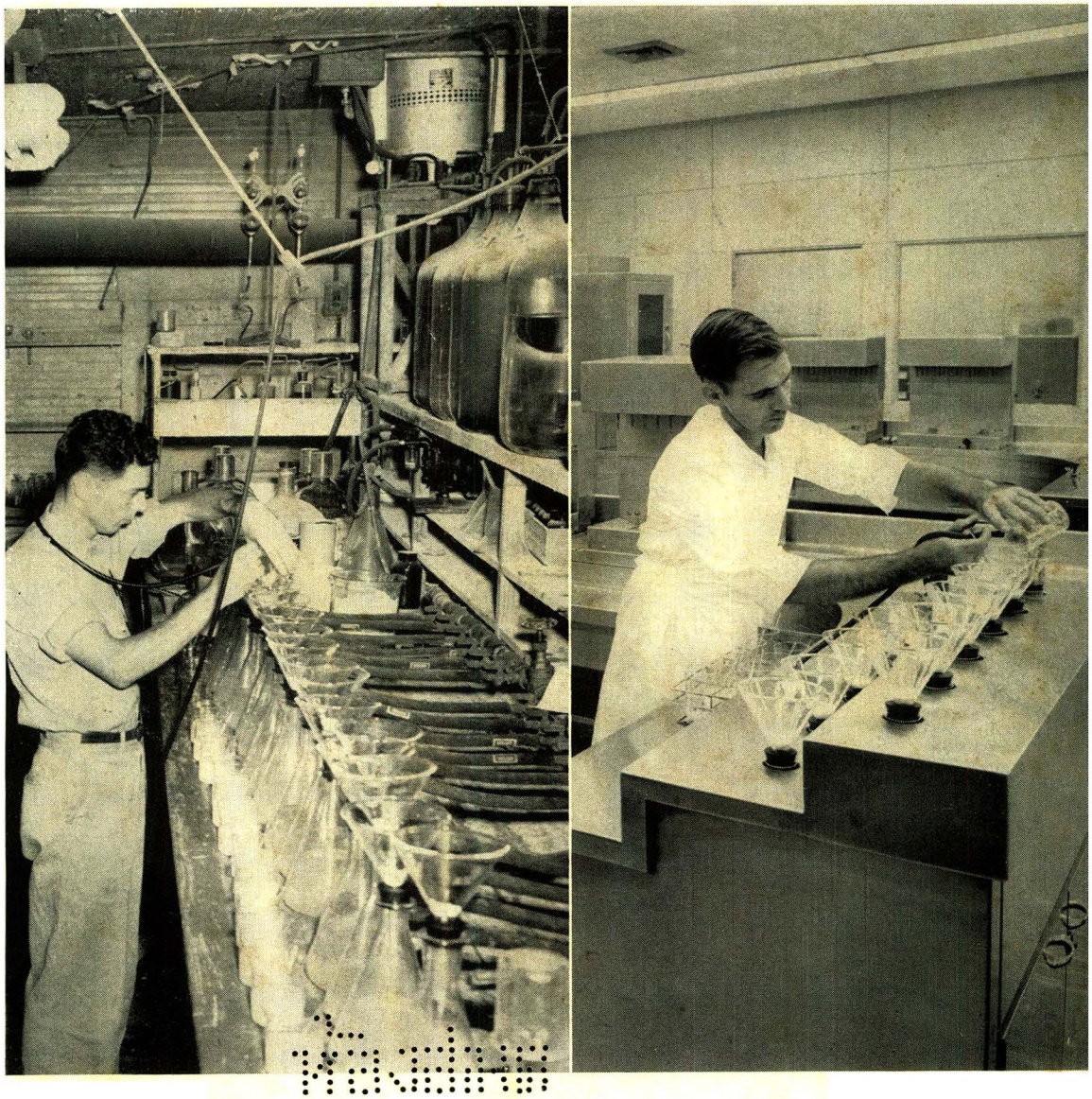
APRIL 1954

ANALYTICAL CHEMISTRY



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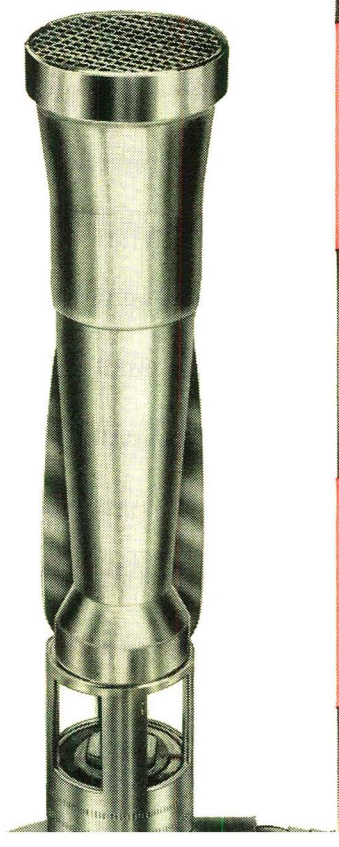

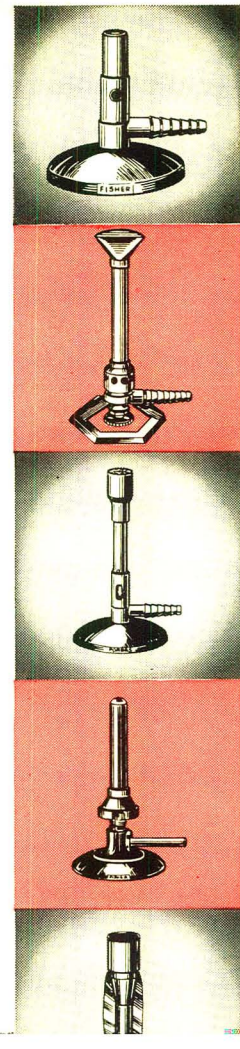

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This Month's Cover. Analytical control of processes and products is one of the most vital aspects of modern industry. The value of studying and reappraising present facilities and methods was sharply accentuated for us when we recently visited the phosphate mining and processing operations of the International Minerals and Chemical Corp. in Florida. Several years ago the company became aware of the inefficiency of its several ill-equipped small control laboratories at several locations. After a thorough study it was decided to build a new control laboratory equipped with the highest quality equipment and apparatus. The study showed that considerable money would be saved every year by the use of new facilities, which would, in a very short period, more than pay for the capital investment required. For further information, see pages 39 A and 41 A.

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Spot News ... of the month

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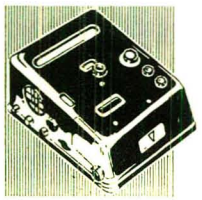

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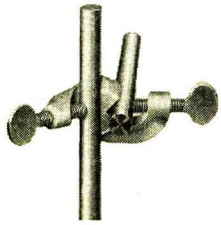

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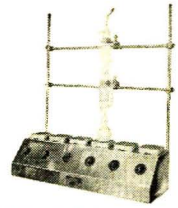

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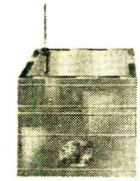

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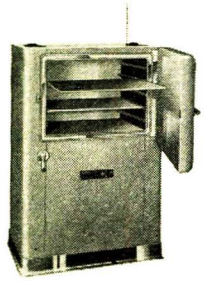

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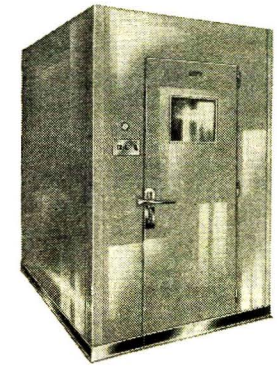

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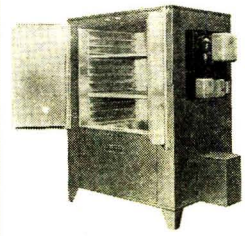

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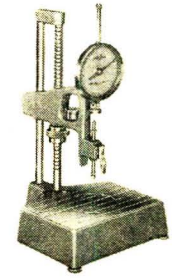

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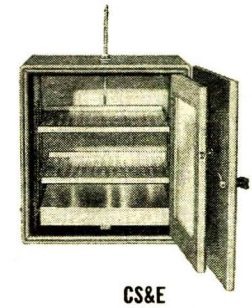

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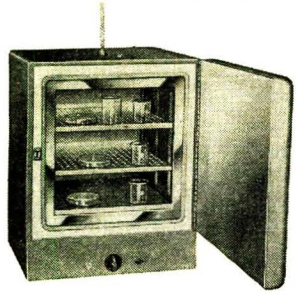

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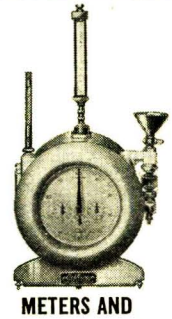

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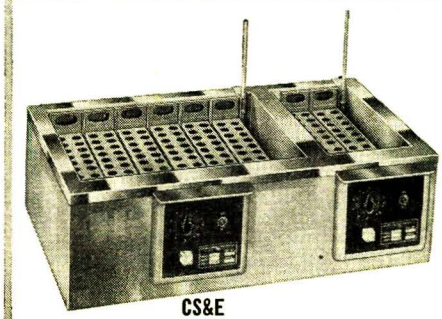

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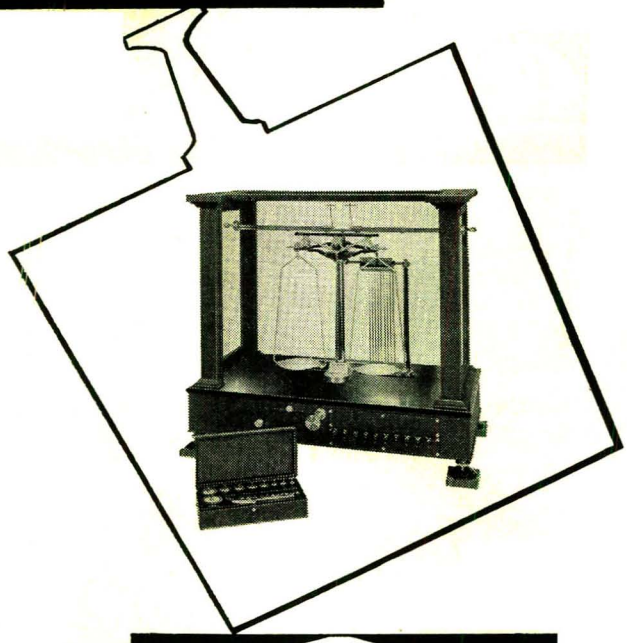

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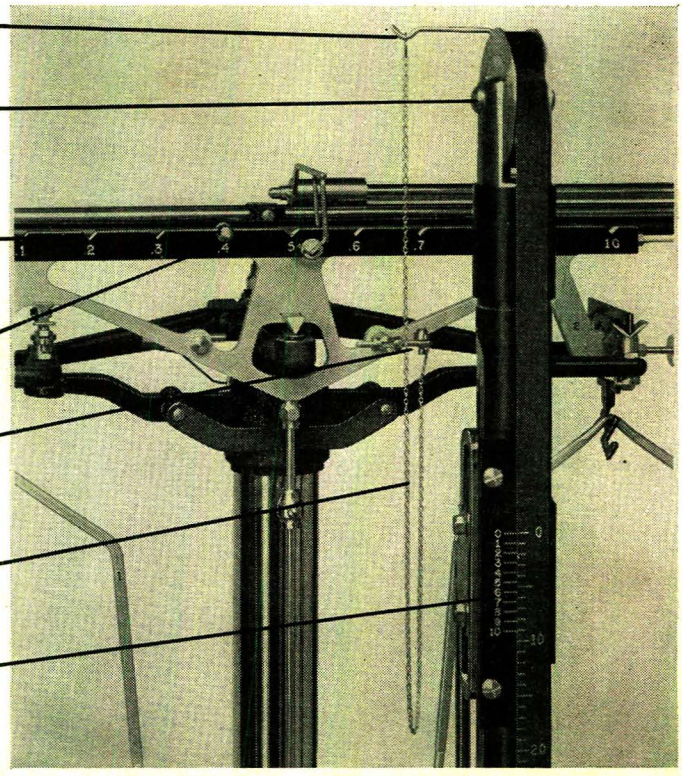

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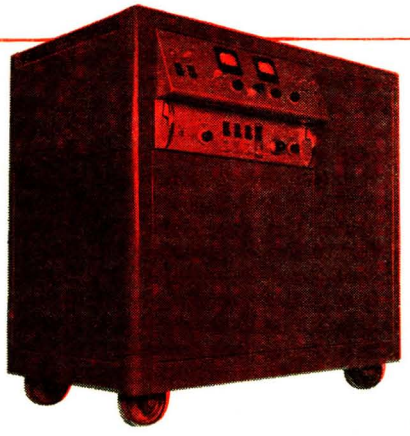
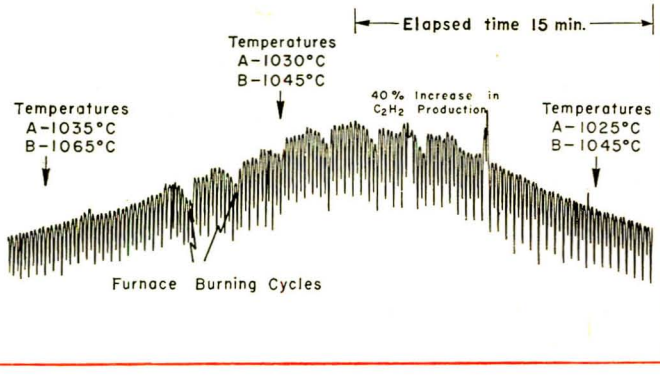
New acetylene production process uses the

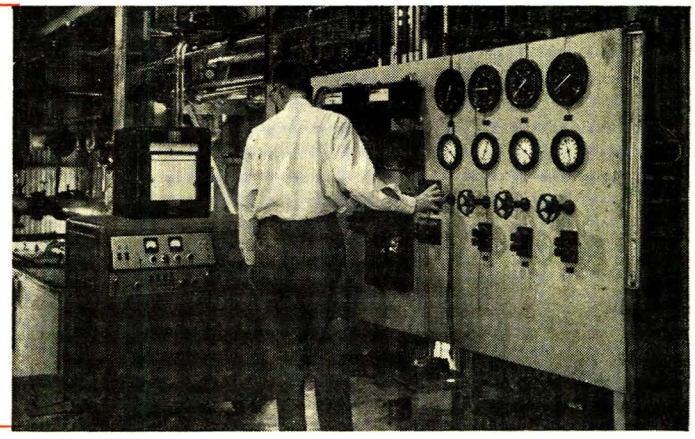
Consolidated continuous process–monitoring mass spectrometer..... for "on the spot" control



The new Consolidated Model 21-610 continuous process monitoring mass spectrometer played a part in the development of the Wulff Process for the commercial production of acetylene. Requiring only 110 volts and a small quantity of cooling water for operation, this self-contained, completely portable instrument was placed on stream in the pilot plant, where it monitored various gas streams under a variety of imposed conditions. Samples from 19 different points, introduced through a common manifold for analysis, made possible among other things: (1) the monitoring of feed stock, (2) evaluation of cracking gas composition versus temperature, (3) determination of fuel gas composition, (4) measurement of acetylene or ethylene content in recycle gas, (5) diacetylene scrubber efficiency, (6) acetylene or ethylene absorber efficiency, (7) solvent recovery and/or loss, (8) final product purity.

The chart, below, left, illustrates the versatility and practical value of the Model 21-610 as a production control instrument. The mass-26 peak of acetylene was monitored in the cracking gas coming directly from the unit as the furnace temperature was varied. From right to left, the temperature was slowly increased. The rise in the cyclically scanned 26 peak indicates rising acetylene content of feed stock. This test showed that acetylene increased approximately 40% with a temperature rise of 5 degrees C. Using the chart as a reference, guesswork was eliminated and maximum future production assured. Write for Bulletin CEC-1824-X17.





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For further information, circle number 9 A on Readers' Service Card, page 49 A

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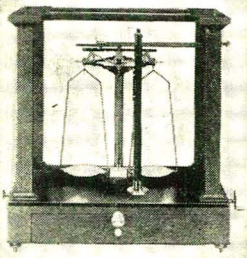

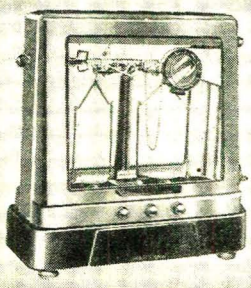

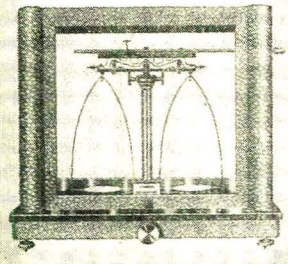

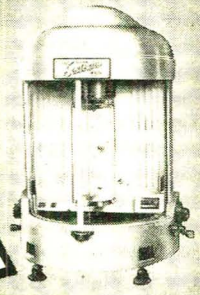

AINSWORTH

H-1550—Type LC $177.00
H-1560—Type LCB 276.00
(Capacity 200 gm., sensitivity 1/10 mg.)

H-1570—Type DL $254.00
H-1580—Type DLB 353.00
H-1600—Type B 285.00
*H-1605—Type BB 384.00
(Capacity 200 gm., sensitivity 1/20 mg. H-1560, H-1580, H-1605 are equipped with chainweight and notched beam. Magnetic dampers extra at $38.50 single end, $60.50 double end.)

CHRISTIAN BECKER

H-1803—Model AB-7 . . . . . $177.00
H-1813—Model AB-4 . . . . . 353.00
(Capacity 200 gm., sensitivity 1/10 mg., 1/20 mg. with loads up to 100 gm.)

*H-1823—Model AB-2 . . . . . $449.00
H-1813-10 Model AB-5 . . . . . 310.00
(Capacity 200 gm., sensitivity 1/20 mg. H-1813, H-1823 are equipped with dial reading chainomatic, notched beam, magnetic damper. H-1813-10 is same, but without damper.)

H-1843—Model AB-1 . . . . . $695.00
(Projectomatic with notched beam. Direct reading 0 to 100 mg. No loose weights required up to 1.1 gm.)

VOLAND

*H-2440—No. 100 . . . . . $105.00
(Ideal for student use. Aluminum cabinet. Single knob releases beam and pan simultaneously. Capacity 200 gm., sensitivity 1/10 mg.)

H-2440-30 . . . . . $235.00
(Same as H-2440 but equipped with notched beam, drum chain, equilibrium adjuster, and magnetic damper. No loose weights required up to 1.1 gm.)

H-2450—No. 200 . . . . . $110.00
(Similar to H-2440 but has a separate pan release.)

H-2450-30 . . . . . $240.00
(Similar to H-2440-30 but has a separate pan release.)

SARTORIUS "SELECTA"

*H-2424 Sartorius "Selecta" $890.00
(Single pan; direct reading; no weight handling at all. Weights are placed on beam by merely rotating external knobs. Last 100 mg. projected on screen automatically.)

Harshaw Scientific stocks many other types of balances including micro, semi-micro, specific gravity, etc. We will welcome your request for literature or specific information.

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For further information, circle number 10 A on Readers' Service Card, page 49 A

New Sealed Accessories

FOR CENTRIFUGING INFECTIOUS MATERIALS

Purpose

Laboratory administrators interested in the health of their laboratory personnel have recently become concerned with infectious aerosols sometimes encountered during centrifuging. Infectious materials sealed in centrifuge tubes or bottles quickly become airborne when they are released by a leak or fracture of the container due to high centrifugal forces. The natural draft created by the fan action of the rotating head acts to distribute the material through the laboratory.

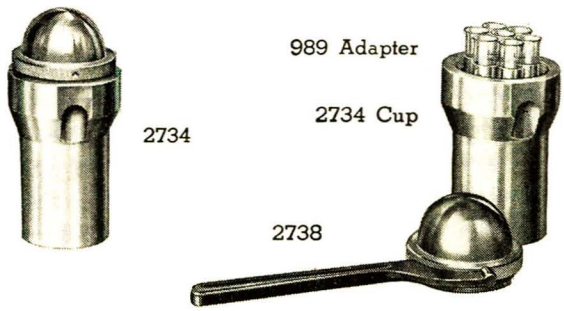
Approach

International Equipment Company engineers have adapted standard accessories to permit sealing of the centrifuge cup. To insure maximum safety, the scientist having completed centrifuging removes the sealed container to a hood for opening. In those instances where a leak or fracture has allowed the material to contaminate the container, immediate decontamination steps may be taken.

Solution

A series of accessories based upon the Hi-speed 250 ml. slotted cup has been designed. The standard cup is threaded to take a dome cover fitted with an O-ring seal. The cup holds one of the standard round or flat bottom 250 ml. centrifuge bottles. Adapters are available for holding: 2–50 ml. centrifuge tubes; 7–15 ml. centrifuge tubes; and 10–13 x 100 mm. serum tubes.

Centrifuge	Head	No. Cups	R.P.M.	R.C.F.
Size 1, Model SBV	277	4	3000	2000
Size 2, Model V...	277	4	2900	1880
Size 2, Model V...	266	6	2300	1410
Model PR-1.....	284	4	2400	1240



2734 — Duralumin Cup, 250 ml., with screw dome cover and gasket, including 582 rubber cushion — $36.00.

2738 — Wrench, spanner type for tightening screw dome on 2734 — $1.75.

2741 989 2740

2741 — Adapter, 2-place, for 50 ml. centrifuge tubes, fits 2734 or any standard IEC 250 ml. centrifuge cup — $4.50.

989 — Adapter, 7-place, for 15 ml. centrifuge tubes, fits 2734 or any standard IEC 250 ml. centrifuge cup — $18.00.

2740 — Adapter, 10-place, for 13 x 100 mm. serum tubes, will fit 2734 or any standard IEC 250 ml. centrifuge cup — $21.50.

277 — Head, 4-place, steel pin type for 2734 or 384 cups — $63.00.

266 — Head, 6-place, steel pin type for 2734 or 384 cups — $95.00.

284 — Head, 4-place, steel pin type for 2734 or 384 cups — $67.00.

OBTAINABLE NOW FROM YOUR LABORATORY SUPPLY DEALER

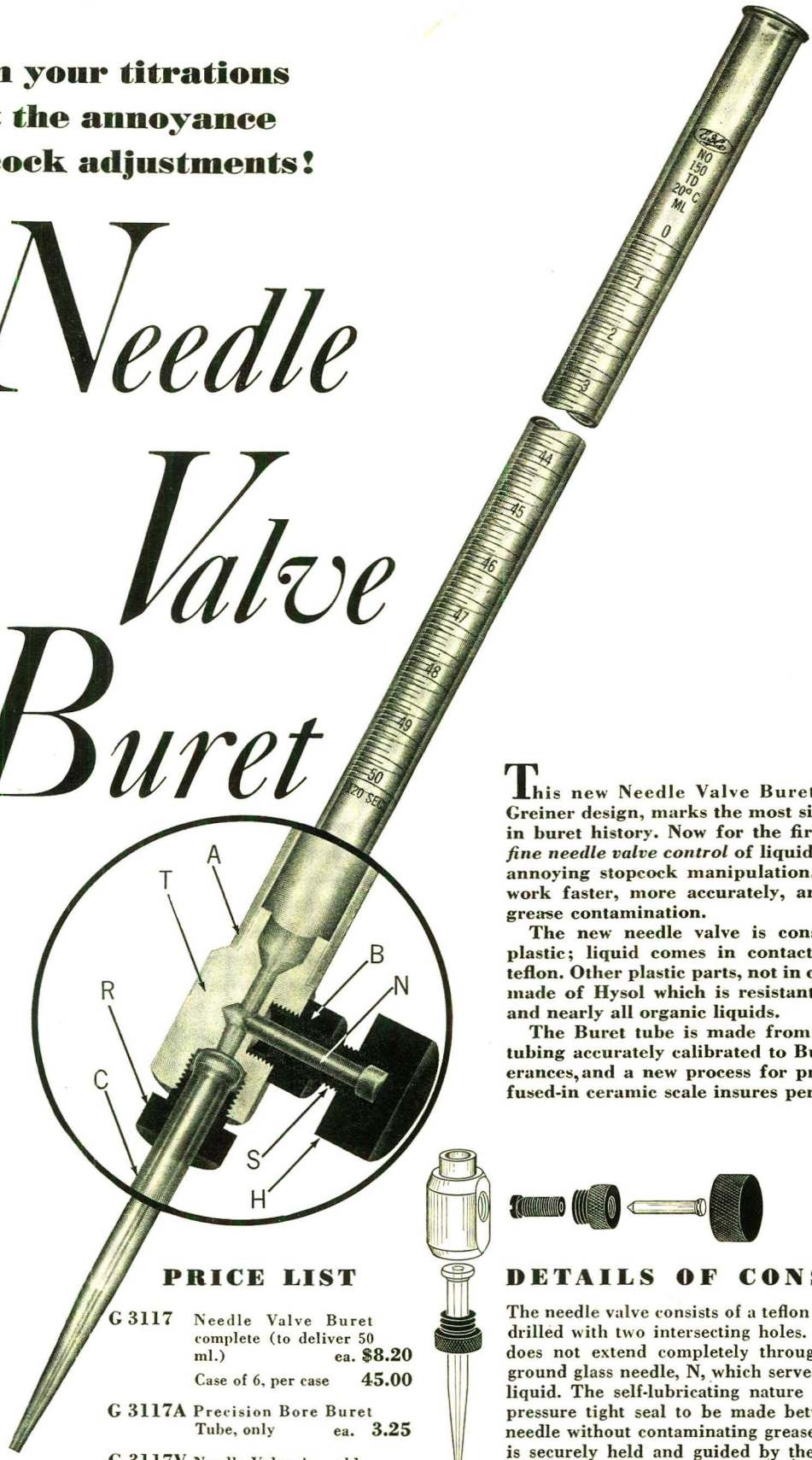
INTERNATIONAL EQUIPMENT COMPANY

1284 SOLDIERS FIELD ROAD, BOSTON 35, MASS.

For further information, circle number 11 A on Readers' Service Card, page 49 A

perform your titrations without the annoyance of stopcock adjustments!

Needle Valve Buret



This new Needle Valve Buret, an exclusive Emil Greiner design, marks the most significant development in buret history. Now for the first time ever you have *fine needle valve control* of liquid flow instead of crude, annoying stopcock manipulation. This means you can work faster, more accurately, and eliminate stopcock grease contamination.

The new needle valve is constructed of glass and plastic; liquid comes in contact with only glass and teflon. Other plastic parts, not in contact with liquid, are made of Hysol which is resistant to acid, alkalis, salt, and nearly all organic liquids.

The Buret tube is made from precision bore pyrex tubing accurately calibrated to Bureau of Standard tolerances, and a new process for producing a permanent fused-in ceramic scale insures permanent linearity.

PRICE LIST

G 3117	Needle Valve Buret complete (to deliver 50 ml.)	ea. **$8.20**
	Case of 6, per case	**45.00**
G 3117A	Precision Bore Buret Tube, only	ea. **3.25**
G 3117V	Needle Valve Assembly, including glass tip	ea. **4.95**

DETAILS OF CONSTRUCTION

The needle valve consists of a teflon body, T, which is cross-drilled with two intersecting holes. One of the holes which does not extend completely through contains a precision ground glass needle, N, which serves to regulate the flow of liquid. The self-lubricating nature of the teflon permits a pressure tight seal to be made between the body and the needle without contaminating grease or gaskets. The needle is securely held and guided by the stem holder, S, which screws into the handwheel, H. A bearing nut, B, guides the stem holder and needle assembly in and out of the teflon body. The precision bore buret tube, A, fits over an accurately machined projection of the valve body to give a tight seal, again without contaminating grease or gaskets. The glass buret tip, C, is firmly attached to the valve body by the retainer nut, R. The buret tip is adjusted to 120 seconds flow time according to Bureau of Standards specifications.

The EMIL GREINER Co.
20-26 N. MOORE STREET E&C Co. NEW YORK 13, N.Y.

For further information, circle number 12 A on Readers' Service Card, page 49 A

THE ANALYST'S COLUMN

L. T. HALLETT, Science Editor

THE warmth of Kansas City's welcome more than compensated for the cold weather. Publicity and arrangements for the 125th ACS meeting were excellent. Comments on the extended 10-day meeting with an intervening week end seemed to be about equally divided between the yeas and nays. The arrangements do make for a less crowded meeting, and, if the majority of your interests coincide with program arrangements, it is an ideal plan.

The Analytical Division's two-day session was rather short compared to other meetings. Actually there was only one day of general papers; the other was devoted to requested papers by former associates and students honoring G. Frederick Smith, this year's Fisher Award winner. While symposia were planned, they had to be abandoned because prior commitments made it impossible to secure chairmen and speakers to undertake such an assignment.

It is true that analytical meetings outside our national meeting are growing apace and offer some competition. We feel that this is just a sign of how fast and important analysis has become and that numerous and competing programs are in order. We believe that the shortness of the analytical sessions that were held at Kansas City was probably due to a unique combination of circumstances.

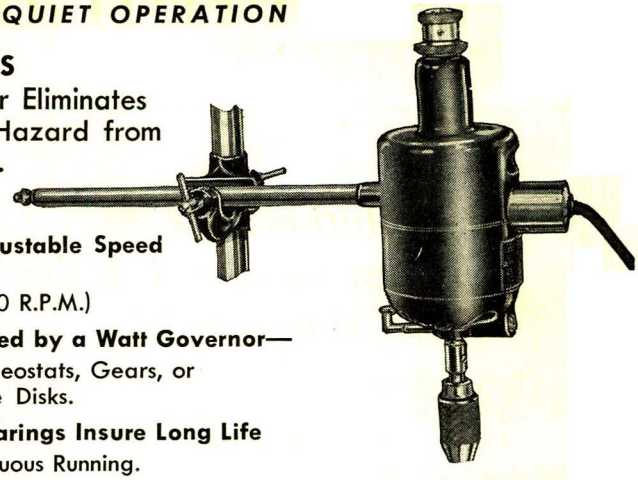
Even if this be true, it does make one pause and reflect that the success of the division (and it is true of every successful venture) has been due to a hard-hitting and far-seeing executive group. More important, such a group must anticipate changing conditions and initiate new programs which so stimulate divisional interest that analysts feel they cannot afford to miss participation in them.

LAST month we wrote about the new instrument developments disclosed at the

Watt-Governor Speed Controlled
LABORATORY STIRRER

LONG LIFE—QUIET OPERATION

SPARKLESS
Induction Motor Eliminates the Explosion Hazard from Brush Contacts.



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- Speed Stabilized by a Watt Governor—Eliminates Rheostats, Gears, or Friction-Drive Disks.
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- Uniform Power Output.

No. 5230. NON-SPARKING MOTOR STIRRER.
60-Cycle, 110-volt A.C. Circuit Each $43.50

No. 5230A. Similar to No. 5230 but for 220-volt, 60 cycle A.C. circuit. A "stepdown" transformer from 220 to 110 volts is provided in the line. Each $54.75

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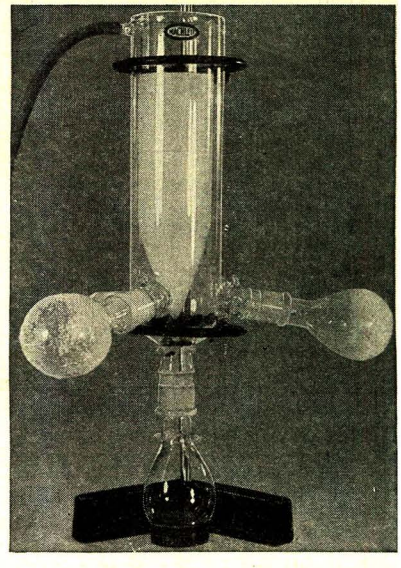
For further information, circle number 13 A-1 on Readers' Service Card, page 49 A

MACHLETT FREEZE-DRY APPARATUS

This economical self-contained unit is ideally suited for freeze-drying operations up to 500 ml. Standing only 21" high, it has a built-in dry ice and solvent chamber and three conveniently located ground, standard taper drying ports around its lower periphery. Standard size for joints is ₹ 34/45, but special sizes can be ground to your specifications.



E36-695 Machlett All-Glass Freeze-Drying Unit with support stand and rings, four flasks, 100, 200 or 250 ml capacity $64.00
E36-695A Machlett Freeze-Drying Unit only $42.00
E36-695B Freeze-Drying Flasks 100, 200 or 250 ml ..... $ 3.00
E36-695F Support Stand and rings $10.00

All prices F. O. B. New York, N. Y.

For further information write for Bulletin F-D.

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ESTABLISHED 1897
APPARATUS • SUPPLIES • CHEMICALS

For further information, circle number 13 A-2 on Readers' Service Card, page 49 A

facts on Infrared *for the laboratory*

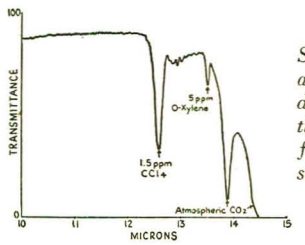
Air Pollution... You must measure it before you can eliminate it!

Before you can take effective measures to eliminate air pollution, you've got to determine its nature and extent. This is no simple task by standard chemical techniques. First, you can't be sure, with the old techniques, of 100 percent extraction of the contaminants from the air sample. Second, your collected sample is so small you can't further separate, and chemical analysis for one component may destroy another.

An infrared spectrometer with a long path gas cell can overcome both of these difficulties. With such equipment you can identify and measure contaminants with speed and accuracy. Usually, no extraction, separation, or concentration steps are involved.

The infrared spectrum shown would result from a concentration of 1.5 ppm CCl_4 and 5 ppm ortho-xylene in room air compressed to 10 atmospheres in a 10-meter path length absorption cell. All components in sample appear simultaneously and their concentrations can be determined from the strength of their absorption bands.

If you have a problem in air pollution control, why not let Perkin-Elmer engineers show you how infrared analysis can help solve it?



Spectrum showing trace amounts of CCl_4 and xylene demonstrates extreme sensitivity of infrared methods for analysis of atmospheric samples.

The Perkin-Elmer Corporation, 800 Main Avenue, Norwalk, Conn.
Offices: New Orleans, La., Chicago, Ill. and Washington, D. C.

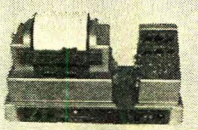
WORLD'S LEADING MANUACTURER OF INFRARED ANALYTICAL EQUIPMENT

PERKIN ELMER

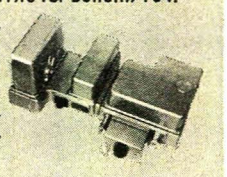
The ONLY complete range of infrared instruments and accessories to meet all research needs!

Model 12-C Infrared Spectrometer—a tested single beam instrument for routine control applications.

Model 112 Double Pass Infrared Spectrometer—single beam, high resolving power, excellent for structural analysis. Suitable attachments for all spectral ranges. *Write for Bulletin 102.*



Model 21 Double Beam Infrared Spectrophotometer—The fastest and most efficient instrument commercially available for the recording of large numbers of spectra. Records directly in percent transmission. *Write for Bulletin 104.*



Model 13 Ratio Recording Infrared Spectrophotometer—Records double or single beam with many features of both the Model 112 and 21. Ideal for the small laboratory with a wide variety of problems. *Write for Bulletin 110.*

ACCESSORIES:

Demountable Cell—may be assembled to any thickness—for liquids, capillary films, mulls of solids—and films and powders.

Fixed Thickness Liquid Cell—for nearly all liquids and solution work. Standard thickness between 0.025 and 1 mm—others to order.

Standard Gas Cells—2, 5, 10 cm and 1 and 10 m path lengths for various absorption studies.

Microcell—obtains good spectra with 25-100 micrograms—available in thicknesses from 0.025 to 3 mm.

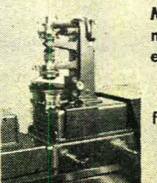
Variable Space Liquid Cell—has accurately variable path length of 0 to 5 mm to bring out features of a spectrum and to compensate for solute absorption in double beam spectrometry.

Reflectance Attachment—for specular reflectance studies of solid materials.

Pressure Cells—for liquids or gasses; path lengths from 0.025 to 50 mm, pressures up to 300 psi. Useful in trace absorption or overtone work. Long and short sizes.

Heating Stage and Heating Stage Power Supply—used with above attachment; permits heating to about 300° C. For studying polymerizations and oxidations. Cycling feature of the Model 21 automatically records reaction stages taking place.

Polarizer—for studies of crystal and molecular orientations. Rotable Cell—To assist in sample orientation for polymerization studies.



Microscope—For analysis of samples of few microns in size as single fibers, tissues, crystals, etc.

Write for Product Bulletin A-3 for more information about these accessories.

For further information, circle numbers 14 A-1, -2, -3, -4 on Readers' Service Card, page 49 A

Pittsburgh Analytical Conference, especially those pertaining to spectrophotometers.

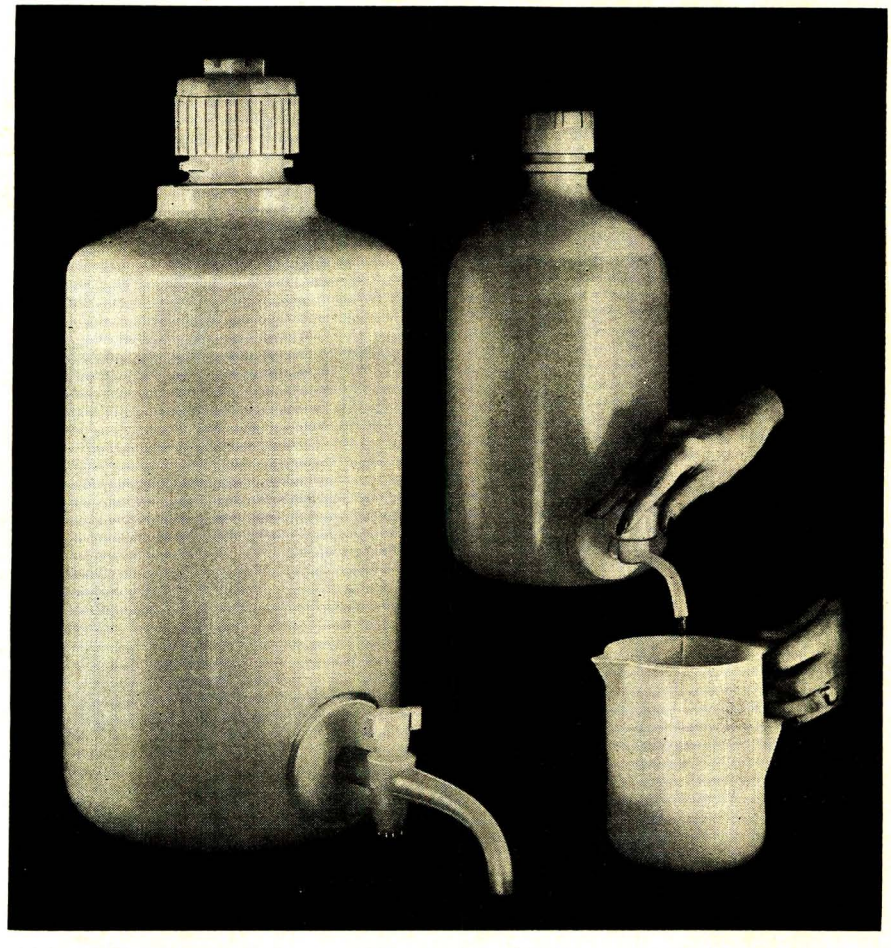
Frederick Brech, director of research for the Jarrell-Ash Co., chose to announce his latest creation in spectrophotometers before the Analytical Division. This instrument, like so many, first had its inception in the research work of David Glick, Department of Physiological Chemistry, University of Minnesota. His researches, like others in this field, deal with secretions such as those from the adrenal glands which are present in very small volumes. Spectrophotometric studies on these samples are important but difficult, because instruments of present-day design have not centered around small volumes, even though many of them have made adaptations. Glick and Brech had small volumes primarily in mind, even though larger volume cells can be used. It is a double-beam spectrophotometer which will handle samples as small as 0.01 ml. with an accuracy of 3.5 parts per billion. A cut of the instrument appears on page 24 A.

The optical system of the instrument comprises a pair of matched monochromatic beams emanating from an *f*4.5 grating monochromator. Each beam passes through a semiconical cell, one of which contains the reference solution and the other contains the sample. The beams emerging from each cell fall upon a photomultiplier, the output of which is amplified logarithmically.

In addition to its use in studies of gland secretion, it can, of course, be used for determination of traces of metals in biological systems and impurities in drugs. Because the instrument is so sensitive, Brech feels that it may also be applied in microdeterminations of corrosion products that are formed in jet engines, with much shorter periods of operations of the engines on test stands than hitherto has been necessary to obtain samples of adequate quantity.

Work now going on is expected to iron out a few minor "bugs" and allow attainment of accuracies within 1 part per billion. When these improvements have been completed, which should be within a few months, the instrument will be marketed, in a nonrecording version, and later a recording model will be added. Both models will be reasonably priced.

Now! Nalge puts Polyethylene stopcocks on Polyethylene Carboys and Bottles for dispensing acids, alkalis, many organics



UNBREAKABLE...PERMANENT...LIGHTWEIGHT

The new Nalgene* polyethylene bottles are blow-molded in a single piece by Plax Corp. and Nalge applies the leak-proof, trouble-proof Polyethylene stopcocks for your convenience.

3 SIZES AVAILABLE

The 2 gallon bottles are fitted with a ¼" needle-type valve made entirely from polyethylene. This valve is welded permanently to the bottle thru the means of a supporting boss.

The 6½ and 13 gallon carboys are fitted with a ½" polyethylene stopcock type valve, threaded to the bottle thru a welded-in boss.

A threaded stopper is available for the 6½ and 13 gallon bottles to screw in place of stopcock for convenience in handling or shipping.

*Brand name for Nalge's Polyethylene ware.

PRICES *Catalog No. 1208*

Size	*Each*	*Lots 2-3*	*Lots 4-9*	*Lots 10-24*	*Lots 25*
2 gallon	$23.00	$21.70	$19.50	$18.60	$17.65
6½ gallon	$46.00	$42.00	$37.80	$36.00	$34.20
13 gallon	$55.00	$51.00	$47.50	$45.80	$43.60

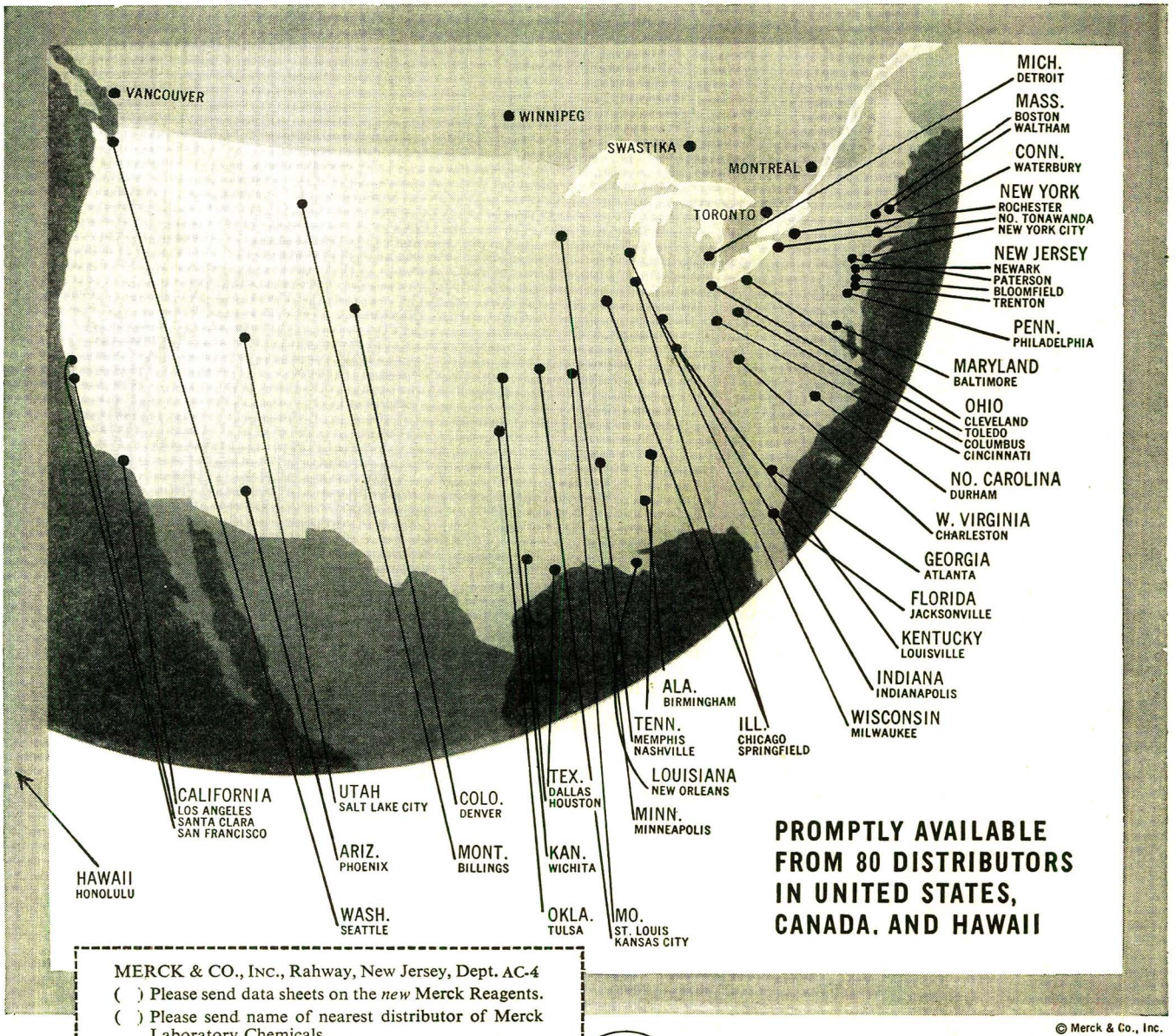
Screw Plugs for the 6½ and 13 gallon carboys $1.00 each.

The NALGE CO.
Sherwood Building
Rochester 2, New York

We're showing many new things - let us show them to you. Ask for the Nalge complete polyethylene listing.
For further information, circle number 15 A on Readers' Service Card, page 49 A

NEW MERCK LABORATORY REAGENTS

- *ACID OSMIC REAGENT*
- *CUPRIC ACETATE REAGENT*
- *SODIUM SULFIDE PENTAHYDRATE REAGENT*
- *CAPRYL ALCOHOL REAGENT*
- *SODIUM AMMONIUM PHOSPHATE REAGENT*
- *AMMONIUM BICARBONATE REAGENT*



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For further information, circle number 16 A on Readers' Service Card, page 49 A

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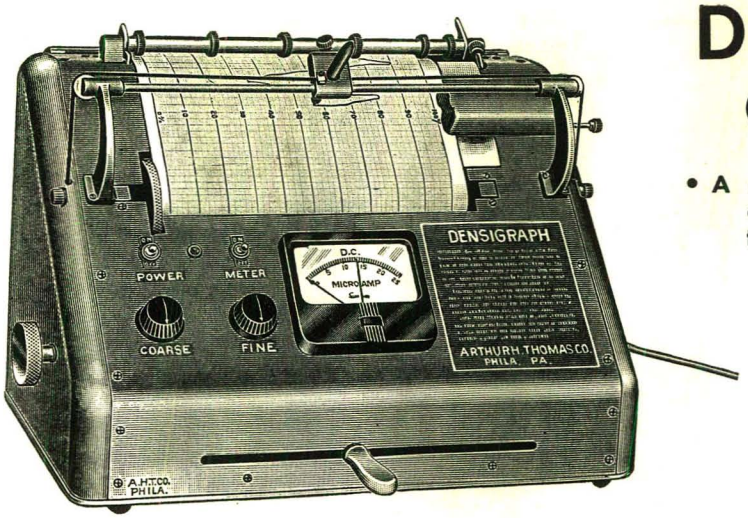

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- **For convenient and rapid photometric analysis of light absorbing materials on *dry* paper strips obtained in electrophoresis and chromatography**
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ANALYTICAL CHEMISTRY

WALTER J. MURPHY, Editor

G. F. Smith—Research Translator

MANY years ago, G. Frederick Smith, as a Ph.D. subject, made a study of the preparation and properties of perchloric acid and its derivatives, particularly with respect to their applications to analytical chemistry. The results were promising. At that time (1922), however, production of the acid was on the order of several hundred pounds a year. A further problem was the difficulty of securing the compounds in a pure form.

Many chemists, after completing their doctoral work, would have dropped the matter and gone on with their careers in industry or academic life. Not so with Smith. He did go into university life at the University of Illinois, but he also decided to manufacture perchloric acid and related products. He established the G. Frederick Smith Chemical Co. at Columbus, Ohio, for this purpose. Other members of the family, including his brothers, A. H. Smith and the late C. M. Smith, Jr., joined in the venture.

During the past three decades, Smith has followed the practice of translating research results into practical techniques and products. The company has prospered and is now the manufacturer of other analytical reagents, including ceric compounds and those from periodic acid.

In the past 30-odd years Smith has also continued his triple career as a stimulating teacher, skillful research chemist, and successful businessman. He has made a success of all three.

Bestowing of the 1954 Fisher Award in analytical chemistry on Smith indicates the high regard in which he is held by his fellow analysts.

Anachems Unite with Detroit Section

ONE OF the dominant characteristics of chemistry during the past half century is the degree of specialization that has occurred. In this respect chemistry is no different from any other fast-moving area of science. Specialization creates new problems and requires new operational facilities.

