined for 1.5 hr., 0.40 mg.; for 2 hr., 0.01 mg.

tributed to the instability constant of the tantalum fluoride complex, the higher degree of dissociation of hydrofluoric acid, and the greater solubility of the tantalum at higher pH values. A tendency toward slightly low results and the greater tendency for niobium coprecipitation at low pH values led to establishing a pH of 1.0 ± 0.1 as optimum. Low results were obtained when large quantities of oxalate ion or chloride ion were present under the conditions recommended in the procedure.

Table II. Influence of pH on Tantalum Recovery

(0.016 mole of HF, 0.35 gram of *N*-benzoyl-*N*-phenylhydroxylamine, 300-ml. volume)

pH	Tantalum Oxide, Gram: Used	Tantalum Oxide, Gram: Found	Ta_2O_5 in Filtrate,[a] Mg.
0.50	0.0182	0.0182	0.03
0.56	0.0228	0.0226	0.20
0.70	0.0228	0.0227	0.10
0.90	0.0148	0.0148	None
1.10	0.0018	0.0017	0.08
1.10	0.0148	0.0148	0.06
2.2	0.0228	0.0154	High
3.0	0.0228	0.0160	High
4.0	0.0228	0.0140	High
4.8	0.0228	0.0117	High

[a] Determined by radioactive tracer method.

Glassware. Repeated dissolution and reprecipitation of tantalum alone in borosilicate beakers gave somewhat erratic high results, which were attributed to the attack on the beaker by hydrofluoric acid. Repeated use of the beakers gave visible evidence of this etching. Polyethylene beakers gave much more satisfactory results.

Quantity of Reagent and Nature of Wash Solution. Preliminary experiments with an alcoholic reagent solution and a water wash of the precipitates gave low results. A hot aqueous reagent solution improved the results, and changing the wash solution to a saturated aqueous reagent solution (0.5 to 0.6 gram per liter) gave quantitative recoveries.

In establishing the theoretical requirements of tantalum for the *N*-benzoyl-*N*-phenylhydroxylamine, samples of the precipitate which had been thoroughly washed with water were dried to constant weight over anhydrous magnesium perchlorate. The loss on ignition was then determined. These data showed that the precipitate contained 2.2 moles of reagent per gram-atom of tantalum. However, experiments showed that a sufficient excess must be added over the theoretical requirement to saturate the final solution at room temperature—i.e., approximately 0.5 gram per liter at 25° C.

Table III. Influence of Niobium on Recovery of Tantalum

(0.0148 gram of tantalum oxide; 0.35 gram of *N*-benzoyl-*N*-phenylhydroxylamine; 300-ml. volume)

Niobium Oxide Present, Gram	HF Present: 1st pptn.	HF Present: 2nd pptn.	Weight of Precipitate, Mg.: 1st	Weight of Precipitate, Mg.: 2nd	Weight of Precipitate, Mg.: 3rd	Nb_2O_5[a] in Final Ppt., Mg.
0.0078	0.011	0.016	0.0157	0.0149	...	0.044
0.0117	0.011	0.016	0.0166	0.0150	0.0148	0.006
0.0195	0.011	0.016	0.0178	0.0156	0.0149	0.005
0.0273	0.020	0.016	0.0161	0.0147	...	0.007
0.0975	0.020	0.016	0.0192	0.0150	...	0.15

[a] Determined by radioactive tracer method.

Presence of Other Metals. The degree of contamination by niobium was determined by the hydrogen peroxide spectrophotometric method of Palilla, Adler, and Hiskey (*14*) and Langmyhr (*12*) or by the radioactive tracer method. The contamination by niobium is also shown by the color imparted to the precipitate by the yellow niobium–*N*-benzoyl-*N*-phenylhydroxylamine complex. Solutions containing much niobium should contain 0.02 mole of hydrofluoric acid for the first precipitation in order to minimize coprecipitation (Table III).

From the weight of sample taken and the weight of the ignited first precipitate, the ratio of tantalum to niobium can be approximated to determine whether or not one or two subsequent precipitations are necessary. Samples containing about 0.1 gram of tantalum oxide give results that are low by about 2 mg. or more.

In Table IV are found data showing the degree of success in the separation of tantalum when admixed with titanium, zirconium, and/or niobium. Second and third precipitations were not carried out on some of these samples because the precipitates were used for the determination of impurities. In all cases where the weights were high, the abnormality was due to the foreign metal present in the original solution.

Temperature. The quantitative precipitation of tantalum with *N*-benzoyl-*N*-phenylhydroxylamine was accomplished with no evidence of temperature effect from 5° to 27° C. Above 27° C. the results appeared to be slightly low. The solubility of the precipitate at higher temperatures was much greater—i.e., when the solution was held at 50° C. Little or no precipitation occurs at 90° to 100° C.

Removal of Molybdenum and Tungsten. Although tungsten alone is not precipitated by cupferron at or above pH 2, considerable amounts are coprecipitated with tantalum, niobium,

Table IV. Influence of Other Metals on Tantalum Recovery

Tantalum Oxide, Gram	Other Oxides, Gram: Niobium	Other Oxides, Gram: Zirconium	Other Oxides, Gram: Titanium	Weight after Pptn., Gram: 1st	Weight after Pptn., Gram: 2nd	Weight after Pptn., Gram: 3rd	Nb[a] in Ppt., Mg.	Ti[b] in Ppt., Mg.	HF[c] Present, Mole
0.0228	None	None	None	0.0228	...	...	...	...	0.012
	0.0014	0.0344	None	0.0235	...	...	0.33	...	0.012
	0.0014	0.0344	None	0.0229	...	...	0.25	...	0.016
	None	None	0.0100	0.0228	...	...	...	...	0.016
	None	None	0.0400	0.0247	0.0228	...	...	0.10	0.016
	None	0.0137	0.0150	0.0239	0.0230	...	...	None	0.016
	0.0143	0.0137	0.0150	0.0262	0.0235	...	0.02	0.06	0.016
0.0200	0.0340	None	0.0260	0.0235	0.0220	0.0204	None	0.06	0.020
0.0041	0.0340	None	0.0260	0.0074	0.0043	0.0040	None	None	0.020
0.0410	0.0340	None	0.0260	0.0478	0.0425	0.0408	None	None	0.020

[a] Niobium and zirconium in precipitate determined by radioactive tracer technique, using mixed Nb^{95}-Zr^{95} tracer and differentiation by use of absorbers when both were present in samples. No zirconium found in any precipitates.

[b] Titanium oxide in final precipitates determined colorimetrically.

[c] 0.012 mole of hydrofluoric acid used in second and third precipitations.

titanium, and zirconium. Molybdenum is precipitated over a wider pH range from pure solutions and also appears with the combined cupferron precipitates. Nevertheless, both molybdenum and tungsten may be removed from the combined cupferron precipitates of tantalum, niobium, titanium, and zirconium by washing the precipitate with 5% ammonium hydroxide (*21*). The presence of hydrofluoric acid minimizes the precipitation of molybdenum and tungsten. Five washings with ammonium hydroxide remove all the molybdenum and tungsten. If hydrofluoric acid is not present and considerable amounts of molybdenum and tungsten are, the ammonium hydroxide washing is inadequate. Table V contains typical data showing the accuracy of this recovery.

DISCUSSION

In this investigation the solutions for precipitation were prepared by pipetting appropriate quantities of the metal stock solutions into polyethylene beakers containing the requisite amounts of water, hydrofluoric, and sulfuric acids. For the purpose of reprecipitation the ignited precipitates were dissolved by the hydrofluoric acid–sulfuric acid treatment described. This method was preferred because the pyrosulfate fusion in Vitreosil crucibles required time-consuming close control of temperature, and a small quantity of silica was picked up from the crucible. Dissolving the precipitate in a near-boiling dilute solution of hydrofluoric-sulfuric acid was unsatisfactory; agglutination of the particles of precipitate to soft masses rendered the method impractically slow.

In order to assure a stock solution of tantalum oxide of the highest purity, the ignited tantalum oxides obtained from studying the optimum conditions for precipitating tantalum alone were used. This material was thus free of the minor impurities of silica, niobium, and alkali metals present in the tantalum oxide from the supply house.

In developing this procedure for determining tantalum, reliable methods were needed for the determination of small quantities of contaminants in the precipitated tantalum, and of the unprecipitated tantalum in the filtrate. The radioactive tracer technique (*4*) appeared to be reliable and was applied where feasible. Radioactive elements—tantalum-182, niobium-95, equilibrium zirconium-95–niobium-95, and tungsten-185—were obtained from Oak Ridge National Laboratory. The activity employed in each sample was a minimum of 1 × 10^6 counts per minute per mg. of the metal oxide tagged. The detection limit of interest in this work was 0.05 mg., which required a counting time of 10 minutes to obtain 5000 total counts with a standard deviation of 41. Isotopic exchange was effected in the stock solutions of the respective metals.

Ignited precipitates and filtrate aliquots were mounted on 2-inch stainless steel planchets. Solid samples were spread evenly with the aid of ethyl alcohol and a glass rod. All mounts were thinly coated with dilute collodion to prevent flaking off and contamination of the counting chambers. The samples were beta-counted using a proportional counter having a background of 58 ± 3 c.p.m. The most serious self-absorption was encountered in determining the niobium impurity in tantalum precipitates. To correct for thick sample absorption for determining the true count—for example, of niobium contamination of ignited tantalum precipitates—the following procedure was used.

To a series of tantalum stock solutions in 10-ml. volumetric flasks was added radioactive niobium-95 solution. The quantity of niobium-95 added was such that all counting samples taken and mounted contained identical quantities of radioactivity. On 2-inch stainless steel planchets were mounted 1-, 2-, 3-, 4-, and 5-ml. aliquots of these solutions. A sixth mount was made of the same quantity of niobium-95 containing no tantalum. These mounts were neutralized with excess ammonium hydroxide, dried under an infrared lamp, and then heated strongly on a hot plate to volatilize ammonium salts. The mounting and evaporation of water were done in increments in order to retain all of the material on the planchets. A 10-minute count was then made on each sample. A curve was plotted of counts *vs.* weight of solids. The counts on all ignited precipitates were corrected by reference to this curve. Proper correction for self-absorption was made in counting all samples containing the different radioactive tracers. The decay factor and the variable sensitivity of the counter were accounted for by comparing sample counts with counts made the same day on aliquots of stock solutions.

In the case of elements for which no suitable radioactive isotope was available, a colorimetric method was applied to the determination of these impurities in the precipitates and the quantity of

Table V. Recovery of Tantalum, Niobium, Titanium, and Zirconium from Molybdenum and Tungsten

Ta, Nb, Ti, Zr Oxides Present, Gram	WO_2 Present, Gram	MoO_3 Present, Gram	Ta, Nb, Ti, Zr Oxides Recovered, Gram	WO_3[a] in Ppt., Mg.	MoO_3[b] in Ppt., Mg.
0.0511[c]	0.0282	None	0.0512	0.088	...
0.0280[d]	0.0282	None	0.0280	0.10	...
0.0432[e]	0.0300	None	0.0431	0.037	...
0.0280[d]	None	0.0300	0.0283	...	0.30
0.0840[d]	None	0.0300	0.0837	...	0.10
0.0385[f]	None	0.0300	0.0385	...	0.10
0.0385[f]	0.0300	0.0300	0.0386	0.030	0.08
0.0385[f]	0.0600	0.0600	0.0386	0.034	0.08

[a] Tungsten determined by radioactive tracer method using W^{185} with beta counting.
[b] Molybdenum determined by thiocyanate method of Grimaldi (*10*).
[c] TiO_2.
[d] ZrO_2.
[e] Mixture of 0.0109 g. Ta_2O_5, 0.0110 g. Nb_2O_5, 0.0111 g. TiO_2, 0.0102 g. ZrO_2.
[f] Mixture of 0.01136 g. Ta_2O_5, 0.01160 g. TiO_2, and 0.01555 g. ZrO_2.

Table VI. Colors of Precipitates of Metals with *N*-Benzoyl-*N*-phenylhydroxylamine

Metal[a]	Valence State	Precipitate Color	pH[b]
Aluminum	3	White	2
Chromium	3	None	0 to 5
Cobalt	2	Pink	4
Copper	2	Chartreuse	4
Iron	3	Rust-red	1
Iron	2	Rust-red	4
Lead	2	White	3.5
Molybdenum	6	White	1
Nickel	2	Light apple green	4
Niobium	5	Buff yellow	1
Tantalum	5	White	1
Tin	4	White	2*N*
Titanium	4	Bright yellow	0.5
Tungsten	6	Cream	0.5
Uranium	UO_2^{++}	Deep orange	1
Vanadium	5	Deep violet	1
Vanadium	VO^{++}	None	0 to 5

[a] Lead precipitated from nitric acid solution, tin from hydrochloric acid solution, others from sulfuric acid solution.
[b] That at which qualitative copious precipitation occurred.

the element remaining in solution. Titanium and niobium were determined by the hydrogen peroxide colorimetric method of Palilla, Adler, and Hiskey (*14*), and molybdenum by the thiocyanate method of Grimaldi and Wells (*10*).

To separate tantalum from molybdenum and tungsten it was necessary to resort to a preliminary separation by the cupferron method described. Preliminary experimentation indicates that probable successful separations can be made from several metals, including iron(III), iron(II), nickel, cobalt, aluminum, chromium(III), tin(IV), and vanadium(IV).

The colors of the pure precipitates of different metals with *N*-benzoyl-*N*-phenylhydroxylamine are found in Table VI. Obviously, the degree of contamination of tantalum precipitates by coprecipitated niobium cannot be assessed by the color imparted to it when other metals are present.

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Determination of Unsaturation in Butyl Rubber Using Carbon-14–Labeled Isoprene

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▶ Various procedures for the determination of unsaturation in Butyl rubber have led to inconsistent results. By preparing Butyl rubber from carbon-14–labeled isoprene, samples of known unsaturation can be produced. Determinations of unsaturation were made on these samples by iodine–mercuric acetate addition and by ozonolysis. The commonly used drastic iodine–mercuric acetate method is reliable but its result must be increased by 15% to estimate accurately the amount of isoprene in the copolymer. The iodine equivalent for this method is thus 2.61 instead of 3.

PROCEDURES for the determination of unsaturation in Butyl rubber have involved chiefly the addition of halogens to olefinic linkages. The iodine monochloride method (*2*, *3*) and the iodine–mercuric acetate method (*2*) have been used most commonly. A procedure based on the reaction of ozone with sites of unsaturation has also been used (*5*). The results of these procedures have not been in agreement, and it was not known which most nearly agreed with the absolute unsaturation of Butyl rubber.

The present investigation measures directly the amount of diolefin entering the polymer by isotope tracer techniques. This should determine unsaturation accurately, assuming that there is one double bond for each molecule of isoprene entering the polymer. This assumption should be sound because there is no evidence of cross linking in the soluble butyl polymers. End group unsaturation is negligible. Previous work (*4*) showed no evidence of dimers of isoprene in Butyl rubber which could cause abnormalities in unsaturation measurements. For this study, carbon-14–labeled isoprene was prepared and copolymerized with isobutylene. Unsaturation results, reported as mole per cent unsaturation (moles of isoprene units per 100 moles of monomer units), are compared with values obtained by standard procedures for the ozonization (*5*) and iodine–mercuric acetate determinations (*2*).

EXPERIMENTAL

Carbon-14–Labeled Isoprene. Isoprene was prepared from acetylene and acetone by the method of Taylor and Shenk (*7*). Radioactivity was introduced into the isoprene molecule by using carbon-14–labeled acetylene as a starting material. Radioactive acetylene was generated by the addition of water to barium C^{14}-carbide. After the gas was collected in a buret, it was injected into a stream of ordinary acetylene for reaction with sodium in liquid ammonia. The sodium C^{14}-acetylide in liquid ammonia was treated with acetone to form dimethyl-C^{14}-ethynylcarbinol. Another product of this reaction is the glycol, 2,5-dimethyl-3-hexyne-2,5-diol. This side reaction was minimized by passing acetylene into the liquid ammonia solution until after the acetone addition was complete (*1*, *7*). When this precaution was used in the present study, it was found that the carbon-14 content of the dimethylethynylcarbinol was much less than should have been obtained. This loss of activity is attributed to interchange

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Table I. Preparation of Radioactive Butyl Rubber

Butyl Type	Feed Charge, Grams			Polymer Yield			
	Methyl chloride	Isobutylene	Isoprene	Olefin-diolefin converted to polymer, %	G. polymer per g. $AlCl_3$	Intrinsic viscosity	Drastic I-HgOAc, cg. I/g.
B-3[a]	255	50	1.55	85	384	1.77	11.2
B-3	255	50	1.55[b]	92	138	1.14	7.19
B-15[a]	145	25	4.4	61	173	0.82	49.3
B-15	145	25	4.4[b]	22	27	0.41	33.6

[a] Control runs with no radioactivity.
[b] Contained radioactive isoprene with specific activity of 0.266 mc. per mole.

between unreacted sodium C^{14}-acetylide and acetylene.

$$\mathrm{NaC^{14}{\equiv}CH + HC{\equiv}CH \rightleftharpoons HC^{14}{\equiv}CH + NaC{\equiv}CH}$$

As ordinary acetylene was used for minimizing the side reaction after the sodium C^{14}-acetylide has been formed, the escaping excess acetylene carried with it radioactive acetylene and left only a fraction of the original sodium C^{14}-acetylide for reaction with acetone.

Dimethylethynylcarbinol was reduced over a palladium catalyst to 2-methyl-3-buten-2-ol, which was dehydrated to isoprene by passage through a column of activated alumina at 300° C. In the dehydration step the activity was diluted somewhat by using nonradioactive 2-methyl-3-buten-2-ol as a "chaser" for the alumina column.

The above reaction sequence was run on 0.20*M* quantities of starting material. The final isoprene product (boiling point, 32.5–33.5° C./758 mm.) weighed 7.2 grams and had a specific activity of 0.266 mc. per mole.

Preparation of Radioactive Butyl Rubber. Butyl rubber samples were prepared in the laboratory by the method described by Rehner, Zapp, and Sparks (*6*) for low temperature polymerization, using a catalyst solution of 0.25% aluminum chloride in methyl chloride. The copper reactor for this work had a capacity of only 750 ml. to accommodate a charge of 180 to 320 ml. The reactor was placed directly into liquid ethylene for cooling so that the reaction took place at −100° C. The charge consisted of 75% by volume of methyl chloride solvent and 25% of olefin-diolefin feed. The catalyst solution was sprayed as a jet stream at 9 ml. per minute onto the vigorously stirred surface of the reaction mixture under a blanket of dry nitrogen. The olefin-diolefin feed for polymerization and the radioactive polymers are described in Table I. Two nonradioactive polymers prepared the same day with a pure grade of isoprene are also shown. The B-number indicates the weight per cent of isoprene in the isobutylene-isoprene feed for polymerization.

Determination of Carbon-14 Content. Isoprene samples were burned to water and carbon dioxide. The latter was precipitated as barium carbonate and counted, using a thin-window Geiger-Mueller tube in conjunction with a commercial scaler. Combustion of Butyl rubber samples gave barium carbonate precipitates too weakly radioactive to be counted with a thin-window tube. Thin films of Butyl rubber, cast on aluminum disks, were counted directly. To obviate the necessity for determining the absorption coefficient of Butyl rubber film, however, the activities were determined by counting toluene solutions of the original isoprene and of the Butyl rubbers in a Packard Tri-Carb liquid scintillation spectrometer using a toluene solution of 2,5-diphenyloxazole as the phosphor medium. Table II shows the radioactive content of these compounds. Comparison of the two methods of counting showed that the absorption coefficient for Butyl rubber was essentially the same as for barium carbonate.

Table II. Carbon-14 Content of Radioactive Samples

Compound	Specific Activity, Mc./G.	Molar Activity, Mc./Mole
Isoprene	0.0039	0.266
B-3 Butyl	0.0000583	0.00328
B-15 Butyl	0.000266	0.01520

Determination of Mole Per Cent Unsaturation. Radioisotope Labeling Method. Mole per cent unsaturation was calculated from specific activity by using the expression

$$\text{Mole per cent unsaturation} = 100\,A_p(M)/A_I \qquad (1)$$

where A_p is the specific activity of the polymer in millicuries per gram, A_I is the molar activity of isoprene in millicuries per mole, and M is the average molecular weight of the monomer unit. For B-3 Butyl samples, the molecular weight of the monomer unit was taken to be that of isobutylene (56.10 grams per mole). For B-15 samples, a corrected molecular weight of 56.82 was used to account for the presence of approximately 6% of isoprene. Results are shown in Table II.

Ozonization Method. The ozonization procedure used was developed by Rehner (*4, 5*). It is based on the reaction of ozone with the polymer in carbon tetrachloride solution to give degraded species, the limiting viscosity of which is governed by the original unsaturation. Values are given in Table III. Due to the limited amount of radioactive polymer available, ozonization values were obtained from a single run and are considered to be approximate. Usually unsaturation values by ozonization are nearly identical with those obtained by 30-minute moderate iodine–mercuric acetate treatment with $F = 3$; here, however, they were quite different.

Iodine–Mercuric Acetate Method. The drastic iodine–mercuric acetate method is the standard procedure used in these laboratories for the determination of Butyl rubber unsaturation; it has been described by Gallo, Wiese, and Nelson (*2*). A solution of Butyl rubber in carbon tetrachloride is reacted for 30 minutes with iodine in the presence of mercuric acetate and trichloroacetic acid. The excess iodine is titrated with sodium thiosulfate. The iodine number (centigrams of iodine per gram of polymer) is calculated from the expression:

$$\text{Iodine No.} = \frac{\text{ml.} \times N \text{ of } Na_2S_2O_3 \times 126.91 \times 100}{\text{grams of sample} \times 1000} \qquad (2)$$

The mole per cent unsaturation is related to the iodine number by the equation:

Table III. Determination of Unsaturation of Butyl Rubber by Various Methods

Butyl Sample	Mole Per Cent Unsaturation					
	Iodine–Mercuric Acetate[a]					
	$F = 3$			$F = 2$, moderate, 1 min.		
	Drastic[b]	Moderate, 30 min.	Moderate, 1 min.		Ozone	C^{14}-Labeling
B-3	1.12	0.93	0.86	1.29	0.71	1.23 (±0.04)
	1.01	0.99	0.85	1.27		
	1.07					
	1.03					
	Av. 1.06	0.96	0.86	1.28		
B-15	5.19	4.16	3.70	5.54	1.88	5.71 (±0.10)
	4.88	4.21	3.76	5.63		
	4.99					
	Av. 5.02	4.19	3.73	5.59		

[a] Calculated from Equations 1 and 2.
[b] Drastic is run in presence of trichloroacetic acid; moderate is not.

Table IV. Determination of Absolute Unsaturation by Various Methods

		Per Cent of Absolute Unsaturation				
		Iodine–Mercuric Acetate Method				
		$F = 3$			$F = 2$,	
Butyl Sample	Unsatn. by C^{14}-Isoprene	Drastic	Moderate, 30 min.	Moderate, 1 min.	moderate, 1 min.	Ozone
B-3	1.23	86	78	70	104	57
B-15	5.71	88	73	65	98	33
		Av. 87	76	68	101	45

$$\text{Mole per cent unsaturation} = \frac{M\,(\text{iodine No.})}{126.91\,F} \quad (3)$$

Here M is the average molecular weight of the monomer unit (56.10 for isobutylene with small amounts of isoprene and 56.82 for a polymer with 6% of isoprene present) and F is a stoichiometric factor depending on the reaction conditions and the nature of the polymer. For the drastic iodine–mercuric acetate method, F has heretofore been assumed to equal 3 (*2*).

The moderate iodine–mercuric acetate method is identical except that no trichloroacetic acid is used. Results from both methods are tabulated in Table III.

DISCUSSION

The addition of halogens to a double bond is often a reliable method for determining unsaturation. In Butyl rubber, however, there are complicating reactions, and the reliability of results from halogenation procedures has been subject to question. Kolthoff and coworkers (*3*) have shown that, when iodine monochloride is added to highly branched olefins and polymers, the reaction is abnormal in that the addition products formed possess steric strain and tend to decompose. The decomposition products react further with iodine monochloride, thus leading to high unsaturation values.

These workers modified the calculation of unsaturation from their iodine monochloride results to give values which were considered reliable for Butyl rubber. This modification was based on the fact that the addition of iodine monochloride to the decomposition product is not so rapid as the addition to the original polymer. The results so obtained gave good agreement with values obtained by the drastic iodine–mercuric acetate method (*3*). These two procedures have been used more extensively for determining unsaturation than the moderate iodine–mercuric acetate and the ozonization methods, both of which give lower unsaturation values than the drastic and the iodine monochloride methods.

Unpublished work in these laboratories (*8*) has shown that the iodine–mercuric acetate methods react with different types of olefins to varying degrees. The drastic method, for example, has been found to consume 3 atoms of iodine for each tertiary double bond ($F = 3$, Equation 2) in lower olefins, and 2 atoms of iodine for primary and secondary double bonds. The moderate treatment consumed between 2 and 3 iodine atoms per double bond, although the moderate procedure with 1-minute reaction time consumed only 2 atoms of iodine for a tertiary double bond ($F = 2$). For some hindered tertiary double bonds, as found in tri- and tetraisobutylene, the iodine consumed was not as high as 3 atoms per double bond (*2*, *8*). The fact that the iodine–mercuric acetate method consumed more than 2 iodine atoms indicates that the same type of unstable addition product is formed with this reagent as with iodine monochloride.

Table III shows that the absolute unsaturation of the two Butyl rubber samples as determined by carbon-14 labeling is greater than indicated by any of the other procedures except moderate iodine–mercuric acetate with 1-minute reaction time using $F = 2$. Table IV indicates the per cent of absolute unsaturation shown by the various methods. Although it appears that the 1-minute moderate treatment with $F = 2$ gives a more accurate indication of absolute unsaturation, it is seen that the drastic procedure is more reproducible at both high and low levels of unsaturation. For routine tests a 1-minute reaction time may be too short to be desirable or reliable, because it is possible that the addition and decomposition reactions have resulted in a coincidental result which agrees with the theoretical at delicately balanced conditions. Since the drastic iodine–mercuric acetate method is convenient and its reproducibility is not easily affected by variations in time, temperature, concentration of reagent, and level of polymer unsaturation, this procedure can be recommended for routine laboratory determination of Butyl rubber unsaturation. However, Table IV shows that the drastic method gives only 87% of the true unsaturation value of Butyl rubber. Values thus obtained should, therefore, be multiplied by 1.15 to give true values for mole per cent unsaturation.

It is recommended that future calculations of unsaturation in isoprene-isobutylene copolymers from iodine numbers determined by the drastic iodine–mercuric acetate method (*2*) employ an F value of 2.61. For low unsaturation (0 to 10 mole per cent) where the molecular weight of the monomer unit is assumed to be 56.1, the conversion from this iodine number to mole per cent unsaturation will be:

$$\text{Mole per cent unsaturation} = 0.1694 \times \text{iodine No.}$$

where iodine number is expressed as centigrams of iodine per gram of polymer.

For a butadiene-isobutylene copolymer, where the double bonds in the polymer are secondary instead of tertiary, a value of $F = 2$ must be assumed until data become available for this type of polymer. The tentative unsaturation equation in this type of polymer is:

$$\text{Mole per cent unsaturation} = 0.2210 \times \text{iodine No.}$$

Attempts to use infrared spectra for measurement of unsaturation in the isoprene-isobutylene copolymers were unsuccessful, even for highly unsaturated B-15 samples. This was using the best technique available with polyisobutylene in the reference cell. The failure is due to the low absorption of the tertiary (Type IV) double bond. However, the absorption of the secondary (Type II) double bond in a butadiene-isobutylene copolymer is strong enough to be seen easily at 10.4 microns and may be used as a measure of unsaturation in these copolymers. Future work with radioactive copolymers of this type would help establish absorption coefficients for this type of double bond in butyl polymers.

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Volumetric Determination of Uranium

Titanous Sulfate as Reductant before Oxidimetric Titration

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▶Need for a more rapid volumetric method for the routine determination of uranium in uranium-rich materials has led to the development of a method that uses titanous sulfate as a reductant before oxidimetric titration. Separation of the hydrogen sulfide group is not necessary. Interfering elements precipitated by cupferron are removed by automatic filtrations made simultaneously rather than by the longer chloroform extraction method. Uranium is reduced from VI to IV by addition of an excess of titanous sulfate solution, cupric ion serving as an indicator by forming red metallic copper when reduction is complete. The copper is reoxidized by addition of mercuric perchlorate. The reduced uranium is then determined by addition of excess ferric sulfate and titration with ceric sulfate. The method has proved to be rapid, accurate, and economical.

Methods in common use for the determination of uranium require reduction of the uranium to a valence of IV and titration to a valence of VI with standard oxidant. This has usually been done by passing the solution through a reductor column filled with metal (*5*, *8*), followed by aeration to reoxidize the uranium to a valence of IV before titration. The uranium can be reduced to the quadrivalent state with cadmium columns (*3*) and lead metal columns (*2*, *9*). Liquid bismuth amalgam will reduce uranium just to the quadrivalent state in 6 to 10*N* sulfuric or hydrochloric acid (*12*). Chemists are aware of the difficulties encountered in using reductor columns. Other workers have investigated the use of titanous sulfate as a reductant for uranium (*1*, *6*, *7*).

The method here described, using titanous sulfate, eliminates the use of the reductor column by making the reduction with simple addition of reagent solutions. The reduction step can be made in this way on a large number of sample solutions at one time.