As far back as the first decade of the present century, the AMERICAN CHEMICAL SOCIETY faced the problem of specialization and solved it successfully by establishing scientific and technical divisions. The solution viewed from today's perspective is a simple one. It is hard to believe that it took more than 10 years filled with bickering before a satisfactory solution was found and accepted. Relatively few ACS members are aware that the Society came very close to dismemberment before the divisional setup was approved.

The divisional plan saved the AMERICAN CHEMICAL SOCIETY and made possible an organization that includes in its membership more than 70,000 chemists and chemical engineers engaged in a wide variety of heterogeneous professional activities. All the needs of specialized groups are provided for and yet the common interests of the chemical profession are served by a strong central organization. The great flexibility of the ACS is its main strength. To the one division authorized in 1908 twenty more have been added, with the result that there are but very few fields of specialization related in any way to chemistry that are not provided for under the banner of the ACS.

If one stops for a moment to think about local sections of the Society, it immediately becomes evident that the vast majority of them in the make-up of membership duplicate the heterogeneity of interests at the national level. Many local sections of the Society today have more members than the Society did in 1908 when the divisional pattern was developed. Does it not follow logically that this pattern which has worked so well at the national level is a desirable one for large and even medium-sized local sections to follow?

Quite a few sections already have found such a move the answer to many perplexing problems and we are particularly proud to say that analysts in a number of instances have taken the lead by creating analytical subdivisions within the operational structure of local sections.

Perhaps the most notable instance was the return of the Pittsburgh analysts to the Pittsburgh Section. Analytical subdivisions have been set up in several sections and in every instance the plan has helped the analysts and has strengthened the section. The latest and most highly satisfactory news is the reported agreement with The Anachems of Detroit, whereby that long established group becomes affiliated with the Detroit Section but like its counterpart in Pittsburgh retains its own name and organizational structure.

It is our understanding that only one of the 14 largest ACS sections has failed to accept to some degree the divisional pattern of the national Society. We hazard the guess that the next great forward movement of the AMERICAN CHEMICAL SOCIETY will be a major expansion of the divisional idea at the local section level with provision for close cooperation and coordination of effort between the national divisions and the local section subdivisions.

This movement already has progressed sufficiently to indicate clearly that it is the practical answer to the problem of how to build greater interest and enthusiasm at the local section or grassroots level.

Obviously smaller sections cannot follow a subdivisional program. Probably none is needed by such sections because usually there is a degree of homogeneity of interest in the very small section that does not exist in the larger ones.

The subdivisional plan providing something for everybody will attract to ACS membership and to local section activity thousands of chemists and chemical engineers who are not now members of the Society. In numbers there is strength for the profession. A united profession can present a united front on matters of common concern to all the members of the profession.

It is plain, at least to us, that the subdivision program at the local section level has many advantages. We may, in our enthusiasm, lack complete objectivity, but we have not been able to discover any disadvantages.

Automatic Coulometic Titration with Electrolytically Generated Silver Ion

Determination of Chloride, Bromide, and Iodide Ions

JAMES J. LINGANE

Department of Chemistry, Harvard University, Cambridge 38, Mass.

Chloride, bromide, and iodide ions can be titrated with silver ion generated electrolytically with constant current at a silver anode immersed directly in the test solution. The equivalence point is detected potentiometrically. The Beckman automatic titrator can be easily adapted to performing these and other titrations automatically in an elapsed time of 1 to 5 minutes. With amounts of the halide ions ranging from 0.2 to 10 mg. in 50 cc. of solution the average error is ±0.005 mg. Coulometric titration with electrolytically generated silver ion should be applicable to all the other established titrations employing silver ion.

ALTHOUGH coulometric titration with constant current has been applied to a variety of oxidation-reduction reactions and to acidimetry and alkalimetry (*4*), application to a precipitation reaction has not heretofore been described. In the present study a method for the automatic titration of the halide ions with electrolytically generated silver ion has been developed. The silver ion is generated at a silver anode immersed directly in the test solution and the equivalence point (e.p.) is detected potentiometrically with a silver indicator electrode. From the measured constant electrolysis current and the measured time required to reach the equivalence point, the quantity of silver ion generated, and thus of halide ion precipitated, is computed via Faraday's law.

Not the least of the several virtues of the coulometric titration technique is its easy adaptability to automatization. Shaffer, Briglio, and Brockman (*5*), DeFord, Johns, and Pitts (*2*), Carson (*1*), and Wise, Gilles, and Reynolds (*7*) have described instruments for automatic coulometric titration. The writer has found that the Beckman automatic titrator (Beckman Instruments, Inc., South Pasadena, Calif.) is very easily converted to coulometric titrations involving all types of reactions and it has been used in this investigation.

Automatic coulometric titrations of chloride, bromide, or iodide ion, in amounts ranging from about 0.2 to 10 mg. or more in 50 cc. of solution, complete themselves in 1 to 5 minutes with an accuracy fully equal to that obtainable more laboriously and less rapidly by the ordinary manual volumetric technique.

INSTRUMENTATION

The required constant current was obtained, as shown in Figure 1, simply by use of a conventional direct current power supply fed from the 110-volt alternating current line through a Sola constant voltage transformer. The power supply employed a 5U4G full-wave rectifier tube and was designed to deliver up to 250 ma. at 350 volts. A large capacitance-input filter in the output reduced the ripple voltage to 1.3 volts at full load and to only a fraction of a volt at the current loads normally used. A 4000-ohm high wattage bleeder resistor, *R*-1, was connected across the output as an aid in stabilization.

The power supply should not be grounded. When the usual practice of connecting the negative side of the power supply output to an earth ground was followed, the operation of the Beckman autotitrator became sluggish, apparently because of coupling through ground of the generator cathode and the calomel reference electrode which is connected through a capacitor to an earth ground via the ground terminal on the instrument case.

The generating current was adjusted to the desired value by the series resistance, *R*-2, which consisted of a bank of five 6000-ohm power resistors connected to a terminal panel in such a way that various series and parallel combinations could be selected to provide a range from 1200 to 30,000 ohms, corresponding to a current range from about 250 to 10 ma. One of the major causes of current drift at constant load resistance with a supply of this sort is temperature variation of the power-dissipating components, particularly resistances *R*-1 and *R*-2. Therefore the latter were selected conservatively with respect to wattage rating so that their operating temperature was relatively low.

The current was indicated approximately by milliammeter, *M.A.*, and was measured precisely by observing the *iR* drop across the precision resistor, *R*-3, with the potentiometer. After about a half-hour warm up, the current variation did not exceed 0.1% per hour.

To employ the Beckman autotitrator as the detecting and control element it was only necessary to disconnect the leads (110-volt alternating current) from the solenoid valve normally used to control the buret outflow and connect them to a 110-volt alternating current double pole–double throw relay of 700 ohms resistance. One side of this relay functions as a single pole–double throw switch to direct the current either to the cell or to the dummy resistor, *R*-4. The other side of the relay acts as a single throw switch to control the electric stopclock, so that the latter indicates the time that the current flows through the cell.

The variable dummy resistor *R*-4 (1000-ohm Helipot) was provided to maintain constant current drain from the power supply during the periods when the cell was switched out of the circuit and it was adjusted so that the current was the same for either position of the relay contacts.

The operation of the Beckman autotitrator for ordinary reagent delivery from a buret has been described by Strickler and Hawes (*6*). Operational technique for automatic coulometric titration is essentially the same—i.e., the instrument is set to operate at

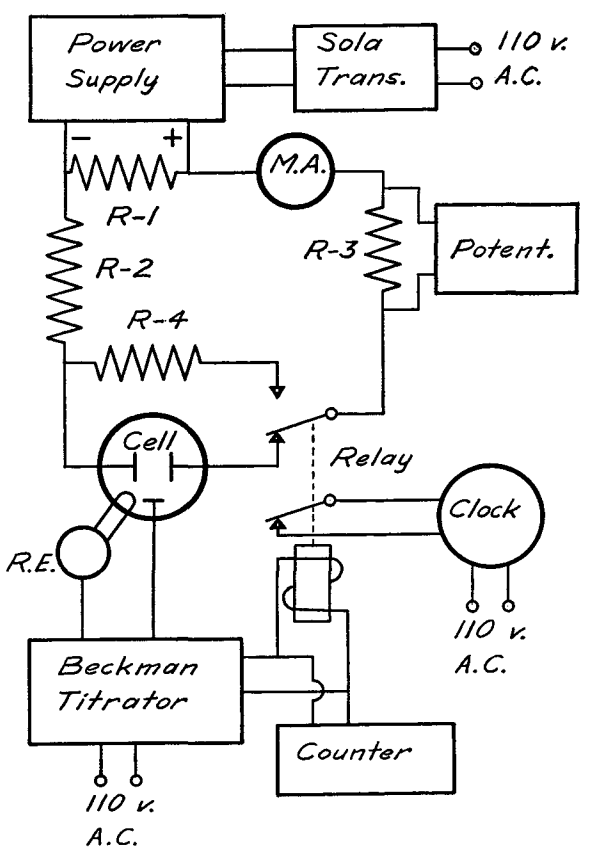

Figure 1. Circuit for Automatic Coulometric Titration

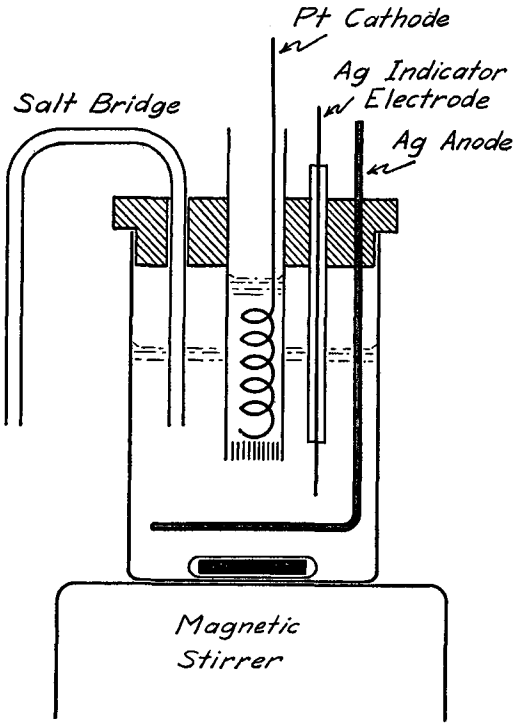

Figure 2. Coulometric Titration Cell

or slightly in advance of the equivalence point potential and the "anticipation control" is adjusted so that the generating current is applied incrementalwise as the equivalence point is approached. In general, for maximum titration speed and to minimize the small error associated with incremental operation discussed in a following section, the anticipation adjustment should be such that no more than about 50 increments are applied. The optimum setting, which depends on the particular titration reaction and the geometrical relation between the generating and indicator electrodes, is easily established by trial. As the equivalence point is approached the size of the increments decreases from a second or more to 0.05 second or less, finally.

As shown in Figure 1, an electric counter (Veeder Root, Model US) was connected in parallel with the relay to the 110-volt alternating current output of the autotitrator to automatically count the number of increments, so that correction for the incremental error could be applied. However, this correction is so small that for most practical purposes it can be neglected.

The electric stopclock was a Model S10 of the Standard Electric Time Co. (capacity 1000 seconds with 0.1-second divisions), equipped with a solenoid brake. According to the manufacturer's specifications the error per unit operation (one start and one stop) is within ±0.02 second.

The titration cell, shown in Figure 2, was a 75-cc. weighing bottle, with a machined plastic cover provided with snugly fitting holes for the several appurtenances. The generator anode was pure silver wire (3-mm. diameter) in the form of a flat spiral positioned horizontally near the bottom of the cell, with a total area of about 20 sq. cm. If silver wire is not at hand, a silver-plated platinum wire will serve equally well. It is important that the anode be of pure silver, since any less noble impurities present detract from 100% current efficiency in direct proportion to their percentage. Quite possibly an electrode of considerably smaller area would function satisfactorily, but this was not investigated.

The silver anode may be used for several successive determinations of the same halide (up to at least 5 coulombs per square cm.) before the silver halide coating becomes thick enough to interfere with the diffusion of the halide ion to the silver surface. The silver halide coating is stripped in cyanide or ammonia solution. An anode coated with a less soluble halide—e.g., silver iodide—may be used for the determination of a more soluble halide—e.g., bromide or chloride—but the reverse is not true.

The generator cathode was a small helix of platinum wire, isolated from the test solution by immersion in a glass tube whose bottom was closed by a sintered glass disk. The catholyte in this tube was the same as, and its level was kept above, the supporting electrolyte in the cell proper.

The purpose of isolating the generator cathode is to prevent the reduction of it at the small concentration of free silver ion in equilibrium with the silver halide, since this would decrease the net current efficiency below the required 100%. In the titration of bromide or iodide the concentration of free silver ion up to the equivalence point is so small that isolation of the platinum cathode may not be necessary.

The indicator electrode was a platinum wire sealed into a capillary tube with Varniton cement with about 1 cm. left exposed, and it was plated electrolytically with silver. Pure silver wire would serve as well.

The saturated calomel electrode supplied with the Beckman autotitrator was used as reference electrode. To prevent contamination of the test solution by chloride ion, the reference electrode was immersed in a small beaker containing sodium nitrate solution and electrolytic connection to the test solution was completed by an inverted U-tube salt bridge filled with approximately 0.1*M* sodium nitrate in a 4% agar gel. Provided the pH of the test solution is kept constant (as it is), it should be possible to use a small glass electrode immersed directly in the test solution as a reference electrode, and this might be more convenient than the calomel electrode and salt bridge.

The test solution was stirred by a magnetic stirrer.

TITRATION CHARACTERISTICS

Just as in ordinary potentiometric titrations, the first step in developing an automatic coulometric titration is the establishment of the equivalence point potential under the particular experimental conditions, since this, in combination with other characteristics of the titration curve, determines the optimum setting of the automatic titrator. This is done once and for all by manually determining the indicator electrode potential versus generation time curve in the vicinity of the equivalent point, under exactly the same conditions that will exist in the proposed automatic titrations. In those cases where the titration curve is symmetrical about the equivalence point, the equivalence point potential corresponds to the point of maximum slope and is independent of both the concentration of the substance titrated and the magnitude of the generating current. This is true in the titration of chloride and bromide ions with electrolytically generated silver ion. The titration curve of iodide ion is asymmetrical because of adsorption of iodide and silver ions by the silver iodide, but even in this case a single setting of the autotitrator suffices for the determination of iodide ion over a wide range of concentration.

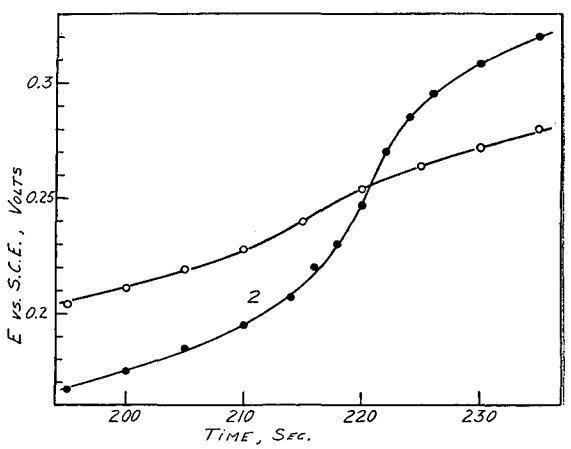

Figure 3. Titration Curves of 1.67 Mg. of Chloride Ion in 55-Cc. Volume Supporting Electrolytes

1. **Aqueous 0.5*M* perchloric acid with 20.52-ma. generating current**
2. **0.4*M* sodium nitrate plus 0.05*M* perchloric acid in 80% ethanol with 20.05-ma. generating current**

Figure 3 shows typical titration curves of 1.67 mg. of chloride ion in a volume of 55 cc., in an aqueous supporting electrolyte (curve 1) and in an 80% ethyl alcohol medium (curve 2). The solubility of silver chloride in water is such that at this small

concentration of chloride ion (about 0.001M) the rate of potential change at the equivalence point is too small to permit precise titration. In the presence of 80% ethyl alcohol the solubility of silver chloride is decreased and the slope of the titration curve at the equivalence point is correspondingly increased to values which permit successful titration. Acetone can also be used to reduce the solubility of silver chloride. Figure 3 shows that the equivalence point potential in the alcoholic medium (+0.255 volt versus saturated calomel electrode) is not very greatly different from its value (+0.246 volt) in the purely aqueous medium, in spite of the much smaller solubility in the former case. This probably is due to change in the liquid-junction potential in the alcoholic medium just about compensating the effect of the decreased solubility.

Although the slope of the titration curve at the equivalence point can be increased either by using a smaller volume of solution or a larger sample of chloride or by a combination of both, the writer prefers the use of the alcoholic medium. Cell manipulation becomes inconvenient when the volume of solution is made very small. The use of larger samples necessitates a correspondingly larger generating current if the titration time is to be kept reasonably short, and with generating currents larger than about 100 ma. a means of current regulation more elaborate than the simple supply used in this study would be needed.

The characteristics of the titration curve of bromide (Figure 4) are similar to those of chloride, except that the slope at the equivalence point is much larger because of the smaller solubility of silver bromide. The use of ethanol or acetone to decrease the solubility is not necessary unless amounts of bromide ion smaller than about 0.5 mg. in 50 cc. are to be determined. In aqueous 0.5M perchloric acid as supporting electrolyte (curve 1) the equivalence point potential is +0.169 volt versus saturated calomel electrode.

As far as solubility alone is concerned, the titration of iodide should be capable of greater precision than that of chloride and bromide. However, this favorable characteristic is offset to a great extent by the deleterious influence of absorption of iodide ion by the precipitate (*3*). The distortion of the titration curve resulting from the adsorption of iodide ion is shown by the curve in Figure 5, which was obtained in the titration of approximately 0.6 mg. of iodide ion in 50 cc. of aqueous 0.4M sodium nitrate plus 0.05M perchloric acid with a generating current of 4.89 ma. The dashed curve is the theoretical curve, based on a value of 1×10^{-16} for the solubility product of silver iodide and +0.558 volt versus saturated calomel electrode for the standard potential of the Ag^+/Ag electrode, and it does not take into account the effect of adsorption. The first inflection in the experimental curve reflects the effect of the adsorption of iodide ion.

It has been definitely established (*3*) that at the stoichiometric equivalence point at pAg = 8.0, precipitated silver iodide still retains adsorbed iodide ion and the isoelectric point corresponding to zero adsorption of both iodide and silver ions is at pAg = 6.0 (E = +0.203 volt versus saturated calomel electrode). Kolthoff and Lingane (*3*) demonstrated that the most accurate procedure for the ordinary potentiometric titration of iodide ion is to titrate to pAg = 6.0 and apply the small correction for the excess silver ion. As discussed in the following section the equivalent procedure yields very satisfactory results by the coulometric method.

The qualifications required of the supporting electrolyte are that it contain no substance which will react in any way with either silver or silver ion or which will undergo electrolytic reaction at the silver anode. It is also desirable that the concentration of the supporting electrolyte be quite large to minimize cell resistance and especially changes in resistance which would change the generating current. It is further desirable that the solution be acidic, because the reaction at the generator cathode is reduction of hydrogen ion. If the catholyte is originally neutral and unbuffered it will become alkaline and the diffusion of hydroxide ion into the anolyte could lead to precipitation of silver oxide. Either 0.5M perchloric acid alone or a mixture of 0.4M sodium nitrate and 0.05M perchloric acid, functions equally satisfactorily as supporting electrolyte.

SYSTEMATIC ERRORS

Only two significant systematic errors have been observed in the halide-silver titrations, an end-point error and an incremental error. Both are small and can either be corrected for or rendered negligible by proper choice of operating conditions.

The end-point error results from slight over- or undertitration—i.e., from failure of the autotitrator to stop the titration precisely at the equivalence point potential. It can be evaluated by noting the potential after the autotitrator stops and comparing with the known titration curve. Representing the discrepancy between the final potential and the equivalence point potential by ΔE and the average slope of the titration curve (over the range ΔE) in millivolts per second by S, the end-point error in seconds is $\Delta E/S$, in coulombs it is $i\Delta E/S$ (where i is the generating current in amperes), and in milligrams of halide ion of atomic weight M it is $Mi\Delta E/96.5\ S$. Thus for a given value of ΔE the end-point error is smaller the greater the slope of the titration curve at the equivalence point—i.e., the greater the degree of completeness of the titration reaction. Expressed in absolute terms (coulombs or milligrams of halide ion) the end-point error in the halide-silver titrations for a given ΔE and given generating current is independent of the quantity of halide ion titrated in a given volume, but it is nearly directly proportional to the solution volume.

When successive titrations are performed by adding the sample solution to a previously titrated solution, the final potential attained in the previous titration, rather than the equivalence point potential, is the reference point used to evaluate the titration error.

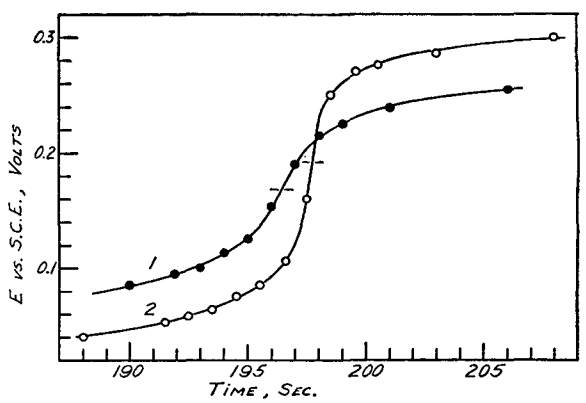

Figure 4. Titration Curves of 3.4 Mg. of Bromide Ion in 55-Cc. Volume Supporting Electrolytes

1. Aqueous 0.5M perchloric acid with 20.50-ma. generating current
2. 0.5M perchloric acid in 75% acetone; 20.34-ma. generating current

In the titration of chloride ion in aqueous medium with a generating current of 20 ma. and a volume of 50 cc., the slope of the titration curve at the equivalence point is approximately 3 mv. per second (see Figure 3). The operation of the autotitrator is such that the reproducibility of the final potential in the chloride titrations is about ±2 mv. Consequently the end-point error or uncertainty is close to 0.7 second. In 80% ethyl alcohol, with other conditions the same, the slope of the titration curve at the equivalence point is increased to approximately 12 mv. per second, and correspondingly the end-point uncertainty is decreased to about 0.2 second or ±0.001 mg. of chloride ion with a 20-ma. generating current.

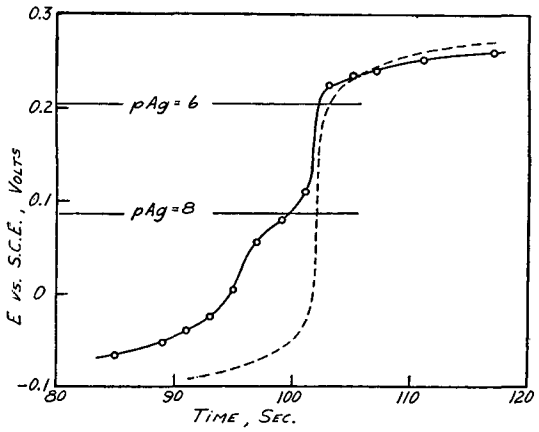

Figure 5. Titration Curve of 0.6 Mg. of Iodide Ion in 50 Cc. of Aqueous 0.4*M* Sodium Nitrate plus 0.05*M* Perchloric Acid with 4.89-Ma. Generating Current

Dashed curve is theoretical curve neglecting adsorption effects

Although the slopes of the titration curves at the equivalence point in the titration of bromide or iodide are greater than in the titration of chloride, this increased slope also leads to a somewhat larger variation of the final potential. The net result is that the end-point uncertainty is about the same as in the chloride titration—i.e., a few tenths of a second.

The incremental error is of more subtle origin and can be more serious than the end-point error. When a series of titrations of bromide ion was performed with the same solution volume but with increasingly larger settings of the anticipation control, so that the number of incremental applications of current near the equivalence point was increased, two effects were noted. First, the magnitude of the individual increments decreased, which is advantageous to obtaining high precision. Secondly, a systemeatic negative error was produced; as shown by the data plotted in Figure 6, the magnitude of this negative error increased in direct proportion to the total number of incremental additions.

It is immediately evident from Figure 6 that when the incremental error is expressed in seconds it is independent of both the quantity of bromide ion titrated and the magnitude of the generating current. Therefore, it must originate in the instrumentation rather than in the chemistry of the titration. The average deviation of the individual points from the best straight line drawn through them is ±0.3 second, and from the slope of this line the error per increment is −0.008 second with a maximal uncertainty of about ±0.003 second.

One likely contributory factor to the incremental error is a net lag in the operation of the electric stopclock (Model S10, Standard Electric Time Co.). According to the manufacturer's specifications the solenoid brake in the clock is adjusted to compensate for the starting lag so that the net error per operation is within ±0.02 second. The observed error per increment of −0.008 second certainly falls well within this tolerance, so that the incremental error could be totally due to a net lag in the operation of the clock.

It also seems likely that the incremental error may result in part from the characteristics of the power supply. During the very brief interval that the current- and clock-controlling relay is open as it switches from one position to the other, the current drain from the power supply is decreased and accordingly the voltage output tends to increase. Consequently, at the moment the relay makes contact, the voltage supplied to the cell and thus the current must be slightly larger than the steady value read by the resistance-potentiometer, although it quickly decays to the steady value. As a result of these small current surges the total quantity of electricity passed is slightly larger than the value computed from the steady current and correspondingly a negative error is produced. This part of the incremental error will, of course, be smaller the faster the relay operates.

Thus the incremental error depends on the characteristics of the particular clock and power supply and must be determined empirically for the particular components used. However, by adjusting the anticipation control so that the number of increments is relatively small—e.g., 50 or less with the particular circuit used in this study—the incremental error can be kept small enough to be practically negligible.

PERFORMANCE DATA

Tables I, II, and III summarize the results obtained in automatic titrations of the three halide ions, over the range from about 0.2 to 10 mg. in a volume of 50 to 60 cc. Known amounts of the halide ions were obtained by weighing out stock solutions which had been prepared by weight from authentically pure samples of the potassium salts, so that the uncertainty in the amount of halide present was smaller than the other uncertainties in the measurements.

In the titrations of chloride and bromide ions the autotitrator was set to stop at a potential 0.025 volt and 0.028 volt, respectively, in advance of the equivalence point potentials. In the titrations of iodide ion the supporting electrolyte was first pretitrated to a potential close to +0.20 volt—i.e., very close to the isoelectric point of silver iodide, before the sample was added,

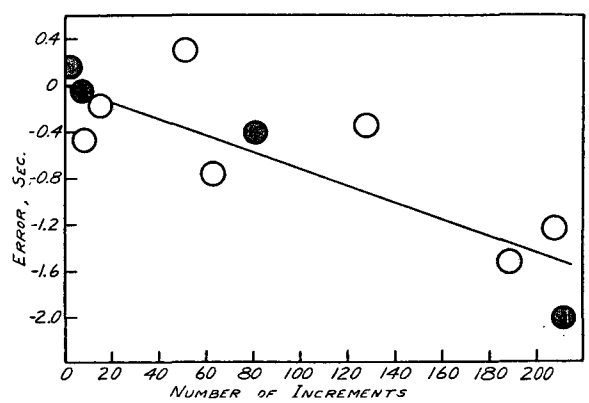

Figure 6. Incremental Error

In all cases the supporting electrolyte was 50 cc. of aqueous 0.5*M* perchloric acid and the autotitrator was set to stop at +0.140 volt *vs.* S.C.E.
The data have been corrected for the small end-point error
The number of incremental additions was varied by changing the setting of the anticipation control
The open circle points were obtained from titrations of 0.9-mg. quantities (accurately known) of bromide ion with a 20-ma. generating current, and the solid points were obtained with 4-mg. quantities of bromide ion and a 70-ma. generating current

Table I. Automatic Coulometric Titration of Chloride Ion

(Supporting electrolyte consisted of 0.4*M* sodium nitrate plus 0.05*M* perchloric acid in 80% ethyl alcohol, and the solution volume was 50 to 60 cc., the autotitrator was set to stop at 0.230 volt *vs.* S.C.E.)

Cl^- Taken, Mg.	Current, Ma.	Time, Sec.	End-Pt. Correction, Sec.	Increment Correction, Sec.	Cl^- Found, Mg.	Error, Mg.
0.495	19.94	66.1	1.3	0.2	0.495	0.000
0.717	19.95	97.0	0.0	0.3	0.713	−0.004
1.343	19.96	181.4	1.6	0.3	1.344	+0.001
2.183	19.96	296.2	0.0	0.3	2.174	−0.009
5.142	19.99	698.4	0.0	0.3	5.131	−0.011

Av. −0.004 ± 0.004

Table II. Automatic Coulometric Titration of Bromide Ion

(Supporting electrolyte consisted of aqueous 0.5*M* perchloric acid and the solution volume was 50 to 60 cc.; the autotitrator was set to stop at +0.140 volt *vs.* S.C.E.)

Br^- Taken, Mg.	Current, Ma.	Time, Sec.	End-Pt. Correction, Sec.	Increment Correction, Sec.	Br^- Found, Mg.	Error, Mg.
0.537	20.53	31.6	−0.2	0.2	0.537	+0.000
0.999	20.52	58.6	+0.2	0.2	1.002	+0.003
1.224	20.46	71.2	+0.4	0.2	1.217	−0.007
1.930	20.48	113.4	0.0	0.2	1.926	−0.004
2.379	20.52	139.9	−0.4	0.2	2.375	−0.004
6.335	20.49	373.2	−0.7	0.2	6.325	−0.010
						Av. −0.004 ± 0.004

Table III. Automatic Coulometric Titration of Iodide Ion

(Supporting electrolyte consisted of aqueous 0.4*M* sodium nitrate plus 0.05*M* perchloric acid; autotitrator set at +0.120 volt *vs.* S.C.E.)

I^- Taken, Mg.	Current, Ma.	Time, Sec.	End-Pt. Correction, Sec.	Increment Correction, Sec.	I^- Found, Mg.	Error, Mg.
0.229	4.882	34.8	0.0	0.2	0.226	−0.003
0.524	4.882	81.1	0.0	0.3	0.523	−0.001
0.968	4.880	150.8	0.0	0.4	0.970	+0.002
2.367	4.880	366.3	0.0	0.4	2.354	−0.013
2.904	4.882	450.3	0.0	0.5	2.894	−0.010
7.848	20.34	295.0	−1.6	0.1	7.851	+0.003
						Av. −0.004 ± 0.006

and the autotitrator was set at +0.12 volt (see Figure 5). In the iodide titrations there is a very pronounced forward drift of the potential (direction of increasing silver ion concentration) in the vicinity of the equivalence point, and with the autotitrator set at +0.12 volt the final potential was in the range +0.20 to +0.23 volt. With all three halides the results obtained by successive additions of samples to previously titrated solutions were indistinguishable from those obtained with fresh supporting electrolyte.

The listed values of the amount of halide found have been corrected for the end-point error (end-point correction) and incremental error (increment correction). It will be noted that in all three cases the average errors are not larger than the average deviation of the errors from the mean, so that there do not appear to be any other systematic errors in addition to the end-point error and incremental error. Even if the small corrections for the end-point and incremental errors had not been applied the average errors would have been only −0.011 mg. in the case of chloride, −0.005 mg. in the case of bromide, and −0.013 mg. in the case of iodide.

These results do not, of course, represent the best attainable accuracy in terms of percentage error. Because the absolute end-point error decreases with decreasing generating current and because the percentage effect of both the end-point and incremental errors decreases with increasing titration time, the percentage error doubtless could be very considerably decreased by employing smaller generating currents for correspondingly longer times.

There is no evident reason why considerably larger quantities of the halides could not be titrated. However, if the titration time is to be kept down to a few minutes, correspondingly larger generating currents would be necessary and little would be gained in the way of accuracy. Indeed, in the case of iodide the complications produced by the adsorption of iodide ion by the silver iodide become more disturbing when relatively large quantities are titrated.

In addition to the halides, the use of electrolytically generated silver ion should be applicable to all the other established titrations employing silver ion, such as the titration of cyanide or thiocyanate ions or the titration of sulfhydryl compounds.

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Titration of Iodide with Electrolytically Generated Silver Ion

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The conditions have been established under which electrolytically generated silver ion can be used for the secondary coulometric titration of iodide; the end point is determined by measuring the current between two silver indicator electrodes with an impressed potential difference of approximately 230 mv. Iodide has been titrated in acetate buffer solutions with an accuracy of ±0.1% for samples from 0.778 to 22.6 mg., and an accuracy of ±0.6% for samples as small as 0.28 mg.

A PROCEDURE for the coulometric titration of halides and halide mixtures by deposition as silver halides on a silver anode, described by Lingane and Small (*2*), was a primary coulometric process, using controlled potentials. An extension of this method for certain halide mixtures has been described recently (*3*).

A secondary coulometric procedure for titrating halides, using constant current, would have the advantages over a primary process discussed by Szebelledy and Somogyi (*7*) and Meier, Myers, and Swift (*4*): simplicity, rapidity, and increased accuracy for semimicro and micro samples. Such a secondary procedure for the titration of iodide with electrolytically generated bromine has been described by Wooster, Farrington, and Swift (*8*); titrations of semimicro samples were much more accurate than with the method of Lingane and Small, or noncoulometric micromethods.

However, oxidation procedures have not been developed for the other halides, and the presence of substances which reduce bromine would interfere with determination of iodide (*8*). For these reasons, and because no work has been reported on constant-current coulometric titrations involving precipitation, it seemed desirable to investigate the usefulness of the silver–silver ion intermediate system in the titration of halides. [While reading proof it was noted that other investigators have titrated bromide with silver ion produced at constant current (*5*).] The present.

paper describes a titration of iodide with this intermediate, using an amperometric end point in which excess silver ion is detected by means of two silver indicator electrodes with a small impressed potential difference. A similar indicator system was used by early workers (*1*) to provide a dead-stop end point.

EXPERIMENTAL

Chemicals. All chemicals used were reagent grade.

Standard potassium iodide solutions, approximately 0.05*F*, were made up by weight from solid potassium iodide which had been dried at 110° C. for 2 hours. These solutions were also made about 0.01*F* in sodium carbonate, for stability to oxidation. They were not kept longer than about 2 months. A dilution of a standard solution was prepared and titrations were run with aliquots of the dilute solution within 1 week. The solid potassium iodide was found to contain no iodate, either before or after the drying. Argentometric titration of a solution prepared from the dried salt showed that no significant amounts of impurities were present.

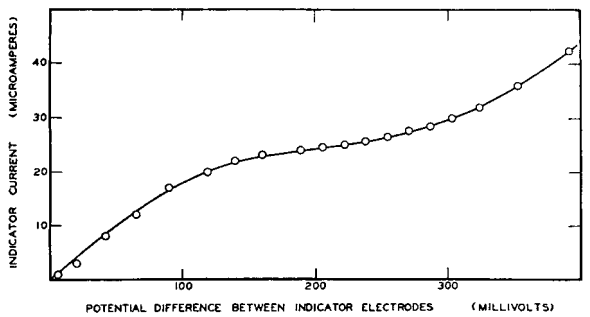

Figure 1. Variation of Indicator Current with Potential Difference between Indicator Electrodes

Silver ion concentration, 4 × 10^{-6}*M*

Electrical Circuits. An indicator circuit similar to that of Meier, Myers, and Swift (*4*) was used in this work, with an electronically regulated generator supply. In all cases the generation current was passed through a standard resistor and the potential drop across the resistor was used to determine the current value.

Electrodes. The generator anode was either platinum foil (1.5 × 2 cm.) plated with silver from a cyanide bath or a spiral of No. 16 gage silver wire (approximately 8 inches). Both types proved satisfactory; however, the spiral lasted considerably longer than the plated electrode. The generator cathode consisted of a piece of platinum foil and was immersed in a shield containing 0.1*F* sulfuric acid.

The indicator anode was prepared by plating silver on platinum foil (5 × 5 mm.) from a cyanide bath for 2 hours at 10 ma.

Indicator cathodes were platinum foil (1.5 × 2 cm.) and platinum gauze (3.5 cm. in diameter, 5 cm. high). The latter was used for increased sensitivity with the smallest quantities.

PROCEDURE

Blank Runs. To 25 ml. of distilled water were added 25 ml. of acetate buffer solution (0.32*M* in acetate ion and 0.027*M* in acetic acid). If the initial indicator current was greater than 10 μa., the electrodes were dipped in cyanide solution and rinsed thoroughly. Silver ion was generated for short intervals of time. Five or six indicator current readings were plotted against time and the best straight line was drawn. The intercept on the time axis was taken as the blank correction. Blank runs were made until the last two or three were consistent within 0.1 second. The blank corrections corresponded to about 3γ of iodide.

Sample Runs. The sample was added to 25 ml. of acetate buffer solution and diluted to 50 ml. with distilled water. In order to prevent oxidation of the iodide, the sample should not stand more than an hour at this point.

Before the generator current is turned on, a reading of the indicator current will give an indication of the best generating rate to be used. The 1 ma. rate should be used if the indicator reading is less than 20 μa., 10 ma. if between 20 and 150 μa., and 50 ma. if more than 150 μa. If the initial reading is less than 150 μa., the indicator current may be left on during the complete titration; otherwise it should remain off for the first half of the titration.

The indicator current remained essentially constant, decreasing slightly, throughout the first 90% of the titration, then decreased sharply as the equivalence point was approached. Generation was stopped when the indicator current dropped below 10 μa. Microammeter readings were taken after every second of generation until the indicator current increased linearly with time of generation. The linear indicator current values were extrapolated back to zero current and the corresponding generation time was corrected by the blank time to find the net titration time.

The microammeter reading must not be taken until it has become constant (with generator current off), as this can be the source of an error as high as 1%. With large amounts of iodide, readings just past the equivalence point may require 3 to 5 minutes to attain a constant value.

DISCUSSION

Potential Difference between Indicator Electrodes. The indicator potential during blank titrations and end-point measurements should be adjusted to give a linear relation between indicator current and concentration of active intermediate, high sensitivity, and stability of current readings.

To find the proper potential, silver ion was generated for 2.0 seconds at 10 ma. in 50 ml. of a 0.2*F* perchloric acid solution, and then the potential was varied from 0 to 392 mv. Values of indicator current are plotted against applied potential in Figure 1. From the curve, it appeared that the best potential would be in the range from 200 to 250 mv. in order to minimize effects due to changes in the resistance of the indicator circuit. A potential of 230 mv. yielded satisfactory indicator current curves in all solutions used in this work.

Solubility Effects. The solubility of silver iodide in water was found to be sufficiently low for accurate amperometric end points, as the minimum currents at the end points were nearly always less than 5 μa. However, preliminary experiments with bromide in 0.02*F* sulfuric acid showed that the solubility of silver bromide in water was too large for an accurate end point. The addition of organic solvents to decrease the solubility of the silver halides should make it possible to titrate bromide and chloride.

Nature of Precipitate and Process. Before the end point in each titration of iodide, the silver iodide precipitate was colloidal, giving the solution a yellowish and slightly cloudy appearance. Near the end point it flocculated, appearing as yellow particles in the solution. Very little if any precipitate formed on the generator anode, which showed that this titration is essentially a secondary process.

Indicator Current Phenomena, Side Reactions, and Effect of Supporting Electrolyte. Titrations of iodide samples of about 2.5 × 10^{-5} equivalent with two indicator electrodes, each 1.5 × 2 cm., were carried out in several supporting electrolytes.

In titrations in 0.2*F* perchloric acid, under nitrogen, a negative error of about 2% was observed. In each case the indicator current before the end point was greater than 50 μa. and then decreased near the end point. In titrations in 0.02*F* sulfuric acid, with or without an atmosphere of nitrogen, a negative error of about 1% was observed with similar indicator current phenomena.

The errors were not due to air oxidation of iodide, as no significant amount of iodine could be detected by the method of Ramsey *et al.* (*6*) when air was present.

If the indicator electrodes were not introduced until the end point, or if the iodide samples were not added until a nearly equivalent amount of silver ion had been generated, the errors were eliminated.

From these results, it was concluded that the errors were due to one or both of the following side reactions, occurring at the silver indicator electrodes:

Anode	Cathode	
$Ag + I^- = AgI + e^-$	$2H^+ + 2e^- = H_2$	(1)
	$O_2 + 4H^+ + 4e^- = 2H_2O$	(2)

In an acetate buffer, with access to air, at a pH of 5.5 (it was calculated that Reaction 1 would not proceed to a significant extent at this pH) satisfactory titrations were performed.

It seems probable that the high indicator currents prior to the end points are due primarily to the side reaction involving reduction of hydrogen ion (Reaction 1). The applied potential increases the driving force behind this reaction, and increases its rate, with a given electrode area. Because of the buffer the hydrogen ion concentration is essentially constant throughout the titration. The over-all potential in favor of Reaction 1 does not change appreciably until the iodide concentration decreases rapidly near the equivalence point. The behavior of the indicator current is consistent with the proposed reactions. Reaction 2 appears to be less probable because the following electrode reactions could take place in the absence of iodide:

Anode	Cathode
$Ag = Ag^+ + e^-$	$O_2 + 4H^+ + 4e^- = H_2O$

If such were the case, it would not be possible to obtain the observed, stable indicator currents of only a few microamperes in the presence of oxygen.

Alternative Procedure. It was also possible to run titrations of iodide in strongly acidic solution (0.02*F* in sulfuric acid), if the side reaction was not allowed to proceed to a significant extent. Preliminary work showed that the use of small indicator anodes, or small indicator potentials, prior to the end point reduced the amount of side reaction. A procedure was developed in which a very small indicator anode, consisting of a 1 × 1 mm. silver wire, *A*, was used prior to the end point. The indicator cathode consisted of a 5 × 5 mm. electrode, *B*, and a 1.5 × 2.0 cm. electrode, *C*, both silver foil, connected together. A small indicator potential (98 mv.) was applied, which provided a small indicator current (10 to 15 μa.). A decrease in this current indicated the approach of the end point. After the end point, *B* was indicator anode, *C* was indicator cathode, *A* was disconnected, and the indicator potential was 230 mv. Using this procedure, samples of about 3 mg. were titrated with an average error of about 0.1%.

Table I. Coulometric Titration of Iodide in Acetate Buffer, pH 5.5

Iodide, Mg. Taken	Iodide, Mg. Found	No. of Titrations	Titration Rate, μa.	% Error
0.2828	0.2811	7	1	−0.60
0.7786	0.7789	3	10	+0.04
1.948	1.950[a]	10	10	+0.10
3.896	3.897	4	10	+0.03
7.792	7.796	3	10	+0.05
7.792	7.800	2	25	+0.10
7.792	7.800	3	50	+0.10
15.58	15.58[b]	8	50	0.0
22.64	22.66	4	50	+0.09

[a] 1.950, 1.948, 1.949, 1.948, 1.949, 1.950, 1.948, 1.950, 1.946, 1.946.
[b] 15.56, 15.59, 15.61, 15.58, 15.57, 15.57, 15.58, 15.57.

CONFIRMATORY TITRATIONS

Table I contains data obtained from confirmatory titrations carried out in acetate buffer solutions. Equally satisfactory titrations can be performed by the alternative procedure, but the manipulations are more complicated.

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Coulometric Titrations with Externally Generated Chlorine, Bromine, and Iodine

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Although chlorine, bromine, and iodine have been prepared by internal generation methods, only iodine has heretofore been prepared by external generation. The work reported in this paper was undertaken to investigate the possibilities of preparing all three of these halogens by external generation. A new type of single-arm cell has been designed for this purpose, and successful generation of all three halogens at currents of 200 ma. or higher has been accomplished. The cell described should also prove useful for the generation of other reagents. High precisions and accuracies have been realized in the titration of arsenite samples with externally generated halogens.

THE general technique of performing coulometric titrations with externally generated reagents has been described in a previous communication (*8*) from this laboratory. This communication reported the successful generation of hydrogen ion, hydroxyl ion, and iodine at currents of 250 ma. in a two-arm electrolysis cell in which the anode and cathode products were completely separated from each other. These are the only reagents prepared by external generation which have been reported to date.

On the other hand, many titrations with internally generated halogens have been reported. Szebelledy and Somogyi (*17*), in their classical papers on coulometric titrations, employed electrolytically generated bromine for the titration of thiocyanate, hydrazine, hydroxylamine, sulfite, bisulfite, and hydroxide on a macro scale. Swift and his coworkers (*2–4, 10, 15, 20*) have employed electrolytically generated bromine for the titration of arsenic, antimony, iodide, thallium, aniline, and thiodiglycol. Shaffer, Briglio, and Brockman (*16*) developed an instrument employing electrolytically generated bromine for the continuous automatic titration of mustard gas in air. Austin, Turner, and Persy (*1*) have described an instrument employing electrolytically generated bromine for the continuous automatic determina-

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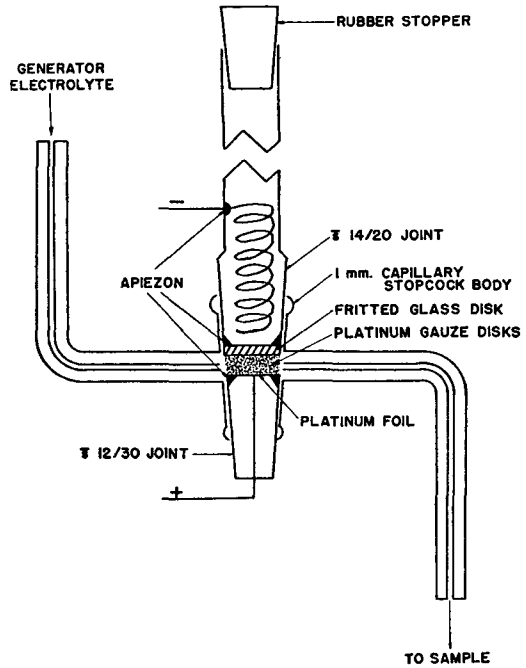

Figure 1. Generator Cell

tion of sulfur compounds in gases. Carson (*5*, *6*) determined 8-quinolinol and uranium by bromometric titration. Swift and his coworkers determined iodide, thallium, and arsenic with electrolytically generated chlorine (*3*, *9*, *20*) and arsenic and thiosulfate with electrolytically generated iodine (*11*, *14*). Wise, Gilles, and Reynolds (*19*) employed electrolytically generated iodine for automatic titrations of arsenic. Tutundzic and Mladenović (*18*) have described the titration of thiosulfate with electrolytically generated iodine and recommend this method for the standardization of thiosulfate solutions.

This paper describes the results of studies on the external generation of chlorine, bromine, and iodine at currents of 200 ma. or more. A general purpose single-arm cell for the generation of these reagents is described; this cell offers several distinct advantages over the two-arm type for the production of halogens.

APPARATUS

Generator Cell. A cross-sectional view of the general-purpose single-arm cell which was employed in these titrations is shown in Figure 1. It is constructed from a 1-mm. capillary stopcock body appropriately fitted with two standard-taper joints. The cathode compartment consists of a standard-taper 14/20 joint sealed to a 24-cm. length of 10-mm. borosilicate glass tubing. The bottom of this joint is ground flat and sealed with Apiezon wax to a 40- to 60-mesh fritted-glass disk about 1 mm. thick. The fritted disk together with the rubber stopper which seals the top opening of the cathode chamber prevent diffusion of the anodically generated halogens into the catholyte. The disk acts as an effective physical barrier, without significantly increasing cell resistance, while the stopper causes a downward displacement of catholyte by trapping the hydrogen evolved from the cathode. The volume of the cathode chamber is sufficiently large so that more than 1 meq. of halogen can be generated without refilling. The cathode consists of a 20-cm. length of 24-gage (B-S) platinum wire wound in a helix about 5 cm. long and sealed through the tube with Apiezon wax.

The construction of the anode section is especially important. The top of a standard-taper 12/30 joint is ground so that, on insertion into the stopcock body, there is a gap slightly greater than 2 mm. between the top of the joint and the fritted disk. This gap comprises the anode compartment and is symmetrically spaced just above and below the capillary outlets. In constructing the anode itself, one platinum foil and six platinum gauze disks are cut to fit the diameter of the anode compartment. One of the gauze disks is then laid on top of the platinum foil and the two are welded together by first heating them to red heat in a gas flame and then striking lightly with a hammer. Each of the remaining gauze disks is successively flame welded in this way to the top of the preceding disk. The bottom of the foil is then welded to a platinum lead wire. The anode foil is 0.003 inch thick, the gauze disks are approximately 50 mesh and are made of 33-gauge (B-S) wire, and the lead wire is 24 gage (B-S). This anode unit, which fits snugly in the anode chamber, is carefully sealed to the top of the standard-taper 12/30 joint with Apiezon wax. The over-all anode design features good electrical contact throughout, maximum anode surface, minimum holdup volume, and efficient anode flushing at low flow rates. The total holdup volume, including the delivery arm, is only about 0.3 ml.

In assembling the cell, all joint surfaces are lubricated with heavy Celvacene Hi-Vac grease (Distillation Products Co.). Extreme care must be taken to avoid getting excess grease on any part of the anode surface. This is especially critical when generating chlorine at currents above 100 ma. A thin layer of glass wool is placed directly on top of the anode and is tucked lightly around its sides in order to obtain more uniform flow through the cell.

Power Supplies. A line-operated, constant-current power supply, similar to the instrument described by Reilley, Cooke, and Furman (*12*), was employed for all titrations in which the current did not exceed 205 ma. The current was checked at frequent intervals with a built-in potentiometer. Generation currents in the range from 205 to 630 ma. were obtained from an unregulated high voltage supply; these currents were continuously monitored during titrations by potentiometric measurement of the IR drop across a standard 1.0000-ohm resistor. The current limiting resistors of the source were manually adjusted as necessary in order to maintain a constant current.

Titration Assembly. The sample to be titrated was placed in a 250-ml. beaker and the indicator electrodes and the delivery tip of the generator cell were immersed in the solution. Vigorous stirring was provided by a magnetic stirrer. The generator electrolyte was supplied to the cell by hydrostatic pressure from a separatory funnel placed about 3 feet above the cell. The funnel was connected through a Tygon sleeve to a stopcock which was used to control the flow of electrolyte. This stopcock was in turn connected by Tygon tubing to the influent capillary arm of the cell. The cell was mounted with a 3-finger clamp. Prior to a titration, the cathode compartment of the cell was filled by removing the rubber stopper and placing a finger over the delivery tip. When the compartment was almost full, the stopper, moistened to ensure a tight fit, was again replaced and the delivery arm was washed with water.

In all cases the flow rate of generator electrolyte through the cell was maintained at a value not less than 0.1 ml. per second (about 1 drop per second). The flow rate was always adjusted before submerging the delivery tip.

End-Point Detection System. Each titration was followed potentiometrically with a platinum-saturated calomel electrode system and a Beckman Model G pH meter.

REAGENTS

All chemicals used were reagent grade. The arsenite samples which were employed were aliquots of standard solutions prepared in the conventional way from weighed quantities of arsenic trioxide.

The generator electrolyte which was employed for the generation of chlorine at currents from 200 to 410 ma. was 2*M* hydrochloric acid. At lower generation currents 1.0*M* hydrochloric acid was satisfactory. For the generation of bromine the electrolyte was a solution 0.2*M* in potassium bromide and 1.0*M* sulfuric acid. For the generation of iodine a solution 0.3*M* in potassium iodide, 0.1*M* in boric acid, and 0.5*M* in sodium sulfate was employed.

EXPERIMENTAL PROCEDURE

When any one of the generator electrolytes is subjected to electrolysis, water is reduced at the cathode to yield hydrogen gas and hydroxyl ion. The acid present in each of the electrolytes neutralizes the base formed and prevents the effluent solution from becoming basic. In addition to the desired oxidation of the halide ions to halogen at the anode, it is possible also that water may be oxidized. In order to determine the current efficiency for generation of the halogens, known quantities of arsenite were titrated with the halogen generated at the anode. Since arsenite is not readily oxidized by oxygen except in strongly basic media, the current efficiency for the generation of halogen could be

readily calculated from the coulombs of electricity required to titrate the sample.

In each case the titration was allowed to proceed without interruption to within a few seconds of the expected end point. Thereafter the generation was carried out in increments of 0.2 to 0.3 second, with sufficient time between increments to permit the indicating electrodes to reach equilibrium. In order to achieve greater precision in the location of the end point, the final incremental portions of the titrations employing currents of 410 and 630 ma. were usually carried out with a current of 204.0 ma. The potential break at the end point was sufficiently pronounced in all cases to permit visual determination of the end point without resort to plotted titration curves.

In all titrations with iodine the sample solution was buffered with sodium bicarbonate according to conventional procedures.

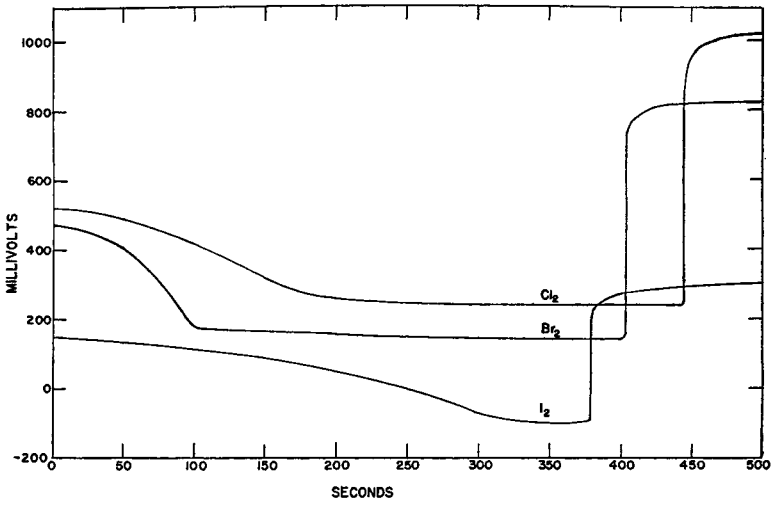

Figure 2. Typical Titration Curves for Determination of Arsenite by Halogen

RESULTS AND DISCUSSION

The results obtained in the titration of arsenite samples with each of the halogens are summarized in Table I. It is apparent from this table that all of the halogens can be generated with 100% current efficiency and that excellent precision and accuracy can be realized in the titration of arsenite samples.

A current of 410 ma. is approximately the maximum which can be employed in the generation of chlorine without simultaneous oxidation of water at the anode. Even at 410 ma., some gas bubbles are formed at the anode but apparently these arise from the evolution of dissolved gases in the generator electrolyte rather than from the oxidation of water, since there is no significant error in the titration of the arsenic samples. At currents of the order of 600 ma. oxygen gas from the oxidation of water is formed in copious amounts. Since the potential for the oxidation of chloride to chlorine is higher than that for the oxidation of water to oxygen, the successful generation of chlorine in an external cell in the absence of a depolarizer is possible only because of the high overvoltage of oxygen on smooth platinum. The high concentration of hydrochloric acid in the generator electrolyte favors the desired reaction both by decreasing the potential for the oxidation of chloride and by increasing the potential for the oxidation of water.

Table I. Titration of Arsenite with Externally Generated Halogens

Reagent	Current, Ma.	No. of Runs	Arsenic Taken, Me.	Av. Arsenic Found, Me.	Av. Deviation from Mean, %	Av. Error %
Cl_2	204.0	8	0.9408	0.9403	0.05	−0.05
	...	15	1.0437	1.0439	0.02	+0.02
	...	6	0.8777	0.8782	0.05	+0.06
	410.0	5	0.8777	0.8787	0.07	+0.11
Br_2	204.0	3	0.9253	0.9259	0.07	+0.06
	...	3	0.7989	0.7991	0.03	+0.03
	...	13	0.8369	0.8375	0.08	+0.07
	630.0	4	0.8777	0.8773	0.05	−0.05
I_2	204.0	3	0.9253	0.9257	0.05	+0.04
		11	0.7989	0.7991	0.03	+0.03
		3	0.8369	0.8374	0.05	+0.06

Generation of bromine proceeds with 100% efficiency at all currents up to 630 ma., the highest current which was tried in this work. The high concentration of sulfuric acid in the generator electrolyte completely suppresses the oxidation of water.

Despite the fact that the anodic oxidation of iodide proceeds at a considerably lower potential than the oxidation of either of the other halide ions, the generation of iodine at currents much greater than 250 ma. is not feasible under the conditions employed in this work. This limitation on the maximum permissible generation current arises from the rather low solubility of iodine in the generator electrolyte. At high currents solid iodine is deposited on the anode. Although the solubility of iodine can be increased by raising the concentration of iodide in the generator electrolyte, the increased consumption of the expensive potassium iodide reagent limits the practicality of this expedient.

When generating iodine it is necessary to add boric acid to the generator electrolyte to neutralize the base produced at the cathode. In the absence of boric acid some of the iodide is oxidized to iodate, which is not suitable for the titration of arsenic. The addition of strong acid to the generator electrolyte is undesirable both because the iodide electrolyte is subject to air oxidation at low pH and because the oxidation of arsenite is not quantitative at low pH. The recommended generator electrolyte has an initial pH of about 5.7; the effluent from the cell during a titration is 7.5 to 8.0, which is ideal for the titration of arsenite. The sodium sulfate in the generator electrolyte merely increases the conductance and thus facilitates the maintenance of a constant current through the cell.

There was no evidence of attack of the platinum anode of the cell by any of the halogens.

Typical titration curves for the titration of arsenite samples with each of the halogens are shown in Figure 2. In all cases the potential starts at a relatively high value, decreases slowly during the initial part of the titration, and rises again sharply at the equivalence point. The titrations with iodine may also be followed satisfactorily with starch indicator. The indicator end point occurs slightly before the potentiometric end point; the difference between the two end points is equivalent to about 0.2 second of generation at 204 ma. The titrations may also be followed amperometrically, but the amperometric method does not appear to be superior in any way to the potentiometric method. In titrations with chlorine the potentiometric method is to be preferred because of its greater sensitivity and reliability. The two methods appear to be equally good in the case of titrations with iodine.

Both iodine and bromine are well-known titrimetric reagents and the utility of these reagents requires no further comment here. However, since standard solutions of chlorine are very difficult to store and to use, chlorine has in the past found little application in titrimetry. Since the coulometric method eliminates the problem of preservation of standard solutions, it was hoped when this work was begun that chlorine could be applied to a variety of titrimetric determinations. Although excellent results have been achieved with this reagent in the titration of arsenite,

the titration of other samples has so far met with little success. The reaction between chlorine and oxalate is very slow and is unsuitable as the basis of a titrimetric determination. Because of the volatility of chlorine, it is not possible to heat the sample to increase the velocity of the reaction. Titrations of iodide to the iodine monochloride end point have likewise been unsuccessful. Iodine was lost by volatilization from the open beaker employed for the titration and results were always low. It might be possible to perform this titration satisfactorily in a closed system. The reaction between ferrous iron and chlorine is too slow to permit a successful chlorimetric determination of iron without a catalyst. Thus it appears that chlorine will find only limited applicability as an oxidimetric reagent because of the generally slow rate of reaction with reducing agents in acid solution. However, since chlorine is a reasonably strong oxidizing agent and since it can be prepared from a very inexpensive electrolyte, it is attractive as a reagent in those cases in which the rate of reaction is sufficiently rapid to permit a successful titration.

Standard solutions of hypochlorite have found some use in the past as an oxidimetric reagent for the titration of such substances as urea, sulfide, nitrite, and hydrogen peroxide in basic solution. Although no titrations of this type were attempted in this work, there is no reason to believe that they could not be performed satisfactorily. It would be necessary, of course, in such titrations to add a sufficient quantity of base to the sample solution to neutralize the acid delivered from the generator cell.

Automatic titrations of arsenite samples with both iodine and bromine have been performed successfully with amperometric indication of the end point. The apparatus used for these titrations was identical with that described previously (*7*) for potentiometric titrations except that the galvanometer, with suitable shunts, was employed as a microammeter to indicate the current flowing between the indicator electrodes. As the apparatus used for these titrations is now obsolete, the details of these titrations are not reported here. An improved apparatus for automatic amperometric titrations is now being developed. An apparatus for automatic amperometric titrations has also been described by Richter and Swift (*13*).

The advantages and disadvantages of external generation of the halogens as opposed to internal generation are worthy of comment. In general, the external generation technique is applicable only to titrations involving relatively large samples in which the introduction of traces of impurities and the dilution of the sample by the relatively large volumes of generator electrolyte are not critical. The internal generation method is, therefore, to be preferred for microanalysis and for trace analysis. Likewise the internal generation method is superior for most batch titrations on a macro scale. The large electrode area which is possible with the internal generation technique, together with the depolarizing action of the sample, permit the use of higher currents than can be employed in an external cell. For example, the authors have found that chlorine can be generated internally with 100% efficiency at currents of 200 ma. in the titration of arsenite samples which are made 0.2*M* in hydrochloric acid. For external generation of chlorine at 200 ma. the concentration of hydrochloric acid must be increased tenfold to achieve 100% efficiency. The generator anode which was employed for the internal generation studies was a cylindrical platinum gauze electrode of the type commonly employed as the cathode in electrodeposition analysis. The cathode was a spiral of platinum wire placed in a borosilicate glass tube with a fritted glass disk at the bottom. The cathode was concentric with the anode so that the generation field was entirely confined within the anode cylinder. This technique made it possible to follow the titration potentiometrically with electrodes placed outside the anode cylinder.

For batch titrations, the method of external generation is probably to be preferred over the internal method only in those cases in which the latter method is not applicable. Such cases include those in which the conditions for the generation of the reagent and for the performance of the titration are not compatible and those in which some constituent in the sample undergoes an undesired reaction at the generator electrode. For example, the external method must be employed for chlorimetric titrations in basic solution since chlorine can be generated only in acid solution. The external generation method is also the preferred method for many continuous automatic titrations in flow processes.

The generator cell which has been described should prove useful for the generation of other reagents in those cases in which mixing of the cathode and anode electrolysis products can be tolerated.

ACKNOWLEDGMENT

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Rotated and Stationary Platinum Wire Electrodes

Residual Current-Voltage Curves and Dissolution Patterns in Supporting Electrolytes

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Polarograms observed at solid wire electrodes in the presence of nonoxidizing or reducing supporting electrolytes often exhibit small cathodic or anodic currents which may interfere with the evaluation of cathodic and anodic diffusion currents. In supporting electrolytes free of added oxidizing or reducing agents a small anodic wave is recorded over the entire pH range when current-voltage curves are measured with automatic registration from negative to positive potentials at stationary and rotated platinum wire electrodes. When the curves are recorded, starting at the evolution potential of oxygen to negative potentials, a small cathodic dissolution pattern is observed starting at a potential which approximately corresponds to the equilibrium value of the platinum–platinous hydroxide electrode. The limiting current of the anodic wave decreases rapidly to zero at a given potential indicating formation of a film at the surface of the electrode. A similar film is formed by placing the electrode in solutions of strongly oxidizing agents; it can be removed by treating the electrode with various reducing agents. Anomalies in automatically recorded residual currents at the rotated platinum wire electrode may impair its analytical applicability as a voltammetric indicator electrode. Simple procedures are given for eliminating these anomalies and for correcting them in current-voltage curves of electroreducible and electrooxidizable substances.

SEVERAL authors (*13, 23*) have observed that polarograms obtained at solid wire electrodes in supporting electrolytes, which are free of oxidizing or reducing constituents, often exhibit small cathodic and/or anodic currents in certain regions between the cathodic hydrogen and the anodic oxygen waves. Also, anodic and cathodic current-voltages curves at these electrodes often exhibit irregularities and are different in shape when run from negative to positive potentials or in a reverse way (*19*). Similar observations have been made by most workers in this laboratory who automatically record current-voltage (c-v) curves at the rotated platinum wire electrode. On the other hand, in measuring current-voltage curves with the manual apparatus irregular and unexpected waves were rarely observed.

Generally a small anodic prewave to the oxygen wave is noticed in supporting electrolytes free of oxidizable or reducible constituents. The starting potential of this prewave varies approximately 60 mv. per unit pH change (see Table I). The appearance of the prewave undoubtedly is closely related to statements in the literature that anodic polarization of a platinum electrode gives rise to the formation of a film of oxygen (*1, 5–7, 9, 20–22, 24, 25*) or platinous oxide (hydroxide) (*4, 8, 11, 12*) on the electrode.

Investigations described in the present study tend to indicate that the film formed on the preoxygen wave is due to platinous oxide. Upon cathodic polarization of an electrode covered with such a film a cathodic dissolution pattern is observed. The characteristics of the film are described and a simple procedure is given for the removal of the film. The film formation accounts for the differences in apparent diffusion currents observed with automatic and manual recording and also for abnormalities in current-voltage curves referred to above.

Upon cathodic polarization with evolution of hydrogen, an anodic dissolution pattern is observed which is due to sorbed hydrogen on the electrode. Although not further discussed here, this pattern has a larger area when a palladium electrode is used, palladium being a good solvent for hydrogen. As shown, sorbed hydrogen can be easily removed by anodic polarization at the proper potential. When the anodically formed film of platinous oxide and sorbed hydrogen are removed from the electrode, only normal residual currents are observed at the platinum electrode in a given range of potentials.

EXPERIMENTAL

Apparatus. A recording polarograph, Sargent Model XII, was used for the measurement of current-voltage and current-time curves. When desired, a manual instrument (*15*) was used for current-voltage curves and potential measurements. All experiments were carried out in a thermostat of 25.0° ± 0.1° C. With the recording polarograph the voltage was varied at a rate of 4.4 mv. per second, unless otherwise stated. Potentials are referred to the saturated calomel electrode (SCE).

Table I. Potentials *vs.* SCE of Cathodic Dissolution Patterns in Various Supporting Electrolytes

Supporting Electrolyte	pH	Starting Potential	Potential of Pt—$Pt(OH)_2$ (*13*)
0.1*M* $HClO_4$	1	+0.67	+0.67
Acetate buffer	5	+0.39	+0.43
Borax buffer	9	+0.17	+0.19
0.1*M* NaOH	13	−0.03	−0.04

A platinum wire electrode was sealed into a glass tube filled with mercury. The electrode was 0.7 mm. in diameter and 4.5 mm. in length, its geometric surface area being approximately 0.1 sq. cm. The electrode was rotated with a synchronous motor at a rate of 600 r.p.m. It gave a diffusion current of 415 μa. per millimole per liter for the oxidation of thallous ion to thallic oxide in deaerated 0.1*M* sodium hydroxide solution (*13*). When being kept stationary, the electrode gave a steady state diffusion current of 14.8 μa. per millimole per liter in the same solution.

A platinum foil electrode was also used of approximately 2.1 sq. cm. geometric area.

Reagents. All reagents used were C.P. grade or better.

Pretreatment of Electrode. Generally, the electrode was stored in 10*M* nitric acid. Before use, it was thoroughly washed with distilled water and short-circuited against the saturated calomel electrode in deaerated 0.1*M* perchloric acid, until the current was nearly zero. This electrode is called a "clean electrode." The electrode was also prepolarized cathodically or anodically at given potentials and current-voltage curves measured after polarization.

Nitrogen from a Linde nitrogen tank (99.99%) was used without further purification for oxygen. It was found that washing the nitrogen through a column containing a sulfuric acid solution of vanadous sulfate and zinc amalgam (*18*) caused contamination of the gas with hydrogen, which in turn was sorbed by the platinum electrode as was evident from the appearance of an anodic dissolution pattern (see Figure 3).

RESULTS

Behavior of Clean Electrode in Various Supporting Electrolytes. Current-voltage curves were obtained with the clean electrode in supporting electrolytes of pH between 1 and 13 in the absence of oxygen by measuring from negative to positive

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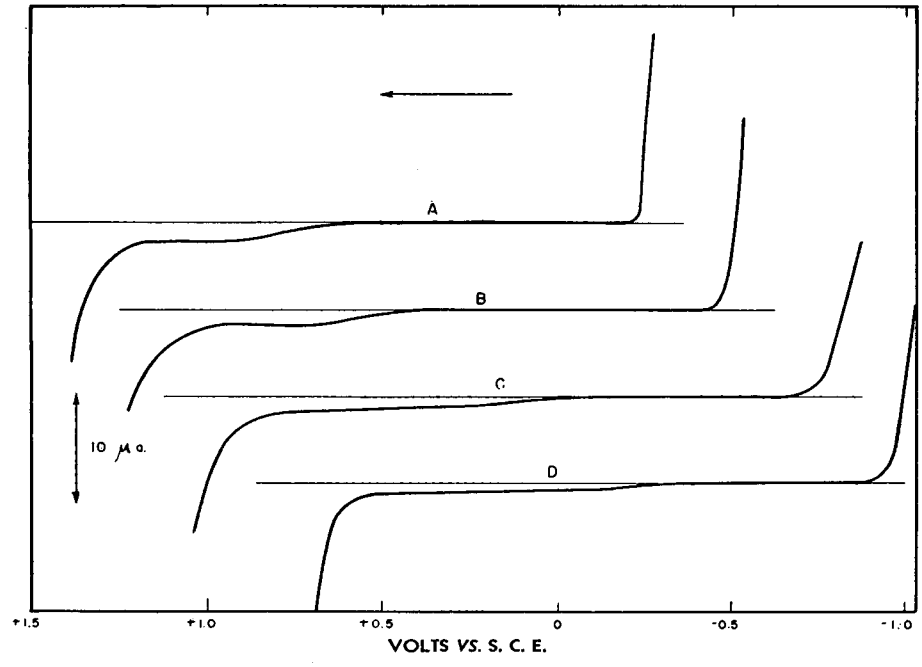

Figure 1. Current-Voltage Curves Measured from Negative to Positive Potentials with "Clean" Electrode in Oxygen-Free Solutions

A. In 0.1*M* perchloric acid
B. In acetate buffer (pH 5)
C. In sodium borate (pH 9)
D. In 0.1*M* sodium hydroxide solution

potentials ("backward"). Some polarograms are reproduced in Figure 1.

Prior to the oxygen evolution wave, a small anodic prewave was observed, the starting potential of which depended on the pH of the solution. Polarograms obtained with the clean electrode by measuring in the direction from positive to negative potentials ("forward") did not exhibit an abnormality, provided the electrode was not polarized at a more positive potential than corresponds to the beginning of the appearance of the prewave. The same behavior was observed when the clean electrode was kept for 30 hours in air- or oxygen-saturated solutions, indicating that no film was formed.

Behavior of Anodically Prepolarized Electrode in Various Supporting Electrolytes. In Figure 2 are shown polarograms measured from positive to negative potentials (forward) in various oxygen-free supporting electrolytes. The polarograms were started at a potential where oxygen was evolved. All current-voltage curves exhibited cathodic dissolution patterns. Their starting potentials were estimated as the point of intersection of the residual current line and the extrapolated line of the beginning part of the cathodic dissolution pattern (see curve *A*, Figure 2). Table I gives these approximate values. For comparison the potential of the reversible platinum–platinous oxide system as given by Latimer (*14*) is tabulated.

Polarograms were also obtained in air-saturated solutions: the dissolution patterns had the same starting potentials as those obtained in the absence of air, the dissolution pattern later overlapping with the reduction wave of oxygen.

No anodic prewave was observed in 0.1*M* perchloric acid from +0.6 volt to more positive potentials (backward) after prepolarization of the electrode at +1.2 volts.

Behavior of Cathodically Prepolarized Electrode. The behavior of the cathodically prepolarized electrode was also investigated. After the electrode was prepolarized in oxygen-free 0.1*M* perchloric acid at −2.0 volts, where hydrogen evolved vigorously at the surface of the electrode, polarograms were recorded in the same solution from negative to positive potentials. A large anodic current was observed following the hydrogen deposition wave (Figure 3).

After a cathodic prepolarization at −2.0 volts, the electrode was washed with air-free distilled water. The polarograms recorded backward starting from −0.3 volt showed a small anodic dissolution pattern. This was eliminated after placing the electrode for 10 minutes in air-saturated 0.1*M* perchloric acid, dilute acid ferric sulfate, ceric sulfate, or bromine water (Figure 3). The dissolution patterns were attributed to the anodic dissolution of sorbed hydrogen. A brief prepolarization at a

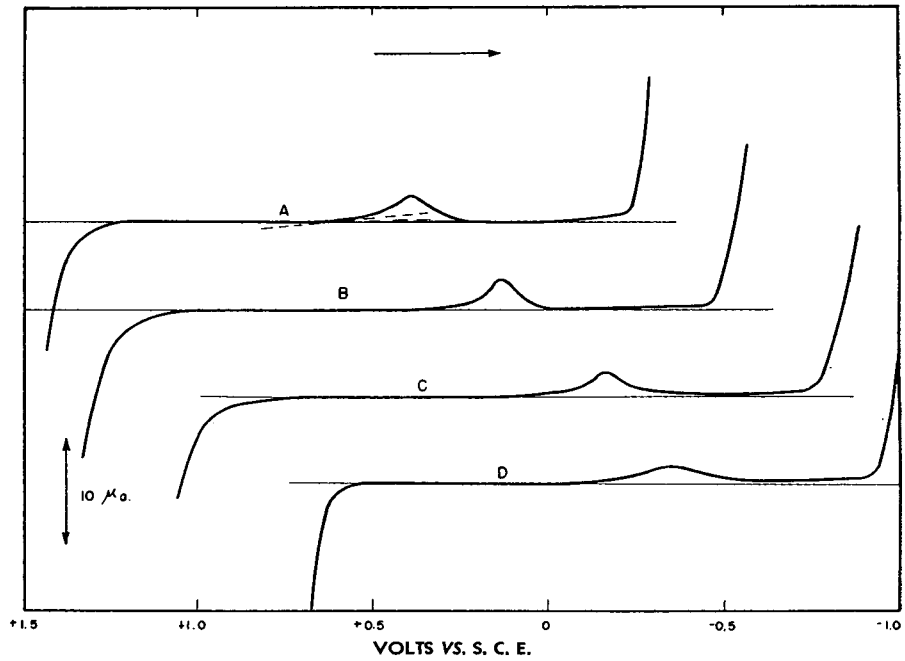

Figure 2. Current-Voltage Curves Measured from Positive to Negative Potentials in Oxygen-Free Solutions

A. From 1.5 volts in 0.1*M* perchloric acid
B. From 1.35 volts in acetate buffer (pH 5)
C. From 1.1 volts in sodium borate (pH 9)
D. From 0.7 volt in 0.1*M* sodium hydroxide solution

small cathodic current was not sufficient to yield a hydrogen dissolution pattern (Figure 1).

When nitrogen, washed through vanadous sulfate in dilute sulfuric acid over zinc amalgam, was passed over the electrode (*18*) in the supporting electrolyte a hydrogen dissolution pattern was found as illustrated in Figure 4. Even a short anodic polarization at +1.5 volts did not remove all the sorbed hydrogen, while the latter did not prevent the formation of the platinous oxide film (curve *B*, Figure 4). On the other hand, the anodically formed film prevented the anodic dissolution of hydrogen as the cathodic dissolution pattern started at the same potential as in the absence of sorbed hydrogen. Only after dissolution of the oxide film was the anodic dissolution of sorbed hydrogen observed (curve *B*, Figure 4).

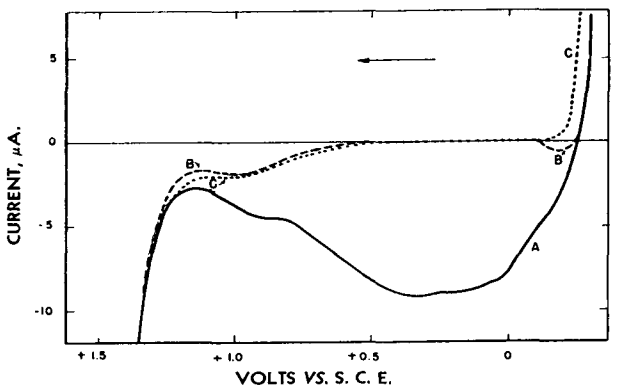

Figure 3. Current-Voltage Curves Measured from Negative to Positive Potentials in Oxygen-Free 0.1*M* Perchloric Acid

A. Electrode prepolarized at −2.0 volts for 10 minutes
B. Same electrode after washing with air-free distilled water, starting at −0.3 volt
C. After treatment with oxidizing agent, starting at −0.3 volt

Characteristics of Anodically Polarized Electrode. CURRENT-TIME CURVES AT POLARIZING POTENTIAL. In Figure 5, current-time curves are reproduced which were measured at the clean electrode at +0.9 and +1.5 volts in air-free 0.1*M* perchloric acid. At the same potential, practically the same curves were obtained whether the electrode was rotated at 600 r.p.m. or was stationary.

Effect of Time of Anodic Polarization at Different Potentials on Area of Cathodic Dissolution Pattern. The rotated and stationary electrodes were prepolarized at +0.9 and +1.5 volts in oxygen-free 0.1*M* perchloric acid for 1 to 10 minutes, whereupon the cathodic dissolution patterns were obtained by measuring from +0.7 volt to negative potentials. The quantities of electricity corresponding to the various dissolution patterns are tabulated in Table II.

Table II. Area of Anodic Dissolution Pattern after Polarization for Various Times at +0.9 and +1.5 Volts

Prepolarization		Electricity Corresponding to Cathodic Dissolution Pattern, × 10^{-4} Coulomb/Sq. Cm.
Potential, volts	Time, min.	
	Rotated Electrode	
0.9	1	3.2
0.9	5	3.9
0.9	8	4.1
1.5	1	10.9
1.5	5	13.4
1.5	10	14.0
	Stationary Electrode[a]	
0.9	8	4.1
1.5	10	14.8

[a] Same electrode without rotation.

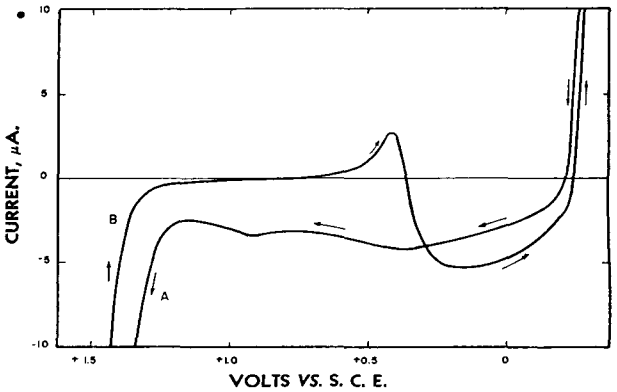

Figure 4. Current-Voltage Curves Measured in Oxygen-Free 0.1*M* Perchloric Acid

A. Negative to positive potentials
B. Positive to negative potentials
Nitrogen washed through vanadous solution over zinc amalgam was passed through

Experiments carried out with the platinum foil electrode with an area about 20 times greater than that of the wire electrode yielded comparable results. For example, after 10 minutes polarization at +1.5 volts the dissolution pattern corresponded to 9.2 × 10^{-4} coulomb per square centimeter as compared to 14 with the wire electrode. Considering the uncertainty in the exact values of the surface areas of both electrodes, the agreement is considered satisfactory.

Formation of Film with Oxidizing Agents. The clean electrode was placed into solutions of several oxidizing agents, washed thoroughly with distilled water, and the cathodic dissolution pattern obtained in oxygen-free 0.1*M* perchloric acid by measuring from +0.7 volt to negative potentials. The dissolution patterns were similar to those obtained with the anodically prepolarized electrode, although their areas were dependent on the oxidizing agent used and the time of contact between electrode and solution.

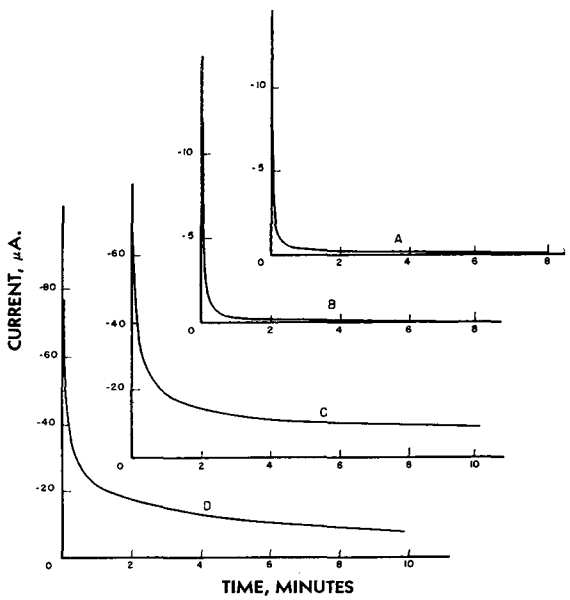

Figure 5. Current-Time Curves Using Clean Electrode in Oxygen-Free 0.1*M* Perchloric Acid

A, C. Electrode rotated at 0.9 and 1.5 volts, respectively
B, D. Stationary electrode at 0.9 and 1.5 volts, respectively

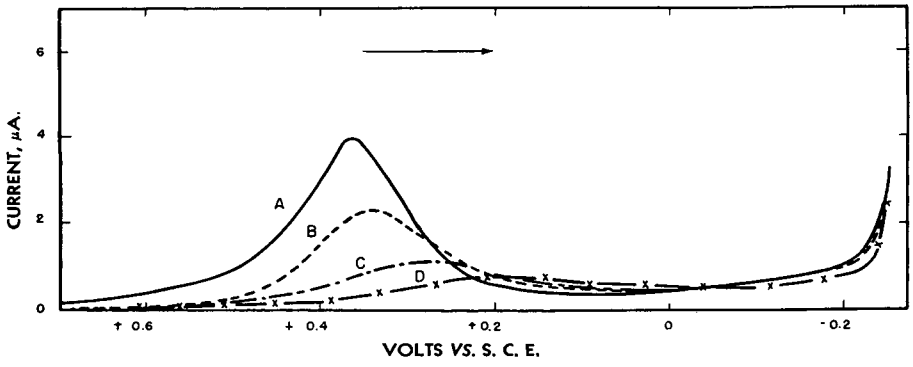

Figure 6. Cathodic Dissolution Patterns of Anodically Prepolarized Electrode (at +1.5 Volts for 10 Minutes) before and after Placing in 0.01*M* Arsenic(III) Solution in 1*M* Hydrochloric Acid

A. Before placing in arsenic(III) solution
B. After placing in 0.01*M* arsenic(III) solution for 2 minutes
C. After placing in 0.01*M* arsenic(III) solution for 10 minutes
D. After placing in 0.01*M* arsenic(III) solution for 60 minutes

The quantity of electricity corresponding to the cathodic dissolution pattern is tabulated in Table III. The presence of air in the oxidizing agent had little or no effect on the oxidation of the electrode. Evidently, the stronger oxidizing agents like cerium(IV), chromic acid, and permanganate, all in acid medium, formed the film while the weaker oxidizing agents like iron(III) did not.

Table III. Formation of Film in Oxidizing Agents

Oxidizing Agent	Time of Contact, Min.	Quantity of Electricity Corresponding to Cathodic Dissolution Pattern, × 10^{-4} Coulomb/Sq. Cm.
Air-Saturated Solution		
$K_2Cr_2O_7$ + H_2SO_4 (cold)	15	4.5
$K_2Cr_2O_7$ + H_2SO_4 (warm)	15	7.5
0.1*M* Ce(IV) in 0.5*N* H_2SO_4	15	8.8
	18 hours	10.7
10^{-3}*M* Ce(IV) in 1*N* H_2SO_4	15	8.7
	60	9.2
10^{-4}*M* Ce(IV) in 1*N* H_2SO_4	15	5.4
	18 hours	9.9
0.1% $KMnO_4$ in 1*N* H_2SO_4	5	8.1
10*M* HNO_3	15	1.1
	18 hours	2.2
Dilute bromine water	10	2.6
0.1*M* Fe(III) in 1*N* H_2SO_4	10	None
0.01*M* $NaNO_2$ in 1*N* HCl	15	None
0.1*M* $NaNO_2$ in 1*N* HCl	10	None
1*N* H_2SO_4	15	None
Deaerated Solution		
0.1*M* Ce(IV) in 0.5*N* H_2SO_4	5	8.1
0.1% $KMnO_4$ in 1*N* H_2SO_4	5	7.8

Removal of Film with Reducing Agents. The electrode which was prepolarized anodically or had been placed in a strong oxidizing agent was treated with a reducing agent, such as ferrous sulfate and arsenic(III) in hydrochloric acid. It was found that ferrous sulfate solution rapidly removed the oxide film. An electrode which had been placed in 0.1*M* ceric sulfate containing 0.25*M* sulfuric acid for 5 minutes was placed in 0.01*M* ferrous sulfate solution 0.05*M* in sulfuric acid for 5 minutes. The current-voltage curve recorded in air-free 0.1*M* perchloric acid from +0.7 volt to negative potentials gave no dissolution pattern.

On the other hand, the removal of oxide film with arsenic(III) was rather slow. The electrode which was prepolarized in air-free 0.1*M* perchloric acid at 1.5 volts for 10 minutes was placed in 0.01*M* arsenic(III) solution 1*M* in hydrochloric acid for 2, 10, and 60 minutes. The dissolution patterns in Figure 6 were then obtained in air-free 0.1*M* perchloric acid. The quantities of electricity corresponding to these dissolution patterns were 14.0 × 10^{-4}, 8.8 × 10^{-4}, 4.8 × 10^{-4}, and 1.9 × 10^{-4} coulomb per square centimeter after 0, 2, 10, and 60 minutes of contact with arsenic(III) solution, respectively.

These results are in agreement with the interpretation of Baker and MacNevin (*2*) in their work on the electro-oxidation of iron(II) and arsenic(III) after anodic (oxygen evolution) and cathodic (hydrogen evolution) polarization.

After prepolarization in 0.1*M* perchloric acid for 10 minutes at +0.9 volt, the electrode was placed for 30 seconds in 0.01*M* hydrogen peroxide and washed with water, and then the cathodic dissolution pattern was measured. A similar experiment was done in which the prepolarization was carried out in 0.022*M* hydrogen peroxide. In both instances a dissolution pattern was observed, the area being about one half of that observed without peroxide treatment. Anodic polarization at −0.06 volt in 0.1*M* sodium hydroxide in the presence of hydrogen peroxide produced oxygen evolution but not film formation. In this medium hydrogen peroxide yields a reversible potential at a platinum electrode (*11*, *12*).

DISCUSSION

After similar treatments the wire electrode, whether stationary or rotated, gave identical current-time curves and also the same area of dissolution patterns. Thus the currents are not diffusion controlled. In case a monomolecular film is formed upon anodic polarization and assuming that an oxygen atom on the surface has the same area as a platinum atom, from the geometric area of the wire electrode a dissolution pattern corresponding to 4.3 × 10^{-4} coulomb per sq. cm. can be calculated. This is the value found after polarization for 10 minutes at +0.9 volt.

Upon polarization at +1.5 volts the value becomes more than three times larger. The reason may be that the true area of the wire electrode is considerably greater than the geometric area, or that the film extends over more than one surface layer.

The potential of the anodically polarized electrode was poorly defined (Figure 1). According to Bornemann (*3*), Grube (*10*), and Lorenz (*16*, *17*), this potential, which slowly drifts with time, is very close to that of the platinum–platinous oxide

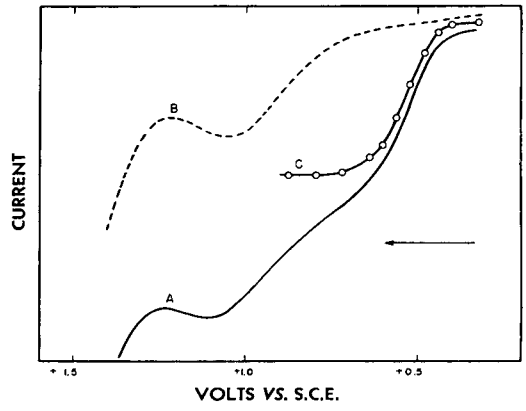

Figure 7. Current-Voltage Curves

A. 0.0001*M* iron(II) in 0.006*M* potassium fluoride and 0.05*M* sulfuric acid
B. Supporting electrolyte
C. Obtained after correction for residual current

electrode. It was also found that the potential of the anodically polarized electrode (Table I) was very close to that of the platinum-platinous oxide couple. The film was not formed when the clean electrode was in contact with oxygen-saturated solutions, but it was formed in oxygen-free solutions of oxidizing agents with high oxidation potential.

The film formation accounts for poorly defined anodic diffusion currents often observed at the rotated platinum electrode with automatic recording. As an example, Figure 7 reproduces a current-voltage curve determined in this laboratory in a dilute ferrous iron solution. Curve *A* does not have a diffusion current plateau. However, when corrected for the "residual" current (curve *B*) a typical diffusion current (curve *C*) is found. The apparent residual current rapidly decreases with time of electrolysis (Figure 5) to the small value of the true residual current.

Similarly, the anodic current of the iron solution at 0.7 to 0.9 volt drops readily to the value of the diffusion current. This diffusion current is proportional to concentration when time is allowed for the formation of the oxide film and correction is made for the true residual current. This behavior should be considered in the measurement of current-voltage curves and anodic diffusion currents at potentials where the oxide film is formed.

The film formation also accounts for the fact that the abnormalities on anodic current-voltage curves are not observed when the measurements are made from strongly positive to more negative potentials, provided that time is allowed for the formation of the oxide film at the starting point. Irregularities in the current-voltage curves can also be observed in the determination of reduction waves of strongly oxidizing agents, like acid solutions of ceric sulfate or permanganate. These curves are obscured by the dissolution pattern of the film unless, at a given potential, time is allowed for the oxide film to be reduced. Also, the difference between the backward and forward current-voltage curves in these solutions is easily accounted for.

ACKNOWLEDGMENT

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High-Frequency Titrations with a Resistance-Type Instrument

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The recent development of a resistance-type instrument for high-frequency titrations has prompted a study of its performance with acid-base titrations and complex formations. The results were very satisfactory for the acid-base titrations, showing extremely good reproducibility and sensitivity. In addition, the results showed that the instrument was promising for the determination of the chemical composition of dimethylglyoxime metal chelates. Its use should be extended to other chelates. The instrument is made very easily. As the change in reading is limited to a high-frequency circuit, this instrument might be of help in the studies of principle of high-frequency titrations. It is also suggested that the method be used when an organic chelating reagent is used for the determination of metal content in a solution.

WITH the progress in high-frequency titrations both in instrumentation and in fields of application, various instruments have appeared which provide a means of following a change in the composition of solutions. With the instruments appearing so far, the measurements have been made indirectly through changes in plate current, grid current, voltage, or frequency. A resistance-type instrument developed by Nakano has appeared (*3*). The design of this instrument is such that whenever any change occurs in plate current, a variable resistance in the high-frequency circuit can be adjusted so as to bring the current reading back to 0; thus the change in plate current can be expressed by the change in resistance which is set in the high-frequency circuit.

Preliminary investigations on the application of high-frequency titrations to the detection of complex formations in solution have shown promising results (*1, 2, 4*) and there are possibilities of future development along this line. The present work was attempted in order to determine chemical compositions of chelate complexes in solutions and to discover whether titration end points could be determined by a high-frequency titration methed

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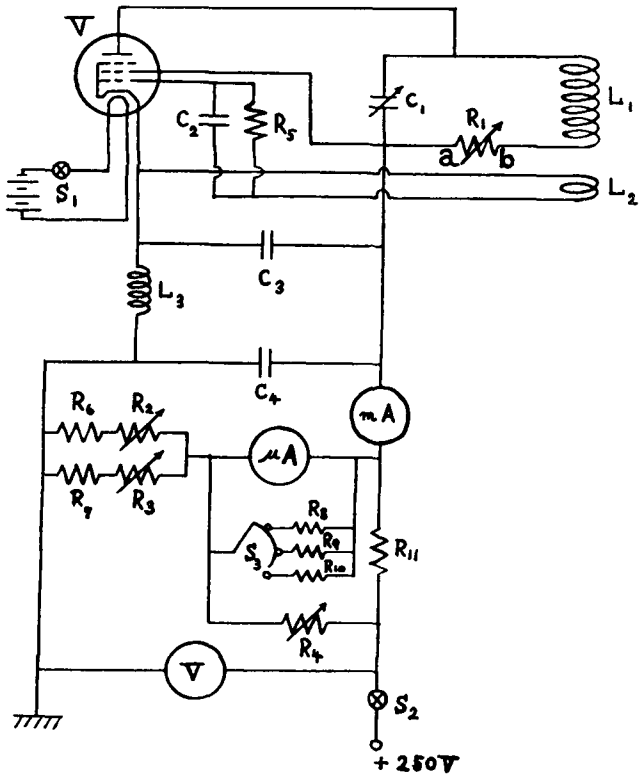

Figure 1. Circuit Diagram of Resistance-Type High-Frequency Titration Apparatus

C_1. Approximately 70 $\mu\mu$f.
C_2. 500 $\mu\mu$f.
C_3C_4. 0.1 μ
L_1. coil, 100 turns, diameter 5 cm.
L_2. coil, 20 turns, diameter 5 cm.
L_3. 4 mh. choke coil
R_1. Variable resistance
R_2. 5 K variable resistance
R_3. 50 K variable resistance
R_4. 10 K variable resistance
R_5. 100 K resistance
R_6. 100 K resistance
R_7. 60 K resistance
R_8. 0.1 Ω resistance
R_9. 1 Ω resistance
R_{10}. 10 Ω resistance
R_{11}. 0.5 K resistance
V. UZ 42 [Power amplifier pentode made by Toshiba Electric Co., Japan. Similiar to 6F6 (RCA)]
$S_1S_2S_3$. Switch
Microammeter, 50 μa.
Milliammeter, 50 ma.
Voltmeter, 300 volts

when an organic reagent is used as titrant for metal ions. In the present report, titrations of dimethylglyoxime with cobalt, nickel, manganese, and lead are discussed.

APPARATUS

The circuit diagram of the instrument is shown in Figure 1. Figure 2 shows the equivalent circuit.

L_1 and L_2 show the coils which are wound on the same bobbin of 50-mm. diameter. S_3 is the microammeter shunt switch with three positions. In the first step of operation, R_8, R_9, and R_{10} are closed. Next R_8 is opened, and in the following step only R_{10} remains closed. In the last step, these three circuits are opened; then as the microammeter has no shunt, its sensitivity becomes highest.

For the filament of oscillator tube, a 6.3-volt battery was used, and the power source was from a voltage-regulated power supply. In carrying out a titration, a beaker containing the test solution was placed in the coil and the current through the microammeter was adjusted to O by regulating R_2, R_3, and R_4. This adjustment is repeated three times, switching off the shunt at each step. Finally, the microammeter is adjusted to O without shunts; thus the instrument is set at its highest sensitivity. If a change occurs in the current through the microammeter, it is brought back to O by adjusting R_1. The change in R_1 is plotted *vs.* milliliters of titrant.

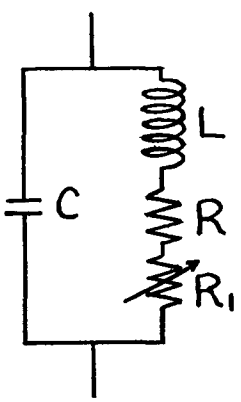

Figure 2. Equivalent Circuit

The variable resistance apparatus is shown in Figure 3. The platinum wire, *A*, is placed in the glass tube, *B*, of 3-mm. diameter. It is set in the high-frequency circuit at the points *a* and *b* (Figure 1). The resistance of 1 meter of this platinum wire is 20 ohms. The wire is in contact with a mercury column in the glass tube, *B*. A liquid hydrocarbon of high viscosity is placed in *D*. The piston, *F*, is raised or lowered by turning a screw handle, *G*. As piston *F* goes down, the mercury column rises in *B*, and a decrease in resistance occurs between *a* and *b*. As *F* moves up, the resistance between *a* and *b* increases.

If a variable resistance such as this is used, there should not be much change in inductance with changes in resistance. This can be used in a high-frequency circuit only if the frequency of the circuit is not especially high. The upper frequency limit for the use of this resistance was 5000 kc.

ACID-BASE TITRATION

Experimental. Five milliliters of a test solution were placed in a beaker, then diluted with 35 ml. of distilled water. The change in the variable resistance was measured and plotted against volume of titrant added.

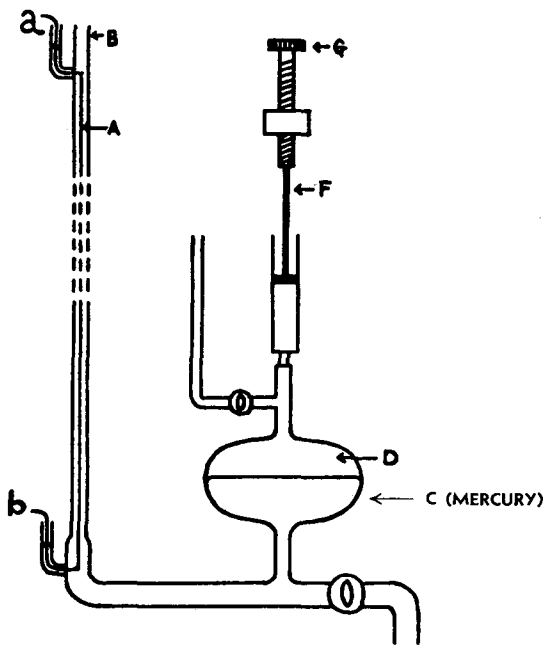

Figure 3. Variable Resistance Apparatus

Results. Various titration curves are shown in Figure 4. The ordinate represents the change in the mercury column height in centimeters. The resistance in ohms is obtained by multiplying the length in centimeters by 0.2. An increase in this length shows an increase in the value of the variable resistance. Figure 4 shows various titration curves of sodium hydroxide with hydrochloric acid. On curves *b*, *c*, *d*, and *e*, the well-defined equivalence points are obtained showing good agreement with the calcuated values. The equivalence point of curve *a* is obtained by extrapolation and agrees with the calculated value. Curve *g* shows no break.