The proposed method not only offers a simple and rapid means of reduction but also eliminates the need for removal of the hydrogen sulfide group, which is required when a metal-column reductor is used. Selenium in quantities greater than 5 mg. interferes with the titration, but it can be quickly volatilized as the bromide during preparation of the sample solution.

The method has been applied successfully to the general sandstone-type uranium ores, both oxidized and reduced, and both high and low in vanadium. Also tested successfully were varieties of uranium ores high in iron, copper, nickel, and cobalt, selenium, low-rank high-ash coals, and petroliferous material. No difficulty with the method was experienced in the analysis of uranium-rich samples containing relatively large amounts of thorium, rare earths, niobium, and titanium, such as might be expected in uranium ores associated with euxenite or brannerite. The method of sample solution described needs to be more elaborate for such refractory materials as monazite or zircon.

CHEMICAL PRINCIPLES

Samples are dissolved by treatment with nitric, hydrofluoric, perchloric, and sulfuric acids, followed by evaporation to fumes of sulfuric acid. In preparing the sample solution boric acid is added, to prevent low results on samples high in rare earths and thorium due to the precipitation of their insoluble fluorides and coprecipitation of uranium. The boric acid forms complexes with the fluoride ion and keeps these elements in solution. The addition of boric acid is much easier than repeated evaporations to eliminate the traces of fluoride left at this stage of the procedure.

Metals precipitated by cupferron are removed by filtration, rather than by extraction, because niobium which may be in solution in appreciable quantity forms an insoluble cupferrate that is difficult to extract (*4*). This filtration is a rapid semiautomatic step using equipment here described. Sufficient niobium occurs in many of the uranium ores from various places in the western United States to make its removal necessary. When solid cupferron is added, the conditions of precipitation approach that of a homogeneous precipitation and occlusion is minimized; addition of cupferron solution tends to form gummy precipitates that are hard to filter and wash.

In the reduction with titanous sulfate cupric ion in the solution serves to indicate an excess of the titanous reagent over that required to reduce the uranium by being reduced to red copper metal. An excess of mercuric perchlorate is then added to oxidize the copper metal to cupric ion, copper(II), an equivalent amount of mercurous ion, mercury(I), being formed in the solution. A trace of ferric iron, too small to cause error in the final titration, catalyzes these reactions. The mercurous ion formed is not oxidized by the ceric sulfate titrant except at boiling temperature (*11*). Because air oxidation of the quadrivalent uranium is catalyzed by the cupric ion in the solution (*7*), the solution is titrated immediately by adding an excess of ferric sulfate and titrating with standard ceric sulfate in the presence of ferroin indicator.

SPECIAL REAGENTS AND APPARATUS

All reagents are of analytical grade.

Ferric sulfate solution, about 0.3*M* in 5% sulfuric acid by volume.

o-Phenanthroline ferrous complex stock solution (ferroin), (0.025*M*). Dissolve 1.5 grams of 1,10-*o*-phenanthroline monohydrate in 20 ml. of water containing 0.7 gram of ferrous sulfate heptahydrate and dilute to 100 ml.

Ferroin indicator solution, (0.001*M*). Dilute 10 ml. of the 0.025*M* solution to 250 ml.

Cupric sulfate solution. Make a 4% cupric sulfate solution and add 5 ml. of 0.3*M* ferric sulfate solution per liter.

Titanous sulfate solution. Mix 20 grams of reagent-grade titanium dioxide with 45 grams of ammonium sulfate. Add 125 ml. of concentrated sulfuric acid. Heat carefully over a Meker burner, in a well ventilated hood, until all foaming stops. Heat to boiling and swirl the boiling liquid vigorously over the full flame of the burner until all or most of the titanium dioxide dissolves. Cool. Add carefully, with swirling, enough cold distilled water to dilute to approximately 500 ml. Decant or filter immediately, before hydrolysis takes place, into a flask containing zinc amalgam prepared by adding 8 grams of zinc to 6 ml. of mercury and 5 ml. of 5% sulfuric acid by volume. Swirl the solution occasionally, cover loosely until the evolution of gas stops, and then stopper the flask tightly. The solution has a deep purple color.

Mercuric perchlorate solution, about 1*M*, 454 grams of mercuric perchlorate trihydrate in approximately 1 liter of 2% perchloric acid.

Standard uranium solution, 1.000 mg. of uranium per ml. in 2.5% sulfuric acid by volume. Prepare from NBL analyzed sample U_3O_8 No. 15, obtainable from New Brunswick Laboratory, New Brunswick, N. J.

Ceric sulfate solution, 0.01*N*. Dissolve 21.2 grams of $Ce(HSO_4)_4$ in 220 ml. of 1 + 1 sulfuric acid. Dilute to 4 liters. 1 ml. = 1.3 mg. of U (approximately). Standardize by titrating with the ceric sulfate solution a number of 50-ml. aliquots of the standard uranium solution, each in 175 ml. of 5% sulfuric acid, in accordance with steps 6, 7, and 8 of the procedure following.

Bulb, for precipitation and filtration of cupferrates. A 500-ml. leveling bulb with the connection for rubber tubing cut off, and the hole made to fit a No. 0 rubber stopper. The top of the bulb is also fitted with a rubber stopper. A 300-ml. Erlenmeyer flask can be substituted for the bulb, if the flask is fitted with a rubber stopper drilled in the center to fit a No. 0 stopper which can be removed for the filtration.

Filter stand. A stand for holding the bulb at the proper distance above the filter paper in a funnel, as shown in Figure 1.

PROCEDURE

1. Accurately weigh and transfer to a 300-ml. Erlenmeyer flask an appropriate weight of the sample, indicated by the figure for equivalent uranium (*e*U) which can be obtained by radiometric measurement. For 0.050 to 0.3% uranium use a 4-gram sample; for 0.3 to 3% uranium use 2 grams; for 3 to 6% uranium use 1 gram; for 6 to10 % uranium, use 0.5 gram; and above 10% use 1 gram. Dilute to volume with 5% sulfuric acid after step 5, and use an appropriate aliquot for titration.

2. Add 20 ml. of 1 + 1 sulfuric acid, 10 ml. of concentrated nitric acid, and 2 to 3 ml. of perchloric acid. Heat to boiling and then add 3 to 4 ml. of hydrofluoric acid (48%). Digest on the hot plate until action on the sample is complete (about 0.5 hour). Smith (*10*) discusses precautions in the use of perchloric acid.

3. Evaporate to dense fumes of sulfuric acid to remove organic matter, and hydrofluoric, perchloric, and nitric acids. Add more nitric and perchloric acids if necessary to ensure complete destruction of organic matter, and again evaporate to dense fumes. If organic matter is present, the solution remains brown after reaching dense fumes of sulfuric acid.

4. Remove the metals precipitated by cupferron as follows: After cooling the solution, add 80 ml. of water and 50 to 100 mg. of boric acid, and heat to boiling to dissolve soluble salts. Oxidize while hot with 2% potassium permanganate solution to a permanent pink. Cool in an ice bath to below 4° C. Transfer to a 500-ml. leveling bulb, rinsing the flask well with water cooled in an ice bath. Add about 4 grams of cupferron to the solution in the leveling bulb and shake thoroughly. If the supernatant liquid is still brown, add more cupferron, again shake the solution, and continue with small additions of cupferron until the supernatant liquid is clear.

Filter the solution into a 500-ml. Erlenmeyer flask through a 15-cm. fast filter paper by removing the lower stopper, washing it into the filter paper, and suspending the leveling bulb above the funnel through a ring in the filter stand (Figure 1), previously adjusted so that the bottom opening of the leveling bulb is well below the top of the filter paper to prevent overflow. The top stopper remains in place.

The solution flows from the bulb onto the filter only as fast as air enters the bulb from below, the level of liquid in the funnel thus being automatically kept below the edge of the filter paper. This filtration is very rapid and little change in the temperature of the solution occurs. Add a few drops of a 6% cupferron solution to the filtrate to test the completeness of the precipitation (shown by a white precipitate). If a brown precipitate appears, add an excess of cupferron and again filter. Wash the interior of the leveling bulb with cold 2% sulfuric acid saturated with cupferron, catching the washings on the paper, and wash the precipitate on the paper eight times with small portions of the same wash solution.

5. To the filtrate add 15 ml. of concentrated nitric acid and 2 to 3 ml. of perchloric acid. Evaporate the solution to dense fumes of sulfuric acid. If the solution is yellow or brown, indicating the presence of organic matter, evaporate to dryness, cool, and add 15 ml. of 1 + 1 sulfuric acid. After cooling, cautiously add 60 ml. of water, heat

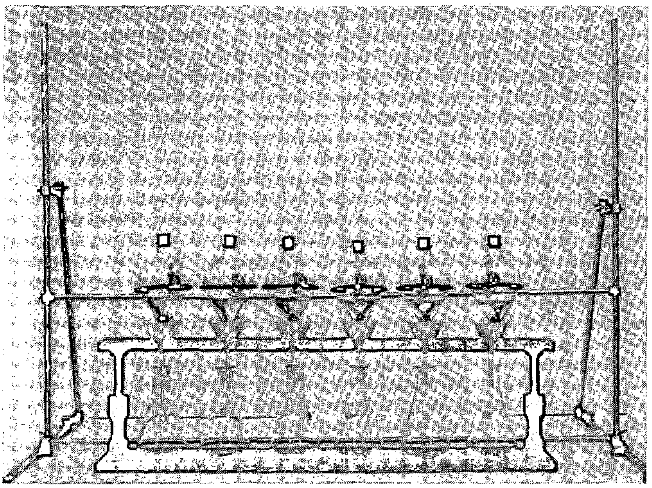

Figure 1. Apparatus for semiautomatic filtration to remove insoluble cupferrates

to boiling, and digest on the steam bath to dissolve all soluble salts. Cool. Filter if there is any precipitate (usually the precipitate is calcium sulfate or manganese dioxide). Transfer the solution to a 400-ml. beaker, rinsing the Erlenmeyer flask with water, and dilute to 175-ml. total volume.

6. Add 1 ml. of 4% cupric sulfate solution, place the beaker on a white surface, and then add the titanous sulfate solution slowly, with vigorous stirring, until a slight excess is shown by the appearance of a red precipitate of metallic copper. Allow the solution to stand for 15 minutes to permit the reaction to reach equilibrium. Add rapidly, with vigorous stirring, 2 ml. of the mercuric perchlorate solution.

If the mercuric perchlorate solution is not added rapidly enough, some metallic mercury forms which gives slightly high results for uranium (equivalent to about 0.2 mg. of uranium). If metallic mercury forms, its effect on the titration can be eliminated by covering it with a small quantity of chloroform or carbon tetrachloride.

7. As soon as the metallic copper disappears, add 2 ml. of the ferric sulfate solution and 2 ml. of the ferroin indicator solution. Titrate immediately with the standard ceric sulfate solution.

8. Run a reagent blank on 175 ml. of 5% sulfuric acid, following the procedure in steps 6 and 7.

9. From the volume of ceric sulfate solution used, after subtracting the blank, calculate the weight of uranium in the sample taken and the percentage of uranium in the ore.

RESULTS

Table I shows that consistently good results can be obtained with the method. In these experiments six samples, representative of the types of material usually analyzed for uranium in the laboratory but containing essentially no uranium, were selected. Solutions were prepared according to the procedure through step 3, and known quantities of uranium (0.0200, 0.0300, and 0.0400 gram) were added as standard solutions.

Table I. Determination of Known Quantities of Uranium

Sample	U Added, G.	U Found, G.	Difference, Mg. U
A	0.0200	0.0199	−0.1
	0.0300	0.0295	−0.5
	0.0400	0.0395	−0.5
B	0.0200	0.0199	−0.1
	0.0300	0.0297	−0.3
	0.0400	0.0393	−0.7
C	0.0200	0.0202	+0.2
	0.0300	0.0297	−0.3
	0.0400	0.0399	−0.1
D	0.0200	0.0202	+0.2
	0.0300	0.0299	−0.1
	0.0400	0.0399	−0.1
E	0.0200	0.0200	None
	0.0300	0.0299	−0.1
	0.0400	0.0398	−0.2
F	0.0200	0.0199	−0.1
	0.0300	0.0297	−0.3
	0.0400	0.0395	−0.5

In Table II, results with the new method are compared with those obtained with the usual method, in which interfering elements are separated with hydrogen sulfide and with cupferron, the solution is passed through an amalgamated zinc column (10% mercury), and the uranium oxidized by aeration to the quadrivalent state before titrating. The standard deviation between the two methods for the samples shown in Table II is 0.014%. The precision of the method may be somewhat greater than this, as replicate determinations on 11 ore-settlement pulps in the range of 0.20 to 0.40% U_3O_8 gave a standard deviation of 0.0034%.

Table II. Comparison of Results by Titanous Sulfate and Amalgamated Zinc Column Methods

	Uranium, %		
Sample No.	Titanous sulfate method, A	Amalgamated zinc method, B	Difference, A − B
1	0.34	0.32	+0.02
2	0.51	0.53	−0.02
3	0.61	0.61	None
4	0.81	0.81	None
5	0.82	0.83	−0.01
6	0.93	0.93	None
7	0.95	1.01	−0.06
8	0.98	0.98	None
9	1.11	1.12	−0.01
10	1.44	1.43	+0.01
11	3.02	3.02	None
12	3.80	3.79	+0.01

Two samples high in rare earths and niobium, which failed to give consistent results with the chloroform extraction of the cupferrates, did give consistent results when the insoluble cupferrates were filtered, as in the new method (0.38 and 0.38%, 1.05 and 1.07%, respectively).

INTERFERENCES

The elements of the hydrogen sulfide group not removed by cupferron do not interfere, unless present in extremely large amounts, and are not usually removed. Tests were made to study the effect of large quantities of these and other ions not removed by cupferron both on the blank and on the titration of known amounts of uranium (Table III). The ions were added in quantities equivalent to 2.5% of each ion in a 2-gram sample.

Silver is reduced to metal by the titanous sulfate, forming a cloud before all of the uranium is reduced. This masks the precipitation of copper metal used as an indicator of the reduction and may cause slightly low results due to incomplete reduction. This cloud disappears on the addition of mercuric perchlorate.

The results in Table III show that selenium, when present in abnormally large amounts, is the only serious interference. Samples known to be high in selenium must be given special treatment because the selenium is reduced to the metal by titanous sulfate and the red color of the selenium metal masks the end point of the ferroin indicator. As much as 5 mg. of selenium causes no difficulty. The selenium can be removed at the time of sample solution by boiling the sample with a mixture of dilute sulfuric acid, hydrobromic acid, and bromine before the addition of the nitric and perchloric acids.

Large amounts of nickel and cobalt do not interfere.

All the halogens cause serious interference because of their complexing action with cuprous ion, which prevents reduction to metallic copper. They are, however, removed during preparation of the sample solution.

A large concentration of nitrate may interfere by preventing the precipitation of metallic copper or by being reduced and consuming the titrant. However, 5 ml. of concentrated nitric acid added to a standard uranium solution caused no error in the titer for uranium. Residual nitrates that may be left in the solution, therefore, cause no serious error.

ACKNOWLEDGMENT

The authors wish to thank Raymond Havens and James E. Wilson for spectrographic and chemical analyses, and Rollin E. Stevens for helpful advice. This study is part of a program being

Table III. Noninterference from Ions Not Removed by Cupferron

	U Found, G.	
Ion Taken, 0.05 G.	U taken, none	U taken, 0.0220 g.
Ag^+	None[a]	0.0216
Hg^{++}	None	0.0219
Sb^{+++}	None	0.0219
As^{+++}	None	0.0219
Cr^{+++}	None	0.0220
Cd^{++}	None	0.0219
Pb^{++}	None	0.0217
Co^{++}	None	0.0219
Ni^{++}	None	0.0219
In^{+++}	None	. . .
Ge^{+4}	None	. . .
Tl^+	None	. . .
Te^{+4}	None	. . .
Se^0	Red color, not titrated	Red color, not titrated

[a] Titration within normal variation for blank.

conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials, U. S. Atomic Energy Commission.

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Determination of Aliphatic Primary and Secondary Plus Tertiary Amines

A Modified Salicylaldehyde Method

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▶ In a modified salicylaldehyde method for the determination of secondary and tertiary amines a chemical indicator is used to detect the equivalence point. The reaction of primary amines with salicylaldehyde to form the salicylaldehyde-imine is conducted in chloroform medium. The unreacted secondary and tertiary amines are titrated with standard perchloric acid in dioxane using bromocresol green indicator. After neutralization of the sample to bromocresol green indicator, the salicylaldehyde-imine, therefore the primary amine, is titrated with the same titrant using Congo red indicator.

Possibly the most versatile procedure yet developed for the determination of secondary and tertiary amines is the salicylaldehyde procedure of Wagner, Brown, and Peters (*5*). Salicylaldehyde reacts with primary amines to form imines. Most secondary and tertiary amines do not react and may be determined by titration in methanol medium with alcoholic hydrochloric acid. Siggia, Hanna, and Kervenski (*4*) modified this method for application to aromatic amines. From the standpoint of control of plant processes, these procedures suffer the disadvantage of requiring a complete potentiometric titration for detecting the equivalence point.

The Wagner, Brown, and Peters method requires a potentiometric titration because of the buffering effect of the weakly basic imines formed by reaction of primary amines with salicylaldehyde. As shown in Figure 1, in the presence of large amounts of primary amines, the titration of the unreacted secondary amine is affected by the basicity and concentration of the imine formed. Therefore, the sharpness of the potentiometric break is a function of the primary amine content of the sample. Attempts have been made to find a solvent system in which the imine does not exhibit appreciable basicity.

DEVELOPMENT OF METHOD

To find an indicator for use in conjunction with salicylaldehyde it was necessary first to find a solvent system in which imines can be distinctly differentiated from secondary amines by direct titration. Fritz (*3*) recommended acetonitrile medium and perchloric acid in acetonitrile as the titrant for this differentiation. Although acetonitrile is a better medium than methanol for this system, the millivolt reading at the equivalence point for the titration of secondary amines is affected to some extent by the concentration of the primary amine. Freeman (*2*) used chloroform medium and perchloric acid in dioxane as the titrant.

The titrant used for Figure 2 was perfluorobutyric acid in benzene and the titration was conducted in chloroform medium. By comparing curves 1 and 2 it can be seen that the presence of the imine has very little effect upon the titration curve. The indicator end point is independent of the amine concentration. This is not the case in methanolic medium, as shown in Figure 1. While perfluorobutyric acid is sufficiently strong to titrate most amines with ionization constants greater than 1 × 10^{-7}, it is too weak to be used for the titration of the salicylaldehyde-imines. This, coupled with the fact that chloroform is a good differentiating medium, no doubt causes the shape of the titration curve to be independent of the imine concentration. The high cost of perfluorobutyric acid prohibits its use in control work. An attempt was made to substitute trifluoroacetic acid but a stable reagent could not be made from this compound.

Figure 3, curve 1, shows the titration of 2-ethylhexylamines using 0.5*N* perchloric acid in dioxane as the titrant. The initial reaction and titration of the first equivalence point were conducted in chloroform medium. Then dioxane was added and the imine was titrated. The bromocresol green indicator end point, *P*, corresponds to the titration of di(2-ethylhexyl)amine. The difference between *T*, the Congo red indicator end point, and *P* corresponds to the titration of the imine. Figure 3, curve 2, is the titration of pure di(2-

ethylhexyl)amine under the same conditions. Although the presence of the imine has a marked effect upon the first equivalence point, the indicator end point coincides with the potentiometric equivalence point. Besides being inexpensive, perchloric acid offers a further advantage in that the second equivalence point is sharp and can be detected by means of an indicator.

APPARATUS AND REAGENTS

All potentiometric titrations were performed using a Leeds & Northrup line-operated pH meter. A sleeve-type calomel electrode with saturated potassium chloride in methanol (*1*) and a glass electrode were used in conjunction with this instrument.

SALICYLALDEHYDE, reagent grade.

DIOXANE, commercial grade, Carbide and Carbon Chemicals Co.

CHLOROFORM, Mallinckrodt Chemical Works analytical reagent.

PERCHLORIC ACID, 0.5N solution in dioxane. Shake the dioxane used to prepare this solution overnight with Amberlite IRA-100 ion exchange resin (*6*). Prepare the solution by diluting 70 grams of 70 to 72% perchloric acid to 1 liter with the special dioxane. Standardize against potassium acid phthalate.

BROMOCRESOL GREEN INDICATOR, 0.5% solution in methanol.

CONGO RED INDICATOR, 0.1% solution in methanol.

PROCEDURE

Add the volume of chloroform specified in Table I to a 250-ml. glass-stoppered Erlenmeyer flask followed by addition of the specified volume of salicylaldehyde. Add 4 to 6 drops of the bromocresol green indicator and neutralize just to the end point with perchloric acid in dioxane or alcoholic potassium hydroxide. Usually the latter step can be omitted, because the blank on the reagent is very small. Weigh into the flask an amount of sample calculated to contain no more than 12.5 meq. of primary amine and 12.5 meq. of secondary plus tertiary amine. If the solution becomes turbid because of the separation of the water of reaction, add the minimum quantity of dioxane necessary to effect solution. Allow the sample to react 15 minutes at room temperature before titrating it with standard perchloric acid in dioxane just to the disappearance of the green color. Record this titration and level the buret at zero. Add the volume of dioxane specified in Table I and 8 to 10 drops of the Congo red indicator. Titrate the sample with the perchloric acid solution to the appearance of a pure green color.

The amount of perchloric acid required for the first titration is a measure of the secondary plus tertiary amine content of the sample. The amount required for the second titration is a measure of the primary amine content.

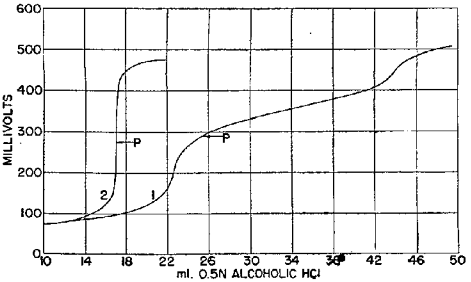

Figure 1. Titration of 2-ethylhexylamines by method of Wagner, Brown, and Peters (5)

1. Mixture containing 33.7% 2-ethylhexylamine and 65.1% di(2-ethylhexyl)amine
2. Di(2-ethylhexyl)amine

P. Bromocresol green indicator end point

DISCUSSION

Salicylaldehyde reacts quantitatively with most of the primary aliphatic amines investigated. The reagent tends to react with certain secondary amines, such as diethanolamine and diisopropanolamine (*5*). Listed in Table I are the amines whose corresponding secondary amines do not react with this reagent under the conditions of the method. In the method of Wagner, Brown, and Peters (*5*) only the secondary alcohol amines caused serious interference while in the present method many more secondary amines caused interference. Evidently these side reactions proceed to a greater extent in solvents of low dielectric constant—for example, the secondary amino nitrogen of diethylenetriamine reacts with salicylaldehyde in chloroform but not in methanol medium—and, have a greater tendency to take place in dioxane than in chloroform.

When salicyaldehyde reacts with primary amines in chloroform medium, water is formed and separates from solution. When this occurs dioxane can be used as a cosolvent to obtain a homogeneous solution, and to solubilize aqueous samples in the reaction medium.

Listed in Table II are purity data for amines that can be determined quantitatively. In Table III are li data for known mixtures of prim and secondary or tertiary amines, obtained as described. In general, the

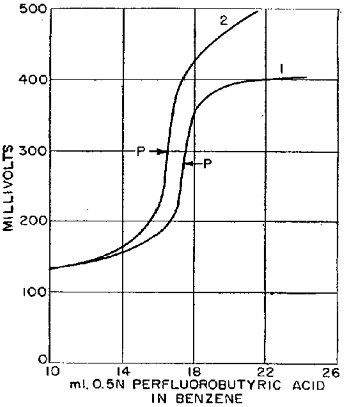

Figure 2. Titration of 2-ethylhexylamines in presence of salicylaldehyde using perfluorobutyric acid

1. Mixture containing 43.9% 2-ethylhexylamine and 55.2% di(2-ethylhexyl)amine
2. Di(2-ethylhexyl)amine

P. Bromocresol green indicator end point

Table I. Reaction Conditions for Determination of Primary, Secondary, and/or Tertiary Amines

	Reagent and Solvent Systems		
Amine Mixtures	Chloroform, ml.	Salicylaldehyde, ml.	Dioxane, ml.[a]
Butylamines	25	5	75
Ethylamines	25	5	75
2-Ethylhexylamines	25	5	75
Isopropylamines	50	10	50
Hexylamines	25	5	75
Methylamines	25	5	75
Propylamines	25	5	75

[a] Add dioxane after titration to bromocresol green indicator end point.

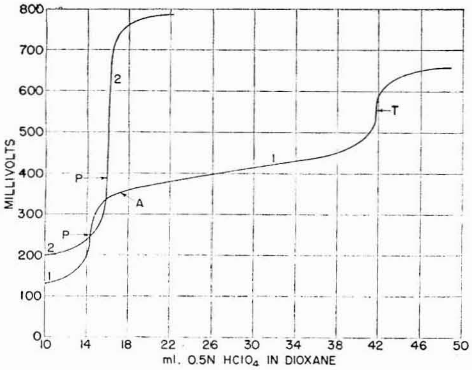

Figure 3. Titration of 2-ethylhexylamines in presence of salicylaldehyde using perchloric acid

1. Mixture containing 48.6% 2-ethylhexylamine and 49.5% di(2-ethylhexyl)amine
2. Di(2-ethylhexyl)amine
P. Bromocresol green indicator end point
A. Addition of dioxane
T. Congo red indicator end point

Table II. Determination of Purity of Primary, Secondary, and Tertiary Amines

Compound	Average Purity, Wt. %	
	Salicylaldehyde method[a]	Other[b]
Butylamine	97.5 ± 0.1 (2)	97.1
Dibutylamine	99.1 ± 0.2 (2)	99.6
Diethylamine	98.6 ± 0.0 (2)	99.1
Di(2-ethylhexyl)amine	99.2 ± 0.1 (2)	99.6
Dihexylamine	92.4 ± 0.0 (2)	92.6
Diisopropylamine	98.8 ± 0.1 (4)	99.4
Dimethylamine	37.7 ± 0.1 (2)[c]	37.8
Ethylamine	70.0 ± 0.1 (4)[c]	70.2
2-Ethylhexylamine	98.2 ± 0.1 (2)	98.0
Hexylamine	99.2 ± 0.2 (2)	99.1
Isopropylamine	98.8 ± 0.1 (3)	99.1
Methylamine	37.5 ± 0.3 (2)[c]	37.5
Triethylamine	99.6 ± 0.1 (2)	99.4
Tripropylamine	96.7 ± 0.1 (2)	96.9

[a] Figures in parentheses represent number of determinations.

[b] By titration with aqueous hydrochloric acid.

[c] Aqueous samples.

average deviation for the determination of both the primary and the secondary amine is ±0.3%. Because both primary and secondary or tertiary amines are determined by using a single sample, the lower limit of detection of each is limited by the total volume of titrant required. Therefore, for small amounts of primary or secondary amines the accuracy of the method is limited by the small net titration. However, fair results can be obtained for concentrations of primary and secondary or tertiary amine as low as 1.0%.

Ammonia does not react quantitatively with the reagent and must be separated before analysis. Heterocyclic secondary amines, such as morpholine, and secondary alcohol amines interfere if present. The method cannot be used for determining the primary and secondary amine content of polyethyleneamines such as diethylenetriamine and triethylenetetramine. However, as indicated in Table III, it is applicable to the determination of mixtures of ethylenediamine and secondary or tertiary amines. In general, it cannot be used for the determination of compounds that contain both primary and secondary or tertiary amino nitrogens in the same molecule.

The method cannot be used for the resolution of mixtures of aromatic primary and secondary amines or of mixtures of primary aromatic and primary aliphatic amines. However, secondary or tertiary aliphatic amines can be determined in the presence of aromatic amines.

Table III. Analysis of Known Mixtures of Primary and Secondary or Tertiary Amines

Mixture	Added, Wt. %		Found, Wt. %		Deviation, Wt. %	
	Primary	Sec. or tert.	Primary	Sec. or tert.	Primary	Sec. or tert.
Benzylamine-ethylcyclohexylamine	12.3	84.4	12.0	84.6	−0.3	+0.2
	83.8	12.4	83.8	12.4	0.0	0.0
Butylamine-dibutylamine	14.2	84.8	14.4	85.4	+0.2	+0.6
	84.2	13.6	84.2	14.0	0.0	+0.4
Ethylamine-diethylamine	9.9	84.6	10.4	84.8	+0.5	+0.2
	58.0	16.9	57.6	16.9	−0.4	0.0
Ethylamine-triethylamine	12.1	82.5	11.9	82.6	−0.2	+0.1
	53.5	24.8	53.0	25.1	−0.5	+0.3
2-Ethylhexylamine–di(2-ethylhexyl)amine	18.9	80.3	19.3	80.7	+0.4	+0.4
	80.0	18.9	80.3	18.6	+0.3	−0.3
Ethylenediamine-tripropylamine	10.3	87.0	10.3	86.7	0.0	−0.3
	81.7	15.2	81.9	14.6	+0.2	−0.6
Isopropylamine-diisopropylamine	2.2	97.1	2.3	97.1	+0.1	0.0
	83.2	15.4	83.4	15.0	+0.2	−0.4
Propylamine-tripropylamine	7.3	80.6	7.3	80.3	0.0	−0.3
	35.0	21.1	35.2	20.7	+0.2	−0.4
				Av. dev.	±0.22	±0.28

Imines formed by the reaction of any of the primary amines listed in Table II and aliphatic aldehydes and ketones can be determined. Usually a longer reaction time is required than for the parent amine. Salicylaldehyde apparently undergoes an exchange reaction with these compounds. For example, dibutylimine, the reaction product between butylamine and butyraldehyde, reacts quantitatively with salicylaldehyde in 30 minutes at room temperature. When the reaction is complete, the salicylaldehyde-imine can be titrated in the same manner as the imine formed from butylamine.

The method appears to be applicable principally to the analysis of mixtures of the simple aliphatic amines.

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Apparatus for Differential Thermal Analysis of Lubricating Greases

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▶ Differential thermal analysis is an excellent technique for the study of phase changes in metallic soap–oil systems such as lubricating greases. An automatic apparatus specifically designed for differential thermal analysis of lubricating greases is described. Experimental results reported include a re-examination of the phase change behavior of pure lithium stearate and a new phase diagram for the model grease system lithium stearate–*n*-hexadecane.

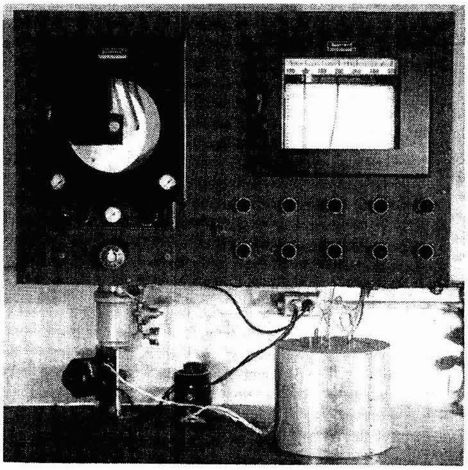

Figure 1. DTA apparatus

Most present-day commercial lubricating greases consist of a lubricating oil thickened to a grease consistency by a colloidal dispersion of a crystalline metallic soap. The application of differential thermal analysis (DTA) to such soap-hydrocarbon systems has been reported by several investigators (*3, 6, 9*). They have shown that several lithium and sodium soaps in various hydrocarbons exhibit distinct phase changes that occur reproducibly when the systems are heated. Such changes are caused by stepwise breakup and solution of the soap crystal structure (*2*). Determination of the phase change temperatures in a given soap-hydrocarbon system permits construction of a phase diagram with its solubility information. Measurements of the latent heat of phase transformation may be made, and the distinctiveness of differential thermograms for specific soaps or soap-solvent mixtures permits their use for identification purposes.

This paper reports the beginning of an investigation into lithium soap-oil systems using differential thermal analysis as the principal tool. The DTA apparatus has two advantages over those described previously (*3, 6, 7*). All experimental data are recorded automatically, and five different samples may be analyzed in a single experimental run.

MATERIALS

LITHIUM STEARATE. Hystrene S-97 stearic acid (Atlas Powder Co.) was recrystallized twice from methyl ethyl ketone, the second time using Norit A decolorizing charcoal. A third recrystallization from Sovasol No. 2 (a light naphtha, boiling point 60° to 90° C.) gave stearic acid with

Iodine No. (Hanus)	Nil
Acid No.	197.6
Melting point (microscope hot stage)	69.5–70.0° C.

A solution of stearic acid in Formula 30 ethyl alcohol was neutralized to a phenolphthalein end point by addition of a carbonate-free, 50% aqueous alcohol solution of lithium hydroxide (lithium hydroxide monohydrate, Foote Mineral Co.). After the crystalline soap precipitate which formed had been stirred and digested for 20 minutes, it was filtered and dried. The soap was recrystallized either from methanol or Formula 30 ethyl alcohol and dried in a vacuum desiccator at room temperature. It was stored in the desiccator over sodium hydroxide and soda lime.

n-HEXADECANE. Du Pont cetane was dried over Drierite.

SOAP-OIL SAMPLES. To ensure intimate mixture of lithium stearate–*n*-hexadecane samples before analysis, the samples were predissolved. The soap and hydrocarbon were weighed into borosilicate glass cells having a ground joint cap with stopcock. The cells were then carefully evacuated to about 2- or 3-mm. pressure to remove entrained air and refilled with dry nitrogen. The evacuation and nitrogen flush were repeated several times. The cells were then heated in an oil bath until all the soap dissolved in the hydrocarbon.

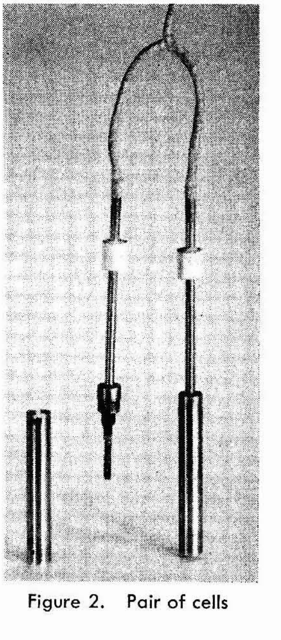

Figure 2. Pair of cells

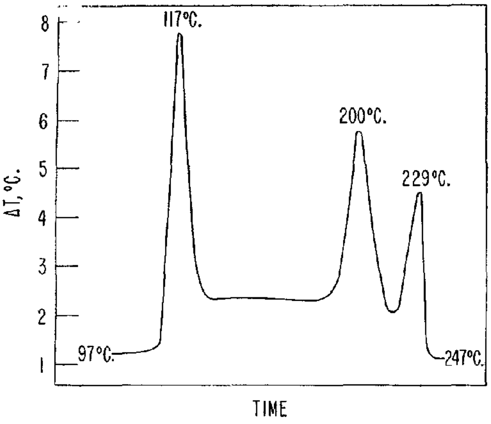

Figure 3. Heating thermogram for pure lithium stearate

Heating rate, 1.5° C. per min.

APPARATUS

Differential Thermal Analysis. The DTA apparatus shown in Figure 1 consists of three basic parts: the sample and reference cells and their thermal environment, the heat-control mechanism, and the temperature recording mechanism.

The heating bath is a cylinder of Duralumin which is heated from the center by a 900-watt, two-element cartridge heater and is insulated on the side and bottom by a thick layer of dense magnesia. The cylinder contains wells for five pairs of sample and reference cells. All wells are parallel to and equidistant from the axis of the cylinder. The sample and reference cells (Figure 2) are made of stainless steel tubing, machined to a wall thickness of 0.03 inch, and have a sample capacity of 4 cc. The cells are closed, but not sealed, by stainless steel, twist-lock caps. The temperature-sensing elements enter directly into the center of the cells through stainless steel shield tubes, integral with the cap. Each sensing element consists of a five-junction, iron-constantan thermopile for differential temperatures plus a single iron-constantan thermocouple to measure the actual cell temperature. The thermopiles and thermocouples are insulated by woven glass sleeves tied into a narrow bundle and coated with Teflon. The Teflon was applied as an aqueous dispersion and sintered to produce a thin, smooth, inert surface on the sensing element.

The heating rate of the Duralumin cylinder is controlled by a Minneapolis-Honeywell Regulator Co. Type 152 Air-O-Line, time-temperature program controller. This unit operates a variable transformer through which current is supplied to the heater. Part of the total heating current is supplied through a second variable transformer which is set manually for each different heating rate. This arrangement permits close automatic control of heating rates throughout the experimental runs. The maximum heating rate of about 2.5° C. per minute is set by the maximum output of the cartridge heater. Lower heating rates may be selected by suitable choice of controller settings. Cooling determinations so far have used the natural cooling rate of the heating block, which varies from about 1° C. per minute at 220° C. to about 0.3° C. per minute at 100° C. However, there is a coil of copper tubing wound around the block inside the insulation through which a fluid coolant may be circulated.

A 16-point potentiometer (Minneapolis-Honeywell Regulator Co.) automatically records all differential temperatures, cell temperatures, and the heating cylinder temperature on the same strip chart. The recorder reads and prints all 16 points in about 30 seconds, thus providing sufficient frequency of reading to define the temperature curves. The range of the recorder is −73° to 260° C.

Visual Observations. Visual features of phase changes in experimental samples were observed in a microscope hot stage using crossed polarizers. The hot stage was based on the design of Vold and Doscher (*8*). All samples were sealed in flat borosilicate glass capillaries to minimize oxidation. Temperatures in the hot stage were measured by an iron-constantan thermocouple connected to a self-balancing precision potentiometer. Calibration of the hot stage with A. H. Thomas Co. melting point standards showed that at temperatures of 200° C. and above, a thermal gradient of about 3° to 4° C. existed within the stage. Melting and other phase changes, therefore, appeared to take place over a wider range than actually exists.

Calibration of DTA Apparatus. The various operational characteristics of the DTA apparatus were determined using pure stearic acid and benzil as melting point standards. At first technical white oil or *n*-hexadecane was used as the reference material. Later, levigated alumina was substituted for the fluids.

The apex of the peak in the differential thermogram marked the completion of melting, and the actual cell temperature corresponding to the peak apex was within 1° C. of accepted values for the melting points of these standards (stearic acid, 70° C.; benzil, 95° C.). This accuracy was independent of either the heating rate or the peak amplitude. The heating rate was varied from 0.55° to 2.5° C. per minute, and the peak size was varied by mixing the standards with alumina. The identity of the peak apex with the accurate phase change temperature follows logically from the placement of the thermopile and thermocouple in the physical and thermal center of the sample.

Calculations of latent heat of fusion for stearic acid and benzil, using either the equation of Evans, Hutton, and Matthews (*3*) or the Vold method (*7*), showed that the present apparatus is not suitable for accurate calorimetry. Best results were only accurate to within ±10% of accepted values.

RESULTS AND DISCUSSION

Lithium Stearate. The phase change behavior of dry lithium stearate was determined by a series of differential thermal analysis runs made under varied conditions. Mixtures of lithium stearate with alumina having a soap content from 10 to 50% were run in addition to 100% soap samples. Also, duplicate samples were run at heat rates which varied from 0.55° to 1.5° C. per minute. In all cases the resulting thermograms showed three distinct peaks.

Figure 3 is a typical thermogram for a pure soap sample, replotted from the strip chart record. In all the runs the first peak occurred at 117° C. and the second at 200° C. However, the third peak's apex temperature varied from 229° to 225° C., depending on the heat rate and the amount of admixed alumina in the sample. The thermograms of soap without alumina all showed 229° C. for the third peak. The variation in the third peak is explained by the fact that there were two different phase changes concealed in the one peak. The first of these occurred probably at 225° C. or slightly higher and the second at 229° C.; the apparatus was not able to resolve the heat effects into two peaks. The existence of the 225° C. transition was verified in three separate batches of lithium stearate by cooling thermograms and by visual observations in the microscope hot stage. Figure 4 shows the cooling thermogram for the same sample heated in Figure 3. The 229° C. peak of Figure 3 was resolved by different amounts of supercooling into two peaks, one at 223° and the other at 207° C. The phase change which occurred at 200° C. on heating was lowered markedly to 137° C. on cooling, while the 117° C. heating transition was only slightly supercooled to 108° C.

The actual physical nature of these phase changes as seen in the hot stage between crossed polarizers is as follows. On being heated, lithium stearate went through a crystalline rearrangement at 117° C. At 200° C. the soap crystal presumably became somewhat disordered, but there was no obvious visual change except for a possible small increase in light transmittance. At 225° C. the soap softened to a jelly-like, brightly birefringent, liquid-crystalline phase, and at 229° C. the soap finally melted to a mobile isotropic liquid. The melting followed the previous change to the liquid crystal state so closely that it was possible to see three phases within the sample at one time. The thermal gradient in the hot stage persisted even with slow heating rates, so the assignment of the two phase change temperatures was based on the first appearance of the liquid crystal phase and on its complete disappearance. On being cooled, the sample went through the reverse sequence of phase changes at temperatures near those found by differential thermal analysis even when the cooling rate was roughly four times as great. The liquid-crystal phase was clearly homogeneous within its temperature range.

Vold and Vold reported only three phase changes in lithium stearate (*9*). These changes, on heating, were said to be an intercrystalline transition at 114° C., the beginning of a mesomorphic or waxy phase at 185° C., and final melting at 224° C. The lower temperatures assigned by Vold and Vold to the phase changes are explained by the fact that they took the sample temperatures at the beginning of phase change peaks in differential thermal analysis thermograms as the phase change temperatures. M. J. Vold had already pointed out (*7*) that this practice gave low results with that apparatus. In the cooling thermogram reported by Vold and Vold for lithium stearate, there were still only three peaks (*9*). The Vold apparatus may not have been able to resolve the two highest phase changes into two peaks.

The existence of two phase changes too close together for resolution by differential thermal analysis on heating was reported by Evans, Hutton, and Matthews (*3*), who observed the phenomenon in a technical lithium stearate in oil. In this case also, the two phase changes were detected when supercooling effects allowed their resolution into two peaks in the cooling thermogram.

Lithium stearate might be expected to have a liquid-crystal type mesomorphic phase on the basis of analogy to other alkali metal soaps. Vold and Vold studied a series of alkali metal palmitates by differential thermal analysis (*10*) and noted that lithium palmitate showed only three phase change peaks (at 103°, 190°, and 223° C.). Lithium palmitate apparently lacked the liquid-crystal phases, called neat or subneat, found in the other members of the series. They interpreted this to mean that lithium palmitate underwent two structural changes at the melting point. Because the palmitates resemble the stearates so closely, perhaps lithium palmitate may have an equilibrium liquid-crystal phase which exists at a temperature slightly below the melting temperature.

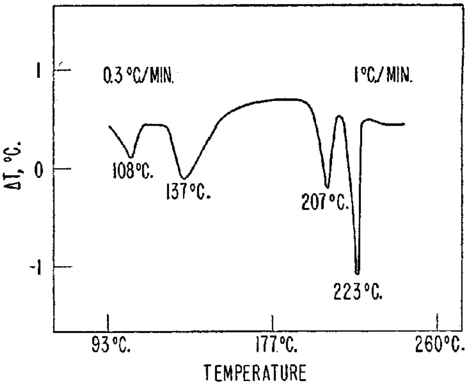

Figure 4. Cooling thermogram for pure lithium stearate

Cooling rate decreased from 1° to 0.3° C. per min.

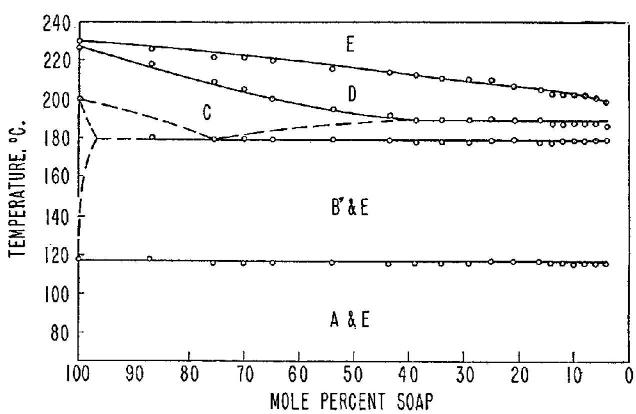

Figure 5. Phase diagram for lithium stearate–*n*-hexadecane

A. Crystalline lithium stearate II
B. Crystalline lithium stearate I
C. Waxy phase
D. Liquid-crystal phase
E. Isotropic soln.

System Lithium Stearate–*n*-Hexadecane. Figure 5 shows an equilibrium phase diagram for the system lithium stearate–*n*-hexadecane. The major boundaries in this diagram were determined by differential thermal analysis of soap-oil samples pretreated as described above. Visual observations of these samples between crossed polarizers in the hot stage supported the differential thermal analysis data. Because the observed phase change temperatures did not vary with the heating rate and were readily reproducible, they were assumed to be equilibrium values. The broken boundaries outline a possible eutectoid system but are not proved experimentally. The nomenclature of the phases was taken from Vold and Vold, except where noted differences occur.

The negligible interaction between crystalline lithium stearate II and *n*-hexadecane was shown by the failure of the solvent to lower the temperature of the intercrystalline shift at any concentration observed. The transition from crystalline lithium stearate I to the waxy phase was lowered from 200° to 179° C. in the dry soap by as little as

12.5 mole % of *n*-hexadecane. The constancy of the temperature of this phase change throughout the concentration range studied suggested a eutectoid between the crystal I phase, the waxy phase, and the liquid-sol phase. The phase boundary marking the transition from waxy phase to the liquid-crystal mesomorphic phase was lowered gradually by increasing percentages of *n*-hexadecane up to about 60 mole %. At lower soap concentrations the boundary was constant at 190° C. The temperature of final solution of lithium stearate in *n*-hexadecane was lowered in a gradual manner by increasing concentration of the hydrocarbon throughout the range studied.

The phase diagram for lithium stearate–*n*-hexadecane reported by Vold and Vold (*9*) showed a phase island called nonaqueous middle soap, by analogy to a similar phase reported for the system sodium stearate–*n*-hexadecane (*1*) and to aqueous, sodium-soap systems (*4*). The middle soap for lithium stearate was described as liquid-crystalline and was said to be completely bounded by the waxy and isotropic solution phases. The experimental observations of the present study clearly indicated that the liquid-crystal phase had the same character as the Vold and Vold middle soap, but that the phase was continuous with the liquid-crystal phase of the dry soap and persisted to as low a soap concentration as measured. There was no evidence for any phase island. The differential thermal analysis thermogram of the 3.9 mole % soap sample still clearly showed four peaks marking all the major phase boundaries. Visual observations of samples of low soap content in the hot stage was somewhat ambiguous because birefringence in the liquid-crystal phase becomes vanishingly dim at these low soap contents. However, there was a sharp transition between the jelly structure of the liquid-crystal phase and the fluid mobility of the solution. The visually observed jelly-sol transition in the low soap samples occurred at the same temperature as the top peak in thermograms.

The present disagreement concerning the phase behavior of lithium stearate in *n*-hexadecane may be compared to a similar case involving the system sodium stearate–*n*-hexadecane. Stross and Abrams (*6*) reported that this system contains no phase islands, all phases being continuous with ones occurring in the pure soap. Their report, which was based mainly on differential thermal analysis data, stands in contrast to those of Doscher and Vold (*1*) and of Smith and McBain (*5*), who reported phase islands in sodium soap–hydrocarbon systems. These latter investigators based their phase diagrams on visual observation alone. Stross and Abrams stated that a possible reason for the discrepancy between their findings and those of Doscher and Vold might lie in the failure of the latter to exclude all traces of water from the system. The major differences between results of the present lithium stearate system and those of Vold and Vold stem from the differing number of phases found in the pure soap and the different shape found for the solution boundary. These differences, in turn, seem to be explained by the greater accuracy and sensitivity inherent in the differential thermal analysis apparatus described above.

SUMMARY

An apparatus for differential thermal analysis of lubricating greases operates automatically in controlling heating rates and recording all pertinent temperatures and differential temperatures. Five different determinations may be run simultaneously, allowing rapid collection of data. The cell and thermopile design permits high sensitivity and accuracy in locating phase changes.

Differential thermal analysis of lithium stearate revealed a previously unreported mesomorphic phase occurring between 225° and 229° C. A differential thermal analysis study of the system lithium stearate–*n*-hexadecane yielded a phase diagram which appears to be more accurate than one previously reported.

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Thoron–*meso*-Tartaric Acid System for Determination of Thorium

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▶ In the spectrophotometric determination of thorium with thoron, *meso*-tartaric acid is used as a masking reagent for zirconium. The effects of different experimental variables such as the concentrations of the reagents, time, and temperature, and the behavior of 35 ions which might be present in thorium ores are discussed. A dilution procedure is given for the direct determination of thorium in zircon ($ZrSiO_4$) that is also generally applicable to other materials.

The determination of thorium in mineral separates such as zircon is important in Geological Survey programs on geochronology. However, the determination is usually lengthy, because zirconium is a serious interference in most methods for the determination of thorium. An earlier paper (*1*) stated that *meso*-tartaric acid should be superior to *d*-tartaric acid as a masking reagent for zirconium in the determination of thorium with thoron.

This paper confirms that statement and shows that no other major change results from the substitution of *meso*-tartaric acid for *d*-tartaric acid and that *meso*-tartaric acid is so effective in masking zirconium that a direct spectrophotometric method can be used to determine thorium in zircon. However, it is advantageous to make a potassium hydroxide separation which reduces the amount of several undesirable ions such as tin and fluorine.

The dilution procedure that follows may be used wherever applicable, but was designed primarily for zircon samples that contain 0.1% or more of thorium dioxide. In the range below 0.1% of thorium dioxide, the results are reliable to only one significant figure.

APPARATUS AND REAGENTS

Spectrophotometer. A Beckman DU spectrophotometer with a housing for 5-cm. cells and with the lamp housing cooled by circulating water thermostatically controlled at room temperature was used.

Sand bath. The temperature of the sand (just below the surface) was 170° to 190° C.

All chemicals used were reagent grade.

Potassium hydroxide (precipitating solution), 50% by weight.

Potassium hydroxide (wash solution). Dilute 2 ml. of the 50% solution to 500 ml. with water.

Hydroxylamine hydrochloride, 10% w./v. aqueous solution.

Cupric chloride (catalyst solution), 1 ml. equivalent to 1 mg. of CuO. Dissolve 0.538 gram of cupric chloride dihydrate in 250 ml. of water.

Thoron [disodium salt of 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid], 0.1% w./v. aqueous solution.

meso-Tartaric acid, 10% w./v. aqueous solution. Filter if necessary. The reagent is available from several suppliers such as The Jasonols Chemical Corp., Delta Chemical Co., and Bios Chemical Co.

PROCEDURE

Mix 50 mg. of a representative finely ground sample with 4 to 5 grams of fresh sodium peroxide in a small crucible and cover the crucible. Sinter and leach (*2*). Then place the covered beaker on a steam bath and digest the solution to remove hydrogen peroxide. After 30 minutes on the steam bath, acidify the solution with (1 plus 1) hydrochloric acid and add about 2-ml. excess. Remove the crucible and lid, police, and rinse them with water.

If the sample is not completely decomposed, add a little paper pulp to the solution, filter off the residue through a slow 7-cm. filter paper, and wash well with water. Reserve the filtrate. Ignite the residue, add sodium peroxide, and repeat the decomposition procedure.

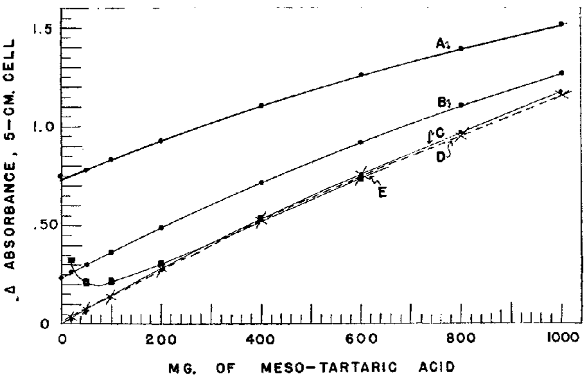

Figure 1. Effect of *meso*-tartaric acid

A. 60.36 γ of ThO_2 + 3 mg. of thoron
B. 20.12 γ of ThO_2 + 3 mg. of thoron
C. 3 mg. of thoron
D. 1 mg. of ZrO_2 + 3 mg. of thoron
E. 5 mg. of ZrO_2 + 3 mg. of thoron

Add the solution from the second sinter to the original filtrate.

Neutralize the combined solutions with 50% potassium hydroxide and add 5-ml. excess for each 50 ml. of solution. Digest the solution on a steam bath for 15 to 20 minutes, then filter it through a fast 7-cm. filter paper, and wash with dilute potassium hydroxide wash solution. Drain the precipitate and funnel stem by placing the palm of the hand over the funnel and pressing down. Dissolve the precipitate from the paper with hot (1 plus 1) hydrochloric acid (total volume about 20 ml.) and heat the solution on a steam bath for several minutes to ensure complete solution. Cool the solution, transfer it to a 25-ml. volumetric flask, and make to volume with (1 plus 1) hydrochloric acid.

Transfer a 3- to 5-ml. aliquot of this sample solution to a 100-ml. beaker and add 1 ml. of perchloric acid. Evaporate the solution on a steam bath until all of the hydrochloric acid has been removed and fumes of perchloric acid appear. Transfer the beaker to a sand bath and evaporate until all of the perchloric acid has been removed. Careful heating at sandbath temperatures is necessary here because heating on a hot plate or fuming over a burner often converts zirconium to an insoluble form that occludes thorium.

Cool the beaker and add 1 ml. of (1 plus 1) hydrochloric acid. Rotate and tip the beaker so that the acid comes in contact with all parts of the residue. Allow to stand 1 to 2 minutes, then add 4 ml. of water. Cover the beaker and place on a steam bath. After 5 minutes, add 1 ml. of hydroxylamine hydrochloride solution and 0.2 ml. of cupric chloride catalyst solution. Recover the beaker and heat on a steam bath for 5 more minutes. Cool to room temperature. If the solution is clear and there is no residue, transfer it directly to a 25-ml. volumetric flask. Otherwise, add a little paper pulp and filter the solution into the flask through a very small slow filter paper and wash. Rinse the neck of the flask with a little water. Add 4 ml. of *meso*-tartaric acid and mix. Add 3 ml. of thoron solution, rinse the ground-glass part of the neck of the flask, and add water almost to volume. Allow 1 to 2 minutes for drainage in the neck of the flask, then make the solution to volume.

Measure the absorbance of the solution at 545 mμ against a reference blank that contains 1 ml. of (1 plus 1) hydrochloric acid, 1 ml. of hydroxylamine hydrochloride, 4 ml. of *meso*-tartaric acid, and 3 ml. of thoron per 25 ml. of solution. Make the measurement within 5 to 10 minutes after adding the *meso*-tartaric acid if a 10-mg. sample aliquot was used. Use 5-cm. matched or calibrated cells for the solutions. If the measurements are made with a Beckman spectrophotometer, use a slit width of 0.15 mm. or smaller. Determine the amount of thorium present in the aliquot by reference to a standard curve or by calculation. Data for a standard curve are obtained from measurements of solutions containing known amounts of thorium chloride.

EXPERIMENTAL

Establishment of Operating Conditions. From the data obtained earlier (*1*), it was decided to develop a thoron–*meso*-tartaric acid system based on 3 mg. of thoron and 1 ml. of (1 plus 1) hydrochloric acid per 25 ml. of solution. With this concentration of thoron there is a sufficient excess to permit the determination of as much as 150 γ of thorium dioxide and tolerances to rare earth and negative ions should be somewhere between those of the two systems using *d*-tartaric acid (*1*).

The effect of the concentration of *meso*-tartaric acid is shown in Figure 1, where the difference in the absorbances due to *meso*-tartaric acid of solutions containing thoron alone (3 mg.), thoron with 20.12 and 60.36 γ of thorium dioxide, and thoron with 1 and 5 mg. of zirconium dioxide are plotted as functions of the concentration of *meso*-tartaric acid. The reference solution for these measurements contained 3 mg. of thoron but no *meso*-tartaric acid. These data indicate that 300 to 400 mg. of *meso*-tartaric acid will mask the effect of 5 mg. of zirconium dioxide.

In the experiments with 5 mg. of zirconium dioxide, a precipitate of zirconium *meso*-tartrate formed with time in sharp contrast to the high solubility of zirconium *d*-tartrate. The effect of the concentration of *meso*-tartaric acid was, therefore, examined further. Absorbance measurements were made periodically on three solutions all of which contained 5 mg. of zirconium dioxide and 3 mg. of thoron and all of which were identical except for their *meso*-tartaric acid contents, which were 200, 400, and 500 mg. The absorbances of these solutions were measured against corresponding reference solutions containing the same amount of *meso*-tartaric acid and other reagents but no zirconium. The data are presented in Figure 2, where the absorbance differences due to zirconium are plotted as a function of the period of time between the addition of *meso*-tartaric acid and measurement of absorbance. Practically no changes in the absorbances of the solutions occur during the first of 5 to 11 minutes following the addition of *meso*-tartaric acid. In this region of the curve, 400 mg. of *meso*-tartaric acid are effective in preventing the formation of enough zirconium-thoron complex to interfere. The break at the end of the regions of almost constant absorbance in each of the curves in Figure 2 corresponds to the time required for precipitation of zirconium *meso*-tartrate to begin. As the break in each of the various curves occurs after the same period of time, the precipitation time is essentially independent of the concentration of *meso*-tartaric acid at these concentration levels.