TITRATIONS OF COMPLEX FORMATIONS

Experimental. All of the reagents used in this study were of reagent grade. Forty milliliters of freshly prepared aqueous dimethylglyoxime solution was placed in a beaker and titrated

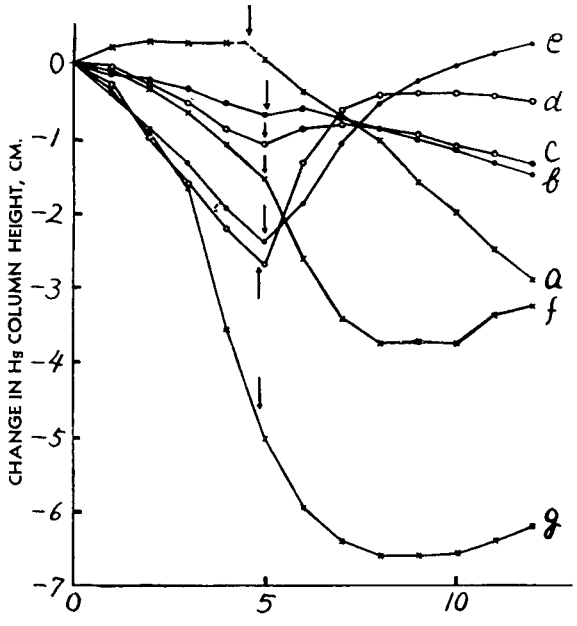

Figure 4. Titration of Sodium Hydroxide with Hydrochloric Acid

a. Titration of 0.91*N* NaOH with 0.98*N* HCl
b. Titration of 0.104*N* NaOH with 0.103*N* HCl
c. Titration of 0.05*N* NaOH with 0.05*N* HCl
d. Titration of 0.0097*N* NaOH with 0.01*N* HCl
e. Titration of 0.005*N* NaOH with 0.005*N* HCl
f. Titration of 0.002*N* NaOH with 0.002*N* HCl
g. Titration of 0.00097*N* NaOH with 0.001*N* HCl
Arrows show calculated equivalence points

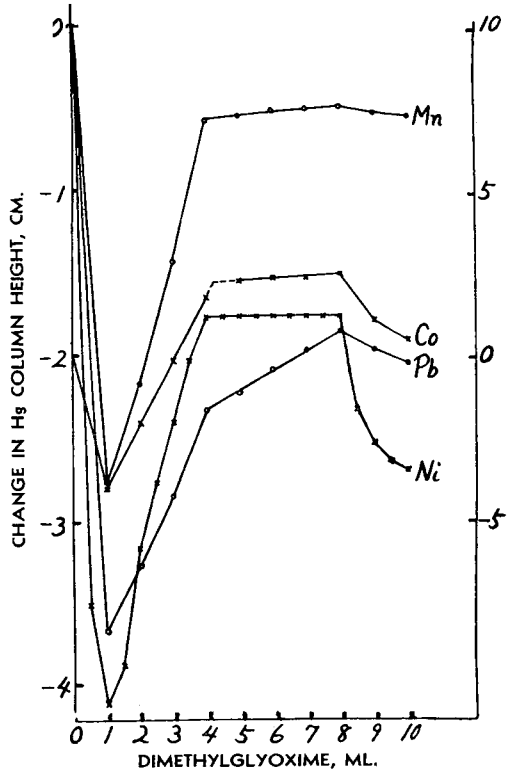

Figure 5. Titrations of Dimethylglyoxime with Cobalt Nitrate, Nickel Sulfate, Lead Nitrate, and Manganese Chloride

40 ml. of 0.001*M* aqueous dimethylglyoxime solution was titrated with 0.005*M* metallic salt solution. Scale on left is for cobalt, nickel, and lead solutions, scale on right for manganese

with metal salt solutions of various concentrations. The solutions were not buffered because electrolytes in the buffer solution might mask titrations.

Results. The titration curves are shown in Figure 5. The scale on the left is for the titration curves of cobalt, nickel, and lead and that on the right is for manganese. The complex salt, whose chemical composition is 1 to 1 (metal to dimethylglyoxime), is formed after 8 ml. of titrant has been added. After 4 ml. of titrant, the chemical composition corresponds to 1 to 2 (metal to dimethylglyoxime). Below 2 ml. of titrant, where the chemical composition is 1 to 4, the reversal is not considered to be an equivalence point.

This instrument has a particular concentration effect which causes reversal at approximately the same total ionic conductance. On all of the titration curves in Figure 5, the breaks appear at 4 and 8 ml. of titrant, where the chemical compositions correspond to 1 to 2 and 1 to 1, respectively.

DISCUSSION

In acid-base titrations, the shape of the titration curves is influenced by concentration (*5*). In a very dilute solution, such as 0.00097*N*, no equivalence point has been observed. On curve *a* of Figure 4, the equivalence point occurs at the maximum peak points. The concentration of the test solution was 0.91*N*. The equivalence point of curve *b*, where the concentration was 0.104*N*, appears at the minimum point. Between these two concentrations, there exists a range of concentration where no marked equivalence point is observed. If a titration curve changes from V shaped to Λ shaped with the dilution of test solution, there exist concentration ranges where the titration curve is linear.

For the titrations of dimethylglyoxime metal chelates, it is evident that a minimum appears at a particular concentration which should be at approximately the same total ionic conductance. This may obscure the end point in a titration. Breaks in the curves occur at points other than these corresponding to known compounds. For example, the breaks of nickel dimethylglyoxime nickel curves occur at 1 to 1 and 1 to 2, although the known compound should occur at 1 to 2.

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Relations between Phase Composition and Partition Coefficients for Some Neutral Steroids

A Nomographic Approach

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Information concerning partition coefficients in various solvent systems must be obtained before countercurrent distribution can be applied to the separation of neutral steroid mixtures isolated from extracts of tissues and body fluids. From the many solvent mixtures available, the quaternary system consisting of ethyl acetate, cyclohexane, ethanol, and water was chosen. By suitable experimental design it was possible to measure partition coefficients over a wide range of phase compositions with relatively few determinations. The data were then converted to a nomographic form. Nomograms for androsterone, 5-isoandrosterone, epiandrosterone, dehydroepiandrosterone, androstanedione, Δ^4-androstenedione, desoxycorticosterone, and 17-hydroxycorticosterone are reported. From the nomograms presented it is possible to predict the behavior of these steroids in countercurrent distribution experiments. It is also possible to select systems suitable for the separation of mixtures. In addition, this general approach may be found useful for the study of other types of solutes and other solvent systems.

THE increasing use of countercurrent distribution procedures for the separation of complex steroid mixtures (*1, 2, 4–6 8, 9, 14–16*) makes it desirable to explore solvent systems which can be used to accomplish these separations. Although an almost infinite number of solvent combinations is available, attention was focused on the quaternary, biphasic system consisting of ethyl acetate, cyclohexane ethyl alcohol, and water. These four solvents meet certain criteria which must be applied to any solvent contemplated for countercurrent distribution. These criteria are discussed by Craig and Craig (*3*) and include availability, ease of purification, adequate solubility of the solutes in the solvent system, a range of partition coefficients suitable for countercurrent distribution, and boiling points of the solvents in the range which permits easy isolation of the solute, as well as the assurance of a relatively constant phase composition throughout a distribution involving several hundred transfers. The partition coefficient, K, is defined as C_u/C_l, where C_u is the concentration of the solute in the upper phase and C_l is the concentration of the solute in the lower phase.

In previous studies of the relation between phase composition and partition coefficients for some steroidal estrogens in ternary and quaternary biphasic solvent systems, it was found that the relationship was linear (*10*) with respect to the logarithm of the partition coefficient. It was hoped that this technique could be extended to some neutral steroids. Unfortunately, in the solvent systems studied, the relationship was not often linear.

$\frac{25\%\ A + 75\%\ B}{25\%\ C + 75\%\ D}$	$\frac{50\%\ A + 50\%\ B}{25\%\ C + 75\%\ D}$	$\frac{75\%\ A + 25\%\ B}{25\%\ C + 75\%\ D}$
$\frac{25\%\ A + 75\%\ B}{50\%\ C + 50\%\ D}$	$\frac{50\%\ A + 50\%\ B}{50\%\ C + 50\%\ D}$	$\frac{75\%\ A + 25\%\ B}{50\%\ C + 50\%\ D}$
$\frac{25\%\ A + 75\%\ B}{75\%\ C + 25\%\ D}$	$\frac{50\%\ A + 50\%\ B}{75\%\ A + 25\%\ D}$	$\frac{75\%\ A + 25\%\ B}{75\%\ C + 25\%\ D}$

Figure 1. Example of Experimental Design for Measurement of Partition Coefficients over a Wide Range of Phase Compositions in a Quaternary Biphasic System

The four components are *A*, *B*, *C*, and *D* and the percentages are by volume of the pure components prior to mutual saturation

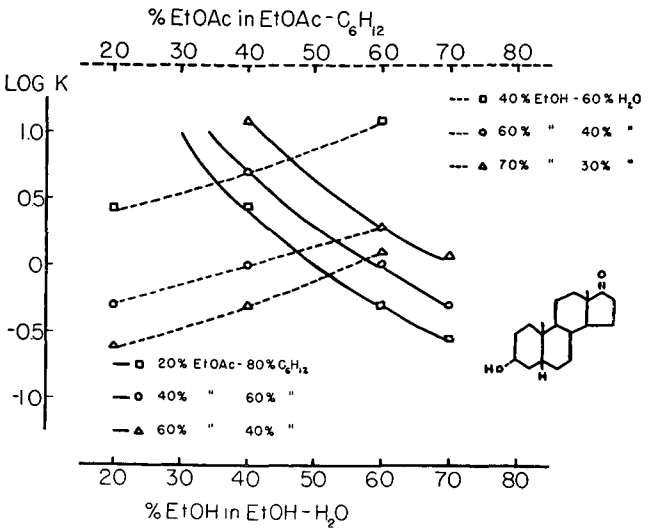

Figure 2. Relation between Phase Composition and Partition Coefficients for 5-Isoandrosterone in the System Ethyl Acetate–Cyclohexane and Ethyl Alcohol–Water

The lower abscissa gives the composition of the lower phase and the upper abscissa gives the composition of the upper phase. The ordinate is the logarithm of the partition coefficient, *K*
—— Variation in log *K* with changing lower phase composition at three fixed upper phase compositions
- - - - Variation in log *K* with changing upper phase composition at three fixed lower phase compositions

By appropriate experimental design, the partition coefficients of the solutes over a wide range of phase composition may be covered with relatively few determinations as indicated in Figure 1. The actual proportions of the four components will be determined to some extent by the solubility of the solute in the two phases, the order of magnitude of the partition coefficients, and the phase composition at the point of miscibility. When the data are plotted as in Figure 2, it is apparent that some extrapolation may be made. These data can then be converted to a nomographic form which permits the determination of a partition coefficient over a wide range of phase compositions (Figures 3 to 6).

EXPERIMENTAL

Solvents. Technical grade cyclohexane was purified by passage through a column of silica gel followed by distillation. Ethyl acetate and ethyl alcohol were purified by distillation.

Partition Coefficient Determinations. Equal volumes of upper and lower phases of the desired composition were equilibrated. Then equal volumes of the two phases were transferred into glass-stoppered test tubes containing a known amount of the steroid to be studied. Equilibration was carried out at room temperature (25° ± 3° C.) by repeated inversion of the test tubes for

Table I. Partition Coefficients of Some Neutral Steroids in Ethyl Acetate–Cyclohexane and Ethyl Alcohol–Water

Compound	Ethyl Acetate in Ethyl Acetate–Cyclohexane, %	Partition Coefficients: Ethyl Alcohol in Ethyl Alcohol–Water, % 30	40	50	60	70	80
Androsterone	20	..	7.3	..	0.89	..	0.29
	40	..	12.2	..	1.6	..	0.54
	60	..	24	..	2.4	1.1	..
5-Isoandrosterone	20	..	2.8	..	0.52	0.28	..
	40	..	5.2	..	1.0	0.51	..
	60	..	12.3	..	2.0	1.2	..
Epiandrosterone	20	..	2.9	..	0.56	0.31	..
	40	..	4.1	..	0.97	0.52	..
	60	..	10	..	1.9	0.95	..
Dehydroepiandrosterone	20	..	2.7	..	0.45	..	0.21
	40	..	6.1	..	0.92	..	0.41
	60	..	13	..	1.7	0.84	..
Androstane-3,17-dione	20	..	5.8	..	1.2	0.60	..
	40	..	8.4	..	1.8	0.88	..
	60	..	17	6.4	2.5	1.2	..
Δ^1-Androstene-3,17-dione	20	..	1.9	..	0.54	0.28	0.25
	40	..	3.4	..	0.92	0.51	0.46
	60	..	8.3	..	1.3	0.89	..
Desoxycorticosterone	30	4.4	..	0.67	..	0.21	..
	50	8.6	..	1.8	..	0.47	..
	60	10	..	2.4	..	0.82	..
	70	17	..	3.2	..	..	..
17α-Hydroxycorticosterone	30	0.31	..	0.08	..	0.04	..
	50	1.1	..	0.39	..	0.16	..
	60	1.8	..	0.59	..	0.31	..
	70	3.1	..	1.2	..	..	..

2 minutes. After the two layers had separated, suitable aliquots of each layer were withdrawn for analysis.

Analytical Methods. 17-Ketosteroids were measured by a modification of the Holtorff-Koch method (*12*) in which the time for color development was extended to 105 minutes. Each steroid employed served as its own standard. The two cortical steroids were estimated by a modification of the Hollander technique (*11*) in which the periodate oxidation and diffusion of the liberated formaldehyde are combined in one step (*7*).

Partition coefficient values were not accepted unless the total recovery of steroid in both phases was 90% or greater. At least three measurements of partition coefficient were made for each compound at each phase composition studied. Values for partition coefficients in the neighborhood of 1.0 are considered to be precise to ±10%. Values differing greatly from 1.0 in which large or very small ratios are measured are less precise.

Construction of Nomogram. The partition coefficients obtained for the eight compounds are shown in Table I. For each compound, the partition coefficients were plotted as functions of phase composition as exemplified in Figure 2. The phase compositions are the compositions of the upper and lower phases prior to mutual saturation. Since no simple function was found to describe the relation between phase composition and partition coefficient, an empirical method was used for the construction of the nomogram.

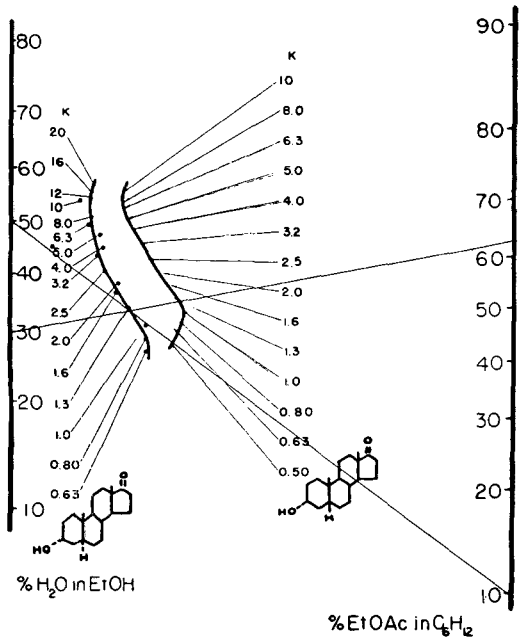

Figure 3. Nomogram for Determination of the Partition Coefficients of Androsterone and 5-Isoandrosterone in the System Ethyl Acetate–Cyclohexane and Ethyl Alcohol–Water

In all the nomograms the points are those which were determined graphically from plots of the type of Figure 2

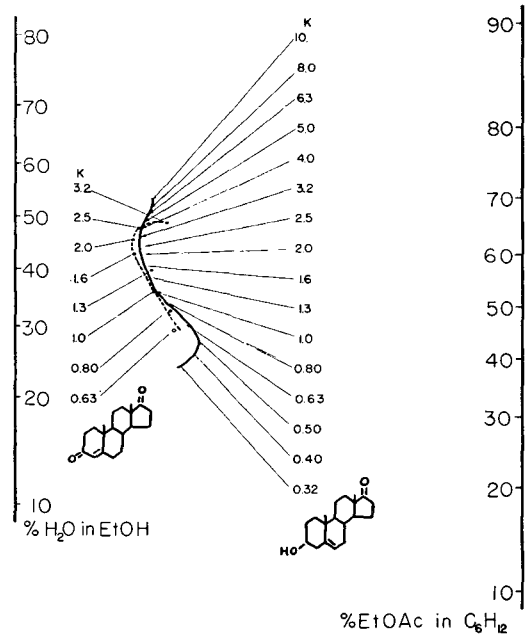

Figure 4. Nomogram for Determination of Partition Coefficients of Δ^4-Androstene-3,17-dione and Dehydroepiandrosterone in System Ethyl Acetate–Cyclohexane and Ethyl Alcohol–Water

In plots of the type of Figure 2, for each value of log K which intersects three or more of the lines, the corresponding compositions of upper and lower phases were read off. For each such set of values the following ratios were calculated: log (per cent water/per cent ethyl alcohol) and log (per cent ethyl acetate/per cent cyclohexane). The two vertical axes were constructed on a linear scale for the range of values of the logarithms of the ratios from 10 to 90% of each component in the other. Three lines were then drawn for the three pairs of log ratio values corresponding to the log K value selected. The point of intersection of the three lines is the locus of that value of log K on the nomogram.

A similar procedure was carried out point by point for other values of log K. The points thus obtained were connected by smooth curves. The vertical scales were then converted to percentage composition scales and the log K curves to K scales. From the finished nomogram it is possible to determine the value of the partition coefficient for any given phase composition within the limits studied. In Figures 3 to 6 are presented nomograms for androsterone, 5-isoandrosterone, epiandrosterone, dehydroepiandrosterone, androstane-3,17-dione, Δ^4-androstene-3,17-dione, desoxycorticosterone, and 17α-hydroxycorticosterone.

DISCUSSION

In practice, the nomograms may be used for the selection of solvent systems to accomplish separations of steroid mixtures, since if the values of any three of the four variables plotted are known the value of the fourth may be obtained. For example, in Figure 3, if it is known that in the system 63% ethyl acetate in cyclohexane and 30% water in ethyl alcohol, androsterone has a partition coefficient of 1.3, then a partition coefficient of 1.3 would be interpolated for 5-isoandrosterone. This system obviously would not be suitable for separating these two steroids.

If then the solvent system were changed to 10% ethyl acetate in cyclohexane and 50% water in ethyl alcohol, androsterone would still have a partition coefficient of 1.3, while that of 5-isoandrosterone would be 0.55. This system clearly would be suitable for achieving a good separation of these two compounds with a reasonably small number of transfers. The number of transfers required to obtain a separation may be calculated using the equation derived by Nichols (*13*).

As was pointed out by Craig and Craig (*3*), differences in polarity of the two solvent phases influence the degree of resolution of solute mixtures. A hydrocarbon-water system would, by this criterion, be ideally suited for separation by countercurrent distribution. However, limitations of solubility make such systems impractical for the steroid compounds under consideration. It was thought that by the addition of ethanol to the aqueous phase and of ethyl acetate to the hydrocarbon phase the solubilities of the steroids would be improved, albeit at the expense of resolution.

Examination of the nomograms discloses that, in general, for a given composition of the ethyl alcohol–water phase greater resolution is obtained as the cyclohexane content of the other phase is increased. Conversely, for a fixed composition of the ethyl acetate–cyclohexane phase, the resolution tends to improve as the water content of the other phase is increased. However, within the limits imposed by the quantity of material available and the sensitivity of the analytical technique, loss in resolution may be compensated for by increasing the number of transfers applied. In the limiting case, when the compositions of the two phases approach identity—i.e., miscibility—the partition coefficients all approach 1 and no resolution can be achieved.

Nomograms prepared by this method are now being used for the selection of solvent systems for the separation of steroid compounds from urinary and tissue extracts. It is anticipated that this general approach will be useful for the study of relations between partition coefficients and phase composition for other solvent systems as well as for other types of solutes.

ACKNOWLEDGMENT

The authors wish to think A. B. Hastings for his generous assistance in the preparation of the nomograms. Thanks are also due the following for the gifts of pure steroids: the late Konrad Dobriner (5-isoandrosterone), T. F. Gallagher (epiandrosterone), Ciba Pharmaceutical Products, Inc. (dehydroepiandrosterone and desoxycorticosterone acetate), the Schering Corp. (Δ^4-androstenedione), and the Upjohn Co. (17α-hydroxycorticosterone). This work was supported by funds from the following sources: National Cancer Institute, U. S. Public Health Service, an institutional grant from the American Cancer Society to the Massachusetts General Hospital, a grant from the American Cancer Society upon recommendation of the Committee on Growth, National Research Council, and the Jane Coffin Childs Memorial Fund for Medical Research.

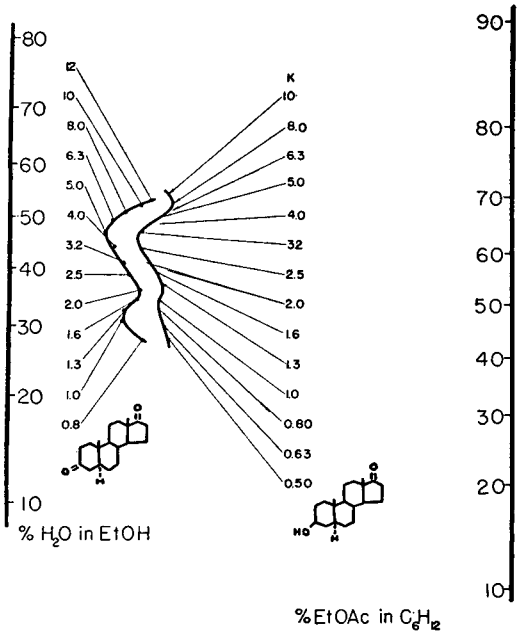

Figure 5. Nomogram for Determination of Partition Coefficients of Androstane-3,17-dione and Epiandrosterone in the System Ethyl Acetate–Cyclohexane and Ethyl Alcohol–Water

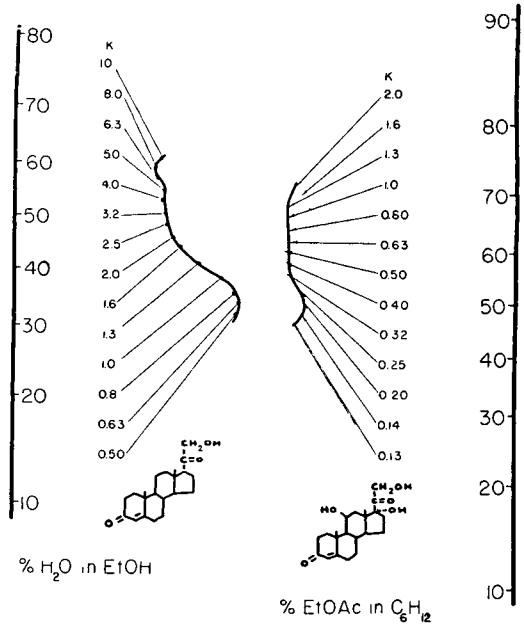

Figure 6. Nomogram for Determination of Partition Coefficients of Desoxycorticosterone and 17α-Hydroxycorticosterone in the System Ethyl Acetate–Cyclohexane and Ethyl Alcohol–Water

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Use of Apparent Dissociation Constants in Qualitative Organic Analysis

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Procedures are described for obtaining and interpreting potentiometric titration data in the form of hydrogen ion binding versus pH curves. Advantages and utility of data in this form are discussed.

THE application of physical methods to qualitative organic analysis during recent years has led to widespread use of ultraviolet and infrared absorption spectrophotometry and, to a lesser extent, polarography in groupwise identification of organic structures. Potentiometric determination of dissociation constants of acidic and basic groups has been exploited far less, in spite of its great utility in such structure studies. Part of this neglect has been due to the lack of a relatively simple means for obtaining and interpreting potentiometric titration curves. Furthermore, the importance of dissociation constants in organic analysis and their relation to other physical methods have not been widely advertised.

Many authors report true dissociation constants (pKa values) which represent extrapolation of apparent dissociation constants (pK_a' values) to zero ionic strength. For the purpose of groupwise identification, pK_a' values obtained experimentally may be compared directly with these data since the ionic strength of the solution under the conditions described is generally less than 0.02 at the end of the titration experiment and deviation from pKa is relatively small. Simms (*4*) has determined the change in pK_a' with changing ionic strength for several typical acidic and basic groups. His data indicate the deviation between pK_a' and pKa corresponding to the ionic strength occurring in the present experiments to be less than 0.1 pH unit. In general, observed pK_a' is lower than pKa for acids and higher than pKa for bases.

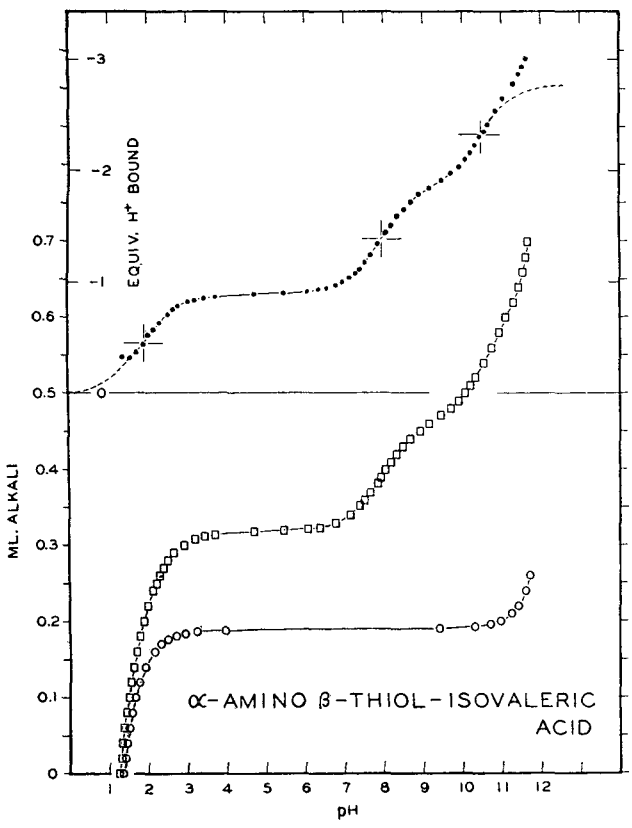

Figure 1. Titration Curves for α-Amino-β-thiolisovaleric Acid

○. Blank titration
□. Sample titration
●. Hydrogen ion-binding curve

TITRATION PROCEDURE

Data given in the illustrative curves were obtained by titration of samples of about 5 mg. for a molecular weight of 300. The sample was dissolved in 3 ml. of water with the addition of one or more equivalents of acid or alkali as needed. A Coleman electrometer with small Beckman glass and calomel electrodes was used for pH measurements. Titrant was with approximately $2N$ hydrochloric acid or potassium hydroxide and was delivered by a Greiner ultramicroburet having a total capacity of 0.1 ml. and reading to 0.0001 ml. on a microgage. A magnetic stirrer kept the solution agitated vigorously.

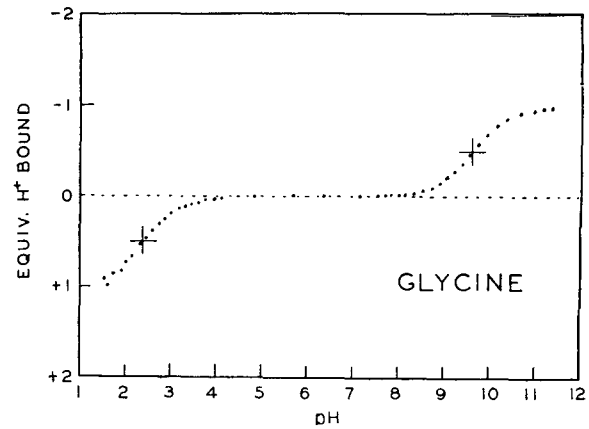

Figure 2. Hydrogen Ion-Binding Curve for Glycine

The use of $2N$ or stronger titrant allows a useful pH range of 2 to 12 to be attained. Additions of titrant should be of such volume to provide an adequate density of points across this pH range. For example, about 5 to 10 points per pH unit are adequate in the region where a group is being titrated. In Figure 1 the curve marked by squares is a conventional titration curve with volume of titrant plotted against pH. Only the inflection at pH 8.0 is immediately apparent. The curve marked by open circles in this figure is a blank titration of a solution prepared like the sample solution, omitting only the sample itself. When the blank curve is subtracted volumewise from the sample curve, the resulting curve (marked by solid circles in Figure 1) shows clearly the presence of two more inflections at pK_a' values of 2.0 and 10.5.

This difference curve, which represents the hydrogen ion-binding capacity of the sample as a function of pH, was calculated and plotted with equivalents of bound hydrogen ion per mole of sample as abscissa versus pH. The units of the abscissa in this and subsequent illustrative titration curves are labeled plus or minus to indicate a hydrogen ion has been removed from solution by the sample or that a hydrogen ion has been donated to the solution by the sample, respectively. Thus the zero hydrogen ion-bound reference line represents the original electrical state of the molecule. Each inflection occurring above this line signifies

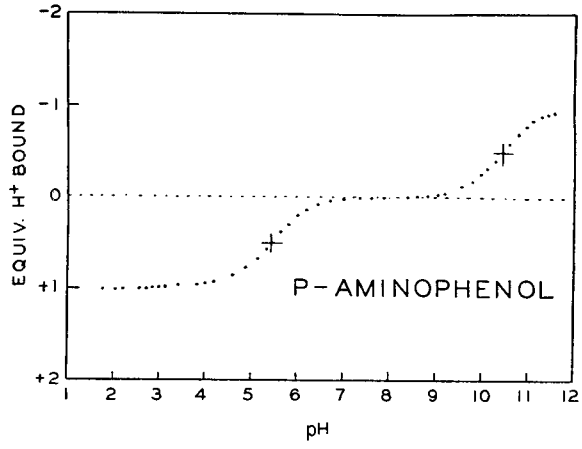

Figure 3. Hydrogen Ion-Binding Curve for *p*-Aminophenol

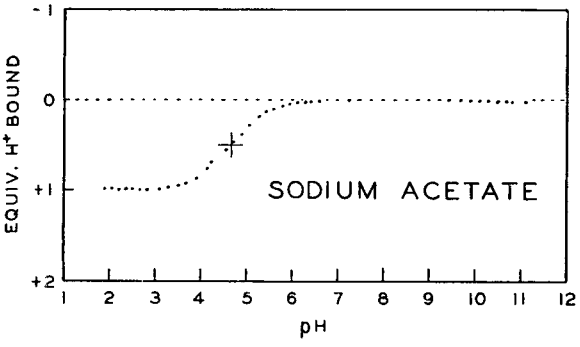

Figure 4. Hydrogen Ion-Binding Curve for Sodium Acetate

release of one equivalent of hydrogen ion to the solution, by ionization of an acidic group or by conversion of the salt of a base to the free base. Likewise each inflection below this line corresponds to the binding of one equivalent of hydrogen ion by ionization of a basic group or conversion of an acid salt to the free acid.

Chemical information about the presence of inorganic anions or cations is necessary for identification of a given inflection as an acidic or basic group. Where inflections occur both above and below the reference line, the numbers of inflections above and below correspond to the numbers of hydrogen ion–releasing and hydrogen ion–binding groups, respectively, but a given inflection may be due to either type of group and further information is necessary to make this distinction. An example of this is shown in Figure 2 with the titration curve for glycine (pK_a' 2.38 and 9.62) and in Figure 3 with the titration curve for *p*-aminophenol (pK_a' 5.41 and 10.4). In the former compound the inflection for the acidic group is found below the reference line, while in the latter compound the acidic group is found above the line.

Two methods are available for facilitating distinction between certain types of acidic and basic groups. By performing titrations at several temperatures, it is possible to calculate the heat of dissociation for a given group. The heat of dissociation for a monocarboxylic acid is generally less than 2000 calories per mole and is about 6000 calories per mole for phenolic groups, while the ΔH for basic groups is generally greater than 5000 calories per mole (*1*). This technique has been used to great advantage in the study of the dissociating groups in proteins.

The second method involves titration in a nonaqueous solvent or a solvent-water mixture. Apparent dissociation constants of 27 carboxylic acids in varying ethyl alcohol–water mixtures have been studied by Michaelis and Mizutani (*2*). Progressive increase in pK_a' values with increasing alcohol concentration was observed for each acid. Variations in the rate of increase with structure adjacent to the carboxyl group was noted. Mizutani (*3*) reports that 11 organic bases show a marked decrease in pK_a' with increasing alcohol concentration. Another solvent which affords a satisfactory distinction between acidic and basic groups and possesses the advantages of lower vapor pressure and better solvent characteristics is dimethylformamide.

Since a few organic acids and bases are so strong that their titration inflections are not observed in the range of reliable pH values, caution must be exercised in the interpretation of hydrogen ion–binding curves. Usually such strong groups can be readily detected by chemical means.

When aqueous titration curves of equivalents of bound hydrogen ion versus pH are plotted on a uniform scale—e.g., 1 inch per equivalent and 0.5 inch per pH unit—any single titratable group produces an inflection having the same shape regardless of its position on the pH scale. The midpoint of the inflection is the pK_a' of the dissociating group. Figure 4 illustrates the bound hydrogen ion curve obtained in a typical potentiometric titration of sodium acetate (pK_a' 4.67). The theoretical curve for this inflection is derived from the following expression:

$$\mathrm{pH} = pK_a' + \log_{10}(a/1 - a)$$

where a is the fraction of the sample in the dissociated state for acids or the associated state for bases.

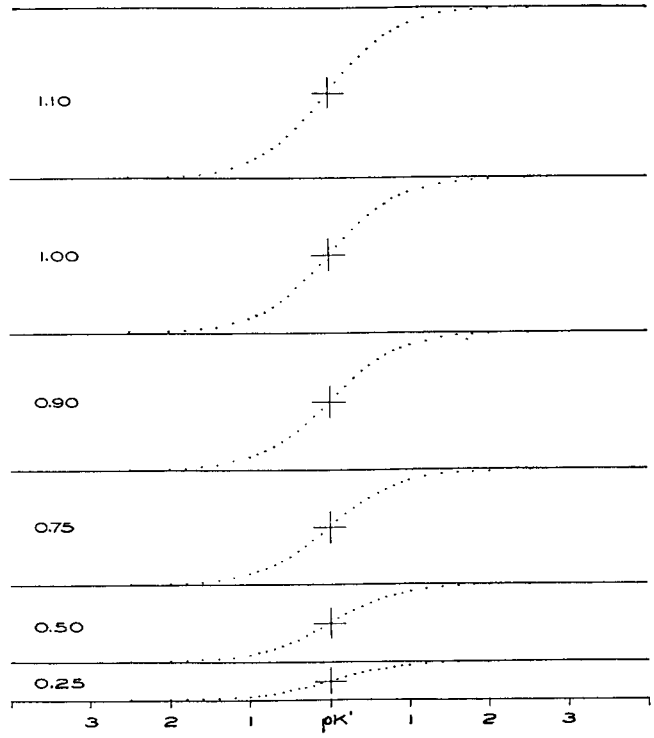

Figure 5. Theoretical Curves from Transparent Mask Used for Graphic Analysis of Hydrogen Ion–Binding Curves

A transparent mask shown in Figure 5 bearing this theoretical curve has been prepared for convenience in interpreting bound hydrogen ion versus pH curves. In addition to the curve for exactly one equivalent hydrogen ion bound per mole of sample, other curves for 1.10, 0.90, 0.75, 0.50, and 0.25 equivalent per mole have been incorporated for use with samples of unknown purity or molecular weight. An index mark at the midpoint of the theoretical curve allows immediate determination of the pK_a' values with an accuracy of about ±0.05 pH unit. Use of this mask permits estimation of pK_a' at the extremes of the pH

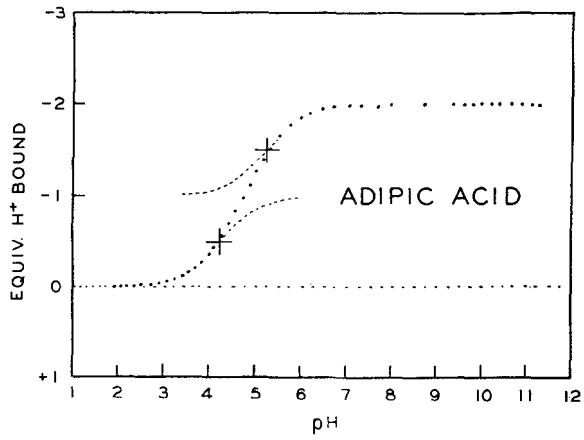

Figure 6. Hydrogen Ion-Binding Curve for Adipic Acid

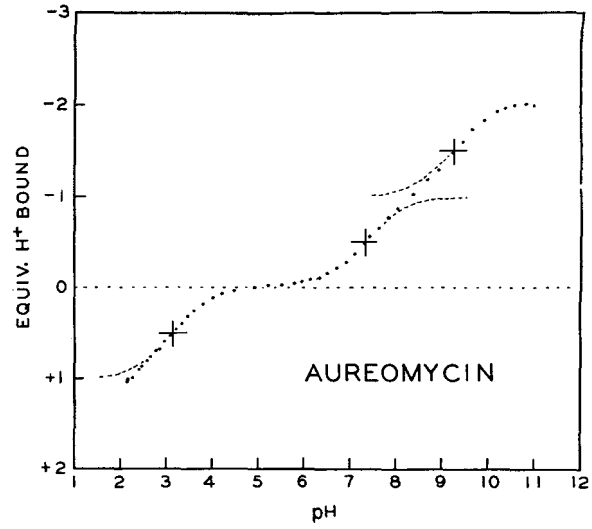

Figure 8. Hydrogen Ion-Binding Curve for Aureomycin

scale where only a portion of the complete theoretical titration curve may be observed. In Figure 2 the midpoint of the inflection for the carboxyl group of glycine occurs at about the lowest pH at which trustworthy values can be obtained, but the pK'_a can be estimated by fitting the observed points to the theoretical curve. Overlapping groups may be readily resolved and their pK'_a values determined accurately by use of the mask. Figure 6 illustrates use of the mask in resolution of the pK'_a values of adipic acid which are separated by approximately one pH unit (pK'_a 4.23 and 5.24). Use of this mask is limited to aqueous titrations because the shape of inflections in nonaqueous titration curves would be expected to vary.

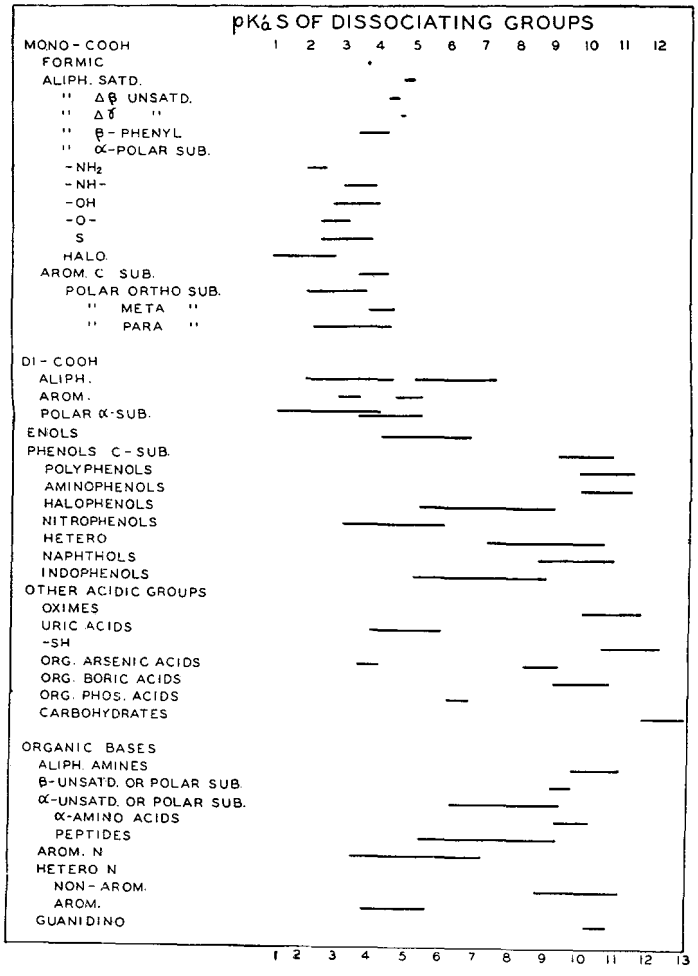

Figure 7. Range of pK'_a of Dissociating Groups from Literature Data

Having determined the pK'_a of the dissociating group and having obtained some information as to its acidic or basic nature, it is frequently possible to make tentative assignments of structure of the dissociating group. The chart in Figure 7 has been drawn from aqueous titration data on 573 compounds taken from the literature. The ranges observed for typical dissociating groups are given and in several cases the effect of neighboring groups or substituents is noted. It has been found helpful to employ a simple Keysort punched card system for indexing these titration data.

While quantitative titrimetry is not within the scope of this paper, some important quantitative information may be obtained from these titration curves. If the purity of the sample is known, the molecular weight can be determined within the limits of accuracy of the method, which is about 5%. Since use of the mask with the theoretical curve distinguishes partially overlapping inflections, a true molecular weight is determined in contrast to a neutral equivalent determined by an indicator titration. An exception would be a compound with two or more titratable groups having pK'_a values separated by less than about 0.4 pH unit. These would appear as a single titratable group and the apparent molecular weight would be the equivalent weight.

Many substances exhibit a marked difference in other physical properties according to the electrical state of their titratable groups. This difference is particularly important in their ultraviolet and visible absorption and in their behavior at the dropping mercury cathode. Figure 8 shows the titration curve for an antibiotic substance, aureomycin (pK'_a 3.14, 7.33, and 9.24), and Table I shows the ultraviolet absorption data for the substance in each of its four electrical states. It can be seen that the effect of electrical state of ultraviolet absorption is profound in the case of this substance. In the investigation of the unknown structure of a new substance, potentiometric titration must precede determination of ultraviolet absorption or

Table I. Ultraviolet Absorption Maxima for Aureomycin

pH 1		pH 5.4		pH 8.4		pH 12	
λ,[a] mμ	a[b]	λ, mμ	a	λ, mμ	a	λ, mμ	a
231	15,200	228	16,700	239	16,200	247	16,600
267	16,900	278	14,300	277	14,800	280	14,000
320	6,700						
368	8,100	368	7,700	380	15,900	385	8,000

[a] λ = wave lengths of absorption maxima.
[b] a = molar absorptivity.

polarographic behavior if these characteristics are to be obtained for each electrical state of the substance.

The electrodes and electrometer used for titrations impose a limitation on the range of dependable pH values. This range may be extended by resort to more accurate but less convenient potentiometer circuits and by use of alternative but likewise less convenient electrode systems. The range of valid pH values is further extended by use of smaller sample volumes and higher concentrations of acid or alkali used as titrant. Excellent data on dissociation beyond this valid pH range can occasionally be obtained by measuring change in ultraviolet or visible light absorption or change in some other physical property as the molecule dissociates.

Many organic substances exhibit inadequate solubility in water to permit satisfactory titration. In such cases it may be necessary to titrate the sample in a water–organic solvent mixture. Alcohols, dioxane, and dimethylformamide have proved useful for this purpose. Since pK_a' values will vary with different solvents, the data in Figure 7 cannot be used for correlation with structure.

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Pharmaceutical Control Laboratory Record System

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A rapid, efficient pharmaceutical control laboratory record system is described. The system is based on two forms: an analytical "work sheet" and a marginally punched permanent record card, both of which contain the complete product formulation and job-identifying information. The marginal punching permits the coding of analytical and production information which aids in the critical evaluation of production and of laboratory operation.

THE authors have developed a record-keeping system for a pharmaceutical control laboratory which has proved extremely efficient. It evolved from a desire to create a system which would emphasize ease of recording of analytical control data and simplification of the study of such accumulated data. The system makes use of two forms: a "work sheet" which has the dual function of indicating to the analyst that a specific assay is to be done and serving as the report form after the analysis has been completed; and a marginally punched card which acts as the permanent record of all analytical control data. An industrial analytical laboratory record system also based on a marginally punched card has recently been described (*2*).

PUNCHED RECORD CARD

A marginally punched 6 × 8 inch Keysort card manufactured by the McBee Co., Athens, Ohio, serves as the permanent record of analytical control data for each product manufactured by the company. The card, which is printed on one side to minimize clerical preparation time (Figure 1), is made of card stock which permits duplication on the blank side with a Ditto duplicator. In this company, production of a pharmaceutical product is initiated by the creation of a manufacturing card which indicates product constituents, concentrations, manufacturing instructions, warnings of dangerous materials, customer's specifications, and all requisite job-identifying data, such as customer, type of product, and code and lot number. At the time the manufacturing card is made, a duplicate copy is Ditto reproduced on the unprinted side of the control laboratory punched card (Figure 2).

Having this complete and accurate copy of each manufacturing card in the control laboratory minimizes routine reference to the master files for the verification of product specifications. In addition, having the complete formula of each product aids the ag-

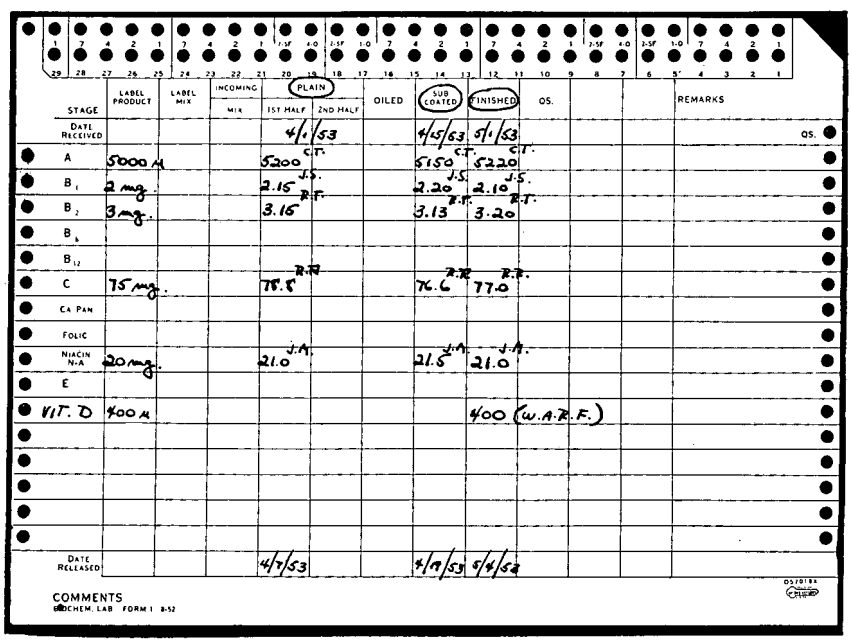
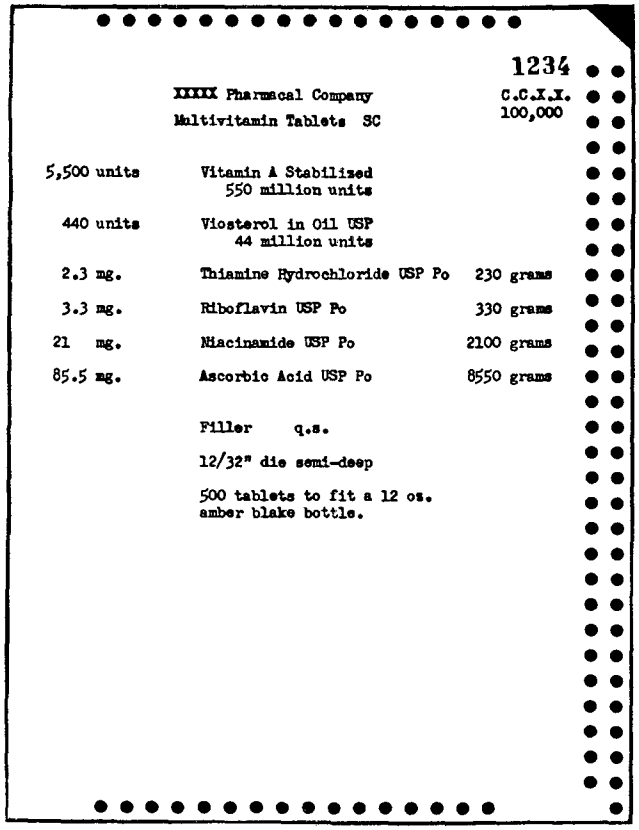


Figure 1. Punched Card for Permanent Record of Analytical Control Data



1234

XXXX Pharmacal Company — C.C.X.X. 100,000

Multivitamin Tablets SC

5,500 units	Vitamin A Stabilized 550 million units	
440 units	Viosterol in Oil USP 44 million units	
2.3 mg.	Thiamine Hydrochloride USP Po	230 grams
3.3 mg.	Riboflavin USP Po	330 grams
21 mg.	Niacinamide USP Po	2100 grams
85.5 mg.	Ascorbic Acid USP Po	8550 grams

Filler q.s.

12/32" die semi-deep

500 tablets to fit a 12 oz. amber blake bottle.

Figure 2. Duplicate of Manufacturing Card Printed on Reverse Side of Punched Card and on Reverse Side of Work Sheet

gregation and analysis of production and control data. When a product comes to the control laboratory for analysis this copy of the manufacturing card also obviates the need for clerical entry of customer, code, lot number, and components, in the control laboratory records. This has not only reduced the time required for record keeping but has eliminated the mistakes inevitable in copying.

Most of the information printed on the reverse side of the punched card (Figure 1) was formerly transcribed by hand for each job received by the control laboratory. Having the card custom-printed to specifications eliminated this nonconstructive copying of information which is unchanging and independent of the specific job. In addition, printing the names of the constituents most commonly assayed by the laboratory has also reduced record-keeping time.

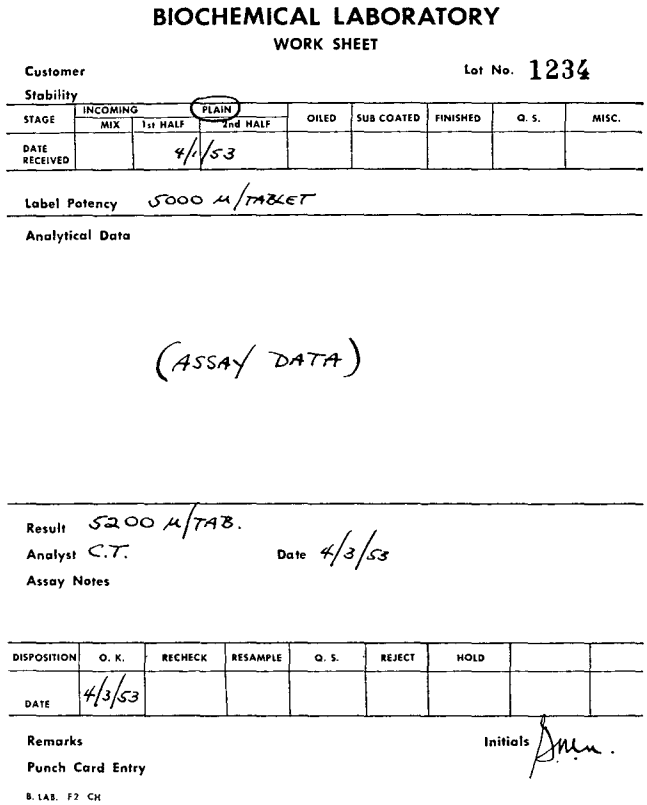
Space is provided on the printed portion of the card for the date of receipt of the sample, stage of production, assay data, analysts' initials, customer's label statement for each component, dates of laboratory release for further processing and, finally, data of laboratory release of the finished product. Sufficient space has also been provided for remarks on assay procedures, production problems, or previous experience with the particular product. At times an additional card is added for more detailed comments on special assay techniques or key points in the handling of the product. Extra cards of this type have even been utilized for the reproduction of memoranda issued by the control laboratory which pertain to the lot. Subsequent reference to such cards helps quickly to clarify the previous history of the product. This punched card system has been found very flexible in this respect and ways of increasing its utility are continually discovered.