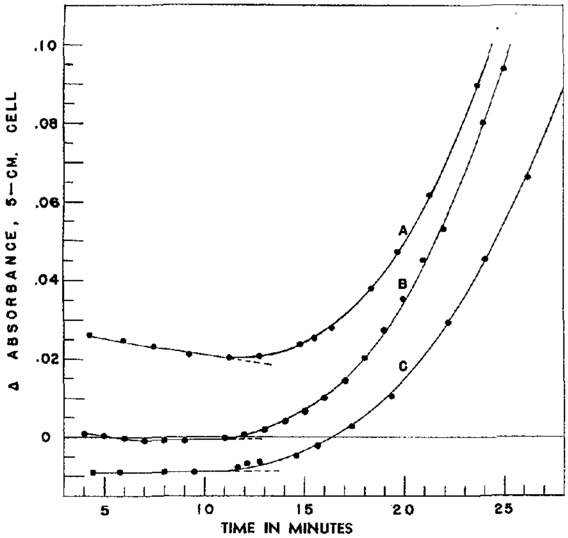

Figure 2. Effect of concentration of meso-tartaric acid on the reaction of 5 mg. of zirconium dioxide

A. 200 mg. of *meso*-tartaric acid
B. 400 mg. of *meso*-tartaric acid
C. 500 mg. of *meso*-tartaric acid

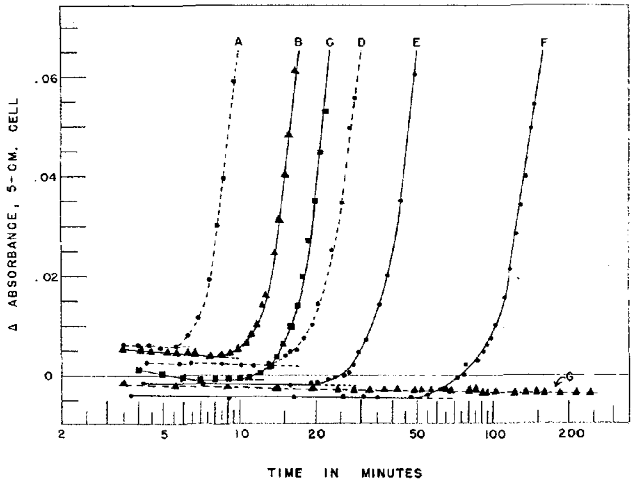

Figure 3. Effect of time on interference from different amounts of zirconium dioxide

A. 8 mg. of ZrO_2
B. 6 mg. of ZrO_2
C. 5 mg. of ZrO_2
D. 4 mg. of ZrO_2
E. 3 mg. of ZrO_2
F. 2 mg. of ZrO_2
G. 1 mg. of ZrO_2

The precipitation was also followed by observation of the Tyndall effect which is evident at the start of the precipitation. The same period of time was required for the appearance of a Tyndall beam in solutions containing 5 mg. of zirconium dioxide and 400 mg. of *meso*-tartaric acid with and without thoron. The precipitation time for zirconium *meso*-tartrate is thus practically independent of the thoron concentration. On the basis of these tests 400 mg. of *meso*-tartaric acid was selected for the final procedure.

Standard Curve. The standard curve relating absorbance and concentration of thorium is linear from 3 to 150 γ of thorium dioxide per 25 ml. of solution. In this range of concentration an absorbance difference of 0.010 is equivalent to 1 γ of thorium dioxide. Below this range the standard curve has a slight heel if the phototube normally supplied with the Beckman instrument is used. The substitution of a photomultiplier tube allows the use of very narrow slit widths (0.015 to 0.045 mm.) and results in a standard curve that is linear over its entire length.

Sources of Error. VARIABLE VOLUMES. For greatest accuracy, the sources of possible error should be recognized and precautions taken to minimize the errors. The reference

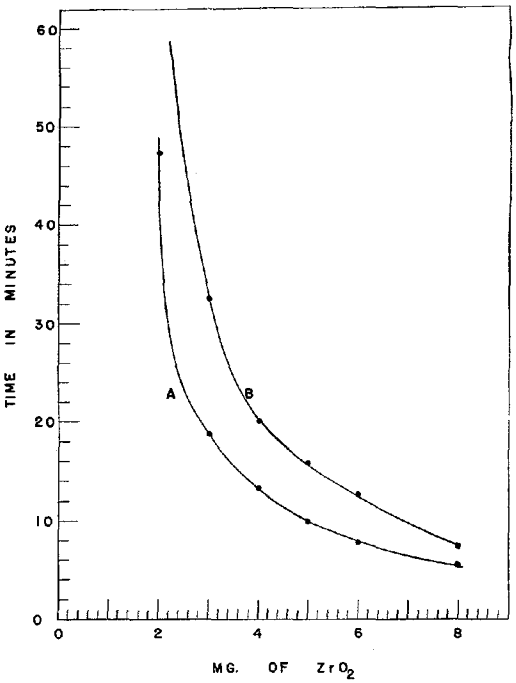

Figure 4. Time-zirconium areas for noninterference of zirconium

A. Time for start of precipitation
B. Time for an increase of 0.010 in absorbance

blank has an absorbance of 1.33 with respect to water. If an absorbance difference of 0.002 between sample and reference solution is to be meaningful, great care must be exercised in preparing each; the volume of thoron added to the reference and sample solutions must be reproduced to 1.5 parts per 1000; the volume of *méso*-tartaric acid added, to 2.5 parts per 1000; and the final volume of the solution, to 1.5 parts per 1000. Because the precision in the reproduction of the measurements of these volumes is the significant factor, the same pipet should be used to add a given reagent to both sample and reference solutions.

TEMPERATURE. If the reference solution is hotter than the sample solution, the sample solution will read too high; if the reference solution is cooler, the sample solution will read too low. The relationship between the difference in temperature of the two solutions and the difference in their absorbances is linear. A difference of ±0.8° C. between the two solutions results in an absorbance difference of ± 0.002.

Behavior of Various Ions Under Operating Conditions. The data on the behavior of various amounts of zirconium are summarized in Figure 3, where the absorbances are plotted against the time between the addition of *meso*-tartaric acid and measurement of the absorbance. The small variations between the absorbances in the horizontal parts of the different curves are probably not significant, as insufficient time was allowed for proper drainage in the necks of the flasks.

In Figure 4, *A*, the time after the addition of *meso*-tartaric acid at which the break occurs in each of the curves in Figure 3 is plotted as a function of the amount of zirconium present. It it safe to measure the absorbance of a solution containing a given amount of zirconium at any time along that part of its ordinate that lies below curve *A* in Figure 4. Figure 4, *B*, represents the total time required for an absorbance increase of 0.010 greater than any point in *A*.

The relationship between time and the beginning of precipitation of zirconium *meso*-tartrate shown by the curves in Figures 3 and 4 holds only if the zirconium used is present as a simple ionic species. The standard zirconium solutions used in these studies were prepared

Table I. Milligrams of Various Elements (as Oxides) Equivalent to an Absorbance Difference of 0.010

(Slit width = 0.15 mm.)

Element Tested	Mg. Equivalent to Absorbance Difference of 0.010		
	0 γ ThO_2	50.3 γ ThO_2	150.9 γ ThO_2
Sc_2O_3	> 2.0	0.11	0.120
Y_2O_3	2.6	2.6	6.56
La_2O_3	0.45	0.70	>10.0
Ce_2O_3	0.37	0.49	1.12
Pr_2O_3	0.43	0.83	1.3
Nd_2O_3	0.68	0.76	1.0
Sm_2O_3	0.60	0.56	3.6
Eu_2O_3	1.25	1.25	4.5
Gd_2O_3	1.45	1.85	7.4
Ho_2O_3	2.2	...	...
Yb_2O_3	3.8	8.5	>10
TiO_2	1.2	0.019	0.009
ZrO_2[a]	8	8	8
Nb_2O_5	0.22	0.20	0.075
Ta_2O_5	> 1.0	0.045	0.035
WO_3	> 10	2.0	1.2
UO_3	0.36	0.42	0.55
Fe_2O_3	0.47	0.10	0.056
Fe_2O_3[b]	> 10	> 10	>10
Au_2O_3	> 5.0	> 5.0	> 5.0
HgO	> 30	> 30	>30
Al_2O_3	5.7	21	25.2
SnO_2	0.062	0.055	0.035
PbO	7.0	11.0	20.0
Bi_2O_3	11.5	12.0	12.5
P_2O_5	> 10	0.42	0.12
SO_3	> 10	1.25	0.65
F	4.1	0.003	0.001
ZnO	> 30.0	> 30.0	>30.0
Pt	5.9	6.8	8.5
Na_2O	40	88	42
K_2O	>500	68	29
MgO	23	>100	30
CaO	10	39	13
MnO	> 40	...	10
CuO	> 5.0	4.0	> 5

[a] Time dependent.
[b] Reduced to Fe^{++} using cupric chloride catalyst..

by boiling zirconyl chloride in (1 plus 1) hydrochloric acid and by maintaining this high acidity whenever weaker zirconium solutions were made by dilution. In more dilute acid solutions of zirconium, unless freshly diluted from strong acid solutions, zirconium is often present in polymerized form. As little as 1.5 mg. of zirconium in this form give a precipitate almost immediately with *meso*-tartaric acid. Provision is made in the detailed procedure to guard against polymerization of zirconium. Using this procedure, 5 to 8 mg. of zirconium dioxide may be present in the spectrophotometric determination of thorium if absorbance measurements are made within the time shown to be safe by *A*, Figure 4.

The behavior of other ions when 0, 50.3, or 150.9 γ of thorium dioxide also are present is summarized in Table I. This table shows the amount of the element, calculated to the equivalent amount of oxide, that causes a change in the absorbance of 0.010 at three concentration levels of thorium.

Fluorine, titanium, tantalum, tin, and niobium are serious interferences. Iron is not included in this group of seriously interfering elements because, as is done in the final procedure, it is readily reduced by hydroxylamine hydrochloride in the presence of cupric chloride which serves as a catalyst for the reduction. When reduced to the ferrous state, as much as 10 mg. of equivalent ferric oxide may be present.

Table II. Test of New Procedure for Determination of Thorium in Zircon

Sample	Thorium Dioxide Found, % Other methods	New method	Sample in Final Aliquot, Mg.
Zircon 2	0.15	0.15	4
Zircon 1	0.065	0.07	8
		0.07	8
Zircon 3	0.059[a]	0.06	8
		0.07	8
		0.06	10

[a] Method described by Grimaldi and others (*2*).

Test of Procedure. The procedure was used to determine thorium in several zircon samples that had been analyzed carefully by other methods. The percentages of thorium dioxide determined by independent means and by the new method are shown in Table II. The size of the sample aliquot used for each determination by the new method is also included.

ACKNOWLEDGMENT

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Determination of Carbon in Bromine

MAURICE CODELL and GEORGE NORWITZ

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▶Carbon in bromine can be determined by passing the sample with oxygen through a tube at 1000° C. to convert the carbon compounds to carbon dioxide. The bromine is frozen out in dry ice traps, and the carbon dioxide is purified by passing it through copper sulfate, manganese dioxide, and Anhydrone.

An accurate method was needed for the determination of carbon in bromine, because bromine frequently contains halogenated hydrocarbons such as chloroform, bromodichloromethane, and bromoform (*5, 7*). The effect of carbon compounds in c.p. bromine in causing a very high blank in the bromination–carbon reduction method for determining oxygen in metals has recently been discussed (*2*).

No accurate method is known for the determination of carbon or carbon compounds in bromine. However, a method has been used since at least 1896 (*1, 6–8, 10*) for the detection of organic compounds in bromine. The method consists of adding 1 ml. of bromine to 25 ml. of 10% sodium hydroxide solution and allowing it to stand overnight. The presence of organic material is indicated by oily drops or a film of oil. This method is of questionable validity. When it was applied to bromine that contained 1% by volume of chloroform, a clear solution was obtained. This is not surprising because chloroform is easily oxidized to carbonyl chloride or carbon dioxide (*4*). An alkaline solution of bromine is a strong oxidizing agent and would be expected to oxidize many organic compounds to water-soluble substances.

In the method proposed here, the sample is treated with oxygen in a tube at 1000° C. to oxidize the carbon compounds to carbon dioxide. The bromine is frozen out in dry ice traps, and the gases are passed through copper sulfate (on asbestos), manganese dioxide, and Anhydrone, and then into a tared bulb containing Ascarite. The copper sulfate absorbs traces of bromine and hydrogen bromide. Previously, copper sulfate was recommended for the absorption of chlorine and hydrogen chloride in the determination of carbon (*3*). The effectiveness of copper sulfate in absorbing bromine is readily demonstrated by passing bromine into a tube packed with the copper sulfate reagent. No bromine will issue from the exit end of the tube. Most of the hydrogen bromide in the bromine would be oxidized to water and bromine in the combustion tube. The purpose of the manganese dioxide is to absorb sulfur dioxide. Manganese dioxide has been used for removing sulfur dioxide in the determination of carbon in steels (*9, 11*). Only high purity manganese dioxide of large surface area should be used. [The following were satisfactory: manganese dioxide, Special, Fisher Scientific Co., or manganese dioxide prepared as described by Pigott (*9*) or U. S. Steel Corp. (*11*)]. Any sulfur trioxide (freezing point, 17° C.) produced in the combustion is frozen out. The oxygen used for the combustion is purified by passing it through copper oxide heated to 600° C. and then through Ascarite and Anhydrone.

APPARATUS

A diagram of the apparatus is shown in Figure 1. All parts of the apparatus that come in contact with bromine are made of glass. The adapter for the combustion tube and the combustion tube are tilted downward at a 10° angle to prevent bromine from flowing back. To avoid clogging of the system with frozen bromine, the combustion tube is connected directly to the first trap which contains no inlet tube. The second trap has an inlet tube that reaches about halfway to the bottom of the trap. The third trap has an inlet tube that extends almost to the bottom of the trap. There is no danger of a pocket of gas forming at the bottom of the first or second traps, because diffusion is rapid when there is a flow of gas. The apparatus should be arranged so that the adapter for the combustion tube, the combustion tube, and the first trap are situated under a hood. This is a safety precaution to prevent possible leakage of bromine fumes into the laboratory.

The joints of the apparatus must be held together by springs. To ensure a perfect fit, the joints and stopcock for the sample flask should be ground together with a paste made from carborundum and water. The stopcock should be lightly greased with Fluorolube grease MG. Fluorolube is the only grease known that is not attacked by bromine. Fluorolube liquid grease S should not be used for greasing the stopcock, because it might be washed mechanically by the bromine into the adapter. All joints between the exit end of the combustion tube and the first bubbler should be well greased with Flurolube grease MG or Fluorolube liquid grease S to prevent leakage of carbon dioxide into the system from the dry ice.

REAGENTS

Oxygen, high purity.

Cupric oxide, fine wire form, reagent grade.

Manganese dioxide, Special, Fisher Scientific Co.

Glass wool, Corning Glass Works, Corning, N. Y.

Fluorolube grease MG and Fluorolube liquid grease S, Hooker Electrochemical Co., Niagara Falls, N. Y.

Copper sulfate reagent. Dissolve 200 grams of copper(II) sulfate pentahydrate in 500 ml. of hot water in a tray. Add 0.5 pound of asbestos that has been ignited at 1000° C. and stir well. Evaporate to dryness on a hot plate and dry in an oven overnight at 200° C. Store in a stoppered bottle.

METHOD

Prepare the train as shown in Figure 1. Heat the copper oxide to 600° C. and the combustion tube to 1000° C. Add pieces of dry ice of about 1/2 cubic inch to the dry ice traps. Fill the first and third traps close to the top with dry ice and fill the second trap half full. Flush the sample flask for about 2 minutes, then turn the stopcock so that the oxygen bypasses the sample flask. Flush the system for a few minutes, then connect the absorption bulb. Adjust the flow of oxygen to about 250 bubbles per minute in the first bubbler. After a few minutes disconnect the absorption bulb, open it momentarily to the atmosphere to equalize the pressure, and weigh. Reconnect the bulb and weigh again after 10 minutes. If constant weight has not been obtained (0.05 mg.), repeat the process.

Add 10.0 ml. of bromine to the sample flask, and stopper. Turn the stopcock so that the bromine falls dropwise into the adapter for the combustion tube. Regulate the bromine flow so that complete addition takes about 30 minutes. After all the bromine has been added, turn the stopcock of the sample flask and brush the adapter with a flame to drive over any residual bromine. Allow the system to sweep out for 15 minutes, disconnect the absorption bulb, and weigh. Determine the blank (usually about 0.2 mg.) by proceeding as above without the bromine.

Calculate the per cent carbon by use of the following equation:

$$\% \text{ Carbon} = \frac{27.29\,(A - M)}{VS}$$

where A = weight of carbon dioxide, grams
M = weight of carbon dioxide for blank, grams
V = volume of bromine taken, ml.

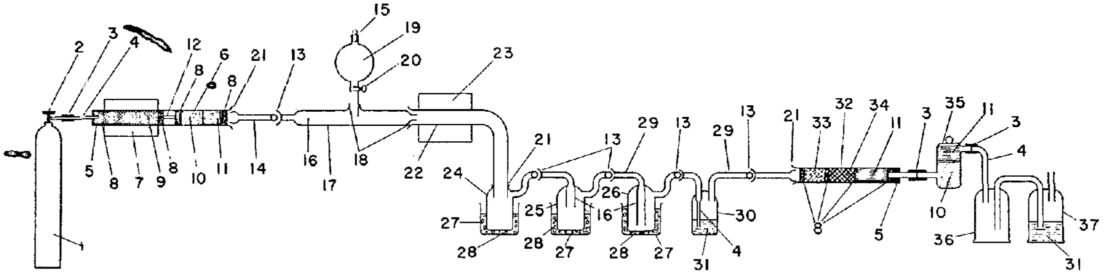

Figure 1. Apparatus for determining carbon in bromine

1. Tank of oxygen
2. Needle valve
3. Gum rubber tubing, small piece
4. Borosilicate glass tubing, 7 mm.
5. Rubber stopper
6. Copper oxide–Ascarite–Anhydrone tube 96% silica, 1 inch in diameter and 22 inches long
7. Electric heater for copper oxide, 600° C., 10 inches long
8. Glass wool
9. Copper oxide
10. Ascarite
11. Anhydrone
12. Borosilicate glass tubing, 0.75 inch in diameter and 2 inches long, to separate copper oxide from Ascarite
13. Ball joint (18/9)
14. Borosilicate glass tubing, 6 inches long and 10 mm. in diameter
15. Ground-glass stopper
16. Borosilicate glass tubing, 18 mm. in diameter
17. Adapter for combustion tube, 6 inches long
18. Ground-glass joint (19/38)
19. Sample flask, borosilicate glass, capacity, 50 ml.
20. Stopcock
21. Ground-glass joint (24/40)
22. Combustion tube, quartz or 96% silica, 1 inch in diameter. Horizontal portion is 15 inches long, vertical portion is 12 inches long
23. Electric heater for combustion tube, 1000° C., 10 inches long
24. First trap, borosilicate glass, 1.25 inches in diameter and 6 inches in height. Side arm is 3 inches long.
25. Second trap, borosilicate glass, 1.25 inches in diameter and 6 inches in height. Inlet tube reaches to 4 inches from bottom. Side arms are 3 inches long.
26. Third trap, borosilicate glass, 1.25 inches in diameter and 6 inches in height. Inlet tube reaches to 0.5 inch from bottom. Side arms are 3 inches long.
27. Thermos beakers
28. Dry ice
29. Borosilicate glass tubing, 10 mm.
30. Sulfuric acid bubble counter, 1.25 inches in diameter and 6 inches in height. Side arms are 2 inches long.
31. Sulfuric acid
32. Copper sulfate–manganese dioxide–Anhydrone tube, 1 inch in diameter and 12 inches long
33. Copper sulfate mixed with asbestos
34. Manganese dioxide
35. Small absorption bulb (U type)
36. Small suck-back trap
37. Small sulfuric acid bubble counter

s = specific gravity of bromine (3.12 for C.P. bromine)

Several determinations may be made without cleaning the traps. When cleaning is desired, allow the traps to thaw until the bromine is completely melted and then add water. Do not add water to the traps while they contain frozen bromine, because this may cause microscopic cracks to develop in the glass. Wash the contents of the traps into a beaker of water and destroy the bromine by adding ammonium hydroxide. Rub off the grease from the ball joints with a cloth and wash the traps in hot water. Dry in an oven at 150° C.

RESULTS

The following results were obtained for carbon in two samples of C.P. bromine from different companies:

	% Carbon	
	Company A	Company B
	0.0086	0.0099
	0.0076	0.0100
	0.0083	0.0099
	0.0077	0.0096
Av.	0.0081	0.0098

There seems to be about 0.009% carbon present in C.P. bromine. If this carbon was present as chloroform, there would be about 0.05% chloroform in the bromine.

To check the validity of the method further, the bromine that had accumulated in the first trap was analyzed for carbon after carefully drawing it up with a pipet (to avoid contact with the grease). No significant amount of carbon could be detected.

Varying amounts of chloroform were weighed in glass-stoppered flasks and portions of purified bromine, recovered from the traps, were added. The samples were then analyzed for carbon and the following results obtained:

Carbon Present, %	Carbon Found, %
0.021	0.020
0.032	0.032
0.074	0.072
0.115	0.118

DISCUSSION

The dry ice is essential for the method. The use of liquid nitrogen or liquid air in place of the dry ice causes the carbon dioxide to freeze. Various salt and ice mixtures were also ineffective in freezing out the bromine. The addition of alcohol or acetone to the dry ice is not necessary, as dry ice alone in thermos beakers is equally effective.

The sample must be introduced by means of a dropping device as shown in Figure 1. If the sample is passed into the combustion tube by bubbling oxygen through a small bottle containing the bromine, some oily material remains that cannot be driven off without charring.

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Interaction of Beta Particles with Matter

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▶ **Of the several phenomena involved in the interaction of beta particles with matter, systematic studies on the relative backscattering of betas by matter have shown that simple regularities obtain for all elements and compounds, and that these can be measured with high precision. The measurements have been applied to solids, liquids, and solutions. Values predicted for pure crystalline solids can be checked to a precision close to that with which the atomic weights are known.**

When beta particles strike matter, some of them are "reflected" and return in the general direction they came from. That this behavior is not a case of ordinary reflection was demonstrated by showing that the backscattering increases with increasing thickness of the target and eventually reaches a limiting value. The early studies showed a slow increase in backscattering with increasing atomic weight of the scatterer and some evidence of periodicity. There was also some evidence that the backscattering by compounds can be predicted from the intrinsic scattering of the constituent atoms (*1*, *3*).

The present studies show that the backscattering of beta particles is a discontinuous function of atomic number, but strictly linear in Z within each period of the periodic system. The backscattering from compounds can be predicted with high precision on this basis.

Some general aspects of backscattering should be discussed before proceeding with the results of these studies. As this phenomenon deals with multiple scattering, excellent reasons could be given to show that the trajectory of a beta particle through an appreciable thickness of a substance is extremely complex, and that one could not hope to predict the over-all behavior from fundamental considerations. In addition, the beta particles are not monoenergetic. They do not interact with matter in any single, simple manner; they are attracted and deflected in their path by the field of the nucleus and deflected by the extranuclear electrons, and those of higher energy can give rise to bremsstrahlung in the process of being slowed down.

Therefore, one is generally advised to confine inquiry to the process of single scattering, with the implication given that multiple scattering leads to answers which are good to order-of-magnitude reliability only. It is astonishing, then, that regularities of a relatively simple nature can be observed and reproduced with high precision.

Figure 1 shows the relationship of the relative backscattering of several elements. These data had been obtained by the middle of 1953. This illustration is schematic; the actual data are given in Table I. The linear equations relating relative backscattering to atomic number within each period were sufficiently precise to establish the inflection points occurring at atomic numbers 2, 10, 18, 36, and 54. From these values, the backscattering of many compounds was predicted and confirmed (*5*).

Since 1953, completely reliable reference materials have been prepared from which the relative slopes of the lines defining each period can be established with high precision.

EXPERIMENTAL

Relatively simple equipment is used. A Lucite sample stage containing a collimated source of beta particles is mounted over a methane proportional counter (Figure 2). A Mylar window about 2.0 inches in diameter admits the beta particles backscattered from the sample within the permitted geometry. The permissible geometry is poor; it represents a compromise between the desire to accommodate rather small specimens and to confine the counting primarily to those betas which are backscattered.

The source consists of a truncated aluminum cylinder with a collimating cylindrical hole 0.5 mm. in diameter. An insert at the base provides a strontium-90 source. A thin stainless steel window cuts off the 0.53-m.e.v. betas from strontium-90 and transmits primarily the 2.18-m.e.v. betas from the daughter element, yttrium-90

The methane proportional counter provides a good plateau between 3600 and 4100 volts. Conventional amplifier and binary scaler are used for manual counting. For the large number of measurements made in these studies, automatic counting and registry were eventually adopted. As shown in Figure 3, the counter could be connected to a five-decade Berkeley decimal scaler. The latter is provided with an automatic read-out which, upon receipt of a command signal, presents the count to a 5-digit printer.

For the automatic system a special timing unit was developed. This utilizes a 60-cycle Invar tuning fork and a gas-tube scaler. The scaler counts cycles from the fork; switching circuits permit the selection of any counting time from 1 to 59 minutes in 1-minute intervals and any dead time from 1 to 10 minutes. These command signals, including a reset signal, are applied automatically to the Berkeley scaler and printer. The timing is accurate to 1 part in 100,000 well in excess of requirements, but inherent in the electrically driven Invar fork.

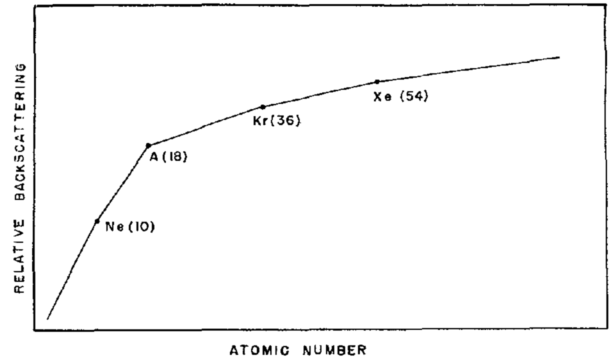

Figure 1. Relative backscattering of beta particles

Discontinuities appear precisely at atomic numbers 10, 18, 36, and 54 corresponding to rare gas configurations of neon, argon, krypton, and xenon

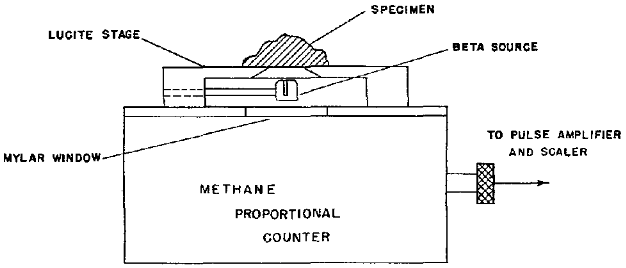

Figure 2. Schematic of apparatus for measurement of beta particle backscattering

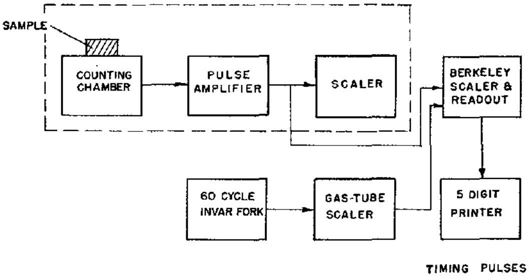

Figure 3. Counting methods for backscattering of beta particles

A. Manual operation (within dotted lines)
B. Completely automatic timing and printing out

The over-all precision of counting could be obtained from examination of the data. The printed data were blocked off into groups of 10 sets. The statistical error to be expected for each set is known from the total number of counts. This applies only to the statistics of nuclear disintegration and has nothing to do with the other characteristics of the system. Statistically acceptable sets of data were then combined to give average values. In critical comparisons of substances for which identical backscattering was expected (isomers), least squares computations of accumulated counts *vs.* elapsed time were made to establish

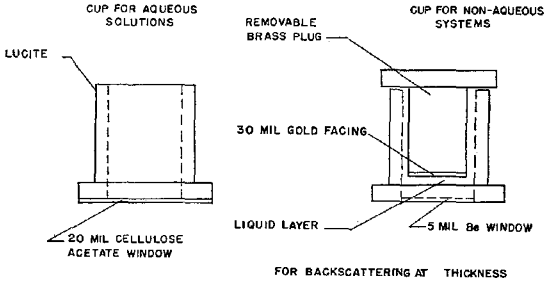

Figure 4. Cells for backscattering and transmission measurements of beta particles used with liquids and solutions

the average count rate. In the early stages of the work, over-all rate was recorded by a count-rate meter which was useful in detecting and correcting sources of count-rate drift. The intercomparison of data sets was considered to be necessary as a true criterion of over-all precision, rather than the sole use of the $\sqrt{n}$ criterion of precision.

Liquids and solutions are measured in thin-window cups. For aqueous solutions a Lucite cup with a 20-mil cellulose acetate window was used (Figure 4). For organic liquids a brass cup with a 5-mil beryllium window was used. Although the studies were concerned almost exclusively with backscattering, some absorption measurements were required, especially to distinguish between isomers. To this end, a brass plunger faced with 30 mils of gold was provided to fit into the brass cup–beryllium window assembly. With this arrangement a thin film of liquid could be trapped between the window and the strongly reflecting gold facing. Betas traversing the liquid twice could be compared for absorption. With this method the calculation of absorption by the liquid is complicated by the need for a small backscattering correction from the thin film of liquid.

An improved system has been developed (7) which consists of a vessel with two thin glass windows soldered to the cell walls. This permits the simultaneous measurement of transmittance (absorption) and the backscattering correction.

The entire system is subject to many refinements and improvements, several of which are now under way.

The relative backscattering values herein reported are characteristic of the particular experimental arrangement, particularly of the geometry of the system. It is possible to devise a system to describe every aspect of the scattering process, including distribution angle and so forth. Such systems can provide elegant and detailed information on one or two specimens but are not particularly suitable for the examination of a large number of elements or compounds in different states of aggregation.

It would be a serious defect if the information were highly dependent upon instrument parameters. Actually this is not the case and the information can be obtained with highly diverse arrangements. One of the most useful results has been the discovery of reference materials which can be used to calibrate a given system in a short time.

PRACTICAL REFERENCE POINTS

Figure 1 shows that the inflection points in the series of linear values connecting backscattering with Z occur at atomic numbers 2, 10, 18, 36, and 54, corresponding to the rare gas configurations of helium, neon, argon, krypton, and xenon. With the exception of atomic number 2, pure single crystals of sodium fluoride, potassium chloride, rubidium bromide, and cesium iodide should exhibit almost identical backscattering at these respective inflection points. In each case, the halogen is one atomic number below, and the alkali one atomic number above, the corresponding rare gas. Calculation and observation confirmed this completely:

	$\bar{Z}$	Z, Nearest Rare Gas
Sodium fluoride	10.092	10 (Ne)
Potassium chloride	18.048	18 (A)
Rubidium bromide	36.034	36 (Kr)
Cesium iodide	54.032	54 (Xe)

The value of $\bar{Z}$ for each crystal is computed from the intrinsic scattering of each element in the compound and its weight fraction in the compound.

Single crystals of the above substances were grown in this laboratory. Precise measurements obtained with them have established the relationship of backscattering *vs.* Z in periods III, IV, and V, and thus have fixed the backscattering values for the 45 elements in these periods.

The intrinsic values for backscattering listed in the tables in this paper are based on these cardinal reference points and are compared with direct measurements on elements as indicated. The reference points are now relied on completely rather than individual measurements of the elements. In few cases can the elements be obtained or fashioned as samples to the degree of purity or excellence of the single crystals. Although early measurements on the elements provided the clue to the inflection points, they are inferior in precision to the crystal values.

The backscattering values listed for all the elements make no specific assumption about the state of aggregation. Thus, the values for helium, neon, argon, krypton, and xenon obviously do not refer to the gaseous state, for which the backscattering would be very small. With the exception of these, for which the values would be valid in the liquid or solid state, the intrinsic scattering for each element refers to the contribution which it would make as a solid (or liquid) or in any compound of that element in proportion to its weight fraction.

There is still no equally useful equivalent for the bottom of period II (helium) or the top of period VI (radon). The neon point is the "anchorage" for the top of period II and the xenon point for the bottom of period VI. In period II it has been necessary to define the linear relationship by additional measurements on beryllium and carbon, and on values of oxygen, nitrogen, and fluorine derived from compounds. Thus, the accurate value for silicon, calculated from period III, combined with precise measurements on quartz, enables one to get an accurate value for oxygen. In similar fashion the value for fluorine can be obtained from fluorite (CaF_2), and so forth. In this connection, an almost equally reliable value for period II has been obtained by combining the computed values of sodium fluoride with those of a crystal of lithium fluoride. Measurements on these two crystals confirm the value.

The problem in period VI is similar because no simple practical equivalent for radon (Z = 86) has been devised. Here one still depends upon a pure metal or a compound to locate enough points to tie with the accurate xenon point. The confidence placed in period VI is enhanced, however, by an empirical expression which relates the backscattering of the rare gas configurations and permits reasonable extrapolation to the radon point. This is not discussed in detail because there is not sufficient evidence for its general validity.

However, periods II and VI are not defined with less certainty than periods III, IV, and V. The direct and indirect measurements to supply the information for periods II and VI were even more extensive than in the other three periods. The principal advantage of the calibrating crystals lies in their purity and crystalline perfection and in the great ease with which they can define the backscattering for the 45 elements within their range.

RELATIVE BACKSCATTERING OF ELEMENTS

Table I gives the relative backscattering in per cent for elements 2 to 83. The linear equations which apply to each period were defined by the cardinal calibration standards described above. For those elements in which a direct observation was made, the observed value is also given. For those elements which were determined indirectly—i.e., in terms of a pure compound—the source is indicated. Of the elements examined, about one third were of spectroscopic purity. Of the remainder the purity cannot be specified; they were of the highest quality obtainable. For this reason the calculated values should be emphasized because they represent the best average within each period. Experience has shown that this is justified. There is now an increasing amount of evidence in this laboratory to show that the most precise value for an element is best obtained indirectly from a pure crystalline compound containing that element.

In the values calculated for the rare earths, only one can be compared directly with a measurement on cerium. This large gap between elements 57 and 72 is unsatisfactory, but no other metals or crystalline compounds have been available. Several of the rare earths are now being investigated by aqueous solution techniques. The author venturer the opinion that there will be no anomaly in their behavior. No attempt has been made to examine thorium, uranium, or the transuranic elements. These are all highly radioactive and would be impossible to handle with the present technique. This does not minimize the importance or interest which attaches to these elements.

Values for the rare gases, except helium, are average values. Each of the linear equations yields slightly different values; the mean is chosen and recorded because these points, marking the inflections of the discontinuous function, are probably important. In no case do the extreme values, from which the mean is taken, differ by more than 0.01% absolute or a few tenths per cent relative.

The relative backscattering values pertain to the geometry prevailing in these studies, but from the foregoing it can be seen that calibration for any other system is relatively easy.

ORGANIC COMPOUNDS

In Table I no value is given for hydrogen, and helium has a small but definite value. Hydrogen exhibits negative backscattering, presumably due to absorption effects. Fortunately, this effect can be evaluated precisely and exact corrections can be applied to the observed backscattering. Müller (*4*) has described backscattering from representative organic compounds. Measurements showed that the carbon in each hydrocarbon accounts for more backscattering than is exhibited by the compound and the deficit is directly proportional to the hydrogen content. The average value so obtained provides the proper correction for other hydrogen-bearing compounds, including hydrates.

Deuterium exhibits a backscattering value which differs from hydrogen. At present, knowledge on this point is confined to the difference between heavy and ordinary water and between polyethylene and deuteropolyethylene. As this difference between hydrogen and deuterium is of considerable theoretical importance, no further discussion is contemplated until a precise value for the effect can be obtained.

These investigations (*4*) have also revealed that isomers exhibit identical backscattering. This result would please most physicists and disappoint all chemists, because many isomers are easily distinguished by a dozen or more criteria. The resources of beta-particle techniques are not barren in this case, because isomers differ in the extent to which they absorb betas and apparently in direct proportion to their respective densities.

SOLUTIONS

Extensive measurements have been made on aqueous solutions of the alkali chlorides and the sodium halides (*6*). Some of the general conclusions are

Table I. Relative Backscattering of Elements 2 to 83

Element	Z	% Backscattering		Source
		Calcd.	Obsd.	
		Period II. $BS = 1.2311Z - 2.157$		
He	2	0.305		
Li	3	1.536	1.529	LiF
Be	4	2.767	2.770	
B	5	3.999		
C	6	5.230	5.223	
N	7	6.461		
O	8	7.692	7.703	Quartz, C, Teflon, Be
F	9	8.923	8.934	CaF_2, NaF
Ne	10	10.152		
		Period III. $BS = 0.96731Z + 0.476$		
Ne	10	10.152		
Na	11	11.116	11.138	NaCl
Mg	12	12.084	12.072	
Al	13	13.051	13.072	
Si	14	14.018	14.042	
P	15	14.986		
S	16	15.953	16.007	
Cl	17	16.920		
A	18	17.895		
		Period IV. $BS = 0.68582Z + 5.556$		
A	18	17.895		
K	19	18.587		
Ca	20	19.272		
Sc	21	19.958		
Ti	22	20.644	20.629	
V	23	21.330	21.260	
Cr	24	22.016	21.829	
Mn	25	22.702	22.624	
Fe	26	23.387	23.445	
Co	27	24.073	24.055	
Ni	28	24.759	24.758	
Cu	29	25.445	25.420	
Zn	30	26.131	26.313	
Ga	31	26.816		
Ge	32	27.502		
As	33	28.188		
Se	34	28.874	28.914	
Br	35	29.560		
Kr	36	30.253		
		Period V. $BS = 0.34988Z + 17.664$		
Kr	36	30.253		
Rb	37	30.610		
Sr	38	30.959		
Y	39	31.309		
Zr	40	31.659	31.763	

given here. As shown in Figure 5, the relative backscattering as a function of weight fraction of solute is linear and permits extrapolation to unit weight fraction of solute, which is the value to be expected for the pure solid. The available concentrations are limited by solubility considerations. That these extrapolations are not too heroic is illustrated in Figure 5. For the five salts which were examined, pure single crystals of three of them were available at the time and their backscattering is indicated by the solid dots.

All solutions do not exhibit linear behavior when backscattering is plotted against weight fraction. The binary system, acetone–carbon tetrachloride, has been studied over the entire concentration range (*7*) and, while the interpretation is not completed, there is unmistakable evidence of nonlinearity just as one finds in general for the colligative properties of this system.

Although solution behavior is interesting in this case for its own sake, the examination of solutions for backscattering has been most useful primarily as a means of determining the intrinsic scattering of those compounds or elements which are difficult to obtain in large crystals.

INTRINSIC BACKSCATTERING OF ELEMENTS

The relative backscattering for the elements (Table I) is derived from measurement and can be expressed in each period by a linear equation of the form

$$BS = aZ + b \qquad (1)$$

where BS is expressed in per cent and Z is the atomic number. The values of the constants a and b which satisfy the experimental conditions in these investigations are as follows:

Period	Z	a	b
II	2 to 10	1.2311	−2.157
III	10 to 18	0.96731	+0.476
IV	18 to 36	0.68582	+5.556
V	36 to 54	0.34988	+17.664
VI	54 to 86	0.26225	+22.396

As described above, these values are readily obtainable for any other similar system in terms of a few cardinal calibrating crystals.

These constants have been evaluated by the method of least squares from a large number of measurements on elements and compounds. The number of significant figures in the constants gives no immediate indication of their relevance. It is best inferred from their ability to predict backscattering in pure crystalline compounds. Also, the observed values given for a and b are not the best criterion of precision, because precise values, obtained from the cardinal calibrating substances, are now used. The calculated values in Table I and the above linear equations are considered to represent the most probable values for the elements.

Table I. Relative Backscattering of Elements 2 to 83 *(Continued)*

Element	Z	% Backscattering Calcd.	% Backscattering Obsd.
	Period V.	$BS = 0.34988Z + 17.664$ *(Continued)*	
Nb	41	32.009	
Mo	42	32.359	
Tc	43	32.709	
Ru	44	33.059	
Rh	45	33.409	
Pd	46	33.758	
Ag	47	34.107	34.167
Cd	48	34.458	34.585
In	49	34.808	34.896
Sn	50	35.158	35.283
Sb	51	35.508	35.768
Te	52	35.858	35.959
I	53	36.208	
Xe	54	36.558	
	Period VI.	$BS = 0.26225Z + 22.396$	
Xe	54	36.558	
Cs	55	36.820	
Ba	56	37.082	
La	57	37.344	
Ce	58	37.607	37.638
Pr	59	37.869	
Nd	60	38.131	
Pm	61	38.393	
Sm	62	38.656	
Eu	63	38.918	
Gd	64	39.180	
Tb	65	39.442	
Dy	66	39.705	
Ho	67	39.967	
Er	68	40.229	
Tm	69	40.491	
Yb	70	40.754	
Lu	71	41.016	
Hf	72	41.278	41.309
Ta	73	41.540	41.556
W	74	41.803	41.818
Re	75	42.065	
Os	76	42.327	
Ir	77	42.589	
Pt	78	42.852	42.790
Au	79	43.114	43.083
Hg	80	43.376	
Tl	81	43.638	43.531
Pb	82	43.901	43.962
Bi	83	44.163	44.148
Po	84	44.425	
At	85	44.687	
Rn	86	44.950	

BACKSCATTERING OF COMPOUNDS

It has been suspected for a long time that the backscattering of compounds is predictable from the intrinsic scattering of their constituent atoms. This investigation shows that, at least in the case of single crystals of high purity, the backscattering of a compound can be predicted with a precision almost equal to that with which the atomic weights are known.

Case I. For any compound in which all the constituent atoms fall in the same period, the backscattering is equal to the intrinsic scattering for each element multiplied by its weight fraction in that compound and summed for all other atoms in the same way. Thus, for sodium chloride,

$$BS = \frac{22.997\,B_{\mathrm{Na}} + 35.457\,B_{\mathrm{Cl}}}{58.454}$$

where B_{Na} and B_{Cl} are the intrinsic scattering of sodium and chlorine, respectively. In this equation 22.997 (atomic weight of sodium) divided by 58.454 is the weight fraction of sodium; similarly, 35.457/58.454 is the weight fraction of chlorine.

Case II. This simple principle does not hold for compounds in which the constituent atoms lie in different periods, a situation which may be apparent from the discontinuous nature of the backscattering *vs.* Z relationship (Figure 1). A more general relationship, which reduces exactly to Case I where all elements are in the same period, has been described previously (*5*). An effective atomic number $\bar{Z}$

can be calculated for any compound which will predict its backscattering with high precision. This quantity is defined as follows:

$$\bar{Z} = \frac{n(A_B.Z_B) + m(A_C.Z_C)}{\text{mol. wt. of } B_nC_m} \qquad (2)$$

where A_B and A_C are the atomic weights of B and C for the compound B_nC_m. So defined, $\bar{Z}$ is simply the sum of each atomic number multiplied by the weight fraction of that atom which is present in the compound.

On this basis the value of $\bar{Z}$ calculated for calcite ($CaCO_3$) is 12.565, which indicates that backscattering should be intermediate between magnesium (Z = 12) and aluminum (Z = 13). When the comparison is made with these substances, calcite yields a value of $\bar{Z}$ within 0.08% of the calculated value.

A more striking example may be chosen. Such diverse substances as halite (NaCl) and fluorite (CaF_2) have the following $\bar{Z}$ values:

For CaF_2, $\bar{Z}$ = 14.646
For NaCl, $\bar{Z}$ = 14.639

These differ by less than 0.05% and indicate that both substances should scatter intermediate between silicon (Z = 14) and phosphorus (Z = 15). Such is the case. [In practice it is more convenient to interpolate between silicon (Z = 14) and sulfur (Z = 16).]

It should not be inferred that the $\bar{Z}$ concept requires direct interpolation between the nearest elements, although this is often convenient. In the above example, the $\bar{Z}$ values for fluorite and halite can be substituted directly in the equation given in Table I for period III ($\bar{Z}$ = 10 to 18). When this is done, the predicted values can be compared with direct measurement.

	% Backscattering		
	Calcd.	Obsd.	Δ
CaF_2	14.643	14.652	0.009
NaCl	14.636	14.628	0.008

If the backscattering for these substances is calculated from the intrinsic scattering of the elements (Table I) and their weight fraction, one gets CaF_2 = 15.944% and NaCl = 14.636%.

This illustrates that it is immaterial which mode of computation is used when both atoms are in the same period.

Another example may be cited to illustrate the general validity of the $\bar{Z}$ concept. In the case of zinc sulfide one gets the value,

$$\bar{Z} = 25.393 \text{ (calcd.)}$$

which indicates that its backscattering should lie between manganese (25) and iron (26). Direct intercomparison with these metals yielded a value of

$$\bar{Z} = 25.368 \text{ (obsd.)}$$

which differs by less than 0.1% from the calculated value. If the observed $\bar{Z}$ value is substituted in the equation for period IV, the backscattering is 22.954% (observed) and 22.971 (calculated). Calculation from intrinsic scattering and weight fraction yields 22.782%, which illustrates again the agreement between the observed value and that predicted by $\bar{Z}$. The elements in this case lie in periods III and IV; hence, calculation from the intrinsic scattering is slightly lower and not in accord with observation.

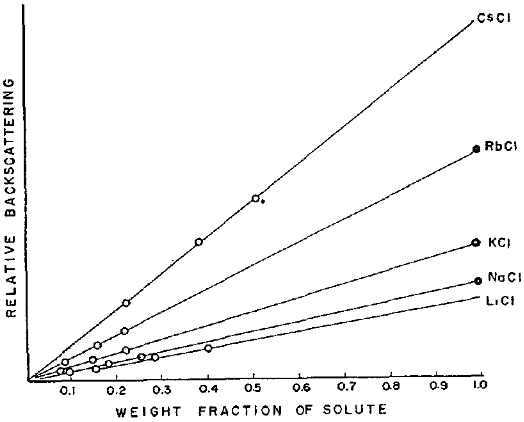

Figure 5. Backscattering of beta particles by alkali halide solutions

○ Validity of extrapolation to unit weight fraction of solute confirmed for NaCl, KCl, and RbCl by synthetic single crystals

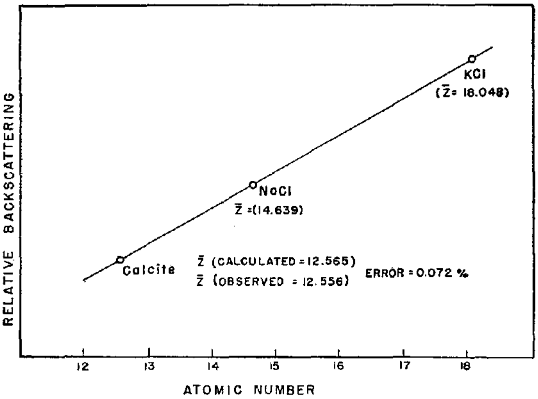

Figure 6. Precise prediction of backscattering of calcite

NaCl and KCl as calibration standards. Equation for straight line is that which holds for all elements in Period III (Z = 10 to 18)

A final example is illustrated in Figure 6. When crystals of potassium chloride, sodium chloride, and calcite are measured for their relative backscattering and plotted as shown, they lie on the straight line defined by the equation for period III. Aside from their conformity to this equation, if sodium chloride and potassium chloride are regarded simply as calibrating substances, then the predicted value of $\bar{Z}$ for calcite is 12.556, whereas it should be 12.565. In this sense, calcite is identified within 0.072% from two substances, neither of which contain the atomic species present in calcite.

RESTATEMENT OF $\bar{Z}$ CONCEPT

From the definition and the evidence presented so far, $\bar{Z}$ defines the backscattering for any compound and indicates that the compound will behave in backscattering as if it were an element of hypothetical atomic number $\bar{Z}$. When $\bar{Z}$ is substituted in the equation for the appropriate period, the per cent backscattering is predicted with accuracy. The alternative method of predicting backscattering from the intrinsic scattering of the elements and their known weight fraction gives an identical answer only if all atoms are in the same period.

The $\bar{Z}$ concept applies also to hydrogen-bearing compounds, and the correction for the hydrogen deficit is straightforward (*4*). This means that if $\bar{Z}$ is calculated for a hydrogen-bearing compound and then substituted in the appropriate equation, the per cent backscattering so computed will be higher than that observed, but in direct proportion to the hydrogen content.

DISCUSSION

The technique described here is susceptible to extensive improvement, particularly from the experimental and instrumental point of view. Until recently such obvious improvements have been held in abeyance until the fundamental facts were established.

Most readers will share the author's dissatisfaction with the empirical nature of these relationships. However, in view of the inherent complexity of the backscattering phenomenon, the author is compelled to regard these regularities as little short of astonishing, particularly because they are so susceptible to precise measurement and have exhibited no single exception to these rules.

If one cannot (*2*), at this moment, deduce these regularities from a simple theory based upon fundamental assumptions, one is at least in possession of the facts from which a coherent theory may be deduced.

Backscattering is not the sole puzzle concerning beta particle phenomena. The very manner in which beta particles are emitted in the process of radioactive decay is not completely understood.

These investigations have raised more questions than they have answered. That the results are highly geometry-dependent has been emphasized. It would be of great interest to know how the scattering is distributed in angle and how the backscattered betas are degraded in energy.

The emphasis in this work has been to gain a broad and comprehensive picture of the relative behavior of most elements and compounds under a restricted but reproducible set of conditions. The results have been interesting, at least, and perhaps not without profit.

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Interaction of Beta Particles with Organic Compounds

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► **The general principles which govern the backscattering of beta particles from atoms and molecules are applied to some representative organic compounds. The anomaly of hydrogen is resolved and a reliable value is fixed for it. The behavior of isomers is described and proof is given that the backscattering of compounds is accurately predictable from the intrinsic scattering of the constituent atoms.**

SYSTEMATIC STUDIES on the backscattering of beta particles by matter have been made in this laboratory for the past 3 years. The general laws and conclusions have been described (*1*, *2*). It is now known that the relative backscattering is a discontinuous function of atomic number, but strictly linear with Z in each period of the periodic system. The scattering by compounds is accurately predictable from the intrinsic scattering of the constituent atoms.

This work deals with the behavior of a few representative organic compounds. While these are in no way different in behavior from other substances, they do afford a simple means of handling the anomaly of hydrogen, which exhibits negative scattering—that is, less than zero scattering, presumably due to absorption effects. It has been possible to establish the exact value and, therefore, to apply the small but definite correction to the observed scattering of hydrogen-bearing compounds. The experimental details and instrumental techniques have been described by Müller (*1*). As before, these results are concerned with the relative backscattering of 2.18-m.e.v. beta particles from yttrium-90.

The relative backscattering for elements in periods II to VI, inclusive, is known (*1*); for the present purpose, only those which are more commonly encountered in organic compounds are listed in Table I. In this table the fourth digit in the values for elements 6 to 9, inclusive, is for computational use only. The values of all elements in Table I are believed to be accurate to somewhat better than 0.1%. No assumptions are to be made about the state of aggregation of each element. The values for nitrogen, oxygen, and fluorine obviously do not refer to the gaseous state, for which the backscattering would be far less. These values are simply those which apply

Table I. Backscattering of Elements Common in Organic Compounds

Z	Element	% Backscattering
6	Carbon	5.230
7	Nitrogen	6.461
8	Oxygen	7.692
9	Fluorine	8.923
16	Sulfur	15.953
17	Chlorine	16.920
35	Bromine	29.560
53	Iodine	36.208

rigorously as the intrinsic scattering for that element, as it may occur, in definite weight fraction in any compound.

From the values in Table I, the backscattering of any compound may be computed by multiplying the intrinsic backscattering of each element by the weight fraction of that element in the compound and totaling for all other atoms in the same way.

As an illustration of the general method for calculating the backscattering of compounds, the case of Teflon is chosen. From Table I the intrinsic backscattering of carbon is 5.230% and that of fluorine is 8.923%. For Teflon, the weight fraction of carbon is 0.24017 and of fluorine, 0.75983. The backscattering is:

$$BS = (5.230 \times 0.24017) + (8.923 \times 0.75983) = 8.037\%$$

Direct observation yields a value of 8.045%, a difference of 0.008% or a relative error of 8 parts in 8037 (0.099%). In many cases the error is greater than this, but in the case of perfect crystals of pure substances, the error is one half to one third of this magnitude.

However, this mode of computation is restricted to compounds in which all the atoms are in the same period. A general approach is afforded by the $\bar{Z}$ concept proposed by Müller (*2*). According to this principle, the compound, B_nC_m, has a value of

$$\bar{Z} = \frac{n(A_BZ_B) + m(A_CZ_C)}{\text{mol. wt. } B_nC_m}$$

where the *A*'s are atomic weights and the *Z*'s, the respective atomic numbers. The denominator is actually the minimal formula weight and the equation could be written:

$$\bar{Z} = Z_Bf_B + Z_Cf_C \qquad (1)$$

where the *Z*'s are atomic numbers and the *f*'s are the corresponding weight fractions of the respective atoms in the compound.

For Teflon, the $\bar{Z}$ value is 8.280, which indicates that it should backscatter as if it were an element of hypothetical atomic number 8.280. Its behavior in this respect should be intermediate between oxygen ($Z = 8$) and fluorine ($Z = 9$). The backscattering for all elements in period II (helium to neon) is expressed by:

$$BS = 1.2311Z - 2.157 \qquad (2)$$

If $\bar{Z}$ for Teflon is substituted in this equation, the predicted per cent backscattering is 8.037, a value identical with the one computed previously. The agreement arises only because carbon and fluorine are in the same period. Further examples of the general validity of the $\bar{Z}$ principle are given by Müller (*1*).

This principle is now applied to the evaluation of the hydrogen anomaly. Accurate measurements on the backscattering of several solid hydrocarbons have supplied the information needed for this purpose. The intrinsic value for hydrogen, so obtained, is satisfactory for the prediction of other hydrogen-bearing compounds.

Measurements on paraffin, naphthalene, *trans*-stilbene, and polystyrene are summarized in Table II. If each $\bar{Z}$ value is substituted in Equation 2 for period II elements, the predicted backscattering is uniformly too high. The anomalous behavior of hydrogen is obtained directly, however, because the deviations are proportional to the hydrogen content. If we add the necessary corrections to the equation for period II in the form:

$$BS = 1.2311\bar{Z} - 2.157 - B_H.f_H \qquad (3)$$

where f_H is the weight fraction of hydrogen and B_H is the desired intrinsic scattering of hydrogen, then the values of B_H so obtained are shown in column 6. The value of B_H is constant to slightly better than 1%. The values in column 7 are expressed in per cent backscattering per per cent hydrogen, a form which is useful in making corrections to observations on substances for which the hydrogen content is expressed in per cent.

The value of −10.38% for the intrinsic backscattering of hydrogen is satisfactory for the correction of all hydrogen-bearing compounds. By comparison with the values of other elements, this "apparent" negative backscattering of hydrogen seems to be rather large; in some compounds of low hydrogen content and for many hydrates, the correction becomes quite small.

Having obtained the absolute value for B_H, it is evident that Equation 3 can be rearranged to compute the backscattering from $\bar{Z}$ for any hydrogen-bearing compound, or if the backscattering has been measured, to compute $\bar{Z}$. It may also be apparent that, when the hydrogen correction is made to the observed backscattering, the $\bar{Z}$ values will all lie on the linear plot relating backscattering to Z (or $\bar{Z}$) as defined by the equation for period II.

In the future it may become profitable to extend this method to other compounds of reasonably high hydrogen content to obtain a more precise estimate for the intrinsic scattering of hydrogen. However, the value given here has been adequate for correcting the observations on the organic compounds.

The question of how the value for hydrogen compares with that of deuterium was studied by comparing polyethylene and deuteropolyethylene and ordinary water and heavy water. There are marked differences in both cases, indicating that hydrogen and deuterium have markedly different backscattering (or absorbing) properties. This effect could probably be accounted for by the neutron which is present in the deuterium nucleus. This problem is the subject of further study. Since the nuclear forces acting upon the beta particles should be profoundly affected by the neutron-proton ratio, at least for the lighter elements, such inquiries would be enhanced by the examination of pure isotopes of some of the lighter elements.

The average value for the intrinsic backscattering of hydrogen so obtained, if applied to those substances from which it was derived, yields values for the prediction of their backscattering as shown in Table III; the average correction predicts the observations within an average error of 0.16% and a maximum error of 0.26%. Similar results with an average error of 0.2% have been predicted for the backscattering of methanol, ethanol, benzene, and acetone.

Compounds involving heavier elements are of interest because these contain elements showing widely different

Table II. Backscattering Measurements on Organic Compounds

Compound	Weight Fraction C	Weight Fraction H	Obsd. *BS*, %	$\bar{Z}$	B_H	*BS* of H per % H
trans-Stilbene	0.93289	0.06711	4.125	5.664	−10.297	−0.1030
Paraffin	0.85175	0.14825	2.778	5.259	−10.381	−0.1038
Polystyrene	0.92257	0.07743	3.956	5.613	−10.293	−0.1029
Naphthalene	0.93709	0.06291	4.178	5.685	−10.551	−0.1055
				Av.	−10.382	−0.1038

Table III. Backscattering Corrected for Hydrogen Defect

Compound	% Backscattering Calcd.	% Backscattering Obsd.	Δ
trans-Stilbene	4.119	4.125	0.006
Paraffin	2.778	2.778	0.000
Polystyrene	3.949	3.956	0.007
Naphthalene	4.189	4.178	0.011
		Av.	0.006

intrinsic scattering. A comparison of chloroform and carbon tetrachloride yielded the expected values. In this case the relative scattering of the two, as calculated from the elements, was in the ratio of $CCl_4/CHCl_3 = 1.0265$, whereas the observed ratio was 1.0278, a relative error of 0.13%.

ISOMERS

Several cases of isomers have been studied. From all available evidence, isomers scatter identically. Fortunately, they differ in transmittance (or adsorption), and in predictable fashion.

Two liquids, diethyl ether and 1-butanol (both $C_4H_{10}O$), have been examined in great detail. Both yield backscattering values agreeing with those computed from the elements, but in this connection, it may be more useful to compare the relative backscattering of the two. The ratio of the observed relative backscattering was found to be:

$$\text{ether/butanol} = 1.00056$$

This means that if any difference exists between the two, it is less than 0.055%. The statistical error in counting (many millions of counts) was of the same order of magnitude, which indicates that there is no difference in these two substances within this limit of experimental error. Conversely, if it would serve any useful purpose, one could extend the counting times severalfold to search for a more precise indication of their identity.

A detailed study in this laboratory (*3*) has established similar results for the isomers of $C_{14}H_{10}$—i.e., anthracene, phenanthrene, and tolane (diphenylacetylene). Their identical backscattering was established independently by measurements on powdered specimens compressed to practically theoretical density in a hydraulic press and also from solutions of these substances in a mixed solvent.

That isomers can be differentiated from one another by beta particle techniques has been established in this laboratory, but not to the high precision with which their identical backscattering can be demonstrated. Because backscattering was of primary interest, transmittance measurements were made with a simple experimental modification of the backscattering system described by Müller (*1*). In this manner the basic backscattering system can be utilized to obtain relative transmittance measurements. Rather elaborate, but straightforward, corrections for backscattering are required in order to obtain the desired transmittancy. Improved cells are being constructed to provide simultaneous transmittancy and backscattering measurements, which are essential for studies on solutions and liquid mixtures.

With this technique the relative transmittancy of diethyl ether and 1-butanol were compared. Contrary to the backscattering results, these substances exhibit different transmittancies (or absorbances). The average of a large number of observations yields the following ratio of absorbance:

$$\text{1-butanol/diethyl ether} = 1.1288$$

The densities at 23.3° C. are 0.80734 for 1-butanol and 0.70966 for diethyl ether. The ratio of the densities at 23.3° C. is 1.1376.

These results show that density is the controlling factor in the relative absorbance, because the ratios agree within 0.86%, which is within the limitations of the backscattering correction and temperature constancy. With respect to the latter, in the Smith and Otvos (*4*) method for determining hydrogen in hydrocarbons a simultaneous measurement of density is made with high precision. In the above measurements temperatures were constant only to the degree afforded by the air-conditioning system.