The marginal punching is conventionally coded (*1*) for all constituents assayed, manufacturing difficulties encountered, type of product, and any additional information which will aid in the critical evaluation and improvement of the company's production.

WORK SHEET

The other form used in the control laboratory record system is a work sheet (Figure 3) which is supplied the analyst for each component to be assayed. The work sheet, which is the same size as the manufacturing and control laboratory punched cards, is made of a paper stock which takes Ditto duplication. A complete copy of the manufacturing card is reproduced on the unprinted side of the work sheet at the same time the manufacturing and punched cards are Ditto printed.

A sufficient number of work sheets are reproduced at this time to provide one sheet for each component requiring assay at every stage of production. The printed side of the work sheet makes provision for indicating the stage of production of the sample, date of sample receipt, analytical data and remarks, analyst's initials, date of assay, disposition and date of disposition by supervisor, supervisor's initials, remarks by supervisor, and supervisor's instructions to the clerk for entry of assay results and comments on the punched card.



BIOCHEMICAL LABORATORY

WORK SHEET

Customer — Lot No. 1234

Stability

STAGE	INCOMING MIX	INCOMING 1st HALF	PLAIN 2nd HALF	OILED	SUB COATED	FINISHED	Q. S.	MISC.
DATE RECEIVED		4/1/53						

Label Potency 5000 M/TABLET

Analytical Data

(ASSAY DATA)

Result 5200 M/TAB.

Analyst C.T. Date 4/3/53

Assay Notes

DISPOSITION	O. K.	RECHECK	RESAMPLE	Q. S.	REJECT	HOLD		
DATE	4/3/53							

Remarks — Initials

Punch Card Entry

B. LAB. F2 CH

Figure 3. Work Sheet for Control Laboratory Record

This form has eliminated the need for extensive clerical preparation of the work sheets before delivery to the analysts. Mistakes made in the recopying of job-identifying information and potencies of components no longer can occur. An appreciable saving of time formerly spent by analysts in verifying data previously copied by the clerk on each work sheet has resulted. The presence of the complete formula on each work sheet also simplifies analytical work by indicating to the analyst the presence of components capable of causing assay interference.

ROUTINE OPERATION

Upon receipt of the sample to be assayed in the control laboratory record office, the clerk removes from the file the punched card and work sheets which had been previously Ditto printed at the time the manufacturing card was made. Since the lot number, job-identifying information, and complete manufacturing formula are already on the punched card, the only additional data requiring entry on the punched card are the label statements of the constituents to be assayed and the date of receipt of sample.

The stage of production involved is merely circled on the punched card. The work sheets also contain the job-identifying data and formula and only require encirclement of the stage of production and entry of date. The component to be assayed is circled on the formula side of the work sheet. One work sheet is prepared for each constituent requiring analysis, and the sheets and sample are delivered to the analysts. The punched card is then numerically filed in the clerk's "in process" file.

Upon completion of the assay the analyst enters the analytical data, results, analytical notes, initials, and date on the work sheet and in the permanent laboratory notebook, and returns the work sheet to the supervisor. The supervisor indicates disposition of the assay, his initials and date, and, if complete, returns the work sheet to the clerk. The assay results, analyst's initials and pertinent comments are then entered on the punched card by the clerk.

When all of the assay work is completed the job is released for further processing or shipment, and the date of release entered on the punched card. When the laboratory's analytical work on a particular job is completely finished the punched card is filed serially by lot number in a standard metal file. The work sheets are retained for a short while before being discarded.

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Visual Control of Analytical Test Scheduling

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A visual system has been developed for use in the scheduling of routine analytical tests and for maintaining a daily status report of each sample in process. This system is based upon an application of a Produc-Trol visual order control board. By means of a series of colored plastic pegs which may be placed on the board, it is possible to visualize the number and type of tests that have been submitted for analysis. Through the use of a color code it is possible to distinguish priority samples, samples which require special techniques or modification of an existing standard procedure, and samples on which the testing is complete but the results have not been reported. Combination of a number code with the color code enables the scheduling supervisor to control the relative order in which the requested analyses on a given sample are to be made. Thus, the supervisor has a complete "picture" of the entire work load requested of his section available at all times for planning and assignment of personnel to the various required tasks. The two outstanding advantages of this scheduling system are its presentation in visual form of a summary of the entire work load of the test section and elimination of the necessity of written test assignments to the testers.

IN RECENT years the scope of analytical chemistry in petroleum refinery laboratories has greatly increased both in variety of analytical functions performed and in the number of analyses required. These increasing demands upon the analytical groups have resulted in a proportionately larger number of routine-type analyses which require detailed technical supervision. Consequently, this trend has increased the amount of time that must be spent in nontechnical work such as sample scheduling, storing, and test reporting. Such housekeeping overhead, while a very necessary function, results in routine, nonskilled use of trained analytical chemists. Further, the inability to visualize readily the exact number and type of tests requested, their relative priorities, and any deviations from specified routine analytical procedures have made the problem of test status and scheduling a complex one.

Continued studies of these problems during the past three years have been made in an effort to develop a more economical and more efficient procedure for the scheduling of routine analyses.

A review of the chemical literature since 1907 reveals that only three papers discuss this important phase of laboratory operation (*2*, *4*, *5*), although a few references to analytical laboratory organization and methods of operation may be found (*1*, *3*). A punch card system similar to that described by Hale and Stillman (*4*, *5*) was developed several years ago, but has been replaced by the system described herein.

REQUIREMENTS OF A CONTROL SYSTEM

Economical utilization of the available manpower and facilities of an organization must be based upon a well-planned program. This plan may be a long-range detailed plan of action or it may be a daily program whose details will be filled in as their need arises. Depending upon the scope of the laboratory program and the degree of supervision desired, the supervisor may be required to maintain a daily status report of each sample in process.

The maintenance of a daily status report for each sample requires:

1. A means of showing each sample for which an analysis is requested.
2. A method of indicating the exact tests required for each sample.
3. A procedure which indicates priority tests, tests requiring special instructions, and tests that must be run in a predetermined order.
4. A method which indicates when a given test has been satisfactorily completed.

In addition to these basic requirements, the control system selected should:

1. Be simple in operation, easy to maintain, and available to all interested personnel during normal working hours.
2. Automatically indicate to each individual his daily work assignment.

3. Require a minimum of clerical operations.
4. Indicate the relative age of each sample awaiting analysis.
5. Provide a record of all test results for the permanent files of the laboratory.
6. Be sufficiently flexible to permit ready addition of new tests and deletion of old tests.

It is the purpose of this paper to describe in detail a sample scheduling system which fulfills all of these requirements with a minimum of technical supervision and clerical man-hours. This system is based upon the application of one or more Produc-Trol visual control boards (manufactured by Wassel Organization, Inc., Westport, Conn.) which present a complete picture of the status of each sample and each test at all times. It is believed that the control system described in this paper is original and that it can be adapted to any type of laboratory operational control.

DESCRIPTION OF EQUIPMENT

The Produc-Trol Board. In general appearance, the Produc-Trol board (Figure 1) resembles a large punch board with a card file attached to one side. The board is 43½ inches wide by 30 inches high and has an index panel containing 100 individual card pockets. The card pockets are numbered from 1 to 100 and are arranged so that the lower quarter inch of each pocket is visible. The index panel is mounted in a slotted metal support which allows it to be removed and placed on a desk for necessary clerical operations. A double row of 200 peg holes extends horizontally across the board for each card pocket. Each double row of holes is numbered on both ends and in the middle to correspond to its card pocket. Figure 2 is a photograph of the upper left section of the board and shows in some detail the general arrangement of the column headings, card pockets, and various types of pegs used. (This photograph and Figure 1 were not taken at the same time, so the location of the pegs in the two photographs is not necessarily the same.) At the left edge of the peg hole section is a round white plastic peg for each of the double rows of holes. These pegs are also numbered to correspond to their designated row and card pocket. Each peg, in turn, is connected by a white string to a concealed spring mounted in the interior of the board. The peg with the attached string when inserted in the desired position on its row forms a white bar which is usually calibrated to measure progress in terms of days, hence the name "progress pegs."

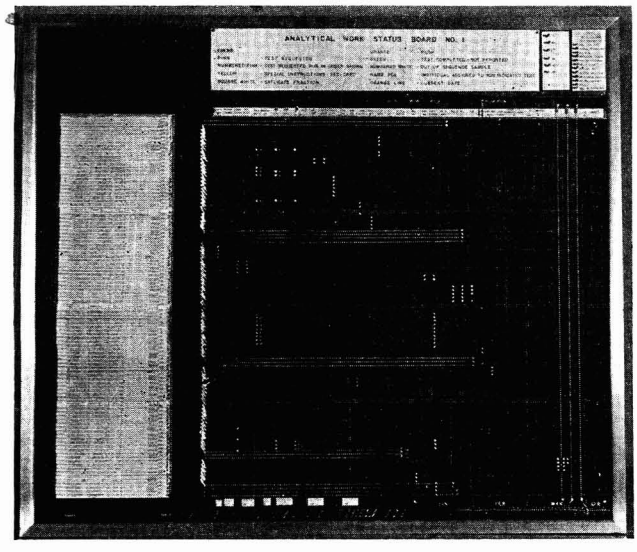

Figure 1. Produc-Trol Control Board

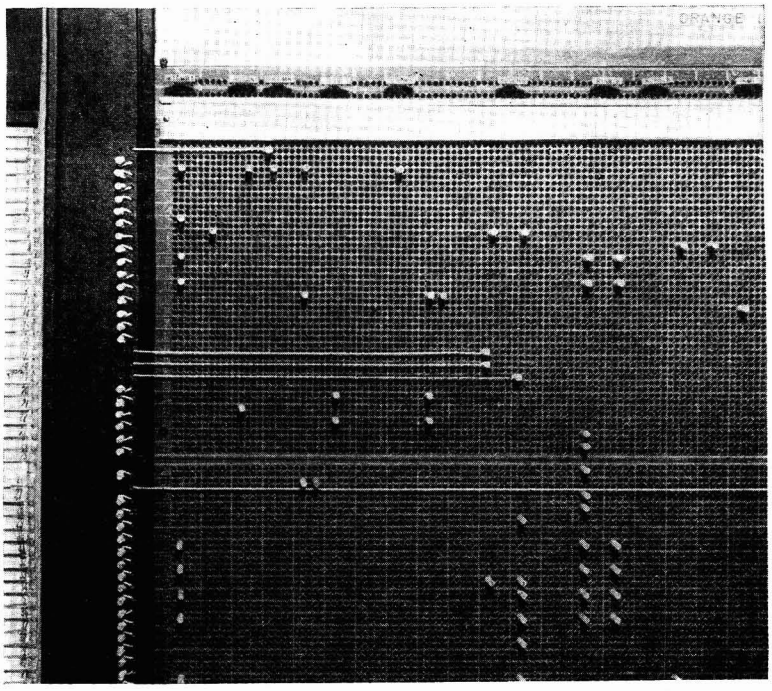

Figure 2. Upper Left Section of Produc-Trol Board

The peg section of the board is divided into 40 vertical columns by light green lines embossed on the face of the board. Each column is 5 peg holes wide, thus giving 10 peg positions in each numbered row. Above these columns is a small section for a column heading strip. Several rows of holes above the heading strip are used in conjunction with similar holes below the last numbered row to divide the board vertically with colored strings supplied with the board.

Signal Pegs. The manufacturer has a wide assortment of plastic pegs of different shapes and colors. The large variety of pegs permits the encoding of many kinds of information on the board. Pegs may be obtained with letters, numbers, or special characters imprinted on their tops. Plain sanded pegs suitable for marking with either ink or pencil may also be secured.

In the system described in this report two types of codes are used to place information on the board. For large-volume routine tests solid color pegs are used to indicate the desired action; for low-volume, miscellanous tests, square pegs of a given color combination are used to indicate the request of a specific analysis. Typical examples of the peg designations used in this system are shown in Table I.

Colored Strings. Three white strings are used to divide several of the columns vertically near the right edge of the board, in order to increase the number of columns available.

A vertical orange string is used with a calendar strip (described in a subsequent paragraph) to indicate the current date.

A horizontal pink string is used to indicate the row of the newest sample on the board.

Column Heading Strip. The column heading strip is lettered on lightweight card stock. The 40 most frequently requested tests are indicated on the column heading by appropriate abbreviations. In addition, columns are provided for inorganic analyses, microanalyses, and miscellaneous tests.

Title Card. Each board is assigned a number to identify it permanently. This same number is placed on the corresponding card file to avoid switching of these files when being replaced upon

the board. The identifying number appears on the title card which contains a master legend for rapid interpretation of the information presented on the board.

Calendar Strip. A three-month calendar strip is pinned to the lower right portion of the board below the peg section. This calendar strip (supplied by the manufacturer) is divided so that each peg hole represents one day. The current date is indicated by pegging the vertical orange strip over the appropriate date. This provides a reference axis which is advanced daily. The significance of this reference axis is explained later in this paper.

Record Cards. Each sample submitted for analysis must be accompanied by a written request (in duplicate). This request form is a 5 × 8 inch lithographed white card (Figure 3) made of lightweight stock to permit making duplicate requests with ordinary carbon paper. The form contains blank spaces for such information as sample description, special instructions, desired tests, desired test order (if necessary), sample source, budget number, and date of request. Spaces are provided for pertinent analytical remarks, the final results, and the location of the original experimental data by laboratory record book and page number. The request form is designed for one sample. Where more than eight tests are desired, the back of the card is used to provide additional space. The lower right corner of the card is reserved for the analytical test order number.

Table I. Designation of Colored Signal Pegs

Color	Shape	Purpose
Pink	Round	Normal routine test (high volume test)
Pink	Round numbered	Normal routine test where order of test is desired in a given sequence
Orange	Round	Priority or rush
Yellow	Round	Test requiring special instructions which are either on request card or must be obtained from supervisor prior to running analysis
White	Square	Saturate fraction for refractivity intercept measurement
Green	Round	Completed test
Yellow	Rectangular imprinted with name	Assigns personnel to specified test
Black-tan triangle	Square	Emission spectroscopic analysis requested
Black-aqua blue triangle	Square	Octane number requested
Black-orange triangle	Square	Resin content requested
White	Round-numbered	Date sample received for out-of-sequence sample

Analytical Test Order Number. Every request for analytical services is assigned a serial number. This number is stamped on the request form and on a gummed label which in turn is placed on the sample container. Each sample in the service section is placed on designated shelving in numerical sequence. Experience has shown that this system reduces the number of lost and misplaced samples to a minimum and the resulting saving of time more than compensates for the time required to place the number on the sample. The test order number also permits keeping all requests in the same sequence in which they are received and provides a convenient method of filing for future reference. In addition, the test order number eliminates confusion caused by original designations of samples.

OPERATION OF THE SYSTEM

Upon receipt of a request for testing, together with the designated sample, an analytical test order number is stamped on the request and on the sample. (The duplicate copy of the request, after being stamped with an order number, is retained by the person submitting the sample.) All requests received prior to 3 P.M. each day are posted daily on the Produc-Trol board by placing the request cards in numerical order in the card pockets beginning with the next vacant pocket. Opposite the request (which now has a numbered line on the board reserved for it) the appropriate types of signal pegs are inserted in the columns corresponding to the requested services. This completes the posting of the sample. Occasionally, an insufficient number of blank envelopes are available to post all new requests in successive envelopes. In such instances, the envelopes already occupied by a request are bypassed and the next vacant envelope is used to post the next sample request. The bypassed sample, which is now considered an old sample, is distinguished by placing the appropriate progress peg over the calendar strip so that the peg indicates the date of receipt of the sample. The length of white string thus exposed is a function of sample age, with the shortest string representing the oldest sample on the board. Conversely, the number of peg holes between the current date line and the progress peg represents the age of the sample. Comparison of the various lengths of white string exposed quickly identifies the old samples for remedial action.

By proper combination of the signal pegs it is possible to indicate several different instructions about a test. For instance, a red, yellow, and pink numbered peg may be used to show that the test is a priority test, that it requires special handling or instructions from the supervisor, and that it is to be run in a certain sequence with reference to the other tests requested on the sample. A yellow peg alone would show that special instructions are on the request card or that the supervisor wishes to give oral instructions regarding the test before it is run.

After the posting of new samples has been completed, the next day's work program is planned by the supervisor and individual personnel assignments are made by placing the individual name pegs above the test columns. This completes the scheduling of the next day's work. Figure 1 illustrates the appearance of the board at this phase of the operation. The outstanding advantages of this phase of the system are that the entire test inventory is visually available to the supervisor at the time the succeeding day's program is being planned and no writing of instructions is required.

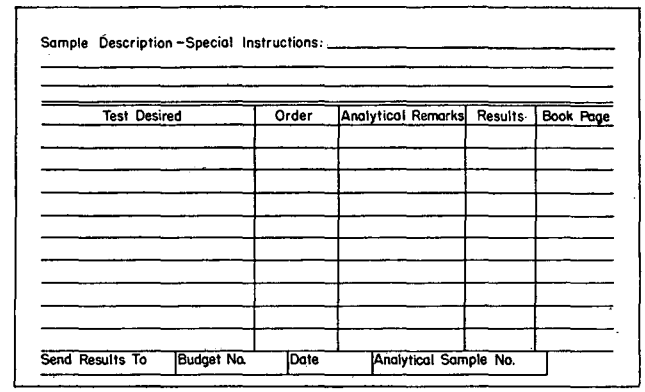

Figure 3. Analytical Test Request Form

Upon reporting for work, each individual assigned to the section proceeds to the boards, determines his work assignment, and notes the order numbers of the samples he will test. In the absence of priority samples or other instructions, the testers are expected to run the tests in numerical sequence. If the assigned samples are pegged with a yellow peg, the tester reads the special instructions on the request card. If these instructions are missing or are not clearly understood, instructions are obtained from the supervisor. If the requested test is pegged with a numbered pink peg the lowest numbered test is run first. For example, the assigned test is pegged with a number 4 peg. The tester checks the status of the other tests requested on the sample to determine whether the tests numbered 1, 2, and 3 are completed. If the latter tests are finished, then the number 4 test is run. However, if any of the lower numbered tests are not complete, the number

4 test is left to be run later. (Posting by numbered pegs thus permits the supervisor to control the test operations where limited sample quantities are available. Also, these pegs can be used in those cases where it is necessary to obtain certain data before another test can be run.) Upon completion of the assigned tests, including the preparation of a report sheet (Figure 4), the tester places a green peg in the appropriate row and column to indicate that the test has been completed. The report of the test is given the supervisor at the end of the day.

REPORT OF ANALYTICAL TEST

DATE: _____

ANALYST: _____

SAMPLE NO.. _____ BOOK AND PAGE NO.: _____

TEST: _____

_____

RESULTS: _____

_____

REQUESTED BY: _____

Figure 4. Form for Report of Analytical Test

The supervisor checks the test results and, if they are satisfactory, he has them entered on the corresponding request card. The pegs representing the reported tests are removed from the board daily. If the test results are unsatisfactory, the supervisor removes the green peg, thus rescheduling the test. Satisfactory test results are distributed daily to the persons requesting the tests. When all of the tests requested on a sample have been satisfactorily completed, the request card is removed for filing as a permanent record. The remainder of the sample (or the empty container, if the sample is consumed) is returned to the submitter. This action relieves the supervisor from any further responsibility for storage of the sample and ensures that only current samples are in the service section's storage spaces.

The lower section of one board has been reserved for samples requiring considerable testing time. This arrangement keeps such samples segregated and reduces to a minimum the number of out-of-sequence samples in the remaining areas of the board.

Personnel on special assignments—e.g., control testing for pilot plants, precision distillation, etc.—or absent are shown in the lower left corner of one board. In this way, the supervisor may determine at a glance the location of all personnel in the service section.

DISCUSSION

The sample scheduling system described in this paper has been tested over a period of two years. It has proved to be a valuable aid in maintaining a daily status report of each request test. The name peg scheduling has been found to be particularly advantageous in reducing the time lag before the section personnel can receive their daily assignments and begin their work. It is simple to maintain and easy to understand, and requires a minimum of clerical time and paper work on the part of the service section.

The visual features of the board enable the supervisors to see which tests are requested, the number to be run, and the position of any sample relative to other samples awaiting analysis. Testing bottlenecks are quickly observed in time to reassign personnel to prevent any one test from holding up completion of a given sample. Priority and old samples are easily located and can be expedited if necessary.

This sample scheduling system is based upon the use of three Produc-Trol boards and was designed for an average sample inventory of about 225 samples. Experience in this laboratory has indicated that the maximum posting time for average samples (six tests per sample) is about 40 to 50 samples per hour and that 95% of the posting can be done by nontechnical personnel after a short training period. With modification this system could be used for the processing of several hundred samples per day but in its present state of development an average daily increase of 100 samples appears to be the maximum economical load. The use of these boards has reduced considerably the amount of paper work required to maintain a daily status record and has, in effect, made a minimum of 3 technical man-hours per day available for other work in the section.

ACKNOWLEDGMENT

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Punched Card System for Radioisotopes

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A simplified punched card system for radioisotopes is presented. The system has been found to eliminate tedious searching of the tables in order to identify an isotope on the basis of its radiation characteristics and half life.

A PUNCHED card system codifying some basic characteristics of radioisotopes has been in use in this laboratory for over a year. While other isotope card catalogs have been devised (*1–3*), it is felt that the one presented here is sufficiently different in purpose and arrangement to warrant description.

The purpose of the isotope card catalog is to facilitate the identification of unknown radioactive isotopes on the basis of half life and radiation. Consideration was taken of minimum half lives encountered in this laboratory, the uncertain quality of counting data when dealing with unknown isotopes, and the possibility that expansion of the system may be desired in the future.

As a result of the above considerations a coding system was devised which selects a small group of isotopes, rather than one or two cards. This allows for the possibility that data reliability and sample history may be important factors. Also, it was decided that unless an isotope had a half life of over 5 hours or was related to a greater than 5-hour-half-life isotope by genesis or isomerism, it would not be cataloged. Stable isotopes were also to be eliminated from the system, since they are not involved in its purpose. As a result of these deletions the number of cards needed for the system was reduced from over 1000 to 375. It is believed that this arrangement excludes only those isotopes not normally worked with or used in either a commercial or a government laboratory. For a particular laboratory dealing in isotopes with half lives shorter than 5 hours, the addition of a few cards would be a simple task.

The case where one wishes to find the characteristics of a certain isotope is correlative to the purpose of the catalog, but is handled adequately by standard isotope tables. For this reason, provision has not been made for the rapid selection of a specific isotope.

The card chosen for the system was the McBee Keysort Form KS 581B, a 5 × 8 inch card with a single row of numbered holes spaced along its periphery. This card is of adequate size to hold a large amount of information and is easy to manipulate. Provision is made on the card for using groups of four holes (adjacent holes numbered 1, 2, 4, and 7) to code numbers from 1 to 14. Because of the generous size of the card there is room for additional information as may be needed. Only slightly more than one half of the available holes are now assigned, assuring the continued and expanding usefulness of the cards. In addition to the description of a radioisotope given by the punched holes, use is made of the face of the card to give more exact half life and energy values. Modes of formation, per cent of total radiation of emission, decay schemes, and conversion coefficients are also given.

Figure 1 shows a sample card of phosphorus-32, and illustrates the coding arrangement. The data used in preparing the cards were obtained from the National Bureau of Standards (*4*).

The code chosen involves simple characteristics which are assigned but one hole each. These simple properties are: (*a*) emits alpha particles, (*b*) emits negatrons (electrons emitted from the nucleus), (*c*) emits positrons, (*d*) emits gamma radiation, (*e*) emits electrons (internal conversion electrons), (*f*) decays by *K* capture, (*g*) decays by isomeric transition, (*h*) is a fission product, (*i*) has a radioactive daughter, (*j*) belongs to the thorium ($4n$) series, (*k*) belongs to the neptunium ($4n+1$) series, (*l*) belongs to the uranium ($4n+2$) series, (*m*) belongs to the actinium ($4n+3$) series, and (*n*) is naturally occurring. Possession of any of these characteristics is signified by punching the appropriate hole.

Certain other properties which the authors have coded may be termed quantitative to distinguish them from the simple characteristics above: half life, maximum gamma energy, predominant gamma energy, maximum positron energy, maximum negatron energy, predominant negatron energy, and maximum alpha energy. The decision to include the predominant gamma and negatron energy stems from the fact that the amount of radiation of maximum energy is sometimes relatively small compared to radiations of lesser energies. Thus absorption or pulse analysis data will often yield predominant energies as better data than maximum energy.

Each of the quantitative properties requires a group of four holes to describe the approximate half life and energies of a given radioisotope. In addition, a group of eight holes is used to designate atomic number.

As mentioned above, there are groups of four adjacent holes numbered 1, 2, 4, and 7 which may be used to codify any number from 1 through 14. By dividing the half lives and energies into classes and assigning a number to each class it was possible to achieve a code with the desired selectivity.

The half life classes with their assigned number are:

Class	No.
Less than 1 minute	1
1 minute up to 1 hour	2
1 hour–1 day	3 (2 + 1)
1 day–3 days	4
3 days–10 days	5 (4 + 1)
10 days–30 days	6
30 days–1 year	7
1 year–10 years	8 (7 + 1)
10 years–100 years	9
Greater than 100 years	11

[Number 10 was not used because it requires three punches for coding (7 + 2 + 1).]

The energy classification for gamma, positron, and negatron emission is as follows:

Class, M.e.v.	No.
0 up to 0.2	1
0.2–0.5	2
0.5–0.8	3 (2 + 1)
0.8–1.2	4
1.2–1.8	5 (4 + 1)
1.8–2.5	6
2.5–5	7
Greater than 5 m.e.v.	8 (7 + 1)

The classification of alpha particle energies necessitated a code involving three punches and is given below:

Class M.e.v.	No.
0 up to 3.0	1
3.0–4.0	2
4.0–5.0	3 (2 + 1)
5.0–5.3	4
5.3–5.6	5 (4 + 1)
5.6–5.9	6
5.9–6.2	7
6.2–6.5	8
6.5–6.8	9
6.8–7.1	10 (7 + 2 + 1)
7.1–7.5	11
7.5–8.0	12 (7 + 4 + 1)
Greater than 8.0	13

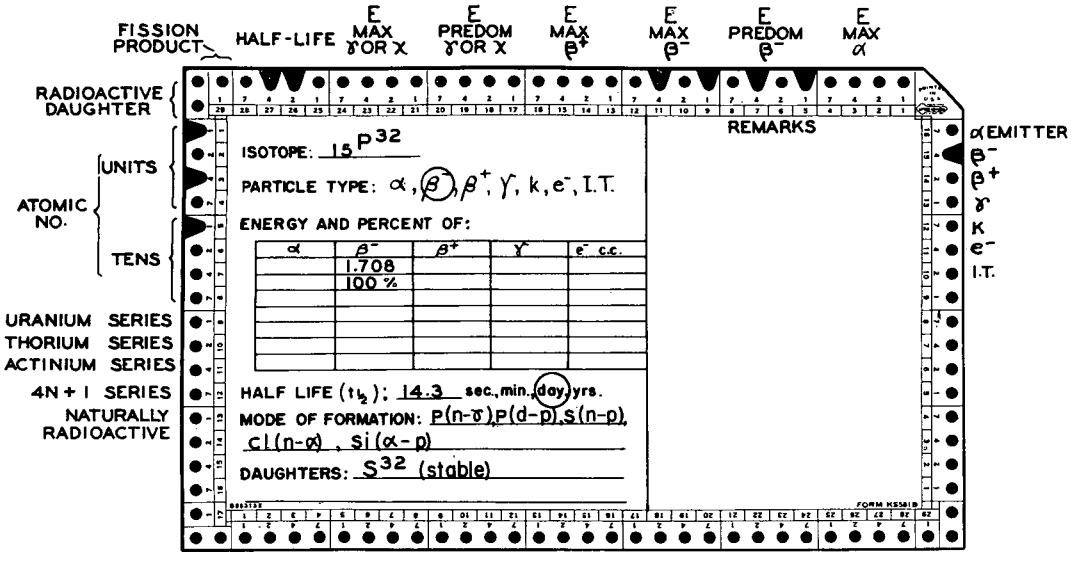

Figure 1. Drawing of Punched Card for Phosphorus-32

Illustrating coding arrangement and punches necessary to describe the isotope

These classifications plus the coding arrangement shown on Figure 1 may be placed on a blank Keysort card. This may be attached to the container holding the cards, where it will serve as a ready index to the system while sorting.

The atomic number designation is accomplished by using two adjacent groups of four holes. The group on the left describes the class of ten, while the group on the right describes the units. For example, 4+2(6) punched in the left-hand group and 7+1(8) punched in the right-hand group designate atomic number 68 (Er). Finding an isotope card for revision purposes is aided by this feature, and is the only reason for the inclusion of this feature in the system.

The cards are manually sorted with a McBee Keysorter needle probe by the standard method of selection and rejection according to the characteristics sought. It is only natural that increased sorting proficiency results from increased familiarity with the system. For example, pure gamma emitters may be found rapidly by first selecting those isotopes which decay by isomeric transition, then rejecting those which emit electrons (to eliminate internal conversion cases); the less experienced would possibly use the more tedious method of selecting the gamma emitters, then rejecting the alpha emitters, positron emitters, etc.

It is felt that the codification of radioisotopes by punched cards is a valuable addition to the scientific library. The modest number of cards needed for the system resulted in a minimum of expense in time and materials, while the time required to identify a certain isotope from a given set of properties has been greatly reduced in the authors' laboratory by this card system.

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Identification of Polyhydric Alcohols in Polymeric Esters

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By a modified saponification procedure, the polyhydric alcohol fraction of a polyester resin can be separated. The component alcohols can be identified by infrared spectral analysis, using the spectra of commercial alcohols as comparative standards. The method provides an effective means of identification for individual polyhydric alcohols and for binary mixtures.

THE original polyester (alkyd) resins contained glycerol exclusively as the polyhydric alcohol component and hence presented no analytical problem in this respect. The gradual replacement of glycerol, in whole or in part, by other polyhydric alcohols, however, soon necessitated a series of analytical investigations which culminated qualitatively in the procedure proposed by Orchin (*8*), which in the past has been applied successfully to polyhydric alcohol fractions isolated according to methods developed in this laboratory (*13*). The Orchin procedure, which is based on the oxidative scission of *vic*-diols with periodic acid, was applicable as follows to the polyhydric alcohols commercially available at that time:

Glycerol, if present, is converted to formic acid by oxidation with a solution of periodic acid which has been carefully neutralized with standard alkali; the formation of formic acid is detected with methyl red indicator.

Ethylene glycol is converted to formaldehyde, which can be detected by a color test involving alkaline phloroglucinol (*12*).

Propylene glycol yields acetaldehyde, which also gives a red coloration with alkaline phloroglucinol. Acetaldehyde may be distinguished from formaldehyde by the iodoform reaction.

Diethylene glycol, which is not a *vic*-diol, is not cleaved by periodic acid oxidation. In the absence of the above polyalcohols, the presence of diethylene glycol can be substantiated by the preparation of the 3,5-dinitrobenzoate.

Periodic acid oxidation has been applied by a number of subsequent investigators, most of whom were concerned with quantitative estimations. Newburger and Bruening (*7*) determined glycerol in the presence of ethylene and propylene glycols by titration of the formic acid liberated upon oxidation with potassium periodate. Pohle and Mehlenbacher (*10*) analyzed mix-

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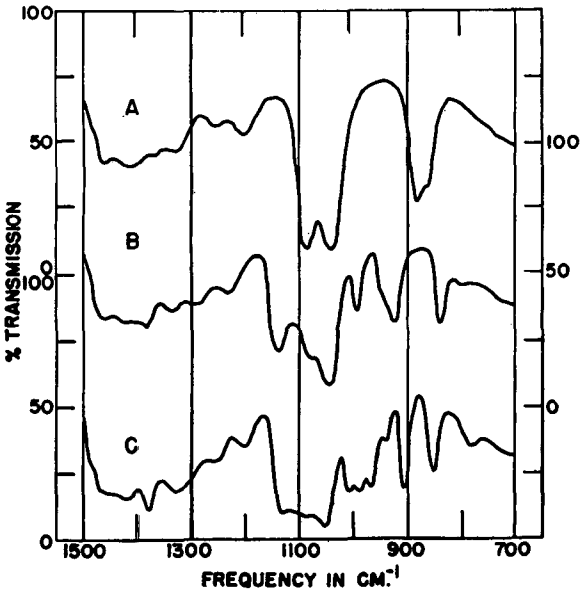

Figure 1. Infrared Spectra of Some Commercial Polyalcohols

A. Ethylene glycol
B. 1,2-Propylene glycol
C. 1,3-Butylene glycol

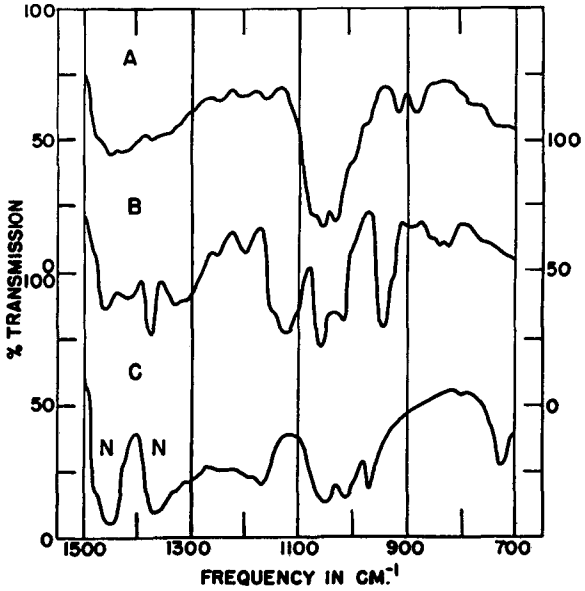

Figure 2. Infrared Spectra of Some Commercial Polyalcohols

A. 1,5-Pentanediol
B. 2,5-Hexanediol
C. 1,10-Decanediol-Nujol

tures of glycerol, propylene glycol, and trimethylene glycol by first determining glycerol as formic acid. Propylene glycol was then measured by titration of the iodine which is liberated when potassium iodide is added to the oxidized solution; trimethylene glycol is determined by acetyl value. Francis (*3*) started with the periodic oxidation procedure in determining the diglycols in mixtures of ethylene and propylene glycols. After the distillation of the resulting aldehydes, the diglycols are oxidized with potassium dichromate and are measured polarographically before and after oxidation. Cannon and Jackson (*2*) have modified the method of Warshowsky and Elving to determine small amounts of 1,2-propylene glycol in ethylene glycol. After oxidation with periodic acid, the aldehydes are removed by distillation and determined polarographically.

Among other approaches which have been suggested for the analysis of polyhydric alcohols may be included the following: Palfray, Sabetay, and Libmann (*9*) have described an entrainment procedure for the isolation (and estimation as such) of polyhydric alcohol fractions. Refluxing with cyclohexane, using a Dean-Stark trap, entrains ethylene glycol, trimethylene glycol, and propylene glycol. Turpentine entrains these, and in addition, diethylene glycol and glycerol. Hough (*5*) has applied paper

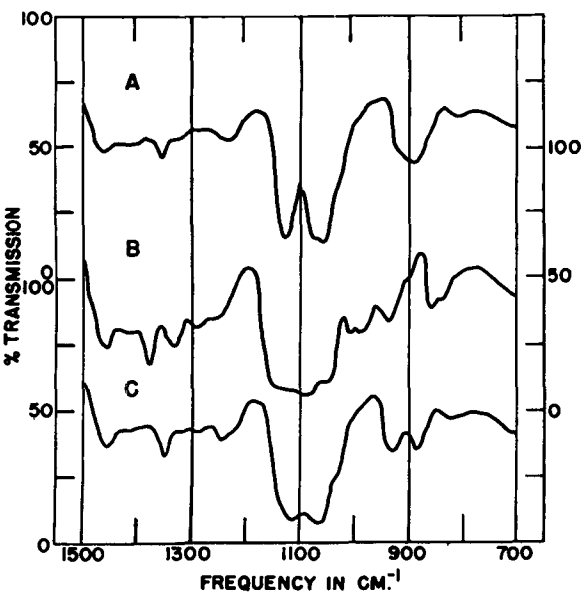

Figure 3. Infrared Spectra of Some Commercial Polyalcohols

A. Diethylene glycol
B. Dipropylene glycol
C. Triethylene glycol

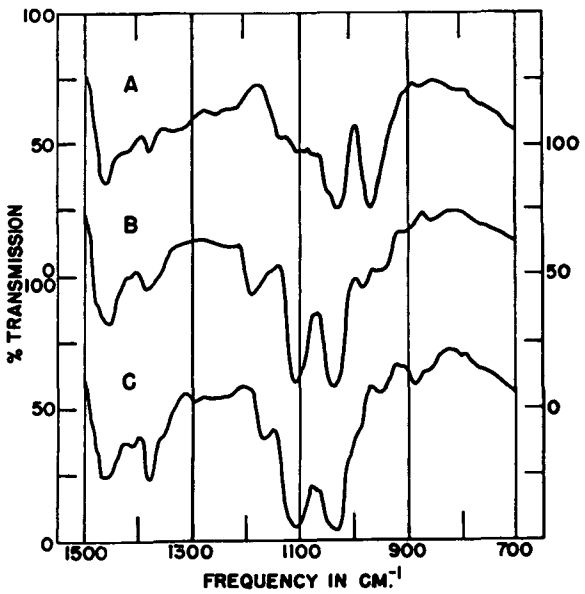

Figure 4. Infrared Spectra of Some Commercial Polyalcohols

A. 2-Methyl-1,3-pentanediol
B. 2-Methoxymethyl-2,4-dimethyl-1,5-pentanediol
C. 2-Ethoxymethyl-2,4-dimethyl-1,5-pentanediol

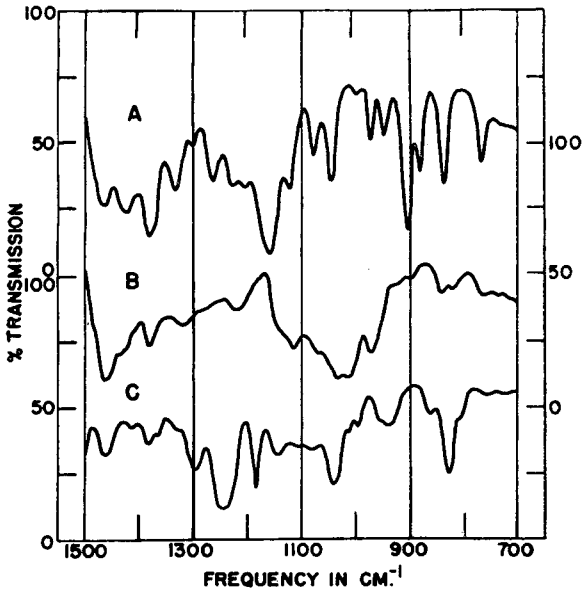

Figure 5. Infrared Spectra of Some Commercial Polyalcohols

A. 2-Methyl-2,4-pentanediol
B. 2-Ethyl-1,3-hexanediol (octylene glycol)
C. 2,2′-(Isopropylidene-bis-*p*-phenylenoxy)dipropanol

partition chromatography to the separation of polyhydric alcohols. Wurzschmitt (*14*) used two methods to analyze mixtures of ethylene glycol, diethylene glycol, and diethylene glycol monoethyl ether: Of these three, ethylene glycol alone reacts with alkaline copper sulfate to give a blue complex; the intensity of the color was used to estimate the quantity of the glycol and the others were determined indirectly from the density; diethylene glycol monoethyl ether is insoluble in 72.5% potassium hydroxide solution. Jaffe and Pinchas (*6*) have estimated dipentaerythritol in the presence of pentaerythritol by the infrared spectroscopy of the corresponding acetates in carbon tetrachloride solution.

The development of unsaturated polyesters during the past few years has demonstrated the great potential flexibility of these polymers, which are apparently restricted only by the available variety of acidic and alcoholic components. Perhaps as a result, the number of commercially available polyhydric alcohols has recently increased greatly. The analytical problems introduced by so many polyalcohols exhibiting such close structural relationship are virtually unsolvable by either chemical methods alone or by the limited approaches already cited. It was the opinion of the present investigators that infrared spectroscopy might be advantageously applied to this problem.

The application of infrared analysis to the identification of organic chemicals (*1, 11*) and specifically to monohydric alcohols in plasticizers (*4*), a problem similar to the one presented here, had been discussed earlier. No attempt is made in this paper to include the theory or fundamental methods involved in infrared analysis. The subsequent discussion is confined to the extent to which the method is successful as applied to the identification of polyhydric alcohols, and the limitations and difficulties encountered.

EXPERIMENTAL

Isolation of Alcohol Fraction. The unsaturated polyester as received is usually dissolved in an inert solvent or potential cross-linking agent. As a preliminary step, it is usually isolated from the solution by precipitation with a nonsolvent such as petroleum ether.

A 10-gram portion of the precipitated polyester is dissolved in a small volume of benzene or acetone and saponified with 250 ml. of an approximately 0.5*N* solution of potassium hydroxide in absolute alcohol.

The insoluble dipotassium salts are removed by filtration and the filtrate is made slightly acid with concentrated hydrochloric acid. The precipitated potassium chloride is removed by filtration and the filtrate is concentrated to approximately 5 ml. The concentrated solution is transferred to a separatory funnel, using 10 to 15 ml. of water, and then extracted with an equal volume of ether. The water layer is made slightly alkaline and then dried by evaporation, using anhydrous alcohol to assist the dehydration. The evaporation residue is extracted with alcohol, filtered, and the filtrate evaporated under a stream of dry air until the added alcohol is removed. The residue from this treatment represents the polyhydric alcohol fraction.

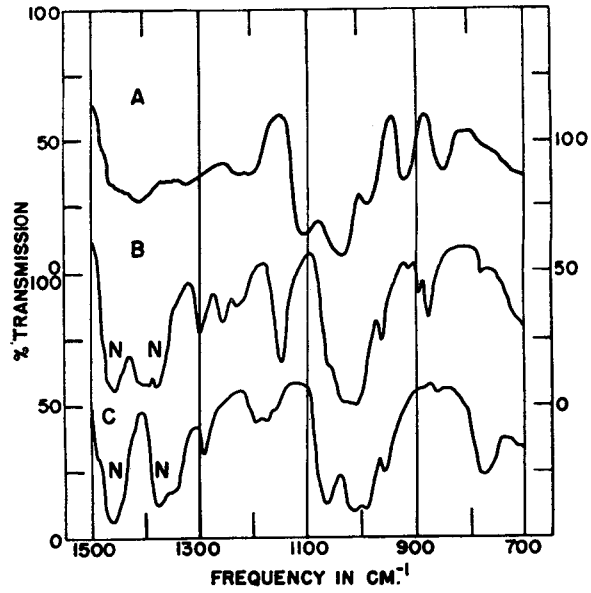

Figure 6. Infrared Spectra of Some Commercial Polyalcohols

A. Glycerol
B. Trimethylol ethane–Nujol
C. Trimethylol propane–Nujol

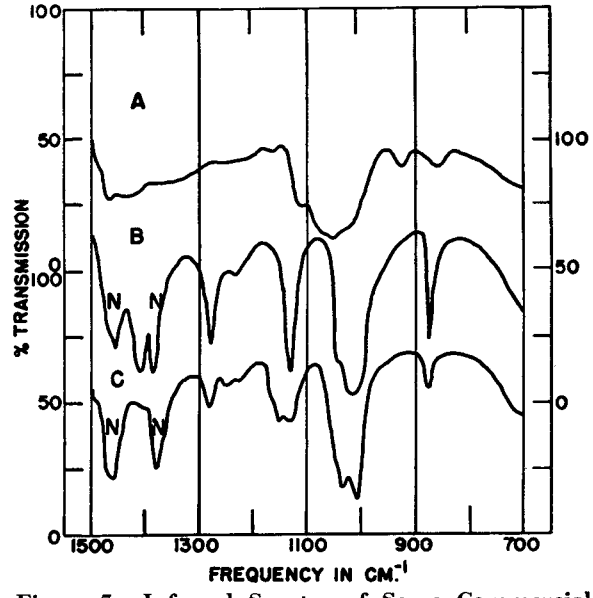

Figure 7. Infrared Spectra of Some Commercial Polyalcohols

A. 1,2,6-Hexanetriol
B. Pentaerythritol–Nujol
C. Dipentaerythritol–Nujol

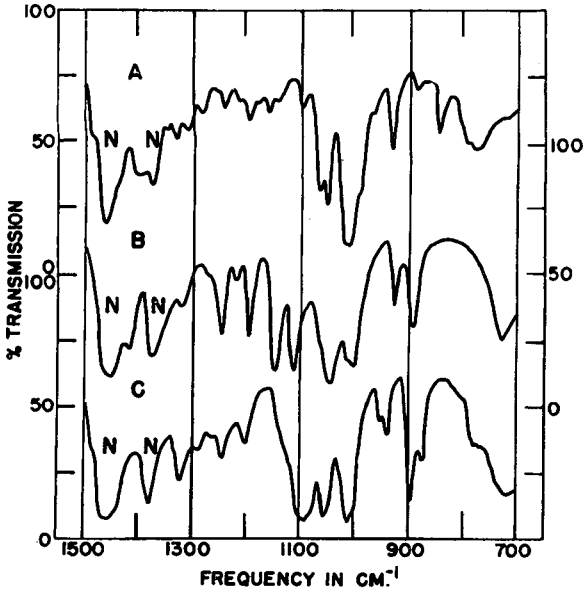

Figure 8. Infrared Spectra of Some Commercial Polyalcohols

A. Tetramethylol cyclohexanol-Nujol
B. Inositol-Nujol
C. Sorbitol-Nujol

Infrared Analysis of Polyhydric Alcohols. Comparison of the infrared spectrum of the separated fraction with the spectra of a selection of commercially available polyhydric alcohols usually permits the identification of the glycol or glycols present in the polyester.

The spectra shown in Figures 1 through 8 illustrate 24 commercial polyalcohols and hence represent a set of comparative standards. These data were obtained on a Perkin-Elmer spectrometer, Model 21, equipped with a sodium chloride prism. The liquid glycols were prepared by spreading a thin film between two rock salt plates and the solids were examined as Nujol mulls on rock salt plates. (Per cent transmission is shown, since spectra are not compensated for cell-window losses nor for Nujol when used.) Before examination, the samples were dried over a desiccant to prevent interference by more than 1 to 2% water.

The curves are presented approximately in order of increasing complexity of structure, with the dihydroxy compounds followed by the tri-, tetra-, penta-, and hexahydroxy alcohols. To conserve space, only the region from 650 to 1550 cm.$^{-1}$ is shown. A few other differences occur in the rest of the spectrum, but this region is the most characteristic for each glycol and the one used for identification purposes. The absorption contributed by Nujol is designated by *N*.

Resolution of Mixtures. The spectra shown in Figure 9 have been included to illustrate the problem presented by mixtures of the common glycols and the manner in which such an occurrence can usually be resolved. The bands are marked with symbols designating the glycol to which the absorption is totally or partially assigned. Ethylene glycol is represented by *E*, diethylene by *DE*, propylene by *P*, and dipropylene by *DP*. Curve *A* represents a mixture of ethylene and diethylene glycols. Inspection and comparison with the curves of the individual compounds (Figures 1*A* and 3*A*, respectively) show that all bands found in both glycols are present in this composite, and account for all absorption bands observed. A 1 to 1 mixture would approximate the observed intensities. Curve B, representing roughly a 1 to 1 mixture of propylene and dipropylene glycols (Figures 1*B* and 3*B*, respectively), shows a spectrum which is less easily resolved into its component absorptions. Since both compounds absorb at nearly the same frequencies in many cases, it is important that a sample thickness be used which shows both the intense and the less intense bands. The usual thickness is less than 10 microns.

Vertical comparison of curves *A* and *B* indicates that a mixture of ethylene and propylene glycols would present a less difficult problem than does the mixture of propylene and dipropylene glycols. The same is true of mixtures involving diethylene and dipropylene glycols.

DISCUSSION OF EXPERIMENTAL RESULTS

The identification of a single, unknown polyhydric alcohol after extraction from the resin, involves only a careful comparison of its infrared spectrum with the set of spectra of known standards. Providing the unknown is one whose spectrum is among the standards, identification is very simple and can usually be accomplished using only the region shown in the curves presented here. The C—O vibrations give the strongest absorption in this region, but since these often overlap from one compound to the next, the lower, weaker bands (below 1000 cm.$^{-1}$) of other single bond vibrations are extremely useful in complete identification.

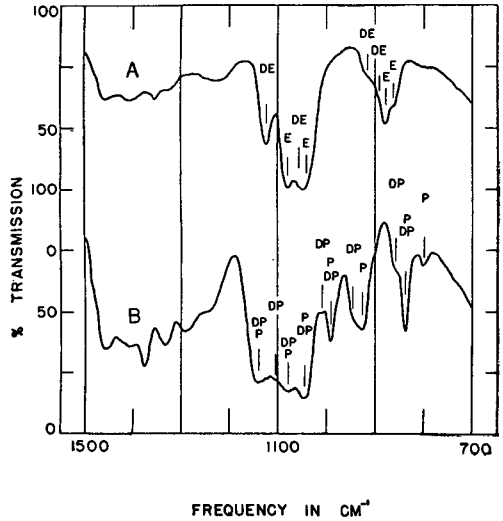

Figure 9. Infrared Spectra of Some Glycol Mixtures

E. Ethylene glycol
DE. Diethylene glycol
P. Propylene glycol
DP. Dipropylene glycol

The infrared spectrum of a mixture of two or more polyhydric alcohols, which do not interact, shows all the absorption bands of each component. This makes possible the identification of certain mixtures, although there are definite limitations to the success of this method. Fourteen mixtures of the more common polyhydric alcohols, in different ratios and different combinations, were examined in the course of this investigation.

Identification of a mixture of two liquid glycols, in ratios of 1 to 1, 2 to 1, and 3 to 1, was found possible and almost always successful. Even combinations of polyhydric alcohols which are closely related structurally could be identified. Propylene and ethylene, dipropylene and diethylene glycols, ethylene glycol, and glycerol were among the mixtures which were identified. The only difficulty encountered was that of regulating the thickness of the sample. It must be thick enough for detection of a small amount of a glycol in the presence of another and not so thick as to cause blanking out or destruction of the well-defined contour of strong absorption bands. Often the shape of a band or the relative intensity of one band to another was the means of detecting and identifying a mixture.

Once a mixture has been identified, the proportions of the com-

ponents may be roughly estimated by comparison with similar mixtures of known composition. In some cases, where each component has some unique absorption without interference from the other, a rough quantitative analysis may be made on the basis of the spectra of pure samples of the components involved.

Mixtures of a solid and a liquid glycol were more difficult to detect. Often the solid did not appear to have dissolved, and so little of it was suspended in the liquid that it probably only scattered light and gave no characteristic absorption of its own. Only the liquid was identified in these cases. In other mixtures, such as that of ethylene glycol and sorbitol, it was sometimes possible to detect a shoulder on the side of a band, indicating the presence of at least one other component mixed with the liquid glycol. However, this was insufficient evidence for complete identification. Probably solvent fractionation means will have to be used to separate solid and liquid glycols, with infrared analysis then being applied to the separate fractions.

Several mixtures of three glycols (in 1 to 1 ratio) were examined. In one case all three were identified (ethylene, diethylene, and triethylene glycols), but as a general rule the evidence is usually inadequate for distinguishing three glycols in a mixture. Unless one of them is particularly unique—e.g., aromatic—and absorbs characteristically without interference from the other two, infrared analysis is not successful in complete identification of most mixtures of more than two polyhydric alcohols.

CONCLUSIONS

Polyhydric alcohols can be readily isolated from unsaturated polyester resins.

The components of the separated alcohol fraction can usually be identified by infrared spectral analysis, using the spectra of dried commercial polyalcohols for comparison.

The infrared method is effective for individual glycols and for mixtures of two liquid glycols, with the components present over a reasonably wide range. Mixtures of a liquid and a solid glycol require further fractionation prior to identification.

The infrared identification of the components of ternary mixtures is only possible in special cases.

ACKNOWLEDGMENT

The contribution of Martha M. Taylor in preparing the illustrative spectra for publication is gratefully acknowledged.

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Identification of Dicarboxylic Acids in Polymeric Esters

Preparation and Properties of Diethyl Esters and Potassium Salts

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The diethyl esters of eight selected dicarboxylic acids were prepared and purified. Various physical properties were determined on the purified products; the potential applicability of these properties to the analysis of mixtures of esters was evaluated. The resolution of mixtures was found possible by the application of distillation and/or ultraviolet and infrared spectroscopy. The dipotassium salts were prepared from the diethyl esters, and the Kappelmeier procedure was evaluated in the process. As characteristic derivatives, the salts were found to be less applicable to the identification of the acids than were the esters.

THE increasing variety of acidic components used in the formulation of polymeric esters has introduced analytical complications which seriously qualify the previously reliable procedures used in the investigation of these commercially important resins. In recognition of the need for modified and/or new analytical procedures for this purpose, a series of investigations was carried out in this laboratory.

Attention was concentrated on the dicarboxylic acids, as represented by eight commercially important compounds. As the initial result of this work, a method employing the infrared spectra of the *N*-benzylamides was proposed (*16*) for the identification of these acids as they occurred in commercial polyesters; the method was based on data obtained during one phase of the broader investigation. In the present paper, data derived from alternative lines of study, performed concurrently on the same eight acids, are reported and discussed.

Originating in 1935, the first reported methods (*3, 5, 8, 9, 11*) for the analysis of alkyd resins were naturally aimed at the determination of phthalic acid. Perhaps the simplest and most reliable of these earlier procedures is that devised by Kappelmeier who subsequently discussed his technique, perfected for the resins commercially available at the time, in some detail (*10*). The method is based on the quantitative precipitation, under controlled conditions, of dipotassium phthalate monoalcoholate during saponification of the polyester with potassium hydroxide dissolved in absolute alcohol. Although primarily

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designed to effect the quantitative estimation of phthalic acid, this procedure possesses the additional advantage that in separating the alcohol-insoluble salt from the soluble monocarboxylic acid salts and other modifiers, it also permits the quantitative separation and estimation of the latter. As a quantitative method for phthalic acid the procedure, in modified form, comprises the American Society for Testing Materials (*1*) (ASTM) standard method of test.

The Kappelmeier procedure suffers from the disadvantage, recognized in the ASTM directions, that the salts of many other dicarboxylic acids are completely or partially insoluble in absolute ethanol under the experimental conditions. As the variety of polycarboxylic acids used in polyester formulation increased, this interference assumed serious proportions. Stafford and Williams (*17*) have suggested a qualitative optical method for the resolution of the Kappelmeier salts of simple mixtures of acids.

In more recent attempts to broaden the scope of the procedure, Swann (*20*) has proposed a method, primarily chemical in nature, which is designed to permit the quantitative estimation of a number of pertinent dicarboxylic acids. Shreve and Heether (*15*) have suggested that the percentage of phthalic acid present in a polyester can be determined by the analysis of the ultraviolet spectrum of the mixture of acids separated as salts by the saponification procedure. The quantitative detection is based on the absorption maximum occurring at 2760 A., and the spectrum of potassium acid phthalate is used as standard. Interferences at this wave length by other aromatic acids and by maleic and fumaric acids are taken into consideration. Both of these approaches, as applied to phthalic acid, have been subjected to collaborative testing by ASTM Subcommittee XI, Committee D-1, and have been accepted by the society as tentative revisions for the standard method (*1*).

Investigators in allied fields have reported on techniques potentially applicable to the current problem. According to Mathews, Warren, and Michel (*14*), their previously reported work on the identification of acids by the x-ray powder diffraction patterns of the corresponding anilides has been extended to include the silver salts and the amides, with the salts preferred because of pattern differentiation and ease of presentation. Castle (*4*) has used the correlation between the index of refraction and the melting point to estimate the probable composition in a homologous series such as that represented by the oxalic-sebacic group of saturated dibasic acids. Marvel has suggested the separation of polybasic acids by fractional extraction (*13*) and partition chromatography (*12*).

Stark, Goodban, and Owens (*18*) have reported on the chromatographic separation of a number of dicarboxylic acids on ascending columns. Most recently, Higuchi, Hill, and Corcoran (*6*), working on the chromatographic separation of the C_4—C_{10} dicarboxylic acids, resolve mixtures of the saturated, straight-chain acids on a partition column using pH 5.4 citrate buffer as the internal phase for the separation of acids above adipic, and water for the separation of acids below adipic.

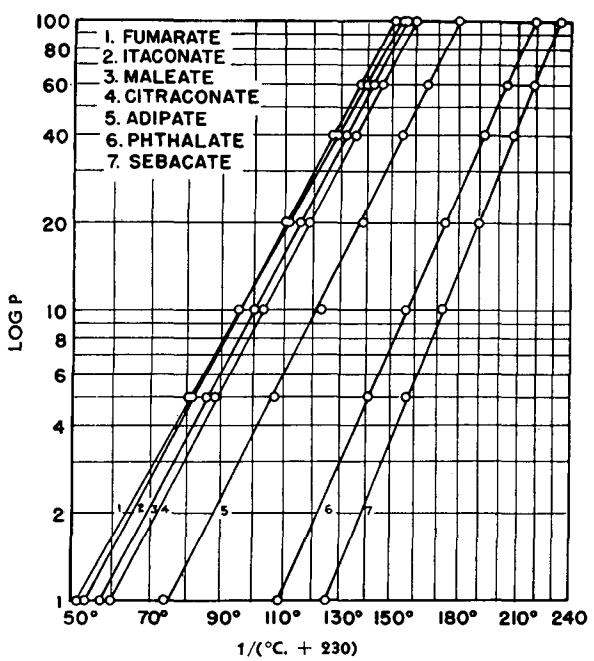
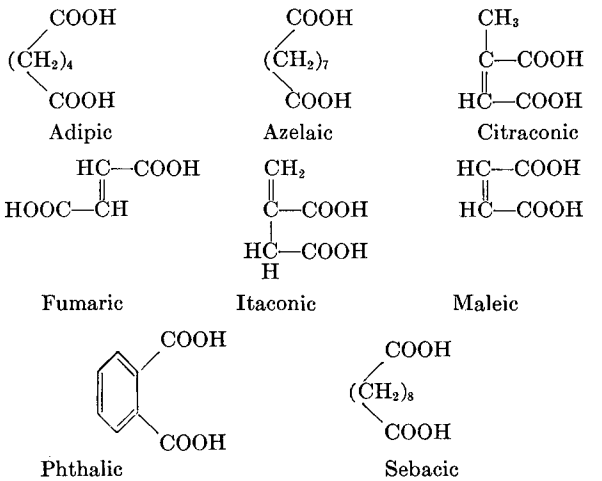


Figure 1. Plot of Stull Vapor Pressure Data

PREPARATION AND PROPERTIES OF DIETHYL ESTERS

As in the earlier study (*16*), eight acids were chosen:



Approximately 1 kg. of the diethyl ester of each of the above acids was prepared and then purified by vacuum fractionation. The usual physical properties were determined on the fractionated esters and are reported together with presumably more accurate comparative data from the literature. The purpose of this itemized treatment is to illustrate the extent to which this set of compounds qualifies as standards for the direct application of infrared and ultraviolet spectral representation and for the evaluation of the Kappelmeier procedure, and as parent compounds for the preparation of derivatives such as the salts and the *N*-benzylamides.

Table I. Vapor Pressure Data of Esters at 50 Mm.

Ester	Temperature, ° C. Observed	Corrected[a]
Fumarate	129.5	131
Itaconate	133.5	137
Maleate	135	139
Citraconate	139.5	143.5
Adipate	156.5	161.5
Azelate	183	189.5
Phthalate	192	200
Sebacate	205	213.5

[a] Corrected to nearest 0.5° for emergent stem.

Preparation. A Fischer-type esterification, using the azeotropic method of Young (*21*) was employed. The reactions were carried out in a 3-liter single-necked flask containing Berl saddles to prevent bumping, and equipped with a 28-inch jacketed column of 1-inch diameter, packed with Berl saddles. The column was connected to a Dean-Stark moisture distillation trap of 50-ml. capacity, fitted with a draining stopcock and a water-cooled condenser.

The technical grade acids used were recrystallized once from water. To an amount of acid calculated to yield approximately 1 kg. of the diethyl ester were added a 100% molar excess of ethanol, 300 ml. of benzene, and 10 grams of toluenesulfonic acid monohydrate as catalyst. Removal of the water of condensation required 20 to 30 hours. The column was then heated,

and the excess ethanol and benzene were stripped off to give a yield of crude ester in excess of 95% in each case. Since the crude esters were practically neutral, with determined acid values of 5 or less, it was not considered necessary to preface distillation with an alkaline wash.

Distillation Procedure and Data. Distillation was carried out in a vacuum fractionation apparatus of conventional design. The apparatus was balanced under total reflux until equilibrium had been reached, and the constant-boiling distillate was removed at 50-mm. pressure. The azelate and sebacate esters foamed so strongly at 50 mm. that after recording the data at this pressure, it was necessary to distill the bulk of these esters at 15 mm. The vapor pressure data are listed in Table I.

Diethyl itaconate polymerized during vacuum distillation, resulting in a reduced yield of monomeric ester. The yields of the other once-distilled esters were in excess of 90%.

From the data collected by Stull (*19*), which were published subsequent to the above experiments, the data in Table II were taken for comparison. No data were listed for diethyl azelate. The data (Table II) were plotted on a Cox chart to give the curves reproduced in Figure 1. The vapor pressures at 50 mm. were taken from the curves for comparison with those determined on the esters. The results are listed in Table III.

Table II. Literature Vapor Pressure Data at Reduced Pressures

	Temperature, ° C.						
Ester	1 mm.	5 mm.	10 mm.	20 mm.	40 mm.	60 mm.	100 mm.
Fumarate	53.2	81.2	95.3	110.2	126.7	137.7	151.1
Itaconate	51.3	80.2	95.2	111.0	128.2	139.9	154.3
Maleate	57.3	85.6	100.0	115.3	131.8	142.4	156.0
Citraconate	59.8	88.3	103.0	118.2	135.7	146.2	160.0
Adipate	74.0	106.6	123.0	138.3	154.6	165.8	179.0
Phthalate	108.8	140.7	156.0	173.6	192.1	204.1	219.5
Sebacate	125.3	156.2	172.1	189.8	207.5	218.4	234.4

Table III. Determined *vs.* Calculated Vapor Pressure Data at 50-Mm. Pressure

	Temperature, ° C.	
Ester	Determined	Calculated
Fumarate	131	132.5
Itaconate	137	135
Maleate	139	137.5
Citraconate	143.5	141.5
Adipate	161.5	160.5
Azelate	189.5	Not listed
Phthalate	200	199
Sebacate	213.5	214.5

Saponification Results. Before saponification values were determined, the esters were redistilled at 25 mm., and the refractive indices before and after distillation were found to agree. The itaconate and citraconate esters were not redistilled because of the partial polymerization of the former during the first fractionation. Preliminary acid value determinations indicated that the twice-distilled esters were neutral to a phenolphthalein end point, whereas the once-distilled itaconate and citraconate showed some slight acidity. This was removed by passing the esters through a column packed with three layers of absorbent, comprising a bottom layer of Hi-Flow Super-Cel diatomaceous earth (Johns-Manville Co.), a middle layer of an aqueous paste of sodium bicarbonate plus the Hi-Flow absorbent, and a top layer of the Hi-Flow absorbent. Two passes through the column yielded neutral esters, the infrared spectra of which showed the presence of 1 to 2% water. The latter was removed by drying in a vacuum desiccator over calcium hydride.

Samples comprising 1.5 to 2.5 grams of neutral ester were weighed into 250-ml. flasks from a Lunge pipet, and 10 ml. of benzene were added to each flask. Alcoholic potassium hydroxide (about 0.5*N*) was next added in at least 100% excess over the amount theoretically required to saponify the ester. A pair of blanks were run in each experiment. The solutions were refluxed under air condensers for 2 hours on a water bath. After washing down the apparatus and cooling, the solutions were back-titrated to a phenolphthalein end point with 0.5*N* hydrochloric acid run in from a 100-ml. buret calibrated by the National Bureau of Standards. The results are listed in Table IV.

Table IV. Saponification Values of Prepared Esters

Ester	Determined	Average[a]	Theory
Fumarate	652.5 652.2	652	652.3
Maleate	652.3 651.4	652	652.3
Citraconate	603.5 602.7	603	603.2
Itaconate	602.7 603.2	603	603.2
Adipate	554.5 555.3	555	555
Phthalate	505.3 504.5	505	505.4
Azelate	457.0 456.4	457	459.8
Sebacate	433.2 433.4	433	434.9

[a] Averaged to nearest integer; results reproducible to nearest ±1.

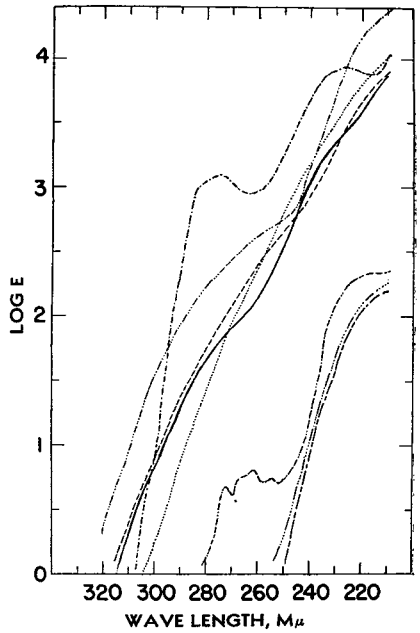


Figure 2. Ultraviolet Absorption Spectra of Diethyl Esters

Other Physical Properties. Refractive Indices and Densities of the esters were determined at 20° ± 0.05°, using an Abbe refractometer for the former and a 5-ml. pycnometer for the latter. Comparative data were taken from Huntress and Mulliken (*7*). The results are listed in Table V.

Ultraviolet Spectra of the esters are reproduced in Figure 2. The data on which the plots are based were obtained by use of a Beckman quartz photoelectric spectrophotometer, Model

Table V. Refractive Indices and Densities of Esters

	Refractive Indices, n_{20}^{D}		Densities, d^{20}	
Ester	Determined	Reported	Determined	Reported
Adipate	1.4275	1.42765	1.007	1.0090
Azelate	1.4351	1.43509	0.972	0.97294
Citraconate	1.4449	1.4442	1.048	1.0491
Fumarate	1.4408	1.44103[a]	1.052	1.05189[b]
Itaconate	1.4408	1.4377	1.045	1.0467
Maleate	1.4413	1.44156[c]	1.064	1.06740
Phthalate	1.5019	1.5019	1.119	1.1175
Sebacate	1.4368	1.43657	0.963	0.9631

[a] 20.1° C.
[b] 20.6° C.
[c] 19.9° C.

DUV, equipped with a Nester water-cooled hydrogen lamp. Fused quartz absorption cells of 5- and 10-mm. light path length were used, as well as adjustable Hilger micrometer Baly cells, variable from 5.00 to 0.01 mm. in length. Redistilled 95% ethanol was employed as solvent as used in the comparison or blank cells.

Beer's law was used in the form:

$$\log P_0/P = A = abc = \frac{\epsilon}{M} bc$$

where P_0 and P are the intensities of the incident and transmitted light, respectively. A is the absorbance (optical density), a is the absorptivity (specific extinction), ϵ is the molar absorptivity (molar extinction), M is the molecular (formula) weight, b is the cell light path length in millimeters, and c is the concentration in grams per 100 ml. The spectra are plotted as the common logarithm of the molar absorptivity *vs.* wave length in Angstroms, which procedure keeps the curve shape independent of concentration.

INFRARED SPECTRA of the esters are reproduced in Figures 3 to 5. The spectra shown were obtained on the esters contained in a cell of 0.01-mm. thickness, using a Perkin-Elmer infrared spectrometer Model 12A. The instrument was equipped with a sodium chloride prism and had been converted to a percentage transmittance spectrophotometer. To conserve space, only the region from 1800 to 700 cm.$^{-1}$ is shown.

DISCUSSION OF EXPERIMENTAL RESULTS

The distillation data led to four conclusions:

Within the limitations of the method, the prepared esters appeared to be sufficiently pure to serve as standards.

The vapor pressures of the unsaturated esters are not sufficiently separated to permit fractionation with the usual laboratory apparatus.

There is sufficient difference between the vapor pressure of the citraconate and the adipate to permit the separation of the unsaturated esters as a group from the saturated esters as a group, assuming 50 to 100 ml. are available for a Podbielniak distillation.

There is sufficient separation among the vapor pressures of the esters of the saturated group to permit further fractionation, assuming each ester is present in an amount exceeding the hold-up of the column employed.

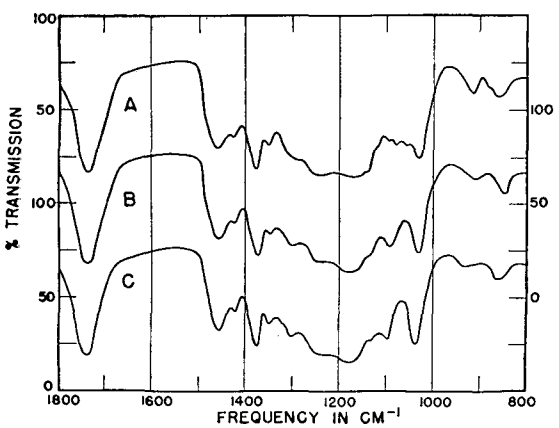


Figure 3. Infrared Spectra of Esters

A. Diethyl adipate
B. Diethyl azelate
C. Diethyl sebacate

The saponification data confirmed the indication of purity by the inherently less accurate and precise distillation data.

The refractive index and density data supplied further confirmation of purity. The high refractive index of the itaconate ester is probably caused by the presence of polymer. Beilstein has pointed out (*2*) that this ester polymerizes during distillation and that this polymerization is characteristic of the pure ester. Since Beilstein reports $n_{20}^{D} = 1.48933$ for the polymer, as little as 5% would be sufficient to cause the increase observed. It is possible that the slightly high value for the citraconate may be similarly explained.

In the ultraviolet spectra both the wave-length positions and intensities fell in the regions expected from the chromophoric groupings of the compounds. This, plus the virtual absence of absorption in the weakly absorbing compounds, furnished additional proof of purity except for a discrepancy noted below. In Figure 2, the curve of the phthalate ester is noticeably different from the others, with a definite maximum near 2750 A. This band is attributed to an electronic transition related to the phenomenon which gives rise to the familar absorption spectrum of benzene—that is, it is associated with the benzene ring.

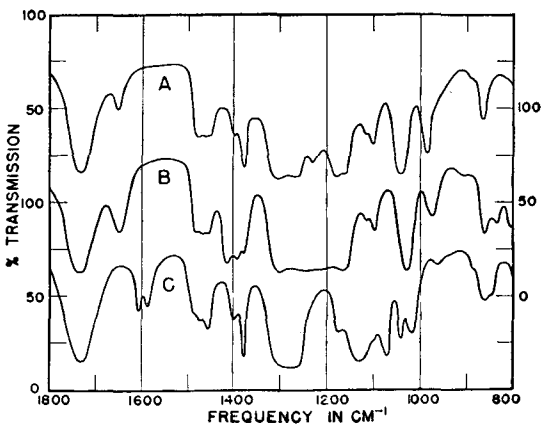


Figure 4. Infrared Spectra of Esters

A. Diethyl fumarate
B. Diethyl maleate
C. Diethyl phthalate

The strong absorption shown by the fumarate, maleate, itaconate, and citraconate esters is attributed to the conjugated carbon and oxygen systems present. The spectra of the maleate and the citraconate esters are, as expected, very similar, since the two structures differ only by a methyl group. The increased intensity of the fumarate spectrum is attributed to the trans configuration as compared to the cis. The close resemblance between the citraconate and itaconate spectra seems surprising, for the itaconate might be expected to absorb at shorter wave lengths because of the shorter formal conjugated resonating system present. This similarity may be due to geometrical effects.

The spectra of the adipate, azelate, and sebacate esters show the expected weak absorption at short wave lengths, because of the lack of conjugation. The series of sharp bands in the azelate spectrum is due to the presence of a small amount of impurity. The concentration of this impurity may be estimated from the band intensities as 0.08% if an aromatic or 0.02% if a triconjugated double bond fatty acid.

The infrared spectrum of each of the esters exhibits the characteristic ester carbonyl absorption at about 1735 cm.$^{-1}$. The absorption at about 1645 cm.$^{-1}$ in the unsaturated esters is associated with the C=C group. The spectrum of diethyl phthalate includes in addition the characteristic absorption of an ortho disubstituted phenyl ring, including bands at 1600, 1580, and 745 cm.$^{-1}$.

Although the spectra of the azelate and the sebacate show such minor differences that it would be difficult to distinguish between these esters when present in mixtures, the spectra of the esters in general are otherwise distinctive, and could be used for identification purposes even in mixtures containing as many as three of these esters. This characteristic absorption can be used to advantage by prefacing the spectral analysis with a fractional distillation of a given mixture to separate the lower boiling unsaturated group from the higher boiling saturated group. Since the presence of more than two acids from each group would

be a rare occurrence in a commercial polyester, spectral analysis of the low and high boiling fractions should permit the identification of the components, respectively, therein.

PREPARATION AND PROPERTIES OF DIPOTASSIUM SALTS

Preparation. The Kappelmeier procedure, comprising the saponification of a dicarboxylic acid ester with an approximately 0.5*N* solution of potassium hydroxide in absolute alcohol under such conditions that the dibasic acid separates as an insoluble salt, was designed for the quantitative estimation of phthalic acid. Since experience has demonstrated that many other dicarboxylic acids yield insoluble potassium salts under the conditions of the experiment, the preparation of the salts was also utilized as a means of investigating the quantitative aspects of the reaction.

Evaluation of Kappelmeier Procedure. As now recommended, the salient features of the Kappelmeier procedure are itemized by the American Society for Testing Materials (*1*). This was followed precisely on the eight esters under investigation. The quantitative data on duplicate experiments are listed and compared with theory in Table VI.

Table VI. Determination of Acid

Ester	Salt, %	Average	Factor	Acid, %	Theory	Detd./ Theory
Fumarate	111.18 111.56	111.37	0.6042	67.29	67.44	99.79
Maleate	124.52 125.84	125.18	0.6042	75.63	67.44	112.14
Citraconate	Indeterminate	...	0.6311	...	69.89	...
Itaconate	Indeterminate	...	0.6311	...	69.89	...
Adipate	112.41 113.52	112.97	0.6577	74.32	72.28	102.8
Phthalate	130.83 131.06	130.95	0.5764[a]	75.48	74.77	100.9
Azelate	Indeterminate	...	0.7121	...	77.05	...
Sebacate	109.45 109.67	109.56	0.7266	79.61	78.29	101.69
Maleic acid	166.37 166.25	166.31	0.6042	100.48	100.00	100.48

[a] Based on monoalcoholate.

Infrared Spectra of Potassium Salts. The various potassium salts, obtained as described above, were examined by infrared spectral methods, using the instrumentation previously described. In this instance, the samples, being solids, were examined in the form of Nujol mulls. As gravimetric reproducibility in the preparation of the salts was not obtained in all cases, and, even when obtained, yielded anomalous data in one instance, it was decided that these salts could not be generally considered as standards for comparison. Reproductions of the spectra are hence omitted at this time.

DISCUSSION OF EXPERIMENTAL RESULTS

The ASTM data led to several conclusions:

The method is satisfactory as now constituted for phthalate, fumarate, sebacate, and adipate, although it was necessary to dry the adipate salt for an additional 4 hours to bring it to constant weight.

The maleate consistently yielded a high result.

The citraconate and itaconate salts were characterized by marked postprecipitation during filtration; the data were hence not quantitative. The salts obtained were sufficiently well crystallized, however, to permit fairly rapid filtration and washing. This suggested that quantitative results may be possible if the procedure were modified.

The azelate was gelatinous and almost impossible to filter. It separated only after the addition of the ether to the saponification solution.

In view of the results, it is apparent that the ASTM method (*1*) is not generally applicable as a quantitative procedure, although it may be so used with certain combinations of acids that have been identified prior to attempting quantitative work.

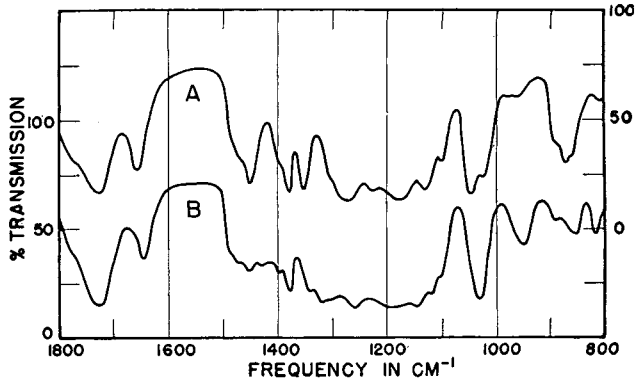


Figure 5. Infrared Spectra of Esters

A. **Diethyl citraconate**
B. **Diethyl itaconate**

The maleate salt, being apparently unique, was investigated further in an attempt to account for the consistently high results obtained. With the exception of the phthalate, which is known to crystallize with one molecule of ethanol per molecule of dipotassium salt, the factors for the conversion of percentage salt to percentage acid were calculated on the basis of the ethanol-free salt. When so calculated, the maleate yielded results about 112% of theory. If potassium maleate crystallized with one molecule of ethanol, the determined percentage acid, calculated with the factor used above, would represent 123.95% of theory. If it were the hemi alcoholate which crystallized, the determined percentage acid would be 111.98% of theory, compared with 112.14% found.

To check this indication, the infrared spectrum of a mull of the maleate salt in perfluokerosene was analyzed. In addition to the expected bands, CH_3, CH_2, and OH absorptions were observed. It is strongly suggested that dipotassium maleate, as prepared from the diethyl ester, contains alcohol of crystallization. This indication was interesting, in view of the fact that the salt prepared directly from maleic acid under the same experimental conditions was in good agreement with theory, and showed no evidence of ethanol in its infrared spectrum. It would therefore appear that the presence of ethanol of crystallization requires the ethyl ester as the starting compound.

Analysis of the infrared spectra of the salts led to the following conclusions:

The various spectra were sufficiently characteristic to permit identification of the individual acids.

Most pairs of salts could be readily identified. Exceptions to this were itaconate plus citraconate, and azelate plus any of the others.

Mixtures including three or more components could be identified only with the greatest difficulty.

In addition to the phthalate and maleate, the itaconate and citraconate salts both apparently contained alcohol of crystallization, judging from the strong hydroxyl absorption evident in their spectra. A method for the quantitative separation of these salts will have to be devised before this indication can be investigated further.

The azelate showed a paucity of characteristic bands.

CONCLUSIONS

Both the diethyl esters and the dipotassium salts are characteristic derivatives which permit the identification of individual dicarboxylic acids. The infrared and/or ultraviolet spectra are the most determinative properties of these derivatives.

When mixtures of acids are involved, the esters permit more effective resolution than do the salts. Neither derivative is as determinative as is the *N*-benzylamide, the application of which has been reported (*16*).

The Kappelmeier procedure for phthalic acid, as represented

by the ASTM standard method (*1*), is not generally applicable as a quantitative method, although it may be so used with certain combinations of acids which have been identified prior to attempting quantitative work.

ACKNOWLEDGMENT

The ultraviolet spectral data herein reported were determined and interpreted by R. C. Hirt. His advice and cooperation are gratefully acknowledged.

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Determination of Triphosphate and Pyrophosphate by Isotope Dilution

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Prior to the present study there has been no solution method capable of determining total triphosphate in the presence of ortho-, pyro-, and trimetaphosphates. Since tracer studies have shown that either triphosphate as $Na_5P_3O_{10}$ or pyrophosphate as $Na_4P_2O_7$ can be adequately purified by three to five crystallizations from water–ethyl alcohol mixtures at room temperatures, both tri- and pyrophosphates can be determined by isotope dilution. No systematic bias is detected in the analysis for pyrophosphate. That observed for triphosphate did not exceed +2% absolute and can be made negligible by suitable correction. Based on replicate determinations the standard deviation is 1.5% absolute for $Na_5P_3O_{10}$ and 1.0% absolute for $Na_4P_2O_7$. The time required for each determination on a sample is 2 to 4 man-hours. The time elapsing before the result becomes available is 1 to 3 days. Since inorganic salts —e.g., sulfate and silicate—and anionic detergents do not interfere with the purification of tri- or of pyrophosphate, the method is applicable to triphosphated detergents as well as to commercial triphosphate.

SOLUTION methods available for the determination of sodium triphosphate and sodium pyrophosphate in mixtures of the two involve precipitation of the two phosphate ions by zinc (*1–3, 8*). In case A (*1–3*) the conditions are arranged so that pyrophosphate is determined by precipitation and triphosphate by titration of released acidity, after correction for the acidity released by pyrophosphate. In case B (*8*) conditions are adjusted so that both pyro- and triphosphate precipitate quantitatively (the latter as $NaZn_2P_3O_{10}$). Analysis of the precipitate for zinc and phosphorus allows calculation of the pyro- and triphosphate content, provided that no other phosphate species are present in the precipitate. Both methods are therefore indirect and, in addition, suffer interferences if higher polyphosphates are present. Thus, in A higher polyphosphates contribute to the titration and in B some of the higher polyphosphates precipitate, especially those just above triphosphate (*10*).

The x-ray method reported recently (*5*) is specific for these species, but requires the sample to be in solid form; it will give the total tri- or pyrophosphate only when both species are present wholly in crystalline form. Furthermore, interference results from the presence of any crystalline ingredient with diffraction lines at the same position as those phosphate lines used for analysis.

Thus, there is a need for a method which is specific for the individual phosphate (pyro- or tri-), which suffers no interference from other soluble phosphates, and which gives the total amount of each species, regardless of physical state of the sample. The present method meets these requirements, and, in addition, suffers no difficulties if sodium sulfate, sodium silicate, and anionic detergents are also present. It is therefore applicable to commercial detergents containing pyro- and triphosphate as well as to commercial sodium tripolyphosphate.

PRINCIPLE OF METHOD

Since the isotope dilution technique does not require full recovery of the species being determined, but merely isolation of some of that species in essentially pure form, ordinary fractional recrystallization procedures found effective in purifying sodium tri- and pyrophosphates have been used for said isolation. To avoid heating or lengthy evaporations, the phosphate species is recovered from a fairly concentrated aqueous solution by adding ethanol to induce precipitation at 25° to 35° C.

To express the principle of the method in quantitative terms, imagine that a mg. of tagged triphosphate of specific activity, S_o, is diluted by b mg. of inactive triphosphate in the sample to be analyzed for sodium triphosphate. The specific activity, S, of the pure triphosphate isolated from the mixture is related to the other quantities by the equation:

$$b = a(S_o/S - 1) = a(Z - 1) \quad (1)$$

When, as is explained later, it often proves necessary to add *also* c mg. of pure inactive triphosphate in order to permit isolation of a pure sodium triphosphate from the system, the equation for calculating the desired quantity b becomes:

$$b = a(Z - 1) - c \qquad (2)$$

Since it is usual to make $Z>>1$, this equation is ordinarily used in the simpler form $b = aZ - c$.

REAGENTS

Triphosphate. In the sodium oxide–phosphorus pentoxide system, sodium triphosphate can be made only by a solid state reaction as shown by the phase diagram (*7*). Tagged triphosphate was prepared by fusing 0.02 mole of NaH_2PO_4, 0.04 mole of Na_2HPO_4, and a negligible weight of $H_3P^{32}O_4$ containing 10 millicuries of phosphorus-32 in a platinum crucible. The melt was held at 900° C. for 2 hours to ensure equilibration of the P^{32} atoms and then was quenched rapidly (10 seconds) to a clear phosphate glass, thus giving an intimate mixture of triphosphate composition. Solid state reaction, induced by holding this glass at 400° C. for 18 hours, yields a crude triphosphate of 96 to 98% purity by inverse isotope dilution, the net result of both heatings being $NaH_2PO_4 + 2Na_2HPO_4 \rightarrow Na_5P_3O_{10} + 2H_2O$. This crude tagged triphosphate was purified by four to six fractional crystallizations from water as the hexahydrate ($Na_5P_3O_{10}.6H_2O$) and air-dried prior to use. The ignition loss at 400° C. for eight different batches of purified hexahydrate ranged from 22.67 to 22.95 (mean 22.78%), theory being 22.71%. X-ray diffraction patterns were identical to those for known triphosphate. About 10^{-8} fraction of the phosphorus atoms were initially phosphorus-32. Close shielding and handling by means of tongs was practiced during preparation and purification of the tracer phosphates in order to limit the radiation dosage to tolerance levels.

Pure inactive sodium triphosphate was made from commercial tripolyphosphate (85 to 95% purity) by a similar recrystallization process.

Pyrophosphate. Sodium pyrophosphate was prepared by adding a 10-mc. "weightless" amount of $H_3P^{32}O_4$ to a Na_2HPO_4 solution, evaporating to dryness, then heating at 400° C. for 2 hours. The reaction $2Na_2HP^{32}O_7 \rightarrow Na_4P_2{}^{32}O_7 + H_2O$ gives a product of more than 99% purity as determined by inverse isotope dilution analysis; a single recrystallization makes its purity at least 99.8% based on purification curves of the type shown in Figure 4. X-ray patterns of the crude $Na_4P_2{}^{32}O_7$ were identical to those of highly purified $Na_4P_2O_7$. All pyrophosphates were ignited to the anhydrous state prior to use, for the decahydrate may lose water at room temperature.

The pure inactive pyrophosphate was reagent grade $Na_4P_2O_7.10H_2O$ or this material once recrystallized.

Trimetaphosphate. Sodium trimetaphosphate ($Na_3P_3{}^{32}O_9$) was prepared by fusing NaH_2PO_4 with a negligible weight of $H_3P^{32}O_4$, quenching to a glass, and then tempering at 535° to 545° C. for 18 hours. The net reaction is $3NaH_2P^{32}O_4 \rightarrow Na_3P_3{}^{32}O_9 + 3H_2O$. The crude product was purified by several recrystallizations from water at 50° to 60° C. Identity was then confirmed by an x-ray pattern. Qualitative tests with silver and barium ions indicated the absence of ortho-, pyro-, and triphosphate.

Orthophosphate. A water solution of $Na_2HP^{32}O_4$, made by dissolving Na_2HPO_4 and a negligible amount of $H_3P^{32}O_4$, was used directly. Untagged C.P. Na_2HPO_4 was also used directly.

Sodium Sulfate. $Na_2S^{35}O_4$ was made by mixing a "weightless" 10-mc. amount of $H_2S^{35}O_4$ with a C.P. sodium sulfate solution, then recovering the $Na_2S^{35}O_4$.

The Quadrafos and anionic detergents were of commercial purity.

The P^{32} and S^{35} in the form of $H_3P^{32}O_4$ and $H_2S^{35}O_4$ solutions were obtained as processed isotopes from the U. S. Atomic Energy Commission, Isotopes Division, Oak Ridge, Tenn.

METHOD

Isolation of Pure Triphosphate. A known small weight (milligrams) of tagged pure triphosphate and a larger amount, usually 5 to 10 grams, of the sample are dissolved in water at room temperature, using 8 ml. of water for each gram of phosphate. In the early work, the practice was to use 8 ml. of water to each gram of anhydrous phosphate; later this was changed to 8 ml. of water per gram of damp hydrate crystals, with a practically negligible decrease in yield of precipitate. Ethyl alcohol is added dropwise at a rate of about 0.5 to 1 ml. per minute until the ethyl alcohol–water volume ratio attains a value of about 1 to 4. The solution is stirred *continuously during* this precipitation step. The precipitated hexahydrate is filtered off—e.g., by using a Gooch filter with a sintered-glass disk (medium). If the mother liquor is fairly completely drawn off by an aspirator, it does not seem to matter greatly whether the precipitates are washed. Some were not, but more often they were washed twice, once with 50% ethyl alcohol, then with 100% ethyl alcohol. The crystals are usually weighed without complete drying, then redissolved in the appropriate amount of water, and the process is repeated until a total of four crystallizations have been made. The loss of triphosphate is 15 to 35% for each crystallization.

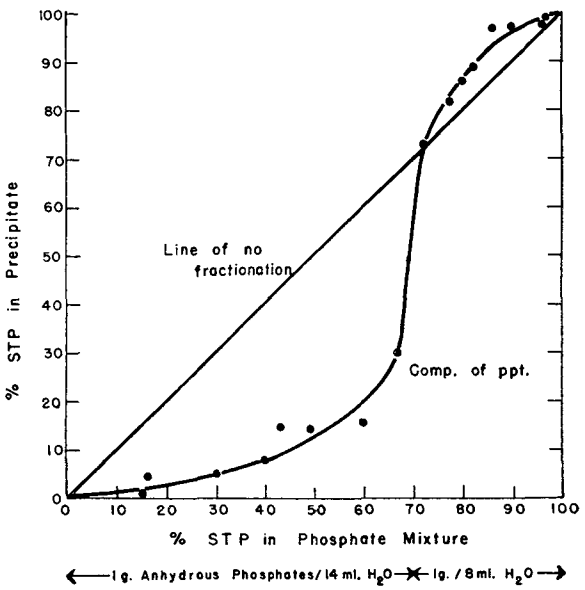

Figure 1. Purification Diagram for Mixtures of Sodium Pyro- and Triphosphates by Fractional Crystallization

Volume ratio ethyl alcohol–water, 1 to 4
Temperature, 25° to 35° C.

Isolation of Pure Pyrophosphate. Analysis for sodium pyrophosphate proceeds similarly except that its decahydrate, $Na_4P_2O_7.10H_2O$, is the precipitated phase and a higher ratio of water to phosphate must be used—namely, about 14 ml. of water per gram of phosphate. When the sample is nearly pure $Na_4P_2O_7$, this is above the saturation limit at room temperature; consequently, either warming to 30° to 35° C. or increasing the water-phosphate ratio to 16 to 1 is necessary to effect solution; most samples contain too little pyrophosphate to require such treatment.

Adjustment of Triphosphate-Pyrophosphate Ratio. As can be seen from Figure 1, this ratio must be in the proper range to allow concentration of the desired species. [In the ordinates and abscissas of the graphs and in some tables the symbols SPP for sodium pyrophosphate ($Na_4P_2O_7$) and STP for sodium triphosphate ($Na_5P_3O_{10}$) have been used.] The weight ratio $Na_5P_3O_{10}$–$Na_4P_2O_7$ must be above 7 to 3 for recovery of pure triphosphate, below this ratio for recovery of pure pyrophosphate. The shape of the curve (Figure 1) shows that it is advisable to make this ratio at least 4 to 1 in analyzing for triphosphate and less than 3 to 2 in analyzing for pyrophosphate. In analyses for both components it is therefore necessary to add some inactive phosphate in at least one of the analyses; sometimes both must be added—i.e., pure inactive triphosphate is added to one portion of the sample which is intended for sodium triphosphate determination and pure inactive pyrophosphate to another portion which is

intended for sodium pyrophosphate determination. A consequence of this required ratio adjustment is that the relative error becomes excessive when the species being determined is present in low concentration. Thus, in determining pyrophosphate the relative error approaches 20% when the pyrophosphate content of the total phosphate falls to 10%. Similarly, in determining triphosphate, 20% relative error is attained when the triphosphate content of the total phosphate falls to 18%.

Analysis of Phosphated Detergents. Only minor variations of the described isolation procedures are required in analyzing detergents containing 35 to 60% total phosphate. A 10-gram sample usually gives sufficient tri- or pyrophosphate recovery for counting—e.g., 0.5 gram, anhydrous basis. The amount of water can be increased somewhat if necessary to effect complete solution of the phosphates, and hence intimate mixing with the tracer. Incomplete solution of the phosphates may result if the sample contains much of other electrolytes—e.g., sodium sulfate—or if the ethanol from a previous crystallization has not been sufficiently removed. It is not necessary that the anionic detergent portion of the sample be dissolved completely in the water, for it will dissolve during the gradual addition of ethyl alcohol, usually before phosphate begins to precipitate. When the concentration of anhydrous phosphate in the sample decreases considerably, the ethyl alcohol–water ratio may be increased on the first crystallization so that the yield of precipitate is maintained. The actual ethyl alcohol–water ratio can be expected to vary between 1 to 3 and 1 to 6 when the damp precipitates are used for recrystallization.

Water-insoluble silicate is removed by filtration (filter aid used), usually between the second and third crystallization. Water-soluble silicate is not precipitated from the ethyl alcohol–water solutions. Thus, pyro- or triphosphate isolated from silicated mixtures (or from commercial detergents containing silicates) probably contained less than 0.1% silica, for no water-insoluble residue was detected in the phosphate after it had been evaporated to dryness twice from an acid solution.

Determination of Specific Activity. The final precipitate (triphosphate hexahydrate or pyrophosphate decahydrate) isolated as outlined previously is converted to the anhydrous salt by heating for 2 hours at 400° C. The specific activity of the isolated anhydrous phosphate is compared to that of the pure phosphate tracer added initially, by counting two or three small portions (usually 200 mg. each) under identical conditions by means of a shielded, end-window type of detector and a standard scaler. The counting rate is corrected for background and, when necessary, for coincidence loss. In order to minimize (or eliminate) the corrections for coincidence loss, the initial tracer phosphate is diluted with an untagged phosphate in a known weight ratio by dry mixing (mortar and pestle), so that the resulting dry mix standard has about the same counting rate as the isolated samples being compared; usually, three or four such dry mix standards covering a 10-fold counting rate range are prepared. Geometry, self-absorption, and decay corrections are the same for all samples and therefore cancel out.

PURITY OF ISOLATED PHOSPHATES

In order to apply the isotope dilution method to unknowns, it is, of course, necessary to isolate a pure phase of the species being determined. It is therefore pertinent to examine the efficiency of the described crystallization processes for phosphate purification. The results of this study provide the best information available relative to the purity of sodium triphosphate and pyrophosphate, showing that each is ordinarily contaminated by the other but not sufficiently to prevent application of the isotope dilution method of analysis. Purification efficiency was determined for pertinent systems by following the removal of a tagged impurity.

Removal of Pyrophosphate from Sodium Triphosphate. Representative purification curves for the system triphosphate-tagged pyrophosphate are shown in Figure 2. Similar curves (not shown) were obtained when the mixtures also contained anionic detergent and sodium sulfate. All show a consistent removal of the added radioactivity—i.e., added pyrophosphate impurity—with repeated crystallizations. The ordinate of Figure 2 is expressed as "apparent per cent added impurity" because other data (see determination of triphosphate purity) show that purified triphosphate still contains 0.4 to 3% pyrophosphate impurity. Another reason for expressing the ordinate as given is that the radioactivity, used to follow the purification, is associated with at least two phosphate species (pyro- and triphosphate). Curves *C* and *D* may be considered either as a measure of the reproducibility of the process or as an indication that the different batches of tagged pyrophosphate contained different amounts of tagged triphosphate impurity. The number of crystallizations was carried to 14 in one case (curve *D*) and led to a specific activity flat in the 12th to 14th crystallizations. The flat is primarily due to tagged triphosphate impurity in the tagged pyrophosphate and is discussed further under determination of pyrophosphate purity. So long as the tri-pyro ratio is 4 to 1 or larger in the initial mixture, four successive fractional crystallizations remove all but 0.2 to 0.5% of the added pyrophosphate, giving a purity adequate for isotope dilution analysis for sodium triphosphate.

Removal of Orthophosphate from Triphosphate. The orthophosphate impurity in the final precipitates of Figure 2 or of similar nontagged batches of purified hexahydrate determined by the Martin and Doty (*6*) method, was about 0.11% Na_2HPO_4. This is a little greater than the level expected from the triphosphate–$Na_2HP^{32}O_4$ curve in Figure 3, but in either case the purity after four crystallizations is adequate.