Lonadier and Müller (*3*) have confirmed the dependence of absorbance upon density for the isomers of $C_{14}H_{10}$. Further work is being carried out with improved methods for absorbance measurements.

Aside from the numerical values in each particular case, it is fortunate that there are measurable differences between isomers in at least one aspect of beta-particle interaction. Otherwise, the identical behavior in the case of backscattering would leave much to be desired for analytical purposes, as these substances are easily differentiated by a dozen or more simple criteria.

Quite a few substances have been examined in the liquid and solid state by the simple expedient of providing a tall, thin-window cell with a cold finger insert. Backscattering can be measured and then, by filling the cold finger insert with a suitable refrigerant, the backscattering of the solid can be measured on the same sample. By removing the refrigerant and allowing the solid to melt, the liquid value can be checked. No significant differences were observed in the backscattering from the liquid and solid phases. Unless far more precise measurements reveal very small differences, it is apparent that the density of the system has no effect on the backscattering. This conclusion is borne out by the behavior of isomers, which show identical backscattering even though the densities are different. It must mean that the beta particles traverse such relatively large distances within the substance that the same fraction of them return to be counted, regardless of the density.

These considerations do not apply to the case of transmittance or absorption, as has been shown above.

The improved system, which is nearly completed, will permit the simultaneous measurement of absorption and backscattering in thin layers of liquid. The backscattering values which the new technique affords are not those which have been discussed, because they do not correspond to a sample of "infinite" thickness, but their precise value is necessary for the calculation of true absorption.

Despite the obvious and necessary improvements to be expected from the newer technique, the present method leaves no serious doubts about the identity of isomeric substances. The backscattering values as observed, combined with the known intrinsic scattering of the constituent atoms, establish the substance as one of several possible isomers. By then measuring the absorbance by use of the gold-faced reflector, one can decide which of the isomers is responsible for the observed value. This presupposes that the densities are known or have been measured. Small differences in densities of two or more isomers would make a decision difficult. Also, in the case of mixtures of isomers, extremely precise measurements would be required and it is possible that the method would be inferior to alternative methods such as infrared spectrophotometry.

ANALYTICAL IMPLICATIONS

The author prefers to express the analytical aspects of this phenomenon as implications rather than applications. The emphasis in these and all related studies on backscattering has been to discover a general relationship between composition and relative backscattering. Because this has been established to the degree that one can predict the relative backscattering in a given experimental assembly, one can speak of applications, their advantages, and limitations for any element or any compound.

The present equipment can be used to examine solids, liquids, and solutions, but it requires samples which are larger than might be desired. The sample stage requires a specimen which must cover a $^3/_8$-inch circular aperture and must have a minimum thickness (t) which can be expressed roughly as 0.422 inch/d, where d is the density. The latter value is approximately "infinite" thickness for the yttrium-90 betas.

With the possible exception of t_∞, there are sample size limitations which can be decreased by improved instrument design.

If the composition of a substance is known or suspected, its identity can be verified in a few minutes. This statement must be qualified by the obvious fact that there can be numerous combinations of atoms present in such relative proportions that their backscattering would be identical or very close, but the possibilities can be calculated. Similarly, if the kinds of atoms present in a compound have been established by elementary qualitative analysis, then the observed backscattering corresponds to a definite limited number of possible compounds. It is obviously impossible, at present, to measure the backscattering and then predict the composition uniquely. This is a limitation comparable to other methods such as electron or x-ray diffraction and infrared spectroscopy, which presuppose that the characteristic pattern has been examined before and can be compared with the new specimen.

As the backscattering of a compound is uniquely and precisely defined by the kind of atoms present and their relative proportions, it is entirely possible that a computer system could be devised to calculate backscattering values for all possible permutations and combinations of atoms in compounds. If restricted to the relatively limited number of atoms commonly found in organic compounds, the requirements of this computer might not be too severe. In cases where only a limited number of compounds would come into consideration, the simple calculation can easily be performed in a few minutes.

Table I shows that large changes in backscattering can be expected for the heavier elements. Halogenated compounds can be distinguished with high precision because of the high intrinsic scattering of the halogens and the large weight fraction which they possess.

Since beta-particle techniques both in backscattering and absorption have been in use for several years in automatic gaging operations, it is obvious that these methods can be utilized in the continuous monitoring of process streams. In such applications direct counting is not used; the counter is connected to a count-rate meter and recording potentiometer. The rate of response to composition changes involves several factors, all of which are well understood. It includes the counting rate and time constants associated with the recording system, and these must be such that the time lag in detecting a change in composition shall have an acceptable value. These are engineering considerations which have been solved satisfactorily for the above-mentioned gaging application.

The studies described here have established the physical and chemical factors from which the feasibility of a process-monitoring scheme could be established.

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Determination of Aluminum in Aluminum-Iron Alloys

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▶ The steadily increasing interest in the Alfenol type of alloy (aluminum-iron containing 5 to 20% aluminum) has necessitated development of an accurate method for determining the high aluminum content of these alloys. Application of these alloys in the field of magnetics requires a high degree of analytical accuracy because the composition of the alloy is critical for the desired magnetic properties. The present method is based on the adsorption of interfering elements by an ion exchange resin; the nonadsorbable aluminum is determined gravimetrically by precipitation with ammonium hydroxide.

The determination of aluminum in the presence of iron has been recently studied by many investigators (*2-4, 8, 9, 11*), who, in most cases, were concerned with determining small amounts of aluminum in the presence of large amounts of iron or large amounts of iron plus other elements. When the aluminum content exceeds 2 or 3%, these methods are either not applicable or inaccurate. The methods in the literature for the separation of large amounts of aluminum from iron yielded inconsistent or inaccurate results—for example, the electrolytic deposition of elements other than aluminum on a mercury cathode and the subsequent determination of aluminum in the solution are frequently erratic and unreproducible. The cyanide-oxyquinolate method has a major disadvantage in the difficulty of handling the aluminum precipitate obtained, due to the coprecipitation of the reagent. The separation of iron from aluminum by the use of sodium hydroxide is a disagreeable procedure and it is difficult to wash the precipitated ferric hydroxide free of aluminum.

Ion exchange is becoming an important tool of the analytical chemist. Although the principle has been known for a number of years, only fairly recently have practicing analytical chemists investigated its use. The separation of metallic ions by an anion exchange resin has become a popular application (*1, 3, 6, 10*). These separations depend on the fact that certain

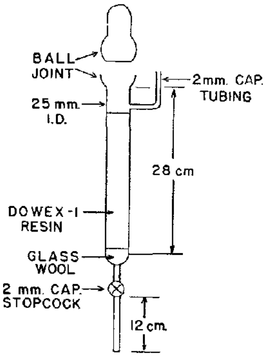

Figure 1. Ion exchange column

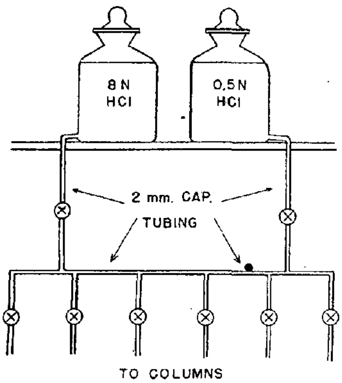

Figure 2. Automatic feed arrangement

metallic ions can exist in solution as cations or chloro anions, depending on the concentration of chloride ions in the solution. The exact mechanism of the exchange has not been established, but it may be related to the existence of these ions as strong acids in solution (*1*).

Kraus and associates (*5*, *7*) have studied the adsorption characteristics of Dowex-1 resin (a quaternary amine, polystyrenedivinylbenzene) and determined that aluminum is not adsorbed on this resin from 9*N* hydrochloric acid. Horton and Thomason (*3*) have determined aluminum in various alloys by adsorbing the interfering elements on a Dowex-1 exchange column and determining the nonadsorbable aluminum spectrophotometrically as the aluminon complex. This method, however, is limited to small percentages of aluminum or requires such a small sample that its accuracy is low.

EXPERIMENTAL PROCEDURE

Preparation of Ion Exchange Column. The apparatus required for an ion exchange separation is simple, utilizing only a glass column to hold the resin, with a stopcock on the lower end to control the flow of liquid, and a means of introducing the sample at the top. A typical column is shown in Figure 1. The use of an automatic feed arrangement is recommended because of the significant time required for each separation. Because the exchange resins used are fine-mesh materials, a several-foot head of liquid is an advantage in providing a fast enough flow rate. This arrangement is shown in Figure 2.

The resin used is Dowex-1, 8% cross-linked, 200- to 400-mesh, prepared for use by settling in 0.5*N* hydrochloric acid to remove the finest and coarsest fractions. After several cycles of successively decanting off the fine and main portions of the slurry, the column is filled with the main portion to a settled height of about 23 cm. The resin is now washed with a few hundred milliliters of 5 to 10% nitric acid and flushed clean with water. There exists some evidence that it is necessary to condition the column to 8*N* hydrochloric acid and it may be necessary to pass several hundred milliliters of the acid through the bed of resin before it is used for the first time, in order to obtain a clean separation of iron from aluminum. As the sample will be introduced into the column dissolved in 8*N* hydrochloric acid, it is also necessary to equilibrate the resin to this acid by flowing about 100 ml. through it preliminary to each separation.

Ion Exchange Separation. A 0.5-gram sample is dissolved in aqua regia, with heating if necessary. This solution is evaporated to dryness four times with dilute hydrochloric acid (1 to 1) and the residue after the last evaporation is dissolved in 20 ml. of 8*N* hydrochloric acid. This solution is transferred to the column (previously equilibrated with 8*N* acid) and the beaker washed well with 8*N* acid. The washings are added to the column. The cap is placed on the column and clamped in place, and the stopcocks are adjusted to deliver 8*N* hydrochloric acid from the reservoir bottle. The bottom stopcocks on the columns are adjusted to permit a flow of 1.5 to 2 ml. per minute. The "scrap" beakers under the columns are replaced with clean 600-ml. beakers and 450 to 500 ml. of solution are collected. These beakers are then replaced with the scrap beakers again, and the iron is washed out of the column with 0.5*N* hydrochloric acid.

Determination of Aluminum. The beakers containing the aluminum solution are evaporated to incipient dryness on a hot plate. Twenty milliliters of nitric acid are added and boiled to destroy any organic matter dissolved from the resin. The solutions are again evaporated to dryness and the residue is dissolved in 20 ml. of dilute hydrochloric acid (1 to 1). The solution is diluted to 150 ml. with water and heated to boiling. The aluminum content is determined by precipitating with ammonium hydroxide to a methyl red end point, filtering, washing with 2% ammonium chloride (made alkaline to methyl red with ammonium hydroxide), and igniting to constant weight at 1100° C. The gravimetric factor for converting Al_2O_3 to Al is 0.5291.

Table I. Recovery of Aluminum from Synthetic Samples

Al Added, Mg.	Fe Added, Mg.	Al Found, Mg.	Deviation, Mg.
75.6	...	75.6	0.0
75.6	...	75.7	+0.1
75.6	...	75.3	−0.3
75.6	...	75.4	−0.2
75.6	...	75.6	0.0
75.6	...	75.7	+0.1
75.6	420	75.3	−0.3
75.6	420	75.2	−0.4
75.6	420	75.5	−0.1
75.6	420	75.5	−0.1
75.6	420	75.8	+0.2
75.6	420	75.3	−0.3
30.2	450	30.4	+0.2
30.2	450	30.2	0.0
30.2	450	30.1	−0.1
30.2	450	30.3	+0.1
30.2	450	30.1	−0.1
30.2	450	30.3	+0.1

RESULTS AND DISCUSSION

The results on some synthetic samples are shown in Table I. Listed in Table II is a series of results on a typical Alfenol sample, containing approximately 14% aluminum.

Table II. Analysis of Typical Alfenol Sample

Sample No.	Sample Size, G.	Al Found, Mg.	Al, %
1	0.5007	71.4	14.27
2	0.5012	71.2	14.21
3	0.5010	71.0	14.18
4	0.5026	71.1	14.15
5	0.5030	71.4	14.19
6	0.5015	71.2	14.20
7	0.5006	71.1	14.21
8	0.5027	71.2	14.16
9	0.5030	71.1	14.14
10	0.5003	70.8	14.16
11	0.5028	71.4	14.20
12	0.5019	71.3	14.20
		Av.	14.19

Std. dev. 0.03

The results shown in these tables indicate that iron can be completely separated from aluminum by using 8*N* hydrochloric acid and an ion exchange column containing Dowex-1.

Although the use of coarser Dowex-1 resin (50 to 100 mesh) was not investigated, its use would decrease the necessity for the large pressure head to provide an adequate flow rate. For routine samples of the sizes shown in Tables I and II, a much smaller column of resin (about 1 x 10 cm.) should suffice. In the case of a smaller column, three column volumes of 8*N* hydrochloric acid should remove all the aluminum. Although the 5 to 10% nitric acid wash was used in this investigation to remove reducing impurities in the resin, according to Nelson (*5*) a dilute hypochlorite solution is better and equilibration of the column requires less 8*N* hydrochloric acid if hypochlorite is used.

Application of this method for determining aluminum in systems containing a third element in addition to aluminum and iron is feasible. Horton and Thomason (*3*) list a series of elements which are retained by Dowex-1 in 9*N* hydrochloric acid. Among these elements is molybdenum (with a valence of 6), which makes this method potentially applicable to the Thermenol type of alloy (aluminum-iron usually containing about 3% molybdenum). The difficulty in removing the molybdenum from the resin mentioned by Kraus and Nelson (*5*) can be overcome by using fresh resin after each sample containing molybdenum. The resin is inexpensive enough to make this procedure practical.

Because of the controlled atmosphere and vacuum melting procedure used in the production of aluminum-iron alloys for magnetic purposes, no insoluble aluminum was found after dissolving the sample in aqua regia.

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Isotopic Method for Determining Oxygen in Chromium

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▶The isotopic method for determining oxygen in titanium, zirconium, copper, and iron has been extended to the determination of oxygen in chromium with an accuracy of 99% or better.

THE methods most commonly used for the determination of oxygen in chromium are those in which the chromium is dissolved in hydrochloric acid; the residue is then either weighed as chromic oxide Cr_2O_3 (*7*), or measured colorimetrically after fusing the insoluble portion with potassium persulfate and potassium hydroxide (*2*). A recent chemical development is the bromination-carbon reduction method (*1*) in which the oxide is converted to carbon monoxide and the chromium to the bromide. These, like all chemical methods, take long periods of time to make a single analysis and require the quantitative separation of definite compounds. A method used with inferior results is a variation of the one used by many to analyze for oxygen in iron, titanium, and zirconium—namely, the vacuum fusion method (*2*).

In the isotopic method used by the author to determine the oxygen content of chromium and chromium oxide, quantitative results are obtained without quantitative separation and recovery of the oxygen from the sample. The only prerequisite is exchange of all oxygen atoms in the system, which is accomplished at the temperatures required.

PRINCIPLE OF METHOD

The method is based on reaction of a sample of chromium metal or oxide mixed with oxygen-18 containing "master-alloy" with graphite above its melting point and liberation of part of the oxygen as carbon monoxide. The oxygen-18–oxygen-16 ratio in the carbon monoxide is determined by a mass spectrometer and the oxygen content is derived from it. The principle, apparatus, and analytical procedure have been described in detail (*3-6*).

PROCEDURE AND APPARATUS

The experimental procedure for chromium is the same as that used for titanium and zirconium, except for the temperature and time. The chromium samples were heated to only 1450° ± 50° C. (300° to 400° C. lower than titanium and zirconium) for 1 hour instead of 2 to 3 hours as in the case of the titanium samples. The maximum time required for complete analysis, including preparation of sample and mass analysis of the liberated carbon monoxide, was 2 hours.

PREPARATION OF CHROMIUM–OXYGEN-18 "MASTER-ALLOY"

The master-alloy was prepared by heating a platinum boat containing chromium metal powder (Eimer & Amend, 98% pure chromium) with a given amount of oxygen gas of known oxygen-18 concentration in a platinum tube at 600° to 700° C. A sample of the master-alloy was then heated with oxygen-free graphite and the carbon monoxide liberated was analyzed for its oxygen-18 concentration. The oxygen content of the master-alloy was determined from the "gain-in-weight" of the master-alloy and the difference in oxygen-18 concentration of initial oxygen gas and the oxygen in the master-alloy. The master-alloy contained 2.766 weight % of oxygen, while the oxygen-18 concentration was 10.0903 atom % ($m = 10.0903 - 0.2150 = 9.8753$).

SAMPLES ANALYZED

The samples analyzed in these studies were: chromium metal powder (Eimer & Amend, 98% pure chromium); three

Table I. Determination of Oxygen in Chromium

Sample	% Oxygen in Chromium, Gain in Wt.			Observed % Oxygen	Difference	Deviation, % of Oxygen Content
	In original Cr	% gain in wt.	Total %			
Chromium powder	. . .	. . .	. . .	0.847	. . .	. . .
Chromium powder heated in oxygen						
(0–1)	0.847	0.104	0.951	0.960	+0.009	0.94
(0–2)	0.847	0.268	1.115	1.104	−0.011	0.96
(0–3)	0.847	1.095	1.942	1.948	+0.006	0.31
Chromic oxide, Cr_2O_3	. . .	. . .	31.575	31.703	+0.228	0.72
					Av.	0.73

samples of the powder heated in oxygen [the amounts of oxygen absorbed by the chromium were (0-1) 0.104, (0-2) 0.268, and (0-3) 1.095 weight %]; and chromic oxide, Cr_2O_3 (Baker & Adamson reagent ACS, 99 + % Cr_2O_3).

EXPERIMENTAL RESULTS

The data obtained upon analyzing the various samples are tabulated in Table I. A study of these values shows that accurate oxygen analyses of chromium samples are obtainable by the isotopic method. The average deviation from the gain-in-weight values is 0.73% of the oxygen content.

These results should be compared with those obtained by Horton and Brady (*2*) using the vacuum-fusion method. The recovery of their method began at 85% and dropped to 70% when the bath contained 5 weight % of chromium. At times their recovery was as low as 40%. With the vacuum-fusion method, lower oxygen values were obtained when nickel was present. Therefore the per cent of chromium in the bath has to be known at all times. Also, periodically, standards have to be run in order to check recoveries. The isotopic method eliminates the need for per cent of chromium determinations and for running standards.

The fast accurate results by the isotopic method are due to the principle of the method—namely, that complete removal and recovery of all the oxygen in the metal is not necessary. Its only requirement is complete statistical exchange between all the oxygen atoms of the various oxygen-containing compounds (metal oxides and carbon monoxide). At the elevated temperatures used, complete exchange is obtained within 30 minutes.

ACKNOWLEDGMENT

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Colorimetric Determination of Glycolate in Carboxymethylcellulose

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► A colorimetric method for determining the glycolate content of crude sodium carboxymethylcellulose is described. The glycolate is washed out of the crude sample with hot 80% ethyl alcohol and determined colorimetrically with chromotropic acid in concentrated sulfuric acid. There is no interference from other impurities in the carboxymethylcellulose.

A COLORIMETRIC method for determining glycolic acid using 2,7-dihydroxynaphthalene as a color reagent was described by Calkins (*1*) who attributed the color development to the condensation of formaldehyde, formed from the glycolic acid, with the color reagent. Using this principle, Eyler, Klug, and Diephuis (*2*) devised a method for determining the degree of substitution of sodium carboxymethylcellulose by hydrolyzing the carboxymethyl group and determining it as glycolate. Chromotropic acid, 4,5 - dihydroxy - 2,7 - naphthalenedisulfonic acid, has been used as a color reagent for formaldehyde in the analysis of polyhydroxy compounds which can be oxidized by periodic acid (*3*, *5*) and in the determination of methoxyl groups (*4*). Fleury, Courtois, and Perles (*3*) determined glycolic acid by converting it to formaldehyde and developing the color with chromotropic acid

A method has been developed for analyzing crude sodium carboxymethylcellulose for glycolate by washing the glycolate out of the crude sample with hot 80% ethyl achohol and determining it colorimetrically by a method similar to that used by Eyler, Klug, and Diephuis, but substituting chromotropic acid as the color reagent.

EXPERIMENTAL

Crude sodium carboxymethylcellulose was washed successively with 30- to 50-ml. portions of hot (50° to 70° C.) 80% ethyl alcohol until chloride-free. For 3-gram samples this required between 200 and 600 ml. of ethyl alcohol depending on the salt content of the carboxymethylcellulose. The wash liquor was collected and diluted to contain between 0.04 and 0.08 mg. per ml. of sodium glycolate, and a 1-ml. aliquot was taken for color development. A purple color resulted when the glycolate sample was boiled with chromotropic acid and concentrated sulfuric acid The absorbance was determined at 570 mμ. Beer's law was obeyed over the range between 0.01 and 0.10 mg. per ml. of glycolic acid.

ANALYTICAL PROCEDURE

Reagents and Apparatus. Concentrated sulfuric acid, 95 to 98%.

Standard glycolic acid solution (Fisher Chemical Index, No. A-130). Accurately weigh 0.1000 gram of glycolic acid, dried overnight in a vacuum desiccator, and dilute to 1 liter with distilled water. For accurate work this solution should be kept no longer than 30 days.

Color reagent, chromotropic salt solution (4,5-dihydroxy-2,7-naphthalenedisulfonic acid disodium salt, Fisher Chemical Index, No. 230-p), 5% aqueous solution, prepared daily. This solution oxidizes readily on exposure to light and air and should be kept stoppered, away from direct sunlight.

Spectrophotometer, Beckman DU, Bausch & Lomb Spectronic 20, or any other that can be used at 570 mμ.

Color Development. Transfer 1 ml. of the ethyl alcohol wash liquor containing 0.04 to 0.08 mg. per ml. of sodium glycolate to a 25-ml. volumetric flask, and add 0.5 ml. of

Table I. Reproducibility of Glycolate Determination in Crude Sodium Carboxymethylcellulose

	CMC Sample A		CMC Sample B	
% Sodium glycolate	3.99	4.15	6.98	7.24
	4.01	4.21	7.03	7.23
	4.12	4.20	7.09	7.21
	4.06	4.04	7.21	7.12
	4.01	4.01	6.99	7.21
	4.07	4.08	7.08	7.05
	3.95	4.11	6.92	7.01
	4.00	4.03	7.10	7.04
Average	4.06		7.10	
Range, %	0.25		0.32	

chromotropic salt solution and 20 ml. of concentrated sulfuric acid. At the same time prepare a reagent blank, using 1.0 ml. of water in place of the sample and a series of standard samples containing 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0 ml. of the standard glycolic acid solution and enough water to make 1.0 ml. Stopper the flasks and mix. Loosen the stoppers and place in a boiling water bath for 30 minutes. Cool to room temperature, dilute to 25 ml. with concentrated sulfuric acid, mix well, and read the absorbance of the unknowns and standards against the blank at 570 mμ on a spectrophotometer.

Plot the standard calibration curve, and from it determine the milligrams per milliliter of glycolic acid in the unknown samples.

$$\% \text{ sodium glycolate} = \frac{\text{mg./ml. of glycolic acid} \times 129 \times \text{dilution factor}}{\text{dry weight of crude NaCMC}}$$

RESULTS AND DISCUSSION

The optimum conditions for color development—those given in the analytical procedure—were determined by running a series of standard solutions. Using those conditions, four standard calibration curves run on different days gave the same curve. Beer's law was obeyed in the range from 0.01 to 0.10 mg. per ml. of glycolic acid. No readable color was developed when sodium chloride, acetic acid, oxalic acid, monochloroacetic acid, dichloroacetic acid, and caustic extract of cellulose were tested.

The reproducibility of this method is shown in Table I. For two samples containing approximately 4 and 7% of sodium glycolate, the standard deviation calculated on the basis of 16 single determinations on each sample was found to be $\sigma = 0.09\%$ sodium glycolate. Table II gives the results of the analysis of carboxymethylcellulose to which known quantities of glycolate were added.

This method can be applied to filtrates or extraction liquors from procedures for determining the per cent of sodium carboxymethylcellulose which involve washing or extracting the crude sample with alcohol to remove impurities.

Table II. Analysis of Sodium Carboxymethylcellulose of Known Glycolate Content

Sodium Glycolate, % Added	Sodium Glycolate, % Found	Difference, %
6.13	5.93	0.20
7.40	7.40	0.00
6.03	6.25	0.22
9.10	8.95	0.15
9.17	8.85	0.32
12.70	12.57	0.13

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Apparatus for Wet Oxidation of Organic Samples and Carbon Dioxide Trapping for Subsequent Radioactive Assay

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▶ An all-glass apparatus allows recovery of partly burned materials, makes possible preparation of high purity barium carbonate samples, avoids transfer of sample from preparation tube, and makes possible gravimetric assay of barium carbonate by use of preweighed centrifuge tubes.

Carbon-14–labeled organic samples are usually put in a uniform form for radioactivity assay by being converted to carbon dioxide or barium carbonate. Most techniques involve the production of barium carbonate or carbon dioxide from the organic material by wet oxidations (*1*, *5*, *7*).

This laboratory has for some time used an all-glass apparatus that has given excellent results. The apparatus consists of a standard-taper centrifuge tube, *A*, in which a sample is placed. The centrifuge tube is then connected to the apparatus as shown in Figure 1. A gentle stream of nitrogen or helium (freed of water and carbon dioxide) is used to flush the gases formed during the oxidation. The separatory funnel, *D*, contains the oxidizing mixture (*2*, *6*). Some refractory organic materials may require catalysts for complete oxidation. They may be added to the mixture at any time by means of the addition tube, *B*.

Finely granulated platinum oxide (Adam's catalyst) gave the most satisfactory results. The catalyst was usually added at the beginning of the reaction. The first scrubber, *F*, contained a 5% potassium permanganate solution in 0.5*N* sulfuric acid and served to trap any sulfur dioxide which might have been carried over. In the receiving tube, *G*, a saturated barium hydroxide solution (layered with toluene) served to trap the carbon dioxide. A simplified version of this apparatus has also been successfully used. In the simplified apparatus an addition tube, *B*, was not present and tube *A* was part of the main digestion chamber (Figure 2). The collecting train is assembled to the cold finger as shown in Figure 1.

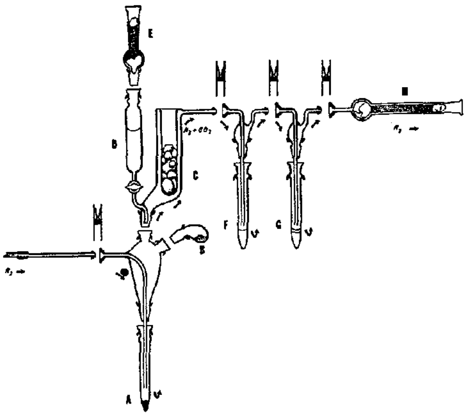

Figure 1. Apparatus for converting organic materials to barium carbonate for carbon-14 counting

The dry ice finger, *C*, is one of the salient features of this apparatus; it serves as a trap for sublimed and partially oxidized materials, some of which—i.e., senecioic acid, etc.—may form barium salts with the barium hydroxide. If a quantity of volatile substances collected on the walls of the finger, it became necessary to "recycle" the material by surrounding test tube *A* with a beaker of dry ice or liquid nitrogen and replacing the cooling agent in finger *C* by hot water. The outside of *C* then was gently warmed, allowing the transfer of incompletely burned materials from *C* to *A*.

Combustion was usually completed after heating test tube *A* at 160° to 170° C. (Wood's metal bath) for 2 hours; test tube *G*, with the formed barium carbonate, was removed from the inlet tube, stoppered, and centrifuged for 10 minutes at 2500 r.p.m. The clean supernatant fluid was decanted and the residue and tube were washed repeatedly until the rinsings were free of barium hydroxide. The yield of barium carbonate was used as an index of the completeness of oxidation. The centrifuge tube and its contents were dried at 200° C. for 10 to 16 hours. After being cooled in a desiccator, the barium carbonate was ground to a fine consistency with a stirring rod, then suspended in acetone and transferred to preweighed planchets with the aid of micropipets. The barium carbonate may also be pressed into uniform wafers as described by Rabinowitz and others (*4*). After drying and weighing, the samples were assayed for radioactivity. For compounds known to oxidize irregularly, it is necessary, prior to assay, to have equal distribution of activity throughout. It may well be necessary that the barium carbonate be regenerated by placing tube *G* in tube *A* position; carbon dioxide is then produced and collected in a fresh tube, *A*.

Table I. Results Obtained by the Use of Different Methods

	% Yield in Recovered Barium Carbonate[a]			
	By Weight		Radioactivity, C.P.M./Mg.C[b]	
Compound, 3 to 10 Mg.	Run	Recycle	Run	Recycle
Rubber (natural)-multilabeled-C^{14} (theoretical[c] 100–120 c.p.m.)	33–38	43–47	100–108	137–150
Rubber (natural) + platinum oxide (theoretical 100–120 c.p.m.)	87–91	97–99	123–132	135–147
Rubber polybromide (theoretical 100–120 c.p.m.)	24–28	29–30	87–120	130–147
Rubber polybromide + platinum oxide (theoretical 100–120 c.p.m.)	89–101	97–102	99–123	130–135
Starch	83–96	93–97	. . .	. . .
Versene (tetrasodium salt of ethylenediaminetetraacetic acid)	79–83	100–102	. . .	. . .
Tris (2-amino-2-hydroxymethyl 1,3-propanediol)	80–86	94–97	. . .	. . .
Senecioic acid-3-C^{14} (theoretical 65–70 c.p.m.)	78–81	100–102	15–39	68–71
Cotton	87–92	94–97	. . .	. . .
4-Nitrobenzimidazole	77–84	94–98	. . .	. . .
Oxalic acid	97–100	. . .	. . .	. . .
Glucose-6-C^{14} (theoretical 130–150 c.p.m.)	96–98	. . .	120–135	. . .
Iodoform-C^{14} (theoretical 40–50 c.p.m.)	84–88	100–101	40–43	40–48
Cholesterol-3-C^{14} (theoretical 100–110 c.p.m.)	. . .	. . .	80–85	100–112
Uracil-2-C^{14} (theoretical 120–125 c.p.m.)	. . .	. . .	116–120	110–108
Methylmethacrylate multi-C^{14} (theoretical 200–220 c.p.m.)	. . .	. . .	185–197	180–185

[a] Barium carbonate weighed in original collecting tube. Adsorbed materials in bubbler were included. Glass apparatus taken to constant weight ± 0.2 mg.
[b] Corrected to infinite thinness. Mica-window Geiger-Müller tube.
[c] Calculated. Corrected to infinite thinness.