Removal of Trimetaphosphate and Sulfate from Triphosphate. Purification curves for the system triphosphate–$Na_3P_3{}^{32}O_9$ and triphosphate–$Na_2S^{35}O_4$ (Figure 3) show that both of these substances are readily removed by the recrystallization process

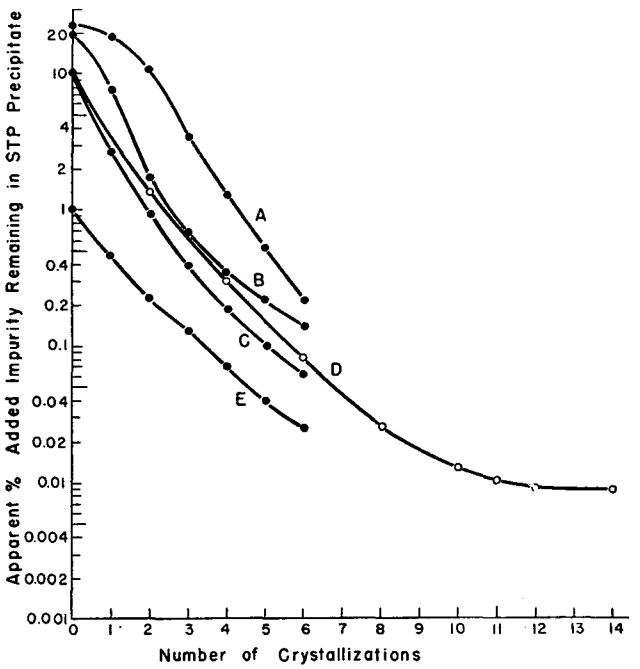

Figure 2. Removal of Added Tagged Sodium Pyrophosphate from Inactive Sodium Triphosphate by Fractional Crystallization

One gram anhydrous phosphate per 8 ml. of water
Volume ratio ethyl alcohol–water, 1 to 4, except for curve *B*, where it was 1 to 5

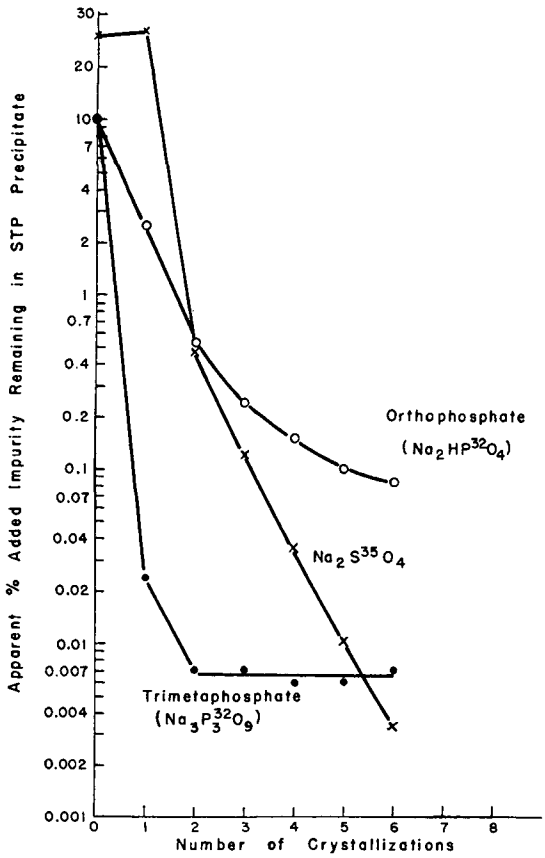

Figure 3. Removal of Added Impurity (Tagged Orthophosphate, Trimetaphosphate, or Sulfate) from Inactive Sodium Triphosphate by Fractional Crystallization

One gram of anhydrous phosphate per 8 ml. of water
Volume ratio ethyl alcohol–water, 1 to 4

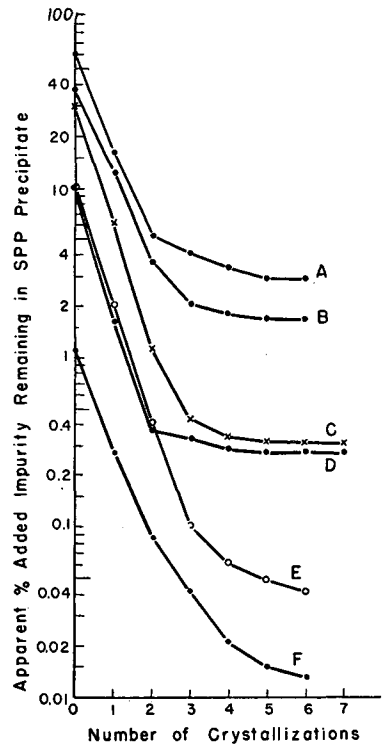

Figure 4. Removal of Added Tagged Triphosphate from Inactive Sodium Pyrophosphate by Fractional Crystallization

One gram of anhydrous phosphate per 14 ml. of water
Volume ratio ethyl alcohol–water, 1 to 4

described. Contrary to the report of Raistrick *et al.* (*8*), these data indicate that trimetaphosphate is not carried along with triphosphate hexahydrate when the latter is precipitated by adding ethanol. However, the leveling of the trimetaphosphate curve at an activity level equivalent to 0.006 to 0.007% of $Na_3P_3O_9$ is probably due to a trace of tagged triphosphate impurity and/or to slight cleavage of the trimetaphosphate ring to produce tagged triphosphate.

Removal of Triphosphate from Pyrophosphate. The purification curves in Figure 4 are typical for the system pyrophosphate-tagged triphosphate. They level off at a higher relative activity than for all other systems studied. This leveling has been traced to tagged pyrophosphate impurity in the tagged triphosphate and is discussed in detail in the section on triphosphate purity. Since the curves are linear for the first two crystallizations, one can infer by extrapolation that sodium triphosphate is readily and essentially completely removed by four crystallizations (final triphosphate level less than 0.5%).

Removal of Orthophosphate from Pyrophosphate. While the purification curve for the system pyrophosphate–$Na_2HP^{32}O_4$ in Figure 5 also gives a flat, it is too low for interference in isotope dilution experiments. Thus, orthophosphate is readily reduced to a negligible concentration in the isolate. In spite of this favorable situation the pyrophosphate–$Na_2HP^{32}O_4$ system was allowed to exchange for 1 and 72 hours, after which the pyrophosphate from both solutions was isolated, giving identical curves for specific activity versus crystallization number. This experiment excludes the possibility of phosphorus atom exchange, which must increase with time until a random distribution of P^{32} atoms is achieved. The activity of *the final flat is less* than 0.5% of the activity which would be present if the phosphorus-32 atoms were distributed randomly between the two species. Combined with the experiments described in determination of triphosphate purity and the data in the literature (*4*, *13*), it is evident that phosphorus atom exchange in solution does not occur between a condensed phosphate and some other phosphate species.

Removal of Trimetaphosphate and Sulfate from Pyrophosphate. Purification curves in Figure 5 for the systems pyrophosphate–$Na_3P_3^{32}O_9$ and pyrophosphate–$Na_2S^{35}O_4$ show that sodium trimetaphosphate and sulfate are readily reduced to negligible levels by the crystallization process described.

DETERMINATION OF TRIPHOSPHATE PURITY

Since both the active and inactive triphosphate reagents were made in the same way, they probably were of comparable purity. As already indicated the orthophosphate content is negligible, about 0.1%. The best available information on pyrophosphate content comes from the data of Figure 4 (and other similar data) on the radioactive triphosphate samples. The activity flats for several batches of tagged triphosphate computed as attributable to $Na_4P_2^{32}O_7$, ranged from 0.37 to 3.1% and averaged about 1%. The high value (3.1%) was obtained on one of the earlier batches; most of the later batches gave results near 1%.

Before accepting pyrophosphate impurity as the explanation for the activity flats in Figure 4, three other hypotheses were considered and shown to be untenable:

1. Occlusion of triphosphate hexahydrate by pyrophosphate decahydrate
2. Atom exchange, $Na_5P_3^{32}O_{10} + Na_4P_2O_7 \rightleftharpoons Na_5P_3O_{10} + Na_4P_2^{32}O_7$
3. Hydrolysis, $Na_5P_3^{32}O_{10} + H_2O \rightarrow Na_4P_2^{32}O_7 + NaH_2P^{32}O$

To test the occlusion hypothesis, pure inactive triphosphate was used to scavenge out active triphosphate. Thus, a mixture of 2 grams of precipitate 7 of curve *C* plus 8 grams of inactive triphosphate was subjected to the triphosphate purification process (12 crystallizations). The activity decreased rapidly during the first seven crystallizations, then leveled out, with only 2% of the initial activity retained. The other 98% of the activity, which was rejected in this triphosphate purification, must have been pyrophosphate, for it had been retained without change during several pyrophosphate crystallizations of the prior purification (curve *C*, Figure 4). Since the apparent level of tagged triphosphate in precipitate 7 of curve *C* was only 0.3% and since only 2% of this is actually triphosphate, the maximum possible occlusion of triphosphate by pyrophosphate is $0.3 \times 0.02 = 0.006\%$. Thus, occlusion of triphosphate hexahydrate

by pyrophosphate decahydrate cannot be the explanation of the relatively high final activity flats of Figure 4.

The inadequacy of atom exchange as an explanation of these flats was shown by allowing 7 days for exchange in aqueous solution at normal pH (9 to 10). The specific activity of the radiotagged species (isolated by the usual four crystallizations) remained unchanged, within a 1% uncertainty, as shown by the data of Table I.

Table I. Search for Phosphorus Atom Exchange between Tri- and Pyrophosphates

Mixture[a]	Spec. Activity, No Exchange	Counts/Min., 7-Day Exchange
8 g. STP^{32} + 2 g. SPP	3437 ± 12	3414 ± 12
3 g. STP + 7 g. SPP^{32}	4375 ± 17	4353 ± 17

[a] STP, sodium triphosphate; SPP, sodium pyrophosphate.

If exchange had effected random distribution of phosphorus-32 atoms, the specific activity would be about 19% lower for the isolated triphosphate (first mixture). Thus if the 1% uncertainty masked a real decrease of 1%, the exchange amounted to but $^1/_{19}$ or about 5% in 7 days. Since the time in solution during isolation never exceeded 8 hours, the proportional change in the shorter time would not exceed 0.3% of the phosphorus-32 atoms. This value is significantly lower than demanded by the flats of Figure 4—i.e., 0.4 to 2.9% exchange of the phorphorus-32 atoms present initially as triphosphate species.

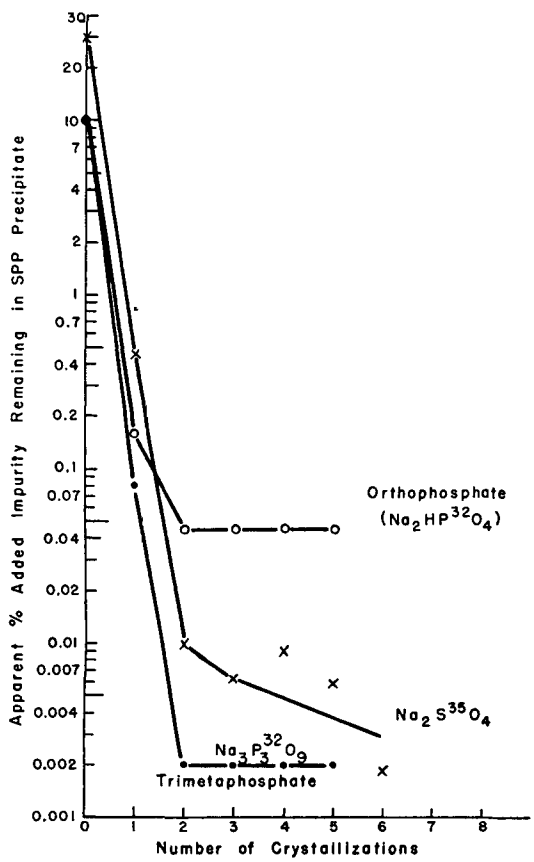

Figure 5. Removal of Added Impurity (Tagged Sodium Orthophosphate, Trimetaphosphate, or Sulfate) from Inactive Sodium Pyrophosphate by Fractional Crystallization

One gram of anhydrous phosphate per 14 ml. of water
Volume ratio ethyl alcohol–water, 1 to 4

If phosphorus-32 atom exchange occurs, it must proceed regardless of which species is tagged initially. The unchanged specific activity of the tagged pyrophosphate isolated from the second mixture (Table I) is confirmatory evidence that exchange is small if it occurs at all. Other data for room temperature exchange in a solution of 10% $Na_4P_2{}^{32}O_7$ and 90% sodium triphosphate adjusted to pH 2.7 showed no exchange. Further confirmatory evidence is given by the work of Hull (*4*) and Wilson (*13*) showing negligible phosphorus atom exchange between a condensed phosphate and another phosphate species.

While triphosphate is known to hydrolyze in solution to form pyro- and orthophosphate, the rate is not great unless the temperature is above 70° C. or the pH below 7 [see Van Wazer (*12*) and references cited by him]. Under the crystallizing conditions, hydrolysis of the triphosphate in solution cannot explain the flats in Figure 4. Thus, the pure pyrophosphate, isolated from the 7-day exchange experiment described for the mixture of 8 grams of $Na_5P_3{}^{32}O_{10}$ with 2 grams of sodium pyrophosphate, contained an amount of activity corresponding to a hydrolysis of not more than 1.5% of the $Na_5P_3{}^{32}O_{10}$. In the shorter time (less than 8 hours) used for the crystallizations, no more than 0.07% of the $Na_5P_3{}^{32}O_{10}$ could have been hydrolyzed. The purification curves of Figure 4 require 0.6 to 4% hydrolysis of the inital tagged triphosphate to give enough tagged pyrophosphate to explain the flats.

The source of the pyrophosphate impurity in the purified samples of triphosphate hexahydrate is not known. The purification curves shown in Figure 2 indicate no significant retention of pyrophosphate impurity initially present in a triphosphate sample. Hence, the pyrophosphate impurity in the purified hexahydrate must be produced in the crystallization process. The mechanism of such pyrophosphate formation has not been established, but it could be due to a slight surface hydrolysis of the triphosphate hexahydrate crystals during air-drying. Samples of hexahydrate were used directly, because heated samples are likely to be less pure (*11*). Once dried the hexahydrate crystals (stored in a closed bottle) suffer no further increase in pyrophosphate impurity over the periods observed (up to 6 months).

DETERMINATION OF PYROPHOSPHATE PURITY

The best information on pyrophosphate purity comes from the data of Figure 2. The activity flat for curve D, computed as $Na_5P_3{}^{32}O_{10}$ impurity, corresponds to 0.084%. By using pure inactive pyrophosphate to scavenge out the tagged pyrophosphate, in a manner similar to that described in the previous section, 97% of the activity in this flat was found to be due to tagged triphosphate impurity. Since the tagged pyrophosphate used for curve *D* had been crystallized once as the decahydrate, it is concluded that such pyrophosphates contain less than 0.1% triphosphate as impurity (anhydrous basis). Occlusion of pyrophosphate by triphosphate is negligible as judged by the same activity flat (curve *D*)—i.e., 0.0094% apparent $Na_4P_2{}^{32}O_7$ × 0.03 actual sodium pyrophosphate = 0.00028% maximum.

ANALYSES OF MIXTURES OF KNOWN COMPOSITION

Analytical results for pyro- and triphosphate in such mixtures are shown in Tables II and III, respectively. Some mixtures contained only phosphates, others were simulated detergent compositions. The compositions of the mixtures were known only in the sense that the phosphate species used to make up the knowns had been purified in the manner previously described. Analyses were made by five different analysts, using different batches of tracer phosphates (eight batches of tagged triphosphate, six batches of tagged pyrophosphate) over a period of about 18 months. The results for triphosphate show a positive bias, the apparent value of which does not exceed 2% absolute; no definite bias in the pyrophosphate results was detected.

The result for pyrophosphate in the mixture of pyrophosphate plus Quadrafos probably indicates the presence of some pyrophosphate in Quadrafos. This has been verified by microscopic examination, for crystals of pyrophosphate decahydrate have been obtained from an aqueous solution adjusted to pH 10 and allowed to evaporate on a microscope slide. The amount of sodium pyrophosphate could be estimated as 7% from this single analysis, but a better result would probably be obtained by an extrapolation of the type illustrated in Figure 6.

ANALYSIS OF UNKNOWN COMPOSITIONS

Analytical results for pyro- and triphosphate in samples of unknown compositions are collected in Tables IV and V, respectively. The tri-pyro ratio in unknown samples will, of course, be outside the optimum purification region for one or both species. To eliminate loss of time by incorrect estimation of this ratio, usual practice is to add a few grams of the pure phosphate species being determined, but for maximum precision this addition should not be very much larger than necessary. Each commercial tripolyphosphate and the first six detergent samples were analyzed by a minimum of two analysts, using different batches of tracer phosphate over a time interval of 6 to 12 months; the other samples were analyzed by a single analyst, using at least two different batches of tracer phosphate over a 2- to 12-month time interval. The standard deviation, s, of the method calculated from all the data in Tables IV and V is therefore a realistic estimate of the precision. The values are 1.0% for pyrophosphate and 1.5% for triphosphate.

The time required for each determination on a sample is 2 to 4 man-hours. The time elapsing before results become available is 1 to 3 days.

Table II. Analysis of Mixtures of Known Composition[a] for Sodium Pyrophosphate

Known Composition	Composition No. 1	2	3	4	5	6	7	8	9
	Weight %								
$Na_4P_2O_7$	90	82	70	70	70	10	10	28	15
$Na_5P_3O_{10}$	10	18	30	..	..	30	30	11	25
Na_2HPO_4	..	..	..	30	..	..	2	..	..
Quadrafos	..	..	..	..	30	..	..	..	..
Anionic detergent	..	..	..	..	..	..	..	35	36
Na_2SO_4	..	..	..	..	..	..	..	22	10
Na silicate	..	..	..	..	..	5	5	4	4
Water	..	..	..	..	..	55	53	..	10
$Na_4P_2O_7$ found, %	91.0	83.2	71.0	70.5	72.0	10.0	9.7	28.2	15.1
	..	..	69.2	..	..	..	..	28.1	14.9
	..	..	70.2	..	..	..	..	..	15.0
	..	..	70.6	..	..	..	..	..	15.4
Analysts	E	D	E,D,B	B	B	B	B	B	C

[a] All phosphate species were treated as 100% pure for calculation purposes.

Table III. Analysis of Mixtures of Known Composition[a] for Sodium Triphosphate

Known Composition	Composition No. 1	2	3	4	5	6	7	8
	Weight %							
$Na_5P_3O_{10}$	95	90	85	80	80	15	25	15
$Na_4P_2O_7$	5	10	15	20	15	25	15	25
Na_2HPO_4	..	..	..	..	5	..	..	..
Anionic detergent	..	..	..	..	..	..	36	36
Na_2SO_4	..	..	..	..	..	..	10	10
Na silicate	..	..	..	..	..	..	4	4
Water	..	..	..	..	..	60	10	10
$Na_5P_3O_{10}$ found, %	98.0	87.8	86.0	81.9	80.7	16.5	26.6	18.2
	..	92.4	..	..	81.4	15.2	27.8	16.0
	..	89.3	..	80.7	..	..	27.2	16.0
	..	93.2	..	81.3	..	..	26.2	16.2
	..	93.0	..	81.1	..	..	..	..
	..	..	..	80.8	..	..	24.7	..
	..	..	..	..	..	..	23.6	..
	..	..	..	80.0	..	..	25.2	..
	..	..	..	80.3	..	..	25.7	..
	..	..	..	79.9	..	..	..	..
	..	..	..	80.3	..	..	..	..

[a] All phosphate species were treated as 100% pure for calculation purposes.

One estimate of reliability has been given in the section on analysis of knowns. Another is given by the data of Figure 6. Varying known amounts of pure pyrophosphate were added to detergent sample No. 2 (Table IV). The total pyrophosphate content of the mixture was then determined by isotope dilution and plotted against the added pyrophosphate in Figure 6. The data fall close to a straight line, thus demonstrating the essential reliability of the method. The intercept on the ordinate axis agrees with the average of the four individual values for the pyrophosphate content (detergent 2, Table IV) within about 1%.

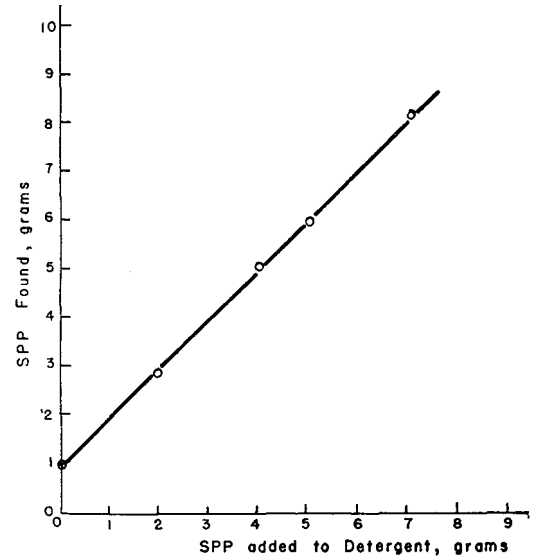

Figure 6. Analysis of a Detergent for Sodium Pyrophosphate, Addition of Inactive Pyrophosphate Required

Sample size, 10 grams of detergent 2 of Table IV

Another measure of reliability can be obtained by adding up all the phosphates found to see if all of the sample is accounted for. Thus, for commercial tripolyphosphate minor impurities are ortho- and trimetaphosphate. The orthophosphate was determined by the method of Martin and Doty (*6*) and reported as Na_2HPO_4. Trimetaphosphate content was not determined, but is known to be small, usually less than 1%. It will be observed (Table V) that the sum of the average values for ortho-,

Table IV. Analyses of Commercial Anionic Detergents for Triphosphate and Pyrophosphate by Isotope Dilution

Sample No.	1	2	3	4	5	6	7	8
$Na_5P_3O_{10}$, % triphosphate	38.1	32.6	42.7	39.9	39.6	25.5	25.9	39.8
	41.4	33.0	42.3	42.4	40.8	24.4	27.7	38.2
	..	36.2	41.2	..	..	23.8	..	..
	..	..	..	..		25.2	..	..
$Na_4P_2O_7$, % pyrophosphate	11.1	8.2	11.5	7.9	7.3	16.2	11.7	6.9
	7.2	10.4	8.6	7.3	8.7	15.2	12.6	6.9
	..	9.3	8.8	5.4	10.6	14.2	..	..
	..	11.2	9.7	5.0	..	..	..	..
Sample No.	9	10	11	12	13	14	15	16
$Na_5P_3O_{10}$, % triphosphate	29.1	31.3	27.1	26.0	27.7	18.2	23.5	21.1
	27.2	32.0	29.4	26.6	26.7	18.5	24.8	20.2
	28.0	30.4	26.0	26.2	..	23	31	23
	28.0	30.9	27.6	25.5	..	19	22	22
	25.0	29.4	..	23.0	..	..	..	..
	24.9	27.6	..	22 6	..	..	..	..
	26	34	..	26	..	..	..	..
	25	27	..	26	..	..	..	..
$Na_4P_2O_7$, % pyrophosphate	11.3	8.4	11.1	11.0	4.3	15.0	15.0	17.0
	11.4	10.0	11.1	11.4	3.7	16.5	16.0	15.
	12.9	8.8	..	11.9	..	17.8	..	..9
	11.2	8.3	..	11.7	..	16.7	..	..

Std. deviation, $Na_5P_3O_{10}$, 1.5%. $Na_4P_2O_7$, 1.0%.

Table V. Analyses of Commercial Tripolyphosphate Samples for Tri- and Pyrophosphate by Isotope Dilution

	Sample No.						
	1	2	3	4	5	6	7
	Weight % Tri- or Pyrophosphate						
$Na_5P_3O_{10}$	91.0	93.4	85.8	92.7	91.8	89.7	84.5
	91.5	91.1	87.6	87.0	90.6	88.5	86.2
	88.5	90.3	..	86.0	92.0	89.4	..
	..	..	..	88.0	..	..	..
	..	..	..	86.2	..	..	..
$Na_4P_2O_7$	10.8	10.0	13.0	7.2	11.2	12.4	14.4
	11.2	10.0	12.0	7.8	12.0	12.4	18.2
	..	12.0	..	9.6	..	12.0	16.0
	..	11.0	..	9.6	..	12.4	14.4
Na_2HPO_4[a]	0.64	0.58	..	0.60	0.57	1.17	..
	0.52	0.56	..	0.53	0.55	1.11	..
Total phosphates	101.9	103.1	99.2	97.2	103.7	102.6	101.1

[a] Martin and Doty method (*6*).

pyro-, and triphosphate usually exceeds 100% slightly, in harmony with the positive bias observed in the determination of sodium triphosphate in known compositions by isotope dilution.

DISCUSSION OF ERRORS

Errors in the final result are systematic, arising from impurities in (*a*) the tracer, (*b*) the isolate, and (*c*) the known phosphate added to adjust tri-pyro ratio, as well as random, arising from measurements of (*d*) specific activities and (*e*) volumes and weights. As indicated by Rittenberg and Foster (*9*), a 1% impurity in tracer or isolate leads to a +1% error in the result; where both occur simultaneously they are additive. An impurity in the known phosphate acts in the opposite direction (see Equation 2). The net systematic error, which is approximately equal to the algebraic sum of errors *a*, *b*, and *c* can be estimated from the purification curves as essentially zero for pyrophosphate and no more than +2% absolute for triphosphate. With conditions all carefully standardized, it would, of course, be possible to improve the accuracy of isotope dilution analyses for triphosphate by applying an empirical correction for this systematic bias.

Random errors affect the precision. Measured by the data of Table IV, these give a standard deviation of 1.0% for pyrophosphate and 1.5% for triphosphate.

ACKNOWLEDGMENT

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Determination of Low Concentrations of Carbon Dioxide in Water

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A modified evolution method has been developed wherein carbon dioxide is stripped from the acidified, heated sample by a stream of recirculating air and is then absorbed in barium hydroxide solution. The method has been studied in the concentration range from 0.00 to 1.50 p.p.m. The error appears to be constant over this range. The standard deviation of results obtained on standard solutions from the true values was found to be 0.045 p.p.m. carbon dioxide. Data on various variables involved in the analysis are presented. This method, useful in the carbon dioxide range below 1.5 p.p.m., augments existing methods of determining carbon dioxide in water. Determinations, made by this method, of carbon dioxide in water which has been treated for the removal of carbon dioxide by a deaerating heater and by a demineralizing plant are presented.

THE analysis of water for fractions of a part per million carbon dioxide is important in the study and control of corrosion of steam condensate systems, since as little as 0.1 p.p.m. carbon dioxide in the condensate can reduce the pH to nearly 6. Hence it was desired, in connection with providing carbon dioxide–free boiler feedwater, to determine carbon dioxide in water at as low a value as possible. Such determinations have been made indirectly by Collins and Dubry (*6*) but a direct method is preferable. A number of methods of determining carbon dioxide for the analysis of water samples have been developed. These range from simple titrimetric procedures (*2*) to more complex methods when greater accuracy is required. The latter generally depends on the evolution of carbon dioxide from the sample after acidification. The excess acid is then back-titrated as in the method of McKinney and Amerosi (*7*) or the evolved carbon dioxide is determined by absorption in barium hydroxide as in the method of Clarke (*5*), which is suitable to below 1 p.p.m. with an accuracy of 0.25 p.p.m. Greater sensitivity than this method provided was desired and a review of the literature indicated that the evolution and reabsorption method would be adaptable to this use.

The present method is derived from that of Clarke, which is also referee method of the American Society for Testing Materials (*3*). The sample volume has been increased to increase sensitivity. A technique has been evolved which reduces introduction of atmospheric carbon dioxide into the system during sampling and avoids such contamination of the sample. The chromate–sulfuric acid trap of Clarke has been eliminated and a new pump employed.

APPARATUS

The apparatus used is illustrated in Figure 1. It consists of a closed recirculating system with sample contained in a flask, *A*,

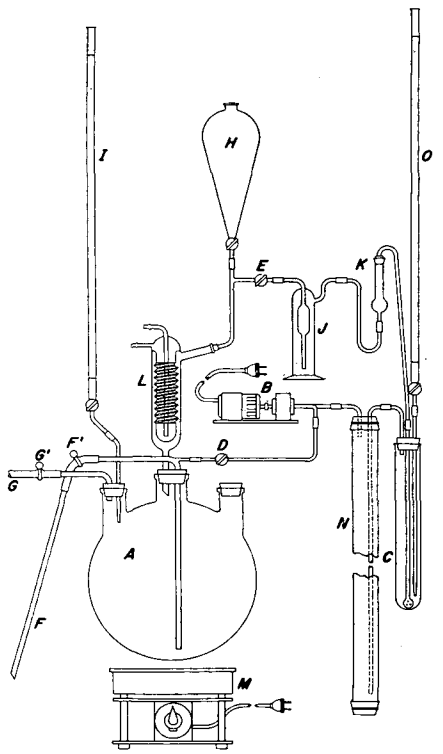

Figure 1. Diagram of Apparatus

A. 3-Liter sample flask, borosilicate glass, 3-necked distillation flask
B. Diaphragm pump (Dynamotor pump), Fisher Scientific Co., Catalog No. 1-092-5
C. 200-Ml. absorption tube.
D, E. Stopcocks, 6-mm. tubing size
F. Sample inlet line, 12-mm. diameter glass tubing
G. Suction line to aspirator, 12 mm.
F', G'. Pinchcocks on rubber tubing
H. Soda-lime tube, 250-ml. separatory funnel
I. 5-Ml. buret for 1.5*N* H_2SO_4
J. Dry trap, 38 × 190 mm., Flemming gas washing bottle
K. Glass wool trap, calcium chloride tube packed with glass wool
L. Friedrichs condenser
M. 2-Kw. hot plate
N. Expansion bladder, 1.5 meters of 5-cm. Gooch tubing with rubber stoppers at ends
O. 50-Ml. buret calibrated at 0.1 ml.

calibrated at 2 liters ± 20 ml. Recirculation is provided by a diaphragm pump, *B*, delivering approximately 2 liters per minute. The most suitable pump used has been the Fisher Dynamotor pump (Fisher Scientific Co., New York, N. Y., Catalog No. 1-092-5), but any leak-proof pressure-tight pump delivering about the same volume would be suitable. The separatory funnel, *H*, filled with soda-lime, is used to admit carbon dioxide–free air when necessary. The dry trap and calcium chloride tube packed with glass wool serve to remove mist. Carbon dioxide is absorbed in barium hydroxide solution in a 200-ml. test tube, *C*, equipped with a 50-ml. buret calibrated to 0.1 ml., which can be estimated to 0.02 ml. for titrating the excess barium hydroxide. A bladder, 1.5 meters long of 2-inch Gooch tubing, stretched over rubber stoppers to close the ends, prevents excessive build-up of pressure when heating a cold sample. The inlet line extends to the bottom to prevent any stagnant pockets. Samples are introduced through the inlet tube, *F*, by applying suction to tube *G*. The tubing is 12 mm. in diameter and is controlled by pinch clamps on heavy walled rubber tubing since stopcocks are not suitable for use with hot water. Other tubing is 6 mm. with plastic tubing joints. Heat is supplied to the sample by a 2-kw. or a 300-watt hot plate as required. The samples are acidified by acid introduced through buret *I*, attached to the sample flask. Additional burets or other apparatus are introduced through the third neck of the flask for various purposes.

REAGENTS

The reagents are 1.5*N* sulfuric acid for acidifying the sample, 0.03*N* barium hydroxide for absorbing carbon dioxide, standard 0.04*N* hydrochloric acid for titrating the barium hydroxide, and phenolphthalein indicator solution. The barium hydroxide is added by an automatic buret protected from carbon dioxide with soda-lime tubes. It is not standardized, but the same solution must be used on consecutive runs. An extension is provided on the tip of the barium hydroxide buret.

PROCEDURE

Blank determinations are first run on carbon dioxide–free samples. Acidify 4 or 5 liters of distilled water to pH 3 or lower and boil vigorously in a 6-liter flask for at least 15 minutes to remove any free or combined carbon dioxide. Remove the boiling blank sample from the source of heat and immediately introduce into the sample flask, *A*, by placing tube *F* in the blank container, closing stopcocks *D* and *E*, and applying suction from an aspirator to tube *G*. Fill the sample flask to the suction outlet. Then siphon the sample volume down to the calibration mark by closing the suction line and allowing air to enter through the soda-lime tube *H*. Close the sampling line, suction line, and soda-lime tube stopcock.

Introduce 40 ml. of barium hydroxide solution into the absorption tube, *C*, from the automatic buret with a precision of at least 0.05 ml. The extension tip of the buret should touch the wall of the tube near the bottom to prevent as much absorption of carbon dioxide from air as possible. Add 0.2 ml. of phenolphthalein indicator and immediately place the tube on the apparatus.

Acidify the sample by the addition of 25 ml. of 1.5*N* sulfuric acid from buret *I* and apply heat to it by means of the 300-watt hot plate. Open stopcocks *D* and *E*. When boiling is incipient, begin recirculation. If the sample becomes too hot before recirculating, the condenser will flood with condensed vapor. Adjust the heat so that condensation is complete in the bottom of the condenser. Minimum heating of the sample consistent with maintaining it near the boiling point is desirable, since excessive reflux of the sample slows stripping of the carbon dioxide.

After recirculation has continued for 15 minutes, titrate the barium hydroxide with 0.04*N* hydrochloric acid, while recirculating to provide agitation. Do not vary the recirculation time, since the hydrochloric acid titration may decrease approximately 0.01 ml. per minute, apparently because of unavoidable pickup of atmospheric carbon dioxide by the system. A white background and good light are necessary for the titration and the end point is taken as the final disappearance of the pink color. Multiple blank titrations should agree within 0.1 ml. of 0.04*N* hydrochloric acid. If the apparatus has been idle, the first blank titration will be low but equilibrium is generally achieved on the next blank.

Following the titration, remove the sample by closing *D* and *E*, opening the soda-lime tube *H*, and applying suction to line *F* to draw the old sample out. The sample and absorption sections of the apparatus are isolated during the changing of tube *C*, since stopcocks *D* and *E* are closed, and only carbon dioxide–free air is allowed in the sample section. Thus the entrance of amounts of carbon dioxide from the atmosphere sufficient to significantly affect the precision is avoided.

After the blank value has been established, perform determinations on samples containing carbon dioxide by the same procedure. Conduct the sample directly from the sampling point to the sample flask by a closed line to avoid any contact with the air. If hot samples such as deaerating heater effluents or steam condensate are being run, a sample cooler is required to prevent flashing, which would tend to remove carbon dioxide, while the sample is being drawn into the system. Draw two or three sample flask volumes through the system before the sample is siphoned down to the proper volume. If cold samples are being run, use a 2-kw. hot plate to avoid excessive sample heating time.

A shield of asbestos paper around the hot plate and flask accelerates heating. Burners may be used, but they may crack the sample flask and tend to contaminate the ambient atmosphere with carbon dioxide. Some pressure may build up in the system with cold samples in spite of the bladder, but this is not troublesome during recirculation and can be safely vented after recirculation before titration of the barium hydroxide. Any such pressure build-up can be minimized by keeping the free volume above the sample as small as is consistent with avoiding entrainment or bumping of the sample into the condenser. Replicate samples containing carbon dioxide should agree within 0.1 ml. of 0.04*N* hydrochloric acid. If the concentration of carbon dioxide is significantly greater than the concentrations determined here, it is

Table I. Determination of Standard Carbon Dioxide Solutions

(Standard deviation of results from known value, 0.045 p.p.m. CO_2; number of determinations, 17)

Sample Temp.	CO_2 Added, P.P.M.	0.04N HCl, Diff. betw. Blank and Sample, Ml.	CO_2 Recovered, P.P.M.	Error, P.P.M. CO_2
Cold	0.00	0.06	0.03	+0.03
	0.00	0.10	0.04	+0.04
	0.00	0.13	0.06	+0.06
Hot	0.08	0.24	0.11	+0.03
	0.08	0.22	0.10	+0.02
	0.08	0.11	0.05	−0.03
Cold	0.23	0.72	0.32	+0.09
	0.23	0.75	0.33	+0.10
	0.28	0.63	0.28	0.00
Cold	0.46	1.04	0.46	0.00
	0.46	1.10	0.48	+0.02
Hot	0.44	0.98	0.43	−0.01
	0.44	0.95	0.42	−0.02
	0.44	0.93	0.41	−0.03
Hot	0.89	1.98[a]	0.87	−0.02
	0.89	1.98[a]	0.87	−0.02
Hot	1.30	2.90[a]	1.30	0.00
	1.30	2.79[a]	1.30	−0.07

[a] Recirculation time, 30 minutes; all others, 15 minutes.

generally preferable to use the method of Clarke (*5*) and the ASTM (*3*).

The total concentration of carbon dioxide is calculated by:

$$\text{Parts per million } CO_2 = 22\,N(B - S)/V$$

where N = normality of HCl
B = blank titration, ml.
S = sample titration, ml.
V = volume of sample, liters

If the pH of the sample is determined by a glass electrode pH meter with suitable precautions for slightly buffered solutions (*8*), the concentrations of free carbon dioxide, bicarbonate, and carbonate can be calculated by some method such as that of Amerosi and McDermet (*1*).

Table II. Effect of Recirculation Time[a]

Recirculation Time, Min.	CO_2 Added, P.P.M.	0.04N HCl, Diff. betw. Blank and Sample, Ml.	CO_2 Recovered, P.P.M.	Error, P.P.M. CO_2
8	0.42	0.88	0.39	−0.03
8	0.42	0.90	0.40	−0.02
8	0.43	1.20	0.53	+0.10
15	0.44	0.98	0.43	−0.01
15	0.44	0.95	0.42	−0.02
15	0.44	0.93	0.41	−0.03
30	0.45	1.04	0.46	+0.01
30	0.45	1.13	0.50	+0.05
30	0.45	1.06	0.47	+0.02

[a] No acid trap used.

DATA AND DISCUSSION

The effectiveness of this method of carbon dioxide-free blank preparation was determined by use of sodium carbonate traced with C^{14} radioactive carbon isotope. Samples containing approximately 31 mg. per liter of sodium carbonate with an activity of 0.5 microcurie were prepared. One sample was prepared by the blank preparation procedure, then reconstituted to 31 mg. per liter. Both were precipitated with a large excess of barium hydroxide, filtered, dried, and counted with a thin mica window Geiger-Müller tube and a scaler counter. Respective counts of 10,730 and 5 counts per minute above a background of 57 counts per minute were obtained, giving a carbon dioxide concentration of approximately 0.005 p.p.m. in the blank. Because of the low count of the blank sample, the error may be 0.02 p.p.m. However, this evidence of freedom from carbon dioxide is supported by the fact that various blanks prepared by boiling 15 minutes to an hour or more gave the same titration.

Laboratory determinations employing samples of known carbon dioxide content are presented in Table I. The standard deviation of the results from the known values is 0.045 p.p.m. The error does not appear to change with sample temperature or concentration. Hot samples were at a temperature near the boiling point and cold samples were at the ambient temperature. All known samples were first prepared by the acidification and boiling technique described. Cold samples were allowed to cool in closed flasks under an atmosphere of argon. Since it was impossible to prevent carbon dioxide contamination of samples manipulated in the atmosphere, known amounts of carbon dioxide were added after the sample was in the evolution flask. A rubber membrane 2 mm. thick was mounted on the third neck of the flask and the needle of a hypodermic syringe was inserted through it. The proper amount of 0.002M sodium bicarbonate stock solution was added from the syringe which was then withdrawn. The syringe was calibrated at 0.2-ml. intervals.

Table II presents data on the effect of varying recirculation time. In all cases blanks and samples were recirculated for the same time. It will be noted that accuracy did not appear to vary between 8 and 30 minutes recirculation and that recovery was complete even at 8 minutes. Therefore, a recirculation time of 15 minutes was standardized.

Table III. Precision of Blank Determination

0.041N HCl, Ml.	Deviation from Mean Equivalent HCl, ml.	Deviation from Mean Equivalent CO_2, p.p.m.
26.60	−0.044	−0.019
26.60	−0.044	−0.019
26.75	+0.106	+0.046
26.65	+0.006	+0.002
26.62	−0.024	−0.011

No. determinations, 5
Average, 26.644 ml.
Standard deviation, 0.056 ml.
P.p.m. CO_2 equivalent standard dev., 0.025 p.p.m.

Table III presents a series of consecutive blank determinations and their standard deviation. The standard deviation is 0.025 p.p.m. for the series. This provides a measure of the precision possible with the method, although the accuracy and precision achieved with known samples as shown in Table I are not so great.

The chromate-sulfuric acid trap of Clarke (*5*) was eliminated because erratic results and excessive drifting of the blank with time were experienced at times with the trap. Figure 2 shows

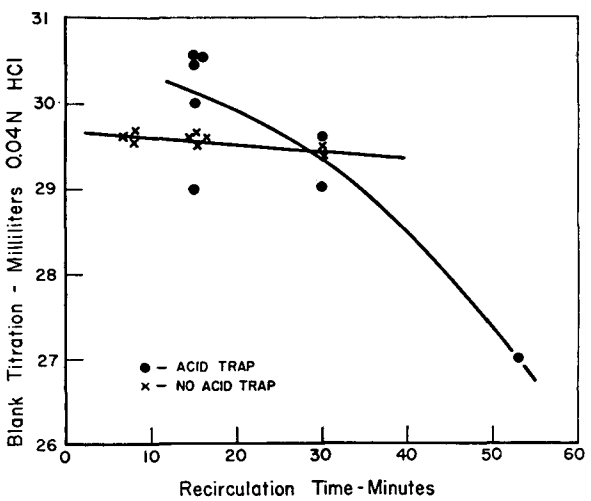

Figure 2. Effect of Chromic Acid Trap on Blank Titration

some representative results. The blank range was 1.6 ml. at constant recirculated time and decreased approximately 0.11 ml. per minute of circulation. In contrast, the blank decreased only 0.01 to 0.02 ml. per minute of circulation without the trap and was much less erratic. The trouble appeared to be due to organic matter entering the trap and being oxidized to carbon dioxide by the strong oxidating solution. That acid mist was not being entrained was shown by operating the apparatus with distilled water and methyl orange indicator in the absorption flask. Even after several hours no evidence of strong acid in the absorption flask was found.

Without the chromate trap, sulfides and sulfites will cause interference. Although water samples pure enough to warrant the use of this method will generally be free of them, steam condensate may contain such compounds which can be evolved from sulfites in the boiler. Some preliminary experiments on interference elimination by addition of 0.2*N* potassium permanganate to the sample in the evolution flask are shown in Table IV. The slightly high results are probably the results of slight volatilization by the acid sample of the interferences which were added as strong solutions by use of the hypodermic syringe before destruction by the permanganate. The permanganate can be added from a buret in the third neck of the flask and a sufficient amount is required to make the sample pink. This method of interference removal is not suitable if organic matter oxidizable by weak permanganate solution is present in the sample.

Table IV. Elimination of Interference

[2.0 p.p.m. Na_2S and 2.0 p.p.m. Na_2SO_3 added to sample (equivalent to 2.3 p.p.m. CO_2); sufficient 0.2*N* $KMnO_4$ added before recirculation to make the sample pink]

CO_2 Added, P.P.M.	0.04*N* HCl, Diff. betw. Blank and Sample, Ml.	CO_2 Recovered, P.P.M.	Error, P.P.M. CO_2
0.46	1.18	0.52	+0.06
0.46	1.43	0.63	+0.17
0.46	1.18	0.52	+0.06
0.46	1.25	0.55	+0.09

The range of concentrations covered is from 0.00 to approximately 1.50 p.p.m. carbon dioxide. A standard deviation of ±0.045 p.p.m. appears to be attainable in this range. Further refinement of technique might improve precision and accuracy. The use of potentiometric, conductometric, or high-frequency titration would allow the use of lower reagent concentrations, which in this case were relatively high to provide sufficient barium ion to repress the solubility of the barium carbonate and give sharp end points. If this is done, the difference of the blank and sample titrations would be higher. Turbidimetric determination of precipitated barium carbonate might be useful as well. Sample volume might be more exactly measured than the ±1% specified. It is felt, however, that precision and accuracy are probably limited by the unavoidable contamination of the system with atmospheric carbon dioxide.

FIELD TESTING

A number of field tests using this method were performed on evaporator feed water treated to remove carbon dioxide. The system has been fully described by Archibald and Purssell (*4*). Basically a hydrogen cation exchange unit converted the salts in the water to acids. The resulting acid water was fed to a 25,000-pound-per-hour stainless steel–clad deaerating heater of the spray type with a scrubber. The carbon dioxide- and oxygen-free water was neutralized with caustic soda and fed to an evaporator which supplied make-up to a high-pressure boiler. The pH of the acid water was approximately 3.

Table V. Carbon Dioxide Determinations on Deaerating Heater Effluent

0.04*N* HCl, Diff. betw. Black and Sample, Ml.	CO_2 Found, P.P.M.	O_2 Found by Winkler Method, P.P.M.
0.7	0.31[a]	0.00
0.2	0.09	
0.1	0.04	
0.0	0.00	0.00
0.1	0.04	
0.0	0.00	
1.0	0.44[a]	0.00
0.2	0.09	
0.1	0.04	
0.05	0.02	0.00
0.15	0.07	

Average, 0.043 p.p.m. CO_2
Standard deviation, 0.034 p.p.m. CO_2
No. determinations, 9

[a] These values were high because of errors in analysis and were omitted from the calculations.

Results of determinations on the heater effluent are presented in Table V. Considerable trouble in analysis was had at times with the pump which was a different type than the one described here. Slow heating of the sample caused by too small a hot plate and the effect of the chromate trap in producing erratic results were also experienced. The results shown are chosen from a period of work when these troubles were not present.

Field tests were also run on the effluent from a two-step demineralizing system supplying water for boiler feed. The system consisted of three cation exchange units containing a carbonaceous cation exchanger (Zeo-Karb H, The Permutit Co., New York) followed by three forced draft degasifiers which preceded two highly basic anion exchange units (Permutit S-2, The Permutit Co., New York). The influent to the anion exchangers contained approximately 0.14 milliequivalent per liter of free mineral acids (sulfuric, hydrochloric), 10 p.p.m. carbon dioxide, and 14 p.p.m. silicon dioxide. The effluent contained approximately 0.05 p.p.m. silicon dioxide and had a pH of 9 and specific resistance of 0.5 megohm-cm. at the time of the test. The carbon dioxide determinations ranged from 0.00 to 0.04 p.p.m. and averaged 0.02 p.p.m.

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Separation of Rhodium(III) from Iridium(IV)

Spectrographic and Spectrophotometric Evaluation

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Rapid and specific methods of analysis were required for the evaluation of the sharpness of separation of rhodium(III) from iridium(IV) by selective reduction of the rhodium(III) to the metal by titanium(III) chloride. Spectrographic methods of analysis were developed, using the porous cup electrode technique with a high voltage spark source and the Rh 3434.9/Co 3455.2 and Ir 2849.7/Co 3455.2 line pairs. Relative analysis errors were about 2.8%, and the lower limits of detection were 0.5 p.p.m. for rhodium and 50 p.p.m. for iridium; smaller amounts of iridium were determined spectrophotometrically. Precipitations of rhodium (III) as metal were made from boiling solutions; the amount of rhodium failing to precipitate was determined spectrographically, while the iridium which coprecipitated with the rhodium was determined spectrophotometrically. Evaluation of separations of disproportionate amounts of rhodium(III) and iridium(IV) showed a separation of about 99.7% for each element. The amount of rhodium failing to precipitate and the amount of iridium coprecipitating were both independent of the quantity of the other element present. The results indicated that, in a gravimetric separation of rhodium from iridium, there exist compensating errors of small magnitude.

THE methods of separation of the platinum metals from each other and their quantitative determination, originally given by Gilchrist and Wichers (*6*), have been generally adopted (*1, 8*). In a previous paper (*3*), some of the difficulties inherent in the precipitation separations and gravimetric determinations were outlined, and spectrographic methods for the determination of palladium, platinum, iridium, and rhodium were proposed as a means of evaluating the sharpness of the separations. These methods have been used in studying the separation of palladium from platinum, iridium, and rhodium with dimethylglyoxime (*4*).

The present report concerns a similar study of the separation of rhodium from iridium by reduction of the rhodium compound in solution to elemental rhodium, using titanium(III) as the reducing agent. Preliminary work indicated that the rhodium line 3323.1 and the iridium line 3220.7 used by Ayres and Berg (*3*), could not be used in the present study on account of interference from lines produced by the titanium reagent; other lines (more exactly, line pairs with cobalt as internal standard) were therefore sought.

The amount of rhodium failing to precipitate at the stoichiometric point was within the range to be adequately evaluated by the porous cup electrode technique, but the amount of iridium contaminating the rhodium precipitate was too small to be evaluated by this method. It was found that a slight modification of the spectrophotometric method given by Ayres and Quick (*5*) was satisfactory for determining the coprecipitated iridium.

APPARATUS

The spectrographic equipment used, the preparation of porous cup electrodes, the exposure conditions and film developing procedures, the densitometer measurements, and the film calibration methods were the same as given by Ayres and Berg (*3*). A sharp rise in film contrast generally occurs for radiation of wave lengths greater than about 3400 A. (*7*). Film calibration curves for the 3400 to 3500 A. region were found to be in very close agreement with the curves for the 2600 to 3400 A. region, over which the film calibration curve is generally valid.

Spectrophotometric measurements of iridium solutions were made with a Beckman Model DU spectrophotometer, operated at constant sensitivity. Matched Corex absorption cells of 1.00-cm. light path were used for samples and blank. Potentiometric measurements were made with a Beckman Model H-2 pH meter, using a standard calomel–platinum electrode system.

REAGENTS

Rhodium(III) chloride tetrahydrate, obtained from A. D. Mackay, Inc., was tested for impurities by direct current arc analysis and found to contain traces of silver, gold, copper, lead, and platinum, but no iridium. A small quantity of concentrated hydrochloric acid was used to dissolve 2.735 grams of the salt; the solution was diluted with distilled water to 1 liter, making a standard solution containing 1000 p.p.m. of rhodium.

Iridium(IV) chloride, stated by the supplier (Mackay) to be of purity 99.5% or higher, was tested for impurities by direct current arc examination; principal impurities were lead, silicon, platinum, and rhodium. The rhodium concentration was estimated to be 0.1%, a quantity which would impair the use of the iridium solution for preparation of spectrographic standards for determination of small amounts of rhodium in the presence of large amounts of iridium.

The rhodium and platinum impurities were removed by precipitation with titanium(III) chloride (*9*). A small quantity of concentrated hydrochloric acid was used to dissolve 3.486 grams of the iridium(IV) chloride, then 100 ml. of concentrated sulfuric acid were added, and the solution was heated until heavy fumes of sulfuric acid appeared and until a clear green solution resulted. The solution was diluted to about 500 ml. and heated to boiling, then 20% titanium(III) chloride solution was added dropwise until the potentiometric equivalence point was reached. The mixture was heated for 2 minutes, and filtered after the addition of paper pulp to gather the precipitate; the precipitate was washed 10 times with hot 2.5% sulfuric acid.

The filtrate (including washings) was heated until dense fumes appeared. After cooling, the solution was transferred to a 2-liter volumetric flask and diluted to volume with distilled water, making a standard solution containing 1000 p.p.m. of iridium. By extensive concentration of some of this solution, the rhodium content of the purified iridium was estimated, by direct current arc examination, to be not greater than 0.01%.

Cobalt(II) sulfate heptahydrate (Merck) was found to be spectrographically free from all platinum metals and to contain only traces of iron and nickel. A solution containing 8000 p.p.m. of cobalt was prepared by dissolving 38.154 grams of the salt in distilled water and about 10 ml. of concentrated sulfuric acid, then diluting to 1 liter. This solution was used as an internal standard.

Titanium(III) chloride was obtained as a 20% solution. Direct current arc analysis showed absence of platinum metals. This solution was used as the precipitant to effect selective reduction of rhodium(III) to the metal in the presence of iridium(IV).