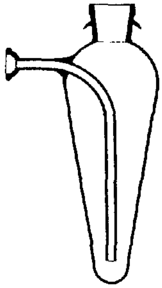

Figure 2. Simplified reaction flask

When a gaseous assay system was to be used, the centrifuge tube containing the anhydrous barium carbonate was placed in a vacuum system suitable for the collection of pure carbon dioxide (*1*, *5*, *7*).

The glass apparatus described has also been successfully used in the isolation of carboxyl-carbon dioxide from organic acids by the Schmidt reaction (*3*). This reaction was carried out by mixing the radioactive organic acid and sodium azide in tube *A*; the tube was then chilled in a dry ice bath and a mixture of fuming sulfuric acid and sulfuric acid was slowly introduced from the separatory funnel. Carbon dioxide in yields 83 to 87% of the theoretical carboxyl carbon were obtained for acetic and propionic acids with the use of this equipment. The apparatus has also been used successfully for trapping pure carbon dioxide from enzymatic reactions (*4*). In these studies, the enzyme system was placed in separatory funnel *D* and introduced to flask *A* (or tube *A*) which contained the substrate. The nitrogen or helium gas was replaced by oxygen or oxygen-nitrogen.

DISCUSSION

The following advantages may be claimed for the apparatus: It allows the recovery of partly burned materials; it makes possible the preparation of high purity barium carbonate samples (free of other barium salts); no transfer of the sample from its preparation tube to the apparatus is necessary if the sample has been collected or prepared in a standard taper centrifuge tube (The preparative or collecting test tube becomes test tube *A*); test tube *G* can be removed and placed in position *A* for the preparation of a uniformly mixed sample or for conversion of the obtained barium carbonate to carbon dioxide for other uses; and by use of preweighed centrifuge tubes gravimetric assay of the resulting barium carbonate is possible.

The results in Table I were obtained with this equipment. Easily oxidizable and refractory materials were utilized and results with or without catalyst and with and without recycling are reported.

ACKNOWLEDGMENT

The author is indebted to Samuel Gurin for his kind encouragement and advice.

This work was carried out with the technical assistance of Herbert D. Strauss.

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RECEIVED for review September 15, 1955 Accepted January 2, 1957. All radioactive materials were obtained on allocation from the U. S. Atomic Energy Commission.

CRYSTALLOGRAPHIC DATA

159. Aluminum Trifluoride, AlF_3

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The University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M.

ALUMINUM fluoride was prepared by reaction of 99.99% pure aluminum metal with aqueous hydrofluoric acid. The compound was oven-dried at 110° C., and then sublimed under vacuum.

The structure of aluminum fluoride was determined by Ketelaar (*1*). The space group is $R32 - D_3^7$ with $2(AlF_3)$ per unit cell. The cell dimensions determined by Ketelaar are, after converting from *kX* to Angstrom units, $a_0 = 5.039 \pm 0.005$ A., $\alpha = 58°31'$.

CRYSTAL MORPHOLOGY

System and Class. Trigonal, trapezohedral.

Habit. Rhombohedrons {110} with the vertex angle 88°49′.

X-RAY DIFFRACTION DATA

Cell Dimensions. $a_0 = 5.030 \pm 0.001$ A.; $\alpha = 58°39' \pm 1'$; volume per formula unit 43.61 A.³ These dimensions were determined by least square methods from the last six lines of the powder pattern in the angular range $\theta = 73°$ to 83°. Absorption and other systematic errors depending on θ were negligible in that range. Dimensions of the hexagonal cell, containing six formula units, are $a_0 = 4.927$ A., $c_0 = 12.445$ A., $c_0/a_0 = 2.526$.

Formula Weight. 83.97.

Density. 3.197 grams per cc. (x-ray).

OPTICAL PROPERTIES

Uniaxial positive.

Refractive Indices (5893 A.). $n_O = 1.3765$; $n_E = 1.3770$; geometric mean 1.3767. Lorentz-Lorenz refraction 6.04 cc.

Colorless.

Powder X-Ray Diffraction Pattern of Aluminum Trifluoride

hkl	*d*, A., Calcd.	*d*, A., Obsd.[a]	I^b
110	3.519	3.52	100
211	2.514	2.512	2
210	2.118	2.119	19
222	2.074	2.074	2
200	2.018	2.019	1
$22\underline{0}$	1.760	1.759	24
$20\bar{1}$	1.599	1.600	2
$32\underline{1}$	1.587	1.587	14
$21\bar{1}$	1.561	1.560	7
332	1.462	1.460	1
$31\underline{0}$	1.432	1.431	2
$11\bar{2}$	1.422	1.422	2
320	1.354	1.355	1
$42\underline{2}$	1.257	1.257	3
$20\bar{2}$	1.232	1.233	1
432	1.206	1.207	1
$43\underline{3}$	1.195	1.195	2
$21\bar{2}$	1.1781	1.1794	1
$411, \underline{3}30$	1.1730	1.1741	1
$30\bar{1}$	1.1626	1.1631	3
431	1.1197	1.1202	1
442	1.0750	1.0700	1
420	1.0591	1.0593	<1
$22\bar{2}$	1.0514	1.0511	<1
444	1.0371	1.0374	1
400	1.0091	1.0096	<1
$53\underline{2}$	0.9853	0.9856	1
$41\bar{1}$	0.9338	0.9338	1
440	0.8798	0.8798	<1
554	0.8703	0.8703	<1
$\underline{5}41$	0.8576	0.8577	1
$43\bar{1}, 510$	0.8495	0.8495	1
552, 633	0.8380	0.8380	1
$53\underline{0}$	0.8285	0.8285	1
$33\bar{2}$	0.8230	0.8229	1
632	0.8178	0.8177	<1
$62\underline{2}$	0.8099	0.8100	<1
$41\bar{2}$	0.80554	0.80559	<1
$40\bar{2}$	0.79969	0.79971	<1
642	0.79334	0.79327·	1
$65\underline{4}$	0.78628	0.78630	<1
$42\bar{2}$	0.78058	0.78061	<1
653	0.77851	0.77849	1

Philips 114.6-mm.-diameter powder camera, Straumanis mounting; $\lambda(CuK\alpha) = 1.5418$; $\lambda(CuK\alpha_1) = 1.54050$ A.

[b] Relative peak intensities above background from densitometer measurements.

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WORK done under auspices of Atomic Energy Commission.

160. Molybdenum Metaphosphate, $Mo(PO_3)_3$

R. M. DOUGLASS and EUGENE STARITZKY

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Euhedral crystals of molybdenum metaphosphate were prepared by B. J. Thamer of this laboratory by reaction of molybdenum metal with metaphosphoric acid at elevated temperature and pressure. Quantitative chemical analysis of a sample gave, by weight, 28.43% molybdenum and 26.5% phosphorus. Considering the small amount of material available and the extreme difficulty with which it is brought into solution for analysis, these values are in satisfactory agreement with those calculated for $Mo(PO_3)_3$: 28.82% molybdenum and 27.92% phosphorus. No physical properties of this compound were found in the literature, except the density (*1*).

Crystal Morphology

System and Class. Monoclinic, prismatic. No piezoelectric effect was detected with a Giebe-Scheibe-type apparatus.

Habit. Prismatic {$23\bar{1}$} with {001}, {100}, and {031}.

X-Ray Diffraction Data

Diffraction Symbol. $2/mI\text{-}/a$, embracing space groups $I2/a$ (C_{2h}^6) and Ia (C_s^4).

Cell Dimensions. $a_0 = 10.76 \pm 0.01$ A., $b_0 = 19.48 \pm 0.03$ A., $c_0 = 9.55 \pm 0.01$ A., $\beta = 97.6 \pm 0.1°$; cell volume 1984 A.^{3}; $a:b:c = 0.552:1:0.490$.

Formula Weights per Cell. 12.

Formula Weight. 332.89.

Density. 3.34 grams per cc. (calculated; weight of unit atomic weight 1.6602×10^{-24} gram); 3.291 (measured); 3.28 [literature (*1*)].

Optical Properties

Refractive Indices (5893 A.). $n_X \approx n_Y = 1.660 \pm 0.001$, $n_Z = 1.680 \pm 0.001$; geometric mean 1.667; $n_Y - n_X = 0.0003$ (calculated from optic axial angle). Lorentz-Lorenz refraction 37.1 cc.

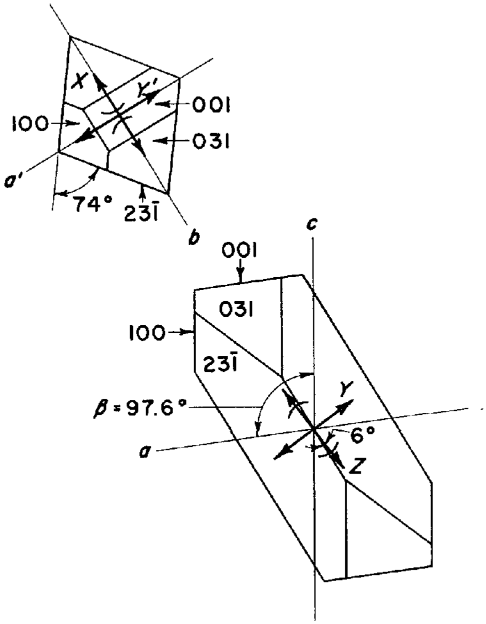

Figure 1. Crystal of molybdenum metaphosphate

Orthographic projections parallel to *b* and to [102]

Optic Orientation. $X = b$; $Z \wedge c = 37°$, $Z \wedge [102] = 6°$.

Optic Axial Angle. $2V_Z = 9.5°$ (5350 A.), 12.3° (5893 A.), 14.4° (6640 A.).

Color. Yellow without pronounced pleochroism.

Partial Powder X-Ray Diffraction Pattern of Molybdenum Metaphosphate

hkl	*d*, A., Calcd.	*d*, A., Obsd.[a]	I/I_1[b]
130	5.547	5.546	5
031	5.355	5.379	40
002	4.735	4.750	25
141	3.931	3.950	100
$23\bar{1}$	3.929		
$13\bar{2}$	3.730	3.752	10
150	3.659	3.661	20
231	3.646		
310	3.499	3.505	45
132	3.484		
202	3.330	3.350	20
222	3.151	3.136	10
330	3.119		
$01\bar{3}$	3.116		
$25\bar{1}$	3.058	3.075	<5
$31\bar{2}$	3.007	3.002	5
$24\bar{2}$	2.996		
$12\bar{3}$	2.990		
$16\bar{1}$	2.986		
251	2.919	2.927	5
161	2.918		
$21\bar{3}$	2.858	2.857	25
033	2.839		
152	2.834		
$34\bar{1}$	2.834		
123	2.800	2.785	25
260	2.773		
		2.690	5
		2.658	5
		2.482	30
		2.438	<5
		2.403	<5
		2.381	10
		2.334	15
		2.299	5
		2.268	20
		2.217	5
		2.140	<5
		2.116	5
		2.070	15
		2.011	<5
		1.9741	10

[a] Philips 114.6-mm.-diameter powder camera, Straumanis mounting; $\lambda(CuK\alpha) = 1.5418$ A.

[b] Relative peak intensities above background from densitometer measurements.

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Work done under auspices of Atomic Energy Commission. Crystallographic data for publication in this section should be sent to W. C. McCrone, 500 East 33rd St., Chicago 16, Ill.

Improved Receiving Assembly and Pot Closure for Laboratory Distilling Columns

Ned C. Krouskop, Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

A RECEIVING assembly and pot closure for laboratory distilling columns (*4*) were used through 1954 in the distillation laboratory of the Petroleum Research Laboratory, Carnegie Institute of Technology, in connection with the work of the American Petroleum Institute Research Project 6. The assembly was designed around high vacuum glass stopcocks, lubricated with either triethylene glycol citrate or tetraethylene glycol citrate grease (*1*, *3*). The pot closure was a lubricated ground-glass cap, which occasionally lost its seal because the lubricant dissolved or melted through contact with hot liquid.

An improved receiving assembly designed around a modified metal diaphragm valve and a pot closure made of Monel metal and a specially treated rubber O-ring have been developed.

The ground-glass stopcocks of the previous receiving assembly required a lubricant that would not contaminate the highly purified distillate, yet would stand up for continuous use for 2 to 6 months without "freezing." It was important that the lubricant should not accumulate in the bore of the stopcock, forming an obstruction in the assembly. The most suitable lubricant found was triethylene glycol citrate for summer use (relatively high ambient temperature) and tetraethylene glycol citrate for winter use (relatively low ambient temperature). These lubricants are slightly soluble in the alcohols and glycol ethers used for azeotropic distillations. In a receiving assembly where glass stop-

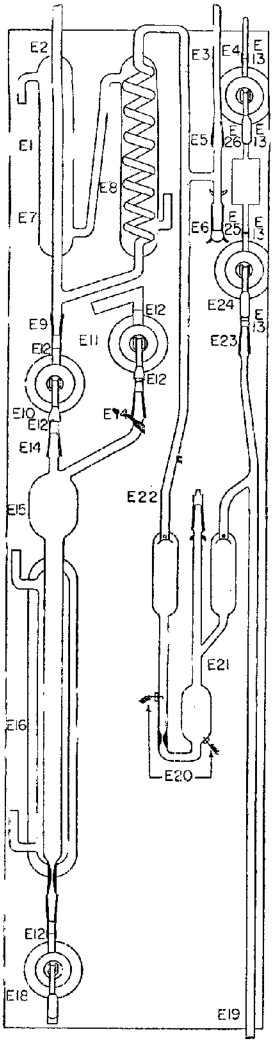

Figure 1. Improved receiving assembly

*E*1. Transite supporting board
*E*2. Product line from head
*E*3. Copper line to controlled pressure system
*E*4. Copper line to source of inert gas
*E*5. Copper-to-glass standard-taper joint (soldered)
*E*6. Outlet to atmosphere, standard ground joint 12/30
*E*7. Condenser for cooling product line, near 10° C.
*E*8. Spiral condenser between receiver and controlled pressure system, near 10° C.
*E*9, *E*14, *E*17, *E*23. Monel-to-glass standard-taper joints (soldered)
*E*10. *E*11, *E*18, *E*24, *E*26. Lever-operated diaphragm valves of Monel
*E*12, *E*13. Connections of Monel (soldered)
*E*15. Overflow portion of receiver
*E*16. Receiver, graduated, water-jacketed
*E*19. Connection to manometer from pot
*E*20. Tungsten contacts
*E*21. Manometer (mercury, with tungsten contacts)
*E*22. Connection from manometer to head through spiral condenser
*E*25. Reservoir for introducing inert gas to pot

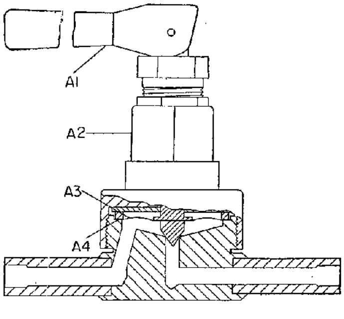

Figure 2. Lever-operated diaphragm valve

*A*1. Lever-operated cam
*A*2. Housing containing spring-loading mechanism
*A*3. Stainless steel diaphragm
*A*4. Teflon gasket

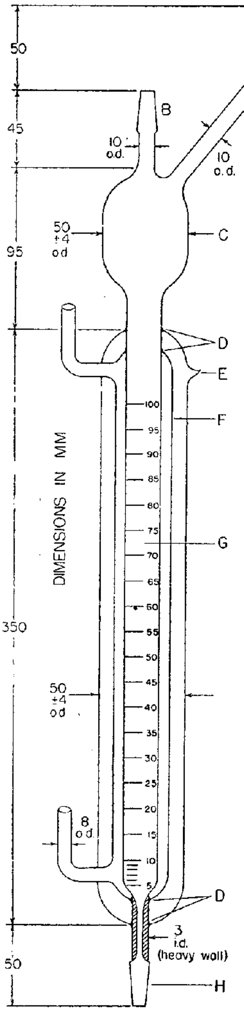

Figure 3. Distillate receiver

A. Standard-taper ground joint 12/30, male portion
B. Standard-taper ground joint 12/30, male portion
C. Overflow reservoir, capacity approximately 100 ml.
D. Ring seal
E. Vacuum jacket
F. Water jacket
G. Graduated receiver tube
H. Standard-taper ground joint 12/30, male portion

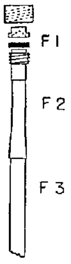

Figure 4. Pot closure

*F*1. Vacuum, metal-to-metal coupling and cap with specially coated rubber O-ring
*F*2. Metal joint, Monel, 14/35 female
*F*3. 14/35 Pyrex joint, male

cocks are used, there is also the difficult problem of supporting and operating the stopcocks without breakage.

A diagram of the new receiving assembly is shown in Figure 1. Details of the diaphragm valves are given in Figure 2. The valves, constructed of stainless steel and Monel metal (Hoke, Inc., No. C413A; modified to eliminate liquid holdup), make a leak-proof system without the use of any type of lubricant, so that contamination is avoided. Diaphragm valves are used both on the receiver (*E*10, *E*11, and *E*18) and on the line from a source of inert gas to the tube connecting the manometer and still pot (*E*24 and *E*26). The design provides much greater mechanical strength and makes all the glass parts more accessible for glassblowing and assembly. The valves are supported through their base and bolted to the Transite panel. An integral overflow receiver eliminates the bulky and cumbersome separate overflow receiver formerly used. A detailed drawing of the new vacuum-jacketed receiver is shown in Figure 3. The oil manometer has been eliminated in the receiving assembly. Experience showed that the mercury manometer was sensitive enough to make the proper adjustments for operating the distillation columns.

The former pot closure, consisting of a 14/35₸ ground-glass joint and cap, sealed to the upper shoulder of the pot to permit charging of material and withdrawal of residue, tended to leak after hot vapors softened or dissolved the lubricant of ethylene glycol citrate (*1*). These disadvantages were eliminated by changing to a stainless steel or Monel closure (Central Scientific Co., Catalog No. 94235) and using a specially treated rubber O-ring (Central Scientific Co., Catalog No. 94236-3, alcohol- and hydrocarbon-resistant) to make the seal. The new metal pot closure, including a specially treated rubber O-ring (Figure 4), is soldered to a Monel 14/35 female tapered joint, which in turn is soldered (*2*, *4*) to the 14/35₸ glass joint attached to the shoulder of the pot. A new O-ring is installed at the beginning of each distillation.

Since installation of the new pot closure, no material has been lost from the pots.

ACKNOWLEDGMENT

The author is indebted to Frederick D. Rossini and Beveridge J. Mair for guidance and suggestions in the work

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Investigation performed as part of the American Petroleum Institute Research Project 6, Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

Head Regulator for Cutoff Valve

Leonard Bean, National Bureau of Standards, Washington, D. C.

Hewitt [Anal. Chem. **27**, 865 (1955)] described an automatic cutoff valve for ion exchange columns utilizing an immersion tube provided with a frit. Two forms were illustrated: one for usual ion exchange columns, the other for analytical work.

A modification of the latter maintains a constant head above the column at all times, while retaining other features.

The bottom of a 250-ml. Erlenmeyer flask (Figure 1) was heated in a blast burner and blown to a slightly rounded shape. A sealing tube with a medium porosity fritted glass disk 10 mm. in diameter sealed into it was cut off just below the disk. The other end of the tube was cut off 8 cm. above the disk bottom. A hole was blown in the bottom of the flask and the end of the tube away from the disk was sealed to the flask. A piece of glass tubing 6 mm. in outside diameter was bent at an angle of about 135° at one end (to keep out dust). The other end was cut off at a suitable length to reach through a rubber stopper and almost touch the fritted glass disk. A rubber stopper was placed over the fritted sealing tube.

In operation, the stopper around the sealing tube is inserted into the top of the column and the liquid in the column is adjusted, as described by Hewitt, so that it is about halfway between the bottom of the rubber stopper and the fritted glass disk. The volume of eluent to be used for the first fraction is poured into the flask and the inner tube is inserted with its stopper. The column is opened at the exit end. This fraction flows through under constant head until the action of the Hewitt valve stops it. The volume of eluent for the next fraction can then be added.

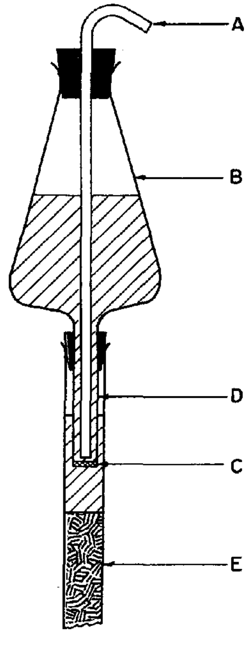

Figure 1. Automatic head regulator for Hewitt valve

A. Inner tube to regulate head
B. Erlenmeyer flask
C. Fritted-glass disk at bottom of sealing tube
D. Fritted sealing tube sealed to flask
E. Resin bed in chromatographic column

The head of liquid above the resin bed at all times is determined by the position of the bottom of the inner tube and does not change with time or volume of eluent placed in the flask. This feature aids in maintaining uniform rate of flow through the column. It is important to maintain a tight fit with the rubber stoppers.

Time Controls for Schroeder and Corey and Gilson Fraction Collectors

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Many separations commonly made in laboratories today would be completely impractical without dependable fraction collectors. Simple changes in two designs are given which remedy difficulties encountered in their practical operation.

SCHROEDER AND COREY FRACTION COLLECTOR

The first design, the automatic weight-driven, time-controlled collector described by Schroeder and Corey [Anal. Chem. 23, 1723 (1951)], is satisfactory where column flow rates are very low, as in the Stein-Moore starch chromatographic methods [*J. Biol. Chem.* 176, 337 (1948)]. However, with higher flow rates, drops of effluent are more apt to be lost as the tube position is changed, since for a period of about 5 seconds during each change, the tubes are out of position and any drop that falls is lost.

Design Changes. The drawings in Schroeder and Corey's paper illustrate minor design changes that might be made to minimize this disadvantage. The pause between tubes can be eliminated if the stops on the trigger bar *O* (Schroeder and Corey, Figure 2, p. 1723), are made the same angular distance apart as are the holes for the test tubes in the turntable. Then, every other index pin is removed so as to make the angular distance between the pins twice that between the test tubes. With these spacings, during stage 2 (Figure 3, p. 1723) tube 2 is in position instead of midway between as in the original design.

The action of the solenoid also must be changed. This can be done by the use of a stepping relay in conjunction with a pulse timer such as that mentioned by Schroeder and Corey (R. W. Cramer Co., Type V-60M). The stepping relay alternately opens and closes a pair of contacts when activated by the pulse from the timer. The stepping relay in turn activates the solenoid during one cycle and deactivates it during the next. (A suitable relay is Type RC-100-AR Guardian locking relay, Almo Radio Corp., Philadelphia, Pa.) The solenoid operating the trigger bar is rated for continuous duty and has not shown any tendency to overheat under the conditions of operation, unless the trigger mechanism jams in some way so that the armature cannot pull into its normal position. To protect the equipment under these conditions, a time-lag fuse or a circuit breaker of the correct size can be installed in the line.

GILSON FRACTION COLLECTOR

The second design is the commercially available Gilson volumetric fraction collector (Gilson Medical Electronics, Madison, Wis.).

The fractions are measured in a volumetric tube fitted with a valve at the lower end, which is operated by a dumping mechanism. A photocell is placed on the opposite side of the volumetric tube from a fluorescent tube used as the light source. When a clear solution fills the volumetric tube, the latter acts as a cylindrical lens and increases the intensity of the light falling on the photocell, which in turn activates the dumping mechanism.

Difficulties arise if the effluent solution becomes colored or turbid and thus causes a decrease in the intensity of the light falling on the opening of the photocell. Even if the solution becomes clear later, further fractionation does not occur, as the remaining effluent overflows at the top of the volumetric tube when the photocell fails to operate the mechanism.

Design Changes. Time Control Operation. One way to obtain fractionation where colored or turbid solutions are encountered, is to convert to time control operation. The dumping operation in the Gilson machine is started by closing a switch in the Weston meter-type relay. A timer which will reset itself and close a switch at the end of its timing cycle thus can be used to control the machine. These requirements are met by the combination of a pulse timer (Type V-60M, R. W. Cramer Co.) and a cycle timer (CF3-2-60S, R. W. Cramer Co.) suggested by Schroeder and Corey. The pulse timer is used to start the cycle timer in the same way as for the Schroeder and Corey design. The second cam of the cycle timer is set to close its switch for a very short period (less than 4 seconds). This switch is then connected in parallel with the output terminals of the Weston meter-type relay of the Gilson machine. (The switch should be isolated from the 115-volt supply to the timer so that a short circuit will not be introduced.) For this method of operation, the fluorescent tube of the Gilson machine is removed so that the photocell does not operate.

Saftey Device. An alternative and better way to operate the Gilson machine is to employ the timer as a safety device which goes into action if the photocell fails to operate the machine. The timer is set for a period slightly longer than is normally required for the collection of a fraction. This method requires that the timer be reset when the dumping mechanism operates; otherwise, if the photocell activates the system the timer soon will be out of step. A simple way of accomplishing this is by use of a timer which will reset itself when the power supply is interrupted.

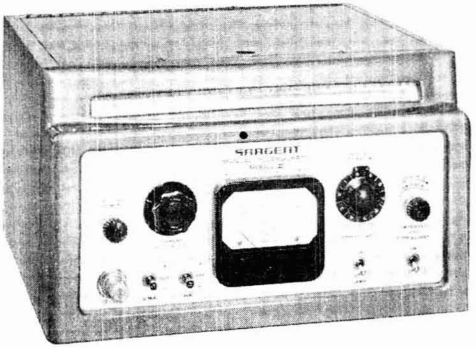
The power supply can be interrupted by use of the microswitch connected to and operated by the dump motor of the Gilson machine. When the machine is turned on but not dumping, the normally open contact of this switch is connected to one side of the 115-volt supply line. When the machine dumps, this connection is broken. Thus if the timer is supplied from this normally open contact and from the other side of the supply line feeding the dumping mechanism, power to the timer is interrupted each time the dumping mechanism operates. (A wiring diagram illustrating this hookup can be supplied upon request.)

The pulse timer mentioned above does not reset itself on power interruption. A suitable timer for this application is the Microflex reset timer (Eagle Signal Corp., Moline, Ill.). This timer contains a switch which can be set so that it is closed at the end of the timing cycle and is open both when the timer is reset and during timing. This switch can be connected across the meter relay output terminals, as mentioned previously. The timer also can be set so that a power interruption will cause it to reset itself to zero time.

If the connections are made through a socket on the dumping mechanism cabinet and a corresponding plug on the end of a four-wire cable to the timer, the timer can be disconnected readily. This is helpful when a chromatogram is being started or at other stages of operation when the flow rate is varying over a wide range. With this method of operation, when a turbid or colored solution passes through the volumetric tube, the timer will cause fractionation to continue until a clear solution again appears, at which time the photocell will resume operation. Although the fractions will be slightly large while the timer is acting, fractionation will be obtained and the effluent will not overflow into the drain.

Mention of commercial products does not imply endorsement by the Department of Agriculture over others of similar nature not mentioned.

SARGENT Polarographs*



MODEL III

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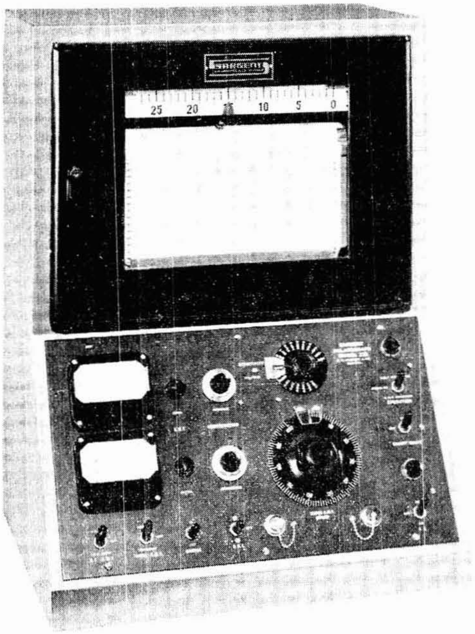

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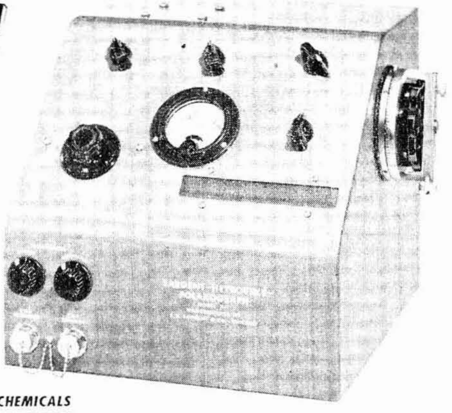

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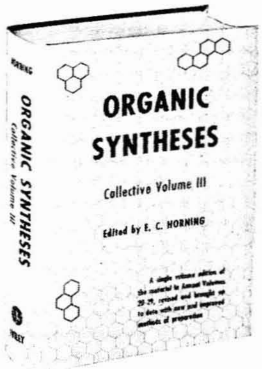

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Blenders. Specifications and applications data available on the gallon-sized Waring commercial "Blendor" cited as being ideal for pilot and experimental runs. Unit has multi-speed 1½ h.p. motor, 7½ foot 3 conductor ground cord, stainless steel container. Waring Products Corp., 25 W. 23rd St., N. Y. 36, N. Y. **26A-2**

Blenders, Twin-Shell. New catalog available on twin-shell blenders. Yoke model is cited as being ideal for small scale batch blending. Yoke arrangements fits standard four or eight quart blender frame, permits two different blends at once. The Patterson-Kelley Co., Inc., 2350 Hanson St., E. Stroudsburg, Pa. **24A-2**

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Casseroles. Coors casseroles are cited as being resistant to chemical attack and thermal shock. Available in various styles with porcelain or wood handles and with or without covers. Coors Porcelain Co., Golden, Colo. **67A-1**

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Cells, Chromatography. Circle 89A-3 for catalog on "Gow-Mac" gas chromatography cells. Catalog contains information on thermal conductivity cells for 225° C. operation, temperature regulated cells for operation at room temperature or 200° C., and power supply and control units. Gow-Mac Instrument Co., 100 Kings Rd., Madison, N. J. **89A-3**

Cells, Glass Absorption. Circle 76A-4 for complete information on Klett glass absorption cells. Klett Manufacturing Co., 177 E. 87th St., N. Y., N. Y. **76A-4**

Centrifuges. Bulletin available on the "Servall SS-1" superspeed angle centrifuge. Up to 16,000 rpm, 32,700 × G, 400 ml. Variable transformer for remote control. Ivan Sorvall, Inc., Norwalk, Conn. **74A-1**

Centrifuges. Complete information on the following table model centrifuges available: "Safety-Head" (3 models), "Safeguard Angle-Head" (5 models), "Safeguard Standard" (5 models), and "Junior" (3 models). Clay-Adams Co., N. Y. 10, N. Y. **90A-2**

Chromatographs, Gas. Data file available on the new Beckman GC-2 gas chromatograph. Instrument provides reproducible sample introduction, reproducible retention times, and reproducible peak configuration. Scientific Instruments Div., Beckman Instruments, Inc., 2500 Fullerton Rd., Fullerton, Calif. **41A**

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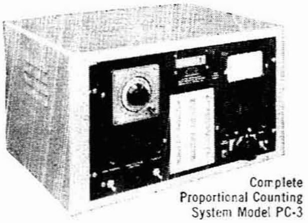

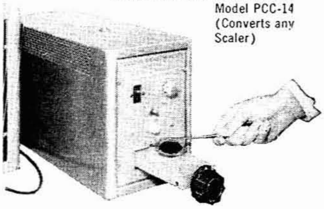

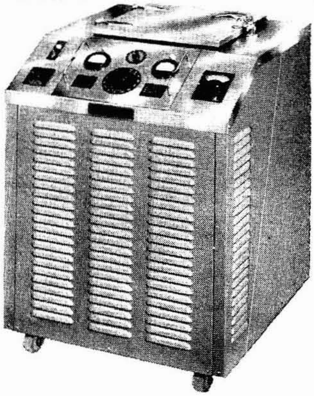

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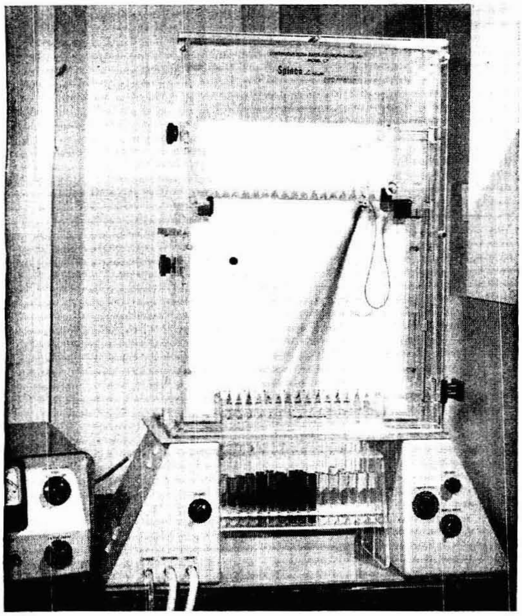


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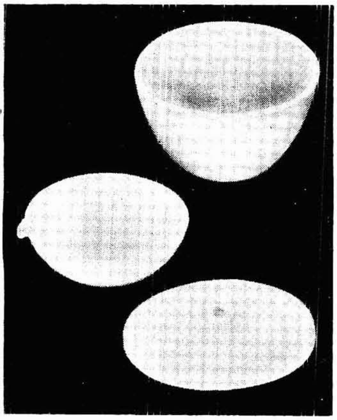

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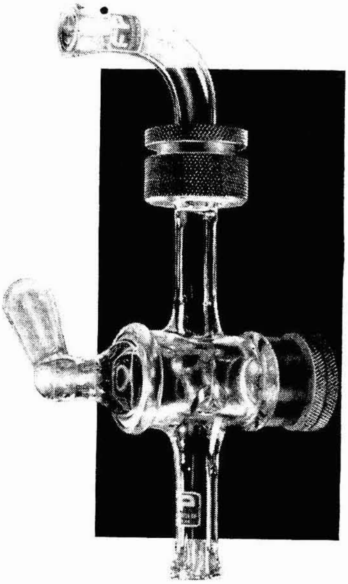

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Mercury Cathode. Circle 43A-1 for bulletin on company's mercury cathode cited as providing rapid, quantitative separation of metals. Eberbach Corp., Ann Arbor, Mich. **43A-1**

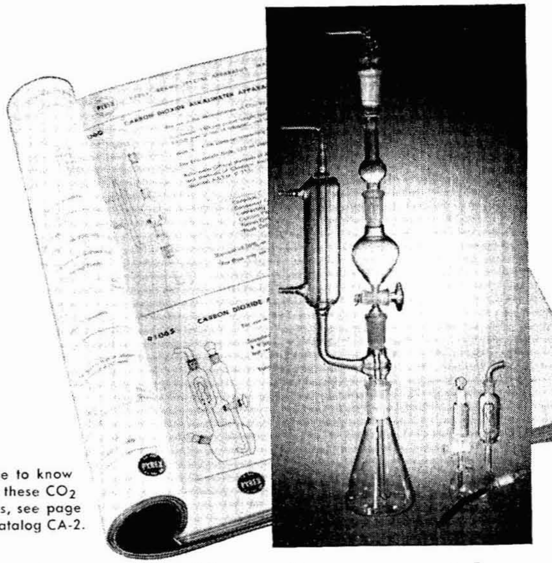
Micro-Microammeters. Circle 17A for a new catalog containing detailed data on the model 412 log micro-microammeter that indicates from 10^{-13} to 10^{-7} ampere on a single 6-decade scale. Accuracy: 0.2 decade. Zero drift: within 0.5 decade in 8 hours. Keithley Instruments, Inc., 12415 Euclid Ave., Cleveland 6, Ohio. **17A**

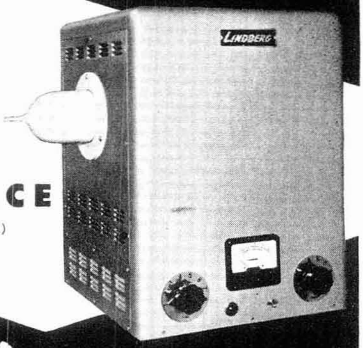
Mixers, Laboratory. Circle 42A for illustrated laboratory mixer bulletin. Contains information on electric or air driven units; single or variable speeds; gear or direct drive; and accessories. Mixing Equipment Co., Inc., 160-c Mt. Read Blvd., Rochester 11, N. Y. **42A**

Monochromators. Bulletin available on double spectrometer-monochromator for the ultra-violet, visible and infrared regions. Range: 0.2–35 microns. Farrand Optical Co., Inc., Bronx Blvd. & E. 238th St., N. Y. 70, N. Y. **43A-2**

Ovens. Complete specifications available on "Thermo-Vac" ovens that feature 2″ thick fiberglass insulation, radiant heating chromalox elements, and hydraulic thermostat controls. Range: room to 200° C. ± 0.5° C. Chamber: 8″ × 8″ × 12″. Schaar and Co., 745 W. Lexington St., Chicago 7, Ill. **59A**

(Continued on page 69 A)

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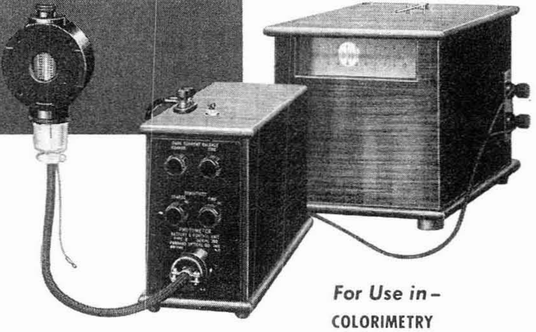

Ovens. Bulletin available describing the complete line of Despatch laboratory and production ovens. The "V-39" is a double-walled, truck-loading, batch type oven with insulated construction. Despatch Oven Co., 341 Despatch Bldg., Minneapolis 14, Minn. **73A-3**

Ovens. Circle 86A-2 for catalog containing information on vacuum oven with "Tuflex" glass window. Capacity: 12″ square by 19″ deep. Temperature range: room to 160° C. National Appliance Co., Portland, Ore. **86A-2**

Paper Electrophoresis System. Circle 46A for new developments which make the Model R paper electrophoresis system more useful for analyses of inorganic and organic mixtures. Analysis time has been reduced by over five hours for serum proteins. Spinco Div., Beckman Instruments, Inc., Palo Alto, Calif. **46A**

pH Meters. Detailed information available on the following Beckman pH meters: pocket, "Zeromatic," Model N-1, Model GS, Model G, and Model N-2. Harshaw Scientific, Div. of Harshaw Chemical Co., 1945 E. 97th St., Cleveland 6, Ohio **3rd Cover**

pH Meters. Bulletin available on company's complete line of battery and line-operated pH meters incorporating modern electronic tubes and circuits. Simple in operation and maintenance, featuring sealed amplifier plug-in units. Photovolt Corp., 95 Madison Ave., N. Y. 16, N. Y. **45A-1**

pH Meters. Bulletin, "Cambridge Research Model pH Meter," available. Instrument measures pH and millivolt values where extreme precision and reliability are required. Cambridge Instrument Co., Inc., 3514 Grand Central Terminal, N. Y. 17, N. Y. **66A-2**

pH Meters. Circle 87A-1 for information on the Beckman pocket pH meter. Circle 87A-2 for information on the "Zeromatic" that features fingertip control. Chicago Apparatus Co., 1735 No. Ashland Ave., Chicago 22, Ill. **87A-1, 2**

Photometers. Complete information available on the Brice-Phoenix light scattering photometer that measures absolute turbidity, dissymmetry, depolarization, and molecular weight. Phoenix Precision Instrument Co., 3803-05 N. 5th St., Phila. 40, Pa. **87A-4**

Photometers. 8-page booklet contains full data on the principles and operation of the Fisher electrophotometer for colorimetric determinations. Fisher Scientific Co., 100 Fisher Bldg., Pittsburgh 19, Pa. **83A**

Phototubes, Multiplier. Du Mont 12-stage multiplier phototubes are cited as providing the high gain of 12 stages plus stability. Available in 2″, 3″, 5″, 12″ and 16″ sizes. Industrial Tube Sales, Allen B. Du Mont Laboratories, Inc., 2 Main Ave., Passaic, N. J. **21A**

Pipet Fillers. New flexible bulb type pipet filler eliminates risks of mouth pipetting dangerous solutions. Holds set level indefinitely, fits any pipette, operates easily with one hand. Instrumentation Associates, 17 W. 60th St., N. Y. 23, N. Y. **84A-3**

Piping, Tin-Lined. Circle 67A-2 for bulletin on company's complete line of tin-lined pipe, valves, and faucets designed for use with distilled or demineralized water distribution systems. Barnstead Still & Demineralizer Co., 9 Lanesville Terrace, Boston 31, Mass. **67A-2**

Polarimeters. Detailed literature available on polarimeter with scale reading to 0.05°. Illumination by either a double filament 40-watt bulb or sodium spectral bulb. Carl Zeiss, Inc., 485 Fifth Ave., N. Y. 17, N. Y. **80A-1**

(Continued on page 70 A)

Product Capsules

Potentiometric Recorders. Automatic, self-balancing potentiometric recorder measures voltages or current and graphically records these variables as a function of time. 40 ranges. 9 standard chart speeds. 21½" wide, 13" deep, 24" high. Weight: 75 lbs. E. H. Sargent & Co., 4647 W. Foster Ave., Chicago 30, Ill. **61A**

Presses, Hydraulic. Circular available on company's automatic 70 ton hydraulic press. 18" × 18" platens heat to 300° with thermoswitch controls. Pasadena Hydraulics, Inc., 1433 Lidcombe, El Monte, Calif. **84A-4**

Presses, Laboratory. Literature available on Carver laboratory presses. Standard 10 ton unit is used for forming KBr pellets, dehydrating, pressing out oils, filtering thick fluids, determining fatty acids, etc. Fred S. Carver, Inc., 54 River Rd., Summit, N. J. **68A**

Pressure Reaction Apparatus. Specifications available on company's "Series 4000" high pressure, rocker type apparatus. For hydrogenation and other reactions at pressures to 6000 psig. at temperatures to 350° C. Furnished with 500 or 1000 ml. stainless steel bombs. Parr Instrument Co., Moline, Ill. **26A-1**

Pumps, Vacuum. Bulletin available on three new models in the Cenco line of high vacuum pumps. Pumps are cited as being free from vibration and balanced for quiet operation. All parts are made to precision tolerances. Central Scientific Co., 1708 Irving Park Rd., Chicago 13, Ill. **28A**

Shakers. Bulletin available on build-up design laboratory shakers with wrist-action motion. Side clamps take various shapes and sizes. Top clamps take bottles and Erlenmeyer flasks. Burrell Corp., 2223 Fifth Ave., Pittsburgh 19, Pa. **72A-1**

Shakers. Bulletin available on heavy duty maintenance-free rotary action shaker for general laboratory work that provides through shaking and vigorous agitation for sustained periods. 140 and 400 oscillations per min. New Brunswick Scientific Co., P. O. Box 606, New Brunswick, N. J. **89A-2**

Spectrographs. Circle 27A-2 for the B&L spectrograph catalog. Contains information on the 1.5 meter stigmatic grating spectrograph, the dual-grating spectrograph, the Littrow spectrograph, the Littrow-Echelle spectrograph, and the Echelle attachment. Bausch & Lomb Optical Co., 60917 St. Paul St., Rochester 2, N. Y. **27A-2**

Spectrographs. Circle 91A-2 for 8-page catalog on company's 3.4 meter convertible spectrograph used for quality control and research analysis. Jarrell-Ash Co., 32 Farwell St., Newtonville, Mass. **91A-2**

Spectrometers. Circle 10A for latest "Radio Frequency Spectroscopy Bulletin." Full technical information on both N-M-R and E-P-R spectroscopy and the complete "N-M-R at Work" series will be included. Instrument Div., Varian Assoc., Palo Alto 4, Calif. **10A**

Spectrometers. Circle 48A-1 for data on Model 12G single beam, single pass and Model 112G single beam, double pass recording infrared fore prism-grating spectrometers. Circle 48A-2 for information on the Model 154-B vapor fractometer. Circle 48A-3 to receive "Instrument News," a quarterly publication on electro-optical instrumentation. Instrument Div., Perkin-Elmer Corp., Norwalk, Conn. **48A-1, 2, 3**

Spectrometers. Circle 19A for bulletin on company's mass spectrometer for process-stream or atmosphere-monitoring applications. Provides accurate readings in the range of mass 2 to mass

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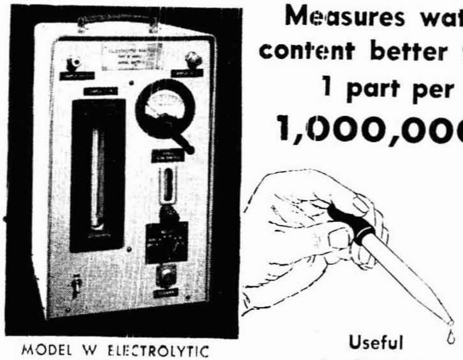

150. Consolidated Electrodynamics Corp., 300 N. Sierra Madre Villa, Pasadena, Calif. **19A**

Spectrophotometers. Circle 6A for latest information on color measurements and data on the General Electric recording spectrophotometer. General Electric Co., Section 585-40, Schenectady 5, N. Y. **6A**

Spectrophotometers. Circle 25A for bulletin containing complete information about Coleman spectrophotometers and other Coleman products. Company's spectrophotometers are cited as delivering precise analyses, at high speed, even in the hands of untrained operators. Coleman Instruments, Inc., Maywood, Ill. **25A**

Spectrophotometers. Circle 31A-1 for data file on the Beckman DK-2 recording spectrophotometer that provides analysis in ultra-violet, visible, or near-infrared ranges with speed and precision. Circle 31A-2 for "Career File" outlining positions available in engineering, manufacturing, and technical marketing. Scientific Instruments Div., Beckman Instruments, Inc., 2500 Fullerton Rd., Fullerton, Calif. **31A-1, 2**

Spectrophotometers. Accurate, direct reading absorbance to 1860A is now provided with the Cary Model 14 recording spectrophotometer through the use of optical elements of increased ultra-violet efficiency in the double monochromator. Circle 56A-1 for bulletin. Also available is information on company's improved vibrating reed electrometer (circle 56A-2). Applied Physics Corp., 362 W. Colorado St., Pasadena 1, Calif. **56A-1, 2**

Spectrophotometers, Infrared. Circle 49A for complete data and specifications on the Model 21 and its accessories. Accessories include 6 different prism materials, gas cells, liquid cells, variable path length cells, polarizers, heatable cells, reflectance attachments, auxiliary source assemblies, etc. Instrument Div., Perkin-Elmer Corp., Norwalk, Conn. **49A**

Spectrophotometers, Infrared. Circle 62A for data file on two low-cost Beckman infrared spectrophotometers: the IR-6, designed for quantitative performance; and the double-beam IR-5, designed for qualitative performance. Scientific Instruments Div., Beckman Instruments, Inc., 2500 Fullerton Rd., Fullerton, Calif. **62A**

Spectrophotometers, Infrared. Circle 70A for complete information on the new low cost "Infracord" double beam optical null system spectrophotometer. Instrument features atmospheric and solvent compensation, differential analysis, linear wavelength vs. transmittance recording, instant wavelength reset, direct recording on notebook size paper, and reproducible performance. Instrument Div., Perkin-Elmer Corp., Norwalk, Conn. **70A**

Stopcocks. Circle 30A for the new catalog which illustrates products featuring the "Lab-Crest" stopcock and includes prices and specifications. Stopcock does not leak, never "freezes," requires no lubrication. Fischer & Porter Co. 1557 County Line Rd., Hatboro, Pa. **30A**

Sulfur Determinations. 16 - page Dietert-Detroit catalog illustrates and describes both sulfur and carbon determinators plus the complete line of accessory equipment and supplies. Circle 34A for copy. Harry W. Dietert Co., 9330 Roselawn, Detroit 4, Mich. **34A**

Titrimeters. Bulletins available on instruments for all electrometric titrations. Includes information on the standard, automatic, high - frequency, amperometric and coulomatic titrimeters.

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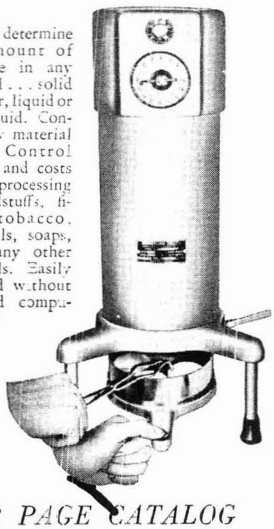

Product Capsules

Fisher Scientific Co., 100 Fisher Bldg., Pittsburgh 19, Pa. **54A**

Tubing, Plastic. Tygon flexible plastic tubing is cited as being glass clear, chemically inert, non-toxic, tough, and easy to couple. U. S. Stoneware, Akron 9, Ohio. **82A**

Tubing, Plastic. New catalog available on company's flexible plastic tubing. Transparent tubing is available in all sizes from 1/8″ ID through 2″ ID. Tubing resists heat, chemicals, and age discoloration. The Nalge Co., Inc., Rochester 2, N. Y. **90A-1**

Tubing, Rubber. Company's pure latex tubing is cited as making strong, air-tight connections. Flexible and resilient. Withstands rough treatment with little danger of tearing or breaking. Available in 24 standard sizes. Rubber Latex Products, Inc., Cuyahoga Falls, Ohio. **18A**

Viscosimeters. Circle 76A-2 for bulletin on the Hoeppler viscosimeter that operates on the falling ball principle. Circle 76A-3 for bulletin on the Ubbelohde viscosimeter that operates on the principle of the suspended level. Fish-Schurman Corp., 72 Portman Rd., New Rochelle, N. Y. **76A-2, 3**

Viscosimeters. Circle 85A for illustrated brochure on the Brookfield 8-speed viscometer and specialized accessories. Portable instrument is cited as being easily operated and as providing precise measurement readings directly in centipoises. Brookfield Engineering Laboratories, Inc., Stoughton 112, Mass. **85A**

Ultramicroburets. Circle 3A for descriptive bulletin on the newly designed Gilmont ultramicroburets. The Emil Greiner Co., 20–26 N. Moore St., N. Y. 13, N. Y. **3A**

X-Y Recorders. Circle 88A for complete information on the "Autograf" X-Y recorder in five models. Instrument is used for curve drawing, point plotting, curve following, card and tape reading, and gain-frequency plotting. F. L. Mosely Co., 409 No. Fair Oaks Ave., Pasadena, Calif. **88A**

CHEMICALS AND MATERIALS

Buffer Tablets. Bulletin available on certified Coleman buffer tablets cited as being always fresh and exact. pH values from 2.0 to 11.40 pH in 0.20 increments. Coleman Instruments, Inc., Maywood, Ill. **78A**

Ether, Reagent. Baker & Adamson reagent A.C.S. ether is readily available in 1-lb. and 5-lb. bottles, 27-lb. and 300-lb. drums. General Chemical Div., Allied Chemical & Dye Corp., 40 Rector St., N. Y. 6, N. Y. **4th Cover**

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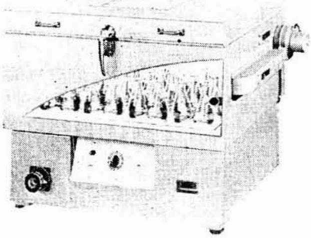

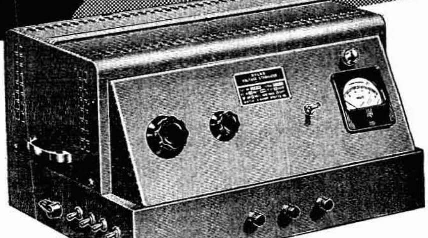

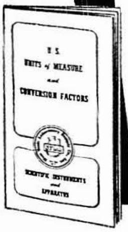
U. S.
UNITS of MEASURE
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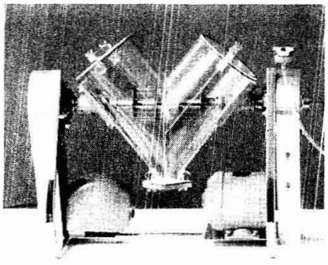


Product Capsules

Filter Papers. Circle 37A-1 for bulletin on company's ultra filters cited as being porous membranes with extremely uniform microstructure and very smooth surface. Circle 37A-2 for free analytical filter paper sampler. Carl Schleicher & Schuell Co., Keene, N. H.

37A-1, 2

Filter Papers. Circle 71A for samples of company's filter papers used for experiments in chromatography, electrophoresis, and qualitative analysis. Papers are available in sheets, rolls, and circles. The Eaton-Dikeman Co., Filtertown, Mt. Holly Springs, Pa.

71A

Radioactive Compounds. Catalog available on company's 50 microcurie C^{14} packages. Ten packages available from stock without AEC license. Research Specialties Co., 2005 Hopkins St., Berkeley 7, Calif. **72A-2**

Reagent Chemicals. The 5 relatively non-hygroscopic "Baker Analyzed" primary standards (arsenic trioxide, benzoic acid, potassium biphthalate, potassium dichromate, sodium oxalate) have an assay greater than 99.95%. J. T. Baker Chemical Co., Phillipsburg, N. J. **2nd cover**

Reagents. DuPont 5-pint reagent bottles have new safety grip, dripless polyethylene sleeve and are packaged in single-trip, throw-away cartons. Colored labels with matching bottle caps. Grasselli Chemicals Dept., E. I. du Pont de Nemours & Co. (Inc.), Wilmington 98, Del. **12A**

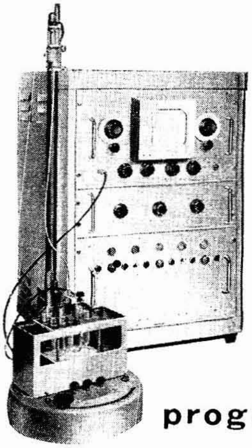
Reagents. Company's line of over 400 analytical reagents are packaged in "Stormor" bottles, and are cited as being of tested, uniform purity. Mallinckrodt Chemical Works, 2nd & Mallinckrodt Sts., St. Louis 7, Mo.

79A

Spectroscopic Electrodes. Circle 14A for free samples and complete information on company's line of spectroscopic graphite electrodes available in three hardness grades: U-2 (soft), U-1 (medium) and UF-4 (hard). Boron-free, they are cited as providing uniformity in diameters, hardness texture, and porosity. United Carbon Products Co., Inc., P.O. Box 269, Bay City, Mich.

14A

Spectroscopic Electrodes. Circle 38A for information on company's complete line of "National" spectroscopic electrodes and powders available in a total of forty performed sizes and shapes, plus stock length and powders. National Carbon Co., Div. of Union Carbide and Carbon Corp., 30 East 42nd St., N. Y. 17, N. Y. **38A**



Researchers:

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Lithium metal, lithium hydride, lithium hydroxide and lithium carbonate are the basis for both experimental and commercial studies as polymerization catalysts in the manufacture of certain plastics, polymers and resins. The polymerization reactions may be "addition" or "condensation" processes.

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Lithium carbonate, to cite another example, is a preferred catalyst for the esterification of tall oils. Again, lithium hydroxide has been found to be a superior catalyst for the manufacture of alkyd resins. And work has been done with lithium hydride for ester interchange reactions.

In case you have a catalyst problem in mind requiring the use of highly reactive lithium, our PR&D department is making available information on this new and highly valuable research tool. Describe your application or request general information.

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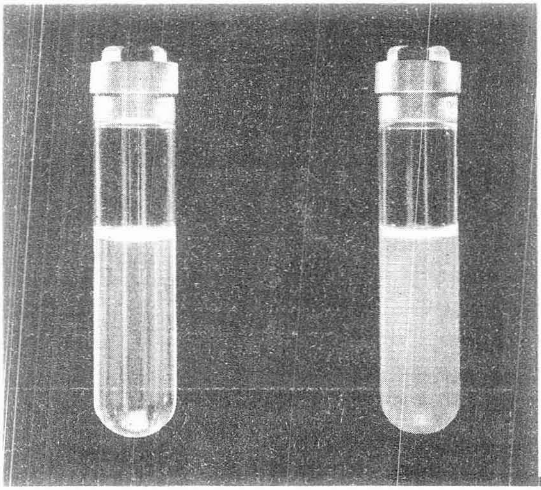
For further information, circle number 75 A on Readers' Service Card, page 77 A

A CLEAR CASE OF SEDIMENTING EFFICIENCY



These two tubes containing 5 mg/ml of tobacco mosaic virus were centrifuged for 1 hour at 25,000 rpm, 51,000 x gravity. In tube at right, run in conventional rotor, 12% of virus remains in supernatant. In tube at left, run in K-25.1 Insulated, Core-Ventilated Model K rotor, only 2% remains in supernatant.

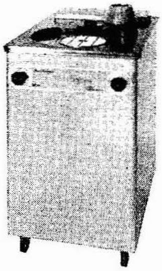
Spinco Model K Preparative Centrifuge

with insulated, core-ventilated rotors*

Here is a general-purpose centrifuge which brings a new type of sedimenting efficiency to the laboratory.

The key: high centrifugal forces (to 51,000 x gravity) plus a unique insulated, core-ventilated* rotor. This new rotor minimizes thermal convection which causes stirring in conventional rotors; it keeps rotor temperatures from rising more than a few degrees above ambient; it protects most labile materials without requiring refrigeration.

The results: sedimenting efficiency is greatly increased; the time for centrifuging routine samples is substantially reduced; many separations are possible with the Model K which cannot be done with conventional centrifuges.



The Spinco Model K introduces other valuable features:

Automatic Operation:
up to speed at the push of a button

New Drive System:
full power always available,
even at low speeds

Versatile Design:
large rotor chamber has room for
special rotors and attachments;
drive is powerful to run heavy loads.

For literature on this new centrifuge write Spinco Division, Beckman Instruments, Inc. Stanford Industrial Park, Palo Alto, California. Ask for Folder K-7.

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**patent applied for*

For further information, circle number 76 A on Readers' Service Card, page 77 A