Titanium dioxide (General Chemical Co.) was found to be spectrographically free from all platinum metals. Concentrated sulfuric acid, 100 ml., was added to 5.17 grams of titanium dioxide and heated until dense fumes appeared for 10 minutes. The solution was then cooled, diluted to about 400 ml., and traces of residue were filtered off. After concentrating the filtrate to about 200 ml., it was transferred to a 250-ml. volumetric flask and diluted to volume, giving a final concentration of about 12,500 p.p.m. of titanium. This solution was used as a diluent for spectrographic standard solutions, to approximate the concentration of titanium present in solutions to be analyzed.

Acids used, nitric, hydrochloric, sulfuric, phosphoric, and perchloric, were of purity in every way satisfactory for use in this study.

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Table I. Accuracy of Rhodium and Iridium Determinations

Rh 3434.9/Co 3455.2			Ir 2849.7/Co 3455.2		
Concentration of Rhodium, P.P.M.		Relative error, %	Concentration of Iridium, P.P.M.		Relative error, %
Taken	Found		Taken	Found	
25.0	26.5	6.0	250	266	6.4
30.0	32.8	9.3	300	290	3.3
35.0	35.7	2.0	350	340	2.9
50.0	50.0	0.0	450	442	1.8
55.0	55.0	0.0	500	518	3.6
60.0	59.0	1.7	550	560	1.8
65.0	66.0	1.5	600	600	0.0
70.0	72.0	2.9	700	700	0.0
75.0	76.0	1.3	720	710	1.4
	Av.	2.8			2.4

EXPERIMENTAL

Preliminary work showed that the line pairs rhodium 3323.1/cobalt 3354.4 and iridium 3220.7/cobalt 3354.4, used by Ayres and Berg (*3*), could not be used in the presence of titanium, because of interference with rhodium 3323.1 by titanium 3322.9, with cobalt 3354.4 by titanium 3354.6, and with iridium 3220.7 by titanium 3320.5. Although the rhodium 3323.1 line could be used in analyzing the dissolved precipitate for rhodium, it would be useless in determining unprecipitated rhodium in the filtrate containing titanium. Interference with the iridium line was not serious if the titanium concentration was kept below 1200 p.p.m., but in order to make the iridium determination highly specific, it was decided to use lines free of interference, because a filtrate containing iridium will necessarily contain titanium in varying amounts depending upon the amount of rhodium precipitated.

Evaluation of New Line Pairs. Because of the general low spectral sensitivity of the platinum group metals, the use of other lines for rhodium and iridium was limited to their other persistent lines: rhodium 3396.9 and 3434.9, and iridium 3513.6, 3437.0, 2924.8, and 2849.7. All cobalt lines appearing in the 3200 to 3500 A. range at a concentration of 3200 p.p.m. of cobalt and the aforementioned rhodium and iridium lines, were checked for interference from each other and from the titanium reagent. This study showed iridium 2849.7, rhodium 3396.9 and 3434.9, and eight cobalt lines to be free of interference. In addition, the lines rhodium 3323.1 and iridium 3220.7 and 2924.8 were examined to determine their behavior relative to the cobalt lines selected.

The cobalt concentration was varied to bring the desired cobalt lines into a moderate range of absorbance; nine replicate spectra were recorded for each concentration used, in order to obtain a statistical variation of a given intensity ratio. All possible intensity ratio combinations were calculated; on the basis of the results thus obtained, the line pairs rhodium 3434.9/cobalt 3455.2 and iridium 2849.7/cobalt 2355.2 were selected for further study. The optimum working range was determined to be 20 to 80 p.p.m. for rhodium, and 200 to 800 p.p.m. for iridium; the lower limits of detection were 0.5 p.p.m. and 50 p.p.m., respectively.

For the preparation of spectrographic standards, suitable aliquots of the rhodium stock solution were fumed down with sulfuric acid, to approximate more nearly the conditions under which the method would be used; the iridium standard solution had already been converted to the sulfate form. Rhodium and iridium standards were prepared in the above working ranges, with the addition of cobalt(II) to give a final concentration of 1600 p.p.m. and sulfuric acid to give a final concentration of 10% by volume. Triplicate exposures were made of each solution. Logarithms of average intensity ratios were plotted against logarithms of the corresponding concentrations. The working curves are illustrated in Figure 1. These curves can be resolved into normal working curves (45° slope on logarithmic coordinates) by applying background corrections. The suitability of the selected

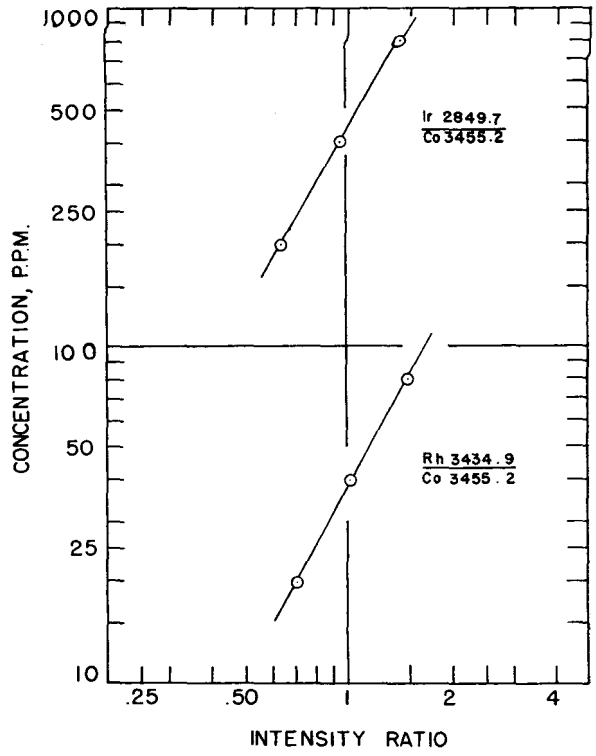

Figure 1. Working Curves for Spectrographic Analysis of Iridium and Rhodium

line pairs was verified by performing analyses in triplicate on nine standards; the results are shown in Table I.

Incidental to this study was the determination of the utility of other line pairs not suited for use in this particular problem. The line pairs most suitable, and their corresponding average relative analysis errors, were: rhodium 3434.9/cobalt 3354.4, 1.5 %; iridium 3220.7/cobalt 3354.4, 2.7%; iridium 3220.7/cobalt 3455.2, 2.1%; iridium 2924.8/cobalt 3354.4, 2.3%; iridium 2924.8/cobalt 3455.2, 2.9%; and iridium 2849.7/cobalt 3354.4, 1.8%.

Table II. Reproducibility of Rhodium Data

Concentration, P.P.M.				No. of Spectra Measured	Intensity Ratio, Rh 3434.9/Co 3455.2		Dev. of Rh Concn., %
Rh	Ir	Co	Ti		Average	Std. dev.	
20.0	0	1600	0	4	0.705	0.015	2.5
40.0	0	1600	0	5	0.997	0.010	1.5
80.0	0	1600	0	6	1.53	0.05	2.5
1.0	400	80	625	3	1.039	0.001	5
2.0	400	80	625	3	1.076	0.009	20
2.5	400	1600	5000	3	0.339	0.003	4
5.0	400	1600	5000	3	0.389	0.020	15
10.0	400	1600	5000	3	0.472	0.043	25
20.0	400	1600	5000	3	0.593	0.015	7.5

The precision with which the rhodium/cobalt intensity ratio could be reproduced is illustrated in Table II; the evaluation includes day-to-day and film-to-film data used for standard curves for determining small amounts of rhodium in the presence of iridium and titanium. For solutions containing 2 p.p.m. or less of rhodium, maximum opening of the grating doors allowed maximum exposure for a given time; the cobalt concentration of 80 p.p.m. was advantageous in giving intensity ratios near unity, thereby minimizing film calibration differences. Preliminary work had shown that the spectral sensitivity of iridium was too low for the determination of small amounts of coprecipitated iridium; hence, Table III shows the reproducibility of the iridium data only in the optimum concentration range.

Spectrophotometric Determination of Iridium. For the determination of coprecipitated iridium, a modification of the method of Ayres and Quick (*5*) was used. The method is based upon a purple color formed when iridium in solution is heated with a mixture of phosphoric, perchloric, and nitric acids, hereafter designated as "mixed acid reagent." Although Ayres and Quick did not use sulfuric acid in the reagent finally selected, it seemed advisable to study the stability and reproducibility of the color in solutions of high sulfuric acid content, because the solutions to be analyzed in the present study contained relatively large amounts of sulfuric acid used for dissolution of the rhodium precipitate.

Table III. Reproducibility of Iridium Data

Concentration, P.P.M.			No. of Spectra Measured	Intensity Ratio, Ir 2849.7/Co 3455.2		Dev. of Ir Concn., %
Ir	Co	Ti		Average	Std. Dev.	
200	1600	0	6	0.668	0.040	10
400	1600	0	6	0.954	0.026	5
800	1600	0	3	1.41	0.04	5
200	1600	625	4	0.638	0.042	15
400	1600	625	6	0.824	0.070	20
800	1600	625	5	1.15	0.06	10
200	1600	5000	3	0.556	0.046	17
400	1600	5000	3	0.703	0.015	4
800	1600	5000	3	1.009	0.024	4

Standard iridium solutions containing from 20 to 60% sulfuric acid (in addition to the mixed acid reagent) were found to have a characteristic absorption maximum at 556 mμ, whereas solutions containing no sulfuric acid showed maximum absorption at 564 mμ; for a given amount of iridium, solutions prepared by the two methods had the same absorbancy at these wave lengths, respectively. Iridium solutions containing 40% sulfuric acid developed maximum color intensity by heating at 150° C. for 40 minutes, and showed no appreciable change in absorbancy over a period of 50 hours.

On the basis of these findings, the following standardized procedure was adopted: An aliquot was taken such that the final iridium concentration would be from 5 to 100 p.p.m., and sufficient mixed acid reagent and sulfuric acid were added to give a final concentration of 20% and 40%, respectively. The resulting solution was heated at 110° C. for 1 hour to eliminate volatile components; the temperature was raised slowly to 150° C. and held at that temperature for 40 minutes. The solution was cooled, transferred to an appropriate volumetric flask, and diluted to volume with 1% nitric acid. Absorbancy measurements were made at 556 mμ.

Separation of Rhodium(III) from Iridium(IV). In the procedure of Gilchrist and Wichers (*6*), the solution containing rhodium and iridium is fumed down with sulfuric and nitric acids to destroy the excess dimethylglyoxime remaining from the previous separation of palladium. To the hot solution, titanium(III) solution is added slowly until it is present in slight excess as shown by the purple color. The precipitated rhodium metal is filtered off and washed with 2.5% sulfuric acid, and the filter paper and rhodium are fumed down with nitric and sulfuric acids; any metal remaining unattacked is filtered off, and again treated with the acids.

In the preliminary work of the present study, observation of the end point of the reduction [purple color of excess titanium(III) reagent] was obscured by the finely divided black rhodium precipitate that coagulated only slowly; the purple color in solution was not observed until after the addition of amounts of titanium(III) far in excess of the stoichiometric requirements for the amount of rhodium present. Furthermore, the precipitate always contained notable amounts of iridium. These difficulties were eliminated by potentiometric detection of the end point of the reduction.

Difficulties were also experienced in completely dissolving the metal precipitate, even by repeated treatments with nitric and sulfuric acids. Direct current arc examination of the insoluble residues showed them to be platinum (impurity in the rhodium and iridium source materials) and rhodium; these residues were found to be completely soluble in aqua regia. On the basis of these findings, the following procedure was adopted.

Aliquots of the rhodium(III) and iridium(IV) standard solutions were heated with 3 ml. of nitric acid and 10 ml. of sulfuric acid. After strong fuming for 1 minute, the solution was cooled, 20 ml. of distilled water were added, and the fuming was repeated. The solution was cooled and diluted to about 200 ml., then heated to boiling, and 20% titanium(III) chloride solution was added dropwise until a reversal in the sign of the potential was observed, using a standard calomel–platinum electrode system. The amount of titanium(III) reagent required for a given amount of rhodium always agreed closely with the theoretical amount.

The electrodes were rinsed, and any adhering metal was wiped off with small pieces of filter paper which were added to the filter to be used later. The mixture was boiled for two minutes, and a small amount of paper pulp was added to gather the precipitate. After filtering, the precipitate was washed 10 times with hot 2.5% sulfuric acid. The filter paper and contents were treated with 10 ml. of sulfuric acid and 3-ml. portions of nitric acid at a low heat until the paper was completely decomposed, and the mixture was then fumed strongly for about 1 minute. After cooling, 20 ml. of distilled water and 20 ml. of aqua regia (1 part of nitric acid to 3 parts of hydrochloric acid) were added, and the mixture was heated gently until evolution of brown oxides of nitrogen ceased. The mixture was then fumed strongly for 1 minute, cooled, and the treatment was repeated. The solution was transferred to a 25-ml. volumetric flask and diluted to volume. Suitable aliquots were taken for the spectrographic determination of rhodium and for the spectrophotometric determination of iridium. The filtrate from the original separation was evaporated to fumes of sulfuric acid, cooled, and transferred to a 25-ml. volumetric flask; the proper amount of cobalt(II) internal standard was added, and the mixture was diluted to volume. This solution was used for spectrographic analysis for rhodium and iridium content; aliquoting and diluting procedures were used as necessary.

RESULTS AND DISCUSSION

Following the above procedure, separations of varying amounts and ratios of rhodium and iridium were performed in quadruplicate. Analyses for the gross amounts of the elements, rhodium in the precipitate and iridium in the filtrate from the separation, indicated that the separation was complete within the limits of the analysis errors of the analytical methods employed (see Table I); because this inherent error is about 2.8%, on this basis alone one can say only that the separations were at least 97.2% complete. However, a more accurate evaluation is obtained from the analysis for the amount of rhodium unprecipitated—i.e., in the filtrate with the iridium—and the amount of iridium coprecipitated with the rhodium. The results are illustrated in Table IV, in which each entry is the average of closely agreeing quadruplicate analyses.

Table IV. Separation of Rhodium from Iridium

Amount Taken, Mg.		Amount Found, Mg.		Separation, %	
Rh	Ir	Rh in filtrate	Ir in precipitate	Rh	Ir
10.00	10.00	0.02	0.02	99.8	99.8
10.00	100.0	0.03	0.30	99.7	99.7
100.0	10.00	0.51	0.04	99.5	99.6
100.0	100.0	0.36	0.30	99.6	99.7

The results indicate that, at least within the tenfold differences in the amounts of rhodium and/or iridium taken, the absolute amount of iridium which coprecipitated with the rhodium was independent of the amount of the latter taken, but was dependent upon the amount of iridium in the solution; also, the absolute amount of rhodium lost in the filtrate was dependent upon the amount of rhodium taken. In terms of percentage separation, the values all ranging from 99.5 to 99.8% indicate

the errors to be essentially proportional rather than additive. The data of Table IV show that there is some compensation of errors in the separation—i.e., some rhodium is lost in the filtrate and some iridium is found in the precipitate. A second precipitation of the rhodium, to effect a more complete separation from iridium, appears to be unnecessary unless results of the highest accuracy are required.

Spectrographic errors were evaluated from the reproducibility of the intensity ratios. For rhodium in the lowest concentration range, the average reproducibility corresponds to a relative error of about 6%. Errors in the spectrophotometric determination of iridium, evaluated from the standard curve as recommended by Ayres (*2*), correspond to a relative analysis error of about 5% for the smallest amounts of iridium determined. Much larger relative errors than these could be tolerated without affecting the final results.

ACKNOWLEDGMENT

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Determination of Vinylidene Cyanide

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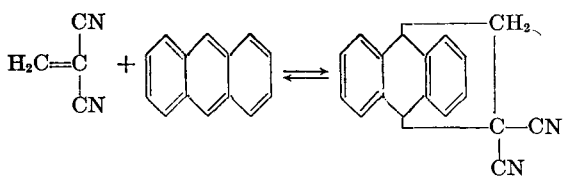
Studies of the preparation and properties of vinylidene cyanide required a method for its determination and also some kinetic studies on the reaction of vinylidene cyanide with anthracene. A method of determination of vinylidene cyanide has been developed based on reaction with an excess of anthracene and determination of excess anthracene by differential colorimetry at 359 mμ. The equilibrium constant of formation of a complex existing between anthracene and vinylidene cyanide in nonpolar solvents has been estimated for one set of conditions. Some kinetic data have been obtained for the anthracene–vinylidene cyanide reaction in benzene. The method is useful as an analytical and a kinetic study tool and should be applicable to the determination of other dienophiles.

THE preparation of vinylidene cyanide, 1,1-dicyanoethylene, as described by Ardis and colleagues (*2–5*) has created a need for a method of determining this substance both in crude reaction product and in purified samples. The extreme ease with which vinylidene cyanide is polymerized by water and many other substances indicates the need for careful handling and suggests a possible gravimetric method based on polymerization in water. Such a method will give approximate results on purified samples but is of little value on crude samples, particularly those containing solvents immiscible with water.

Vinylidene cyanide functions as a dienophile in Diels-Alder reactions (*4, 5*), for example, with butadiene, cyclopentadiene, and anthracene. None of the reactions tried yielded adducts sufficiently insoluble in the possible solvents to be useful in a gravimetric method. The reaction with anthracene is quantitative under proper conditions.



Vinylidene cyanide can be determined by a spectrophotometric measurement of the excess anthracene, since the adduct has no absorption in the region of the 360 mμ absorption band of anthracene. The principle of this method can undoubtedly be applied to the determination of other dienophiles which react quantitatively with anthracene or with other dienes whose concentration can be readily measured.

The spectrophotometric method used for determination of the unreacted anthracene is based on the differential or precision colorimetry method described by Bastian *et al.* (*7, 9*) and Hiskey *et al.* (*12, 13*).

APPARATUS AND REAGENTS

The spectrophotometer used in developing this method was a Beckman Model DU instrument, using either a tungsten lamp or hydrogen discharge tube and 1-cm. Corex or quartz cells. Although the scattered radiation filter is recommended for the wave length used, it was advantageous to omit it as a higher light intensity was thereby obtained. Spectrophotometers with a wider pass band than the Beckman have been used but with some loss in precision.

Anthracene, Eastman Kodak No. 480-X (blue-violet fluorescence) was used in developing the method and in routine testing. Less pure grades introduce errors.

The reaction solvent was anhydrous toluene. A grade of toluene which does not discolor upon standing over phosphorus pentoxide is necessary. Removal of water by azeotropic distillation followed by storage over phosphorus pentoxide for 24 hours before use is advisable. The azeotropic distillation may be omitted for some better grades of toluene. Keep stored over phosphorus pentoxide. Do not use other drying agents.

The diluting solvent was commercial or reagent grades of toluene or benzene. The solvent must have no absorption in the 360 mμ region.

CALIBRATION

Prepare the reference standard by exact weighing of anthracene so as to give 45 mg. (within a few tenths of a milligram) per liter upon proper dilution with toluene or benzene. Prepare a series of known solutions containing increments above 45 mg. per liter in steps sufficient to get as accurate a curve as is required. The upper limit for routine control work is about 65 mg. per liter and for precise work about 55 mg. per liter.

Measure the absorbance of each known solution against the 45-mg.-per-liter reference standard. Plot the calibration curve. The wave length used should be that of maximum absorption in

the 360 mμ region. This will vary somewhat with the concentration of the standard. The slit width should be the optimum one, allowing sensitivity leeway in both directions so that the slit can be kept constant for calibrations and runs when light intensity varies somewhat. Change the solution in the comparison cell frequently to avoid temperature and evaporation errors. Use clean matched 1-cm. cells or unmatched cells which are always used in the same position for calibration and runs.

Since aromatic solvents have a large coefficient of thermal expansion and the reference standard may be used for several days, the temperature at which it was diluted should be recorded. Use at some other temperature must be corrected for in precise work. New reference standards need not be exactly the same concentration as the original, since a direct correction can be made for a small difference in concentration of the standard.

Rerun the calibration, or at least check several points, when a new bottle of anthracene is used or when a new slit width is advisable or necessary because of a change in light source.

Other standards of different dilution, 15 to 90 mg. per liter, varying only in slit width settings and in possible precision of the measurement, may be used.

PROCEDURE

Weigh accurately, from a dropping bottle, a sample containing approximately 1 gram of vinylidene cyanide into a dry 100-ml. volumetric flask nearly full of dry toluene. Wet the sides of the flask neck with toluene before adding the sample. Dilute to the mark with dry toluene.

Into a dry 125-ml. Erlenmeyer flask with a standard-taper joint, weigh accurately sufficient anthracene to provide an excess of 91 to 130 mg. after equimolar reaction with one tenth of the sample weighed previously. The excess should not exceed 110 mg. for precise work, but must be over a 35% excess in all cases. Pipet a 10-ml. aliquot of the sample solution into the flask and wash the sides of the flask down with about 5 ml. (not more than 10 ml.) of dry toluene. Place a dry condenser on the flask and reflux gently for 45 to 60 minutes.

At the end of the reaction period, remove the flask from the heat, rinse down the condenser with 10 to 15 ml. of toluene, and cool the flask. Quantitatively transfer the solution to a 100-ml. volumetric flask and dilute to the mark with toluene. Dilute a 10-ml. aliquot of this solution to 200 ml. with toluene or benzene, using the same diluent as was used for the final dilution of the 45-mg.-per-liter reference standard.

Measure the absorbance of the diluted solution relative to the reference standard. Read the concentration of unreacted anthracene from the calibration curve. Calculate the amount of unreacted anthracene in the aliquot of sample used for analysis. From this value obtain the weight of reacted anthracene and calculate the vinylidene cyanide content by use of the gravimetric factor, 0.4381.

If the absorbance of the unknown does not come within the limits of the calibration curve, a new dilution must be made. Results obtained with less than a 35% excess will be questionable. Occasionally, the absorbance does not fit the calibration curve by any dilution because of an inaccurate estimate of sample purity. In that case, run a new aliquot of the sample, using the correct amount of anthracene as calculated from the first approximate run.

If the temperature of dilution of the unknown is different from that of the calibration, make the proper correction for temperature effects as required by the desired precision.

Dilute solutions of vinylidene cyanide in aromatic solvents may be analyzed, usually without prior dilution. The reaction mixture should contain at least 10 ml. of toluene (or of solvent boiling at the same temperature) and not over 20 ml. of total volume. Any attempt to use less than 100 mg. of vinylidene cyanide per 20 ml. of reaction mixture under the described conditions will give low results.

EXPERIMENTAL CONDITIONS

In developing this method it was necessary to determine the conditions required for complete reaction in a reasonable time. When reaction at room temperature was found to be much too slow, aromatic solvents which do not react with vinylidene cyanide were tried under reflux. Boiling benzene did not give a rapid enough reaction but toluene gave essentially complete reaction in 45 to 60 minutes. On the other hand, xylene gave incomplete reaction, apparently because of thermal dissociation of the adduct.

The sample size, 0.1 gram, is convenient from the standpoint of subsequent dilutions, solubility of the anthracene and of the adduct, and the weight of anthracene used (320 to 360 mg. for 0.1 gram of vinylidene cyanide). Other combinations of sample and reagent amounts could be used but the minimum anthracene concentration should be 15 to 20 mg. per ml. in the reaction mixture.

The vinylidene cyanide concentration in the reaction mixture should not be less than 5 mg. per ml. and should be 6 to 7 mg. per ml. for accurate analysis with a 45-minute reaction period. For the most accurate analyses, a 60-minute reflux should be used. At 2 mg. per ml. the results were about 1% low after 2 hours of refluxing.

For complete reaction in 45 minutes, a 35% excess of anthracene is required. Results drop off below this point. (See the section discussing kinetics of the reaction.)

The use of anthracene reference standards other than the 45-mg.-per-liter solution is possible. In fact, a large amount of routine analysis was carried out in this laboratory using a 90-mg.-per-liter standard. While somewhat less precise, the higher concentration standard has advantages in control work. Less solvent is used for dilution and the spectrophotometer slit is always used wide open (2 mm.), sometimes requiring that the light source be purposely somewhat out of focus. However, changes in light intensity from time to time have less effect on the ability to adjust the slit, an advantageous condition for routine analysis. The lower precision obtained is discussed later.

The temperature coefficient of absorbance, including the effect of temperature change on the concentration, was roughly measured for anthracene solutions in benzene. Its value for a 45-mg.-per-liter solution was estimated to be between −0.0006 and −0.001 per degree Centigrade, about half that of the least sensitive system, potassium dichromate at 350 mμ, studied by Bastian (*8*). A relative temperature control between reference standard and unknown solution of about 1° C. would be required to obtain an anthracene concentration precision of 1 part per thousand.

PRECISION AND ACCURACY

If one assumes that the reaction is quantitative and that all operations prior to spectrophotometric measurement are precise to 1 or 2 parts per thousand, there is still a large relative error in the optical measurements, frequently 0.6 to 1%, if direct comparison with the solvent is used. For this reason and because of simplified dilutions, the differential or precision colorimetry method was chosen for this work.

The theory of errors for this method developed by Hiskey (*12*) and expanded by Hiskey and Young (*13*) is particularly useful in this work, since relatively high concentrations of anthracene exhibit negative deviation from absorption laws. The data used by Hiskey and Young as an example in their development were supplied by the present authors because of the need for an understanding of the errors in this case.

The problem was solved by Hiskey and Young when they demonstrated the method of finding the optimum concentration for the reference standard. Thus, the optimum concentration of the reference standard, that is, the concentration at which the product of anthracene concentration and absorptivity is a maximum, is seen to lie in the 40- to 50-mg.-per-liter region. The error will not be appreciably greater in the 80- to 90-mg.-per-liter region. The method cannot be so effective in this case as in cases where absorption law deviations at high concentrations and wide spectral bands are small. For example, the concentration-absorptivity product, which is actually equivalent to the effective absorbance of the reference standard, is 0.99 at 90 mg. per liter, whereas it would be $90 \times 0.046 = 4.14$, if there were no absorption law deviation. However, it would not be possible to use a solution of such high absorbance in most spectrophotometers.

Table I shows a comparison of the theoretical precision of the spectrophotometric part of the analysis for cases which may be encountered in normal practice. The data are calculated from

the equations and data in (*12*) and (*13*). The total error in transmittance reading inherent in filling, emptying, refilling, positioning the cuvette, and taking a transmittance reading has been chosen as ±0.002, an average value for the instrument used in this work. Thus, Table I gives the per cent relative error which can be expected from the spectrophotometric readings only.

Table I. Theoretical Precision of Spectrophotometric Measurement

Concn. of Std., Mg./ Liter	Effective Absorbance of Std.	Concn. of Unknown, Mg./Liter	Absorbance Reading	Transmittance Ratio, I_2/I_1	Relative Error, %
0	0	0	0	1	
		2.5	0.115	0.767	0.98
		5.0	0.230	0.589	0.64
		10.0	0.460	0.347	0.54
		20.0	0.920	0.120	0.79
45	1.04	45.0	0	1	0.08
		47.5	0.059	0.873	0.09
		55.0	0.235	0.582	0.12
		65.0	0.470	0.339	0.17
90	0.99	90.0	0	1	0.09
		95.0	0.055	0.881	0.095
		100.0	0.110	0.776	0.10
		110.0	0.220	0.603	0.12
		130.0	0.440	0.363	0.17

The precision calculated for concentrations which are 10 mg. per liter or more above the concentration of the standard are somewhat idealized, since the calibration curves are definitely curving above this value. However, it is safe to say that the precision obtainable by the differential method under the worst probable conditions is about three times the precision obtainable under optimum conditions by the solvent comparison method.

In applying the above data to the determination of vinylidene cyanide, it must be remembered that the spectrophotometric measurement involves the excess anthracene only. The relative error of this measurement becomes $^1/_2$ to $^1/_3$ as great when the vinylidene cyanide content is calculated. Thus, the differential method has cut the error caused by the spectrophotometric measurement to a negligible value compared with other normal sources of error.

In practice, the precision of replicate analysis shown in Table II has been obtained. It would appear that most of the error is due to weighing, stoichiometry of the reaction, dilutions, and other factors besides spectrophotometry.

Table II. Precision of the Determination

Range in % Purity	Number of Results	Std. Deviation, Parts per Thousand
All	1036	4.1
10–100	985	3.0
0–10	51	13.4
90–100	212	2.7

There is no absolute proof of the accuracy of the method. However, three samples which were carefully purified by distillation followed by fractional crystallization gave purities of 99.7, 99.7, and 100.1%, respectively, by this method.

SOURCES OF ERROR, INTERFERENCES

Anthracene Quality. Positive errors up to 2% have been obtained in the use of Eastman No. 480 anthracene. This error did not occur with the 480-X grade which has a higher absorptivity.

Polymerization and Volatilization of Vinylidene Cyanide. Errors from these sources are lowered by using an aliquot of a dilute solution for analysis. Direct weighing of 0.1-gram samples of high purity vinylidene cyanide invariably led to low results. Samples should normally be analyzed as soon as received, although samples stabilized with phosphorus pentoxide are often stable for weeks at room temperature if kept in a dry atmosphere. Cooling or freezing aids stability. Solutions in dry toluene are stable for several days without using extra precautions.

Of materials which could be present in a crude reaction product, the following do not affect the analytical method: acetic acid, pyruvonitrile, 1,1-dicyanoethyl acetate, hydrogen cyanide, and 1-cyanovinyl acetate.

It is vitally important to prevent the presence of most polar compounds, especially water and organic bases, which will cause polymerization of vinylidene cyanide before reaction with anthracene can occur.

KINETICS OF THE REACTION

The kinetics of the vinylidene cyanide–anthracene reaction in various solvents is of interest from the quantitative viewpoint and also because of the possibility of studying other less easily followed reactions of vinylidene cyanide through competing reaction data.

Preliminary investigation has revealed some interesting facts concerning the kinetics of the reaction. At 24.2° C., where the reaction can be followed in relatively high concentrations by quenching samples of the reaction mixture by high dilution, there is some deviation from the expected second-order reaction, particularly in the early stages of the reaction. While the deviations were not large compared to expected experimental error, they could indicate intermediate complex formation. This question was investigated and the results are herewith reported.

The second-order rate constant was calculated from nine rate experiments using three anthracene–vinylidene cyanide ratios of about 1 to 1, 1 to 2, and 1 to 3. The average value obtained is $4.63\ (\pm 0.25) \times 10^4$ liters moles^{-1} second^{-1} at 24.2° C.

At 24.2° C. there is no evidence of reversibility of the reaction in 140 hours. However, in boiling toluene the Diels-Alder adduct dissociates to the reactants to the extent of about 5% in 30 minutes. This fact demonstrates the necessity of a large excess of anthracene in quantitative analysis.

The existence of a complex between anthracene and vinylidene cyanide in benzene solution was clearly demonstrated by a series of experiments on mixtures of the reactants in the 0.01 to 0.15*M* concentration range. The mixtures absorb much more strongly in the 390 to 420 mμ region, and probably at lower wave lengths, than anthracene alone. One set of data used to prove this point was obtained by examining the absorbances of six solutions, 0.01*M* in anthracene and from 0.039 to 0.13*M* in vinylidene cyanide, at 395 mμ. Mathematical treatment of these data by a method similar to that described by Heller and Schwarzenbach (*11*) revealed that the equilibrium constant of complex formation, *K*, at 23° C. must lie between 0 and 2.0 liters mole^{-1}, but cannot be zero. The most probable value is about 0.5 liter mole^{-1}. The inherent errors of measurement in this system do not permit of any greater precision in determining *K*. Recalculation of the rate constant by use of the equilibrium constant does not appreciably change the rate constant or the slight deviation from true second-order reaction when *K* is as small as indicated above.

The molar absorptivity of the complex at 395 mμ can be calculated from the data. For $K = 0.5$, the average value, the molar absorptivity is 425 as compared to 26.6 for anthracene. The high absorptivity in this region prompted a study of the absorption curve. It was possible to follow the absorption of the complex roughly by using the differential colorimetry technique. However, it was only possible to demonstrate that there is a maximum 13 mμ below that of anthracene and that it absorbs quite strongly in this region. The absolute wave length of this maximum is difficult to be certain of because of the shift of the curves to higher wave lengths when using 0.0008*M* anthracene as a comparison standard, but 346 to 348 mμ would be a good estimate.

Preliminary measurements indicate that the complex formation equilibrium constant or the absorptivity of the complex is considerably higher in carbon tetrachloride solution than in benzene.

After completion of this complex formation study, the papers by Andrews and Keefer (*1*) and Garrett and Guile (*10*) appeared and the paper by Barb (*6*) was noted, all dealing with complexes of dienophiles with aromatic compounds. Their methods of estimating equilibrium constants were essentially the same as used in the present paper. Vinylidene cyanide also forms a complex with benzene having an absorption maximum at about 280 mμ and no absorption at 359 or 395 mμ. The molar absorptivity of the benzene–vinylidene cyanide complex at 280 mμ appears to be lower than that of the benzene–maleic anhydride complex, unless the equilibrium constant for the formation of the former complex is extremely small.

ACKNOWLEDGMENT

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Three-Level Capillary Viscometer

For Study of Non-Newtonian Flow in Sealed Systems

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A problem involving the rheological behavior of oil-soluble soaps in a volatile hydrocarbon has prompted the design of a viscometer which would exclude moisture and oxygen over extended time intervals, allow repeated measurements on a given solution, yield reproducible results over a 250-fold viscosity range, and characterize quantitatively deviations from Newtonian flow. The absolute dimensions of the instrument have been determined from x-ray photographs and direct measurements, permitting specification of shearing stress and rate in absolute units. The rheological properties of non-Newtonian systems can usually be specified by a pair of constants, one describing the consistency level of the systems under specified shearing conditions and the other characterizing the deviation from Newtonian flow. The method for obtaining these constants from an equation fitting the flow data is illustrated for typical data. Such constants present data for non-Newtonian flow in a more compact and comparable form than do the graphs usually employed.

THIS viscometer was designed to study the rheological properties of dispersions of certain oil-soluble soaps in nonpolar solvents. The relative viscosity of these systems may vary from 250 to 1.06 with an increase of a few hundredths of a per cent in the water content of the system (*1*, *10*) or with moderate changes in temperature. The instrument was required to exclude atmospheric moisture and oxygen for extended intervals, to yield reproducible results over a wide range of viscosities, and to detect deviations from pure Newtonian flow.

Couette-type viscometers have been widely used for non-Newtonian systems; they have an advantage over capillary viscometers in that they give more easily interpreted data because under suitable conditions the rate of shear is uniform from wall to wall of the annulus. It is difficult, however, to design a rotational viscometer providing as rigid exclusion of moisture and other atmospheric constituents as preliminary experiments had shown to be necessary for this study. Since the more viscous systems also required days or weeks to come to equilibrium, it was advantageous to carry on measurements simultaneously in several relatively simple instruments.

Modifications of the more common capillary-type instruments have been reported (*8*, *12*, *15*, *16*, *20*) which meet some but not all of the above requirements. The viscometer described here was designed for simplicity and compactness. The only opening provided is on the end of the filling arm; this is closed with a glass stopper and can be sealed easily; the system can be observed under three different driving pressures and determinations can be repeated simply by inverting the instrument and refilling the bulbs.

DESCRIPTION OF INSTRUMENT

The viscometer (Figure 1) consists of five bulbs as follows: three measuring bulbs, a large reservoir bulb on the bottom, and a small auxiliary bulb at the top whose lower outlet, *C*, is closed by a small steel ball; this ball is lifted magnetically to start each run. The three measuring bulbs have volumes which vary in the ratio of 4 to 2 to 1 from top to bottom, respectively. They are spaced so that the time-average head prevailing during the emptying of each bulb varies in the same ratio. Thus with Newtonian liquids, approximately equal flow times are obtained for each bulb. The bulbs are shaped to provide good drainage conditions and still keep the range of hydrostatic pressure for each bulb to a minimum. The capillary tube has a sharp-edged exit. Positioning errors are reduced by placing the measuring bulbs directly above each other and the reservoir.

The diameter and length of the capillary tube are chosen to give flow rates low enough for the kinetic energy correction to be small under all useful conditions as well as to ensure that the flow of the least viscous liquid used will not be turbulent. The diameter is kept as large as possible both to reduce excessively long flow times and to minimize the obstruction of the capillary by foreign substances such as lint or soap gel.

CALIBRATION AND PROCEDURE

A solution is filtered into the reservoir bulb to remove suspended material, and then the measuring bulbs are filled by inverting the instrument; when it is returned to an upright position the steel ball closes the opening, *C*, preventing flow until it is removed to position *D* by means of a small magnet.

Since the hydrostatic head varies with the volume of the liquid charged to the viscometer and since the presence of a fiduciary filling mark would complicate the design of the instrument considerably, either a measured and constant amount of liquid has to be used in charging or a working curve has to be determined. This working curve, which gives the viscometer constants as a function of volume charged, was obtained using high and low viscosity oils from the National Bureau of Standards. These constants, A and B, were found in the usual manner from the equation

$$\eta = A\rho t - \frac{B\rho}{t} \qquad (1)$$

where η is the absolute viscosity of the solution, ρ is its density, and t is the flow time of the solution through each bulb. The reproducibility for repeated runs is within ±0.3%.

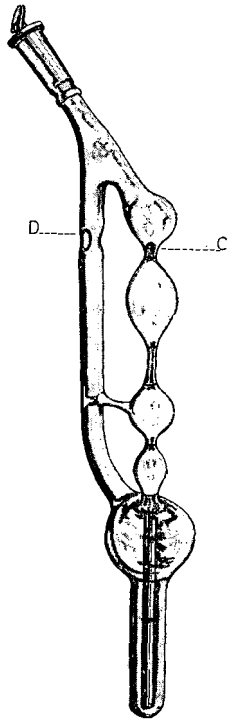

Figure 1. Three-level Capillary Viscometer for Sealed Systems

Although the instrument so calibrated serves for relative viscosity measurements, the fact that the instrument is applied to the study of anomalous flow makes it desirable to determine the absolute values for the radius and the length of the capillary tube, the volume delivered from each bulb, and the time-average hydrostatic heads prevailing during the flow from each bulb. A knowledge of these dimensions permits calculation of the rate of shear, shearing stress, and of rheological constants characteristic of a specific non-Newtonian fluid.

The time average hydrostatic head for each bulb was determined by measuring the liquid head above the reservoir level at small time intervals during flow of a highly viscous calibration liquid and integrating the data graphically. The results for the example instrument are shown in Table I. The slope of the curve in Figure 2 shows the time-rate of change of the hydrostatic heads during a determination. The time average hydrostatic head is constant for equal filling volumes of all liquids exhibiting Newtonian flow but is slightly less for non-Newtonian liquids which exhibit an anomalously large decrease in shearing rate as the shearing stress is decreased. The variation, however, is a second-order effect for most systems.

The volumes of the bulbs and the length of the capillary were found by measuring x-ray photographs taken from two directions 90° apart about the major axis and integrating the data graphically. This procedure avoids the difficulties caused by refraction when the bulbs are measured by conventional optical methods. The volumes of the bulbs in the example instrument were found to be 8.16, 3.21, and 2.24 ml., respectively. The radius of the capillary tube in the example instrument was 0.0309 cm. and its length 12.0 cm. The radius was measured directly on a retained sample of the capillary. To verify the laminar nature of the flow, the Reynolds number was determined at 25.0° C. using the least viscous liquid (benzene, η = 0.602). The values are found in Table I.

The viscosities of colloidal systems suitable for study with the viscometer described often approach equilibrium slowly or are otherwise time-dependent. In such cases the measurements are repeated at suitable intervals until equilibrium is demonstrated or the nature of the time dependence determined. One advantage of the sealed instrument is that with proper choice of inert atmosphere this observation of time dependence may be extended over several weeks without loss of volatile solvent or deterioration of the solute. The time required to reach a stable rheological state must be established experimentally for each system studied. The first sodium phenylstearate solution of Table I, for example, required 30 days, whereas the second showed no changes after a 24-hour period.

CORRECTIONS

To cover the wide range of viscosities at which the instrument was required to function, some measurements were made at flow rates for which the kinetic energy losses could not be neglected; others were made at a low hydrostatic head for which errors from surface tension effects require consideration. Both kinetic losses and surface tension errors are compensated when the instrument is calibrated with reference fluids of known viscosity but must be considered when calculating the absolute shearing stress and shearing rate for the analysis of non-Newtonian flow. The kinetic energy correction (*9*) was calculated to be less than 0.3% for kinematic viscosities greater than 2.05 centipoises. An appropriate correction is applied to measurements of less viscous systems. The surface tension effects, computed by Sugden's method (*21*), were negligible for the upper bulb but significant for the middle and lower bulbs (Table I). The resistance to flow arising in the connecting necks between bulbs, and also the drainage errors, were found to be negligible. Reasonable care in keeping the instrument vertical prevents appreciable alignment errors (*5*).

The directly measured dimensions of the viscometer and the corrections indicated above were used to compute the viscosity of two standard viscosity oils. The results are compared with the viscosities reported by the National Bureau of Standards in Table I. The agreement between the computed values and the NBS values indicates that the measured dimensions of the instrument may be used safely in the analysis of the behavior of non-Newtonian systems.

TREATMENT OF RHEOLOGICAL DATA FOR NON-NEWTONIAN SYSTEMS

The three-level capillary viscometer was designed primarily for the characterization of non-Newtonian systems in units that are

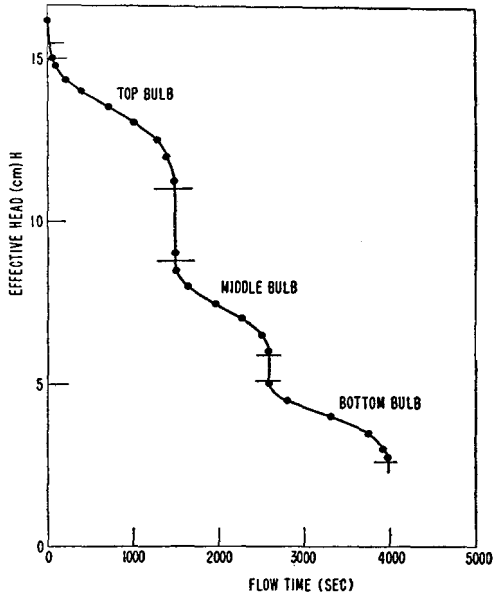

Figure 2. Plot for Determination of Time-Average Heads

Table I. Performance Data for a Three-Level Capillary Viscometer

	Top Bulb	Middle Bulb	Bottom Bulb
Time average hydrostatic heads (Newtonian liquid), cm.	13.47	7.39	4.03
Surface tension correction (S = 30 dynes/cm., density = 0.7774 at 25° C.), cm.	−0.02	−0.045	−0.076
Reynolds No. (benzene)	80.94	44.16	24.06
Viscosity of oil D-8 calculated from viscometer dimensions (NBS value 1.750 cp.), cp.	1.762	1.773	1.774
Deviation from NBS value, %	0.7	1.3	1.4
Viscosity of oil I-9 calculated from viscometer dimensions (NBS value 10.24 cp.), cp.	10.27	10.37	10.32
Deviation from NBS value, %	0.3	1.3	0.8
1.7% sodium phenylstearate in benzene with 0.1 mole of water per mole of soap			
Flow time, seconds	2553	3142	3957
Relative nominal viscosity	26.76	33.04	37.19
1.7% sodium phenylstearate in benzene with 1.5 moles of water per mole of soap			
Flow time, seconds	291.6	302.3	344.2
Relative nominal viscosity	3.026	3.169	3.234
1.7% sodium phenylstearate in benzene with 3.3 moles of water per mole of soap			
Flow time, seconds	1177	3634	28.080
Relative nominal viscosity	12.35	38.22	263.8

independent of the particular instrument employed. A simple numerical description of such systems is inherently difficult, but it is possible whenever the data, over a significant range of shear rates, can be fitted by one of the numerous equations that have been proposed. The characterizing numbers are then the two (or more) constants of the fitted equation; one of the constants usually specifies the consistency level of the system at either a low or an infinitesimal shearing rate; the other is an index of the departure from Newtonian behavior with increasing rate of shear, to which it is difficult to assign a simple physical significance.

The rheology of a wide variety of pseudoplastic systems may be described by the empirical equation of Ostwald-deWaele

$$\gamma_w = \frac{1}{\eta_{\tau=1}} \tau_w^n \tag{2}$$

where γ_w is the actual rate of shear at the wall of the capillary, τ_w is the maximum shearing stress at the wall of the capillary, and $\eta_{\tau=1}$ is a constant equal to the viscosity of a Newtonian system exhibiting similar flow rates at unit shearing stress. When n is equal to unity (Newtonian systems) Equation 2 reduces to the equation for Newtonian flow. Rewriting Equation 2 in the form

$$\log \gamma_w = \left[\log \frac{1}{\eta_{\tau=1}}\right] + n \log \tau_w \tag{3}$$

it will be seen that, when this equation holds, a plot of log γ_w *vs.* log τ will yield a straight line whose slope, n, is an index of the deviation from Newtonian behavior.

The y intercept at $\tau_w = 1$ is $\left[\log \frac{1}{\eta_{\tau=1}}\right]$

Because of the anomalous nature of the flow in the capillary the nominal rate of shear, as determined generally, using the equation

$$\gamma_{nom} = \frac{4}{\pi r^3} \frac{V}{t} \tag{4}$$

will not give a value for the rate of shear of the system corresponding to the actual flow conditions. It is, therefore, necessary to convert the nominal shear rate, γ_{nom}, to the actual shear rate, γ_w, which is used in Equations 2 and 3. Bestul and Belcher (*2, 3*) reported the relationship

$$\gamma_w = \frac{3}{4}\gamma_{nom} + \frac{1}{4}\tau_w \frac{d\gamma_{nom}}{d\tau_w} = \frac{\gamma_{nom}}{4}\left(3 + \frac{d \log \gamma_{nom}}{d \log \tau_w}\right) \tag{5}$$

since $\frac{d \log \gamma_{nom}}{d \log \tau_w}$ is equal to n (assuming that γ_w is proportional to γ_{nom}) then

$$\gamma_w = \frac{n+3}{4}\gamma_{nom} \tag{6}$$

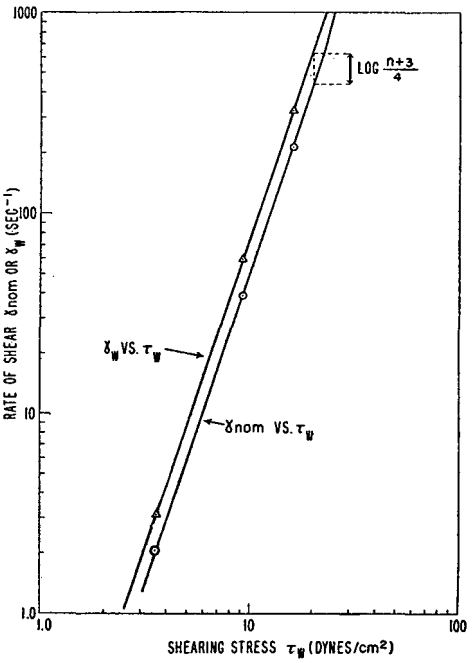

Figure 3. Alternative Determinations of Index of Non-Newtonian Flow (n) Using Nominal (γ_{nom}) and Actual (γ_w) Rates of Shear

Using this relationship the viscosity, η_τ, can be found from the nominal viscosity, η_{nom}, which is numerically equal to the viscosity of a Newtonian system with the same flow rate under the same shearing stress. For practical convenience in plotting, the

$$\eta_\tau = \frac{4}{n+3}\eta_{nom}(\tau^{n-1}) \tag{7}$$

log of any quantity which is proportional to γ_w may be substituted for log γ_w—e.g., γ_{nom}, V/t, $1/\eta_{nom}$. Similarly the log of any quantity proportional to τ may be substituted for τ such as P or $h\rho$ (Figure 3). The slope of the line, n, will be unchanged by such substitutions but the y intercept of the curve must be taken at a value corresponding to $\tau = 1$. The intercept will require multiplication by a suitable conversion factor to obtain a value of $\eta_{\tau=1}$ comparable with that obtained from Equation 7. When the ordinates are log γ_{nom} *vs.* log τ, instead of log γ_w *vs.* log τ then

$$\log \frac{1}{\eta_{\tau=1}} = Y + \log \frac{n+3}{4} \tag{8}$$

where Y is the y intercept at $\tau = 1$. If log V/t is plotted against log $h\rho$ the y intercept at $h\rho = \frac{2l}{gr}$ (i.e., where $\tau = 1$) should be examined and

$$\log \eta_{\tau=1} = -\left(\log \frac{V}{t}\right)_{\tau=1} - \log \frac{n+3}{\pi r^3} \tag{9}$$

Krieble and Whitwell (*11*) have integrated Equation 2 and shown that the quantity, $\eta_{\tau=1}$, which they designate as ζ, the "viscosity-counterpart," may be computed directly from the index of non-Newtonian behavior, n (determined graphically), the dimensions of the instrument, and the pressure-flow data. Using the symbols of the present paper, their equation is

$$\eta_{\tau=1} = \zeta = \frac{\pi r^3}{(n+3)} \frac{t}{V} \left(\frac{Pr}{2l}\right)^n = \frac{\tau^n}{\gamma_w} \qquad (10)$$

The graphic method of obtaining $\eta_{\tau=1}$ will be preferred if there is an appreciable scatter of the plotted points, since it leads in one operation to a weighted value determined by the choice of the best straight line through the points, and in combination with n will describe that line exactly.

The use of this method of summarizing rheological data for non-Newtonian systems is illustrated by Figure 4 and Table II, which utilize raw data that are presented in Table I for solutions of sodium phenylstearate and various amounts of water in benzene.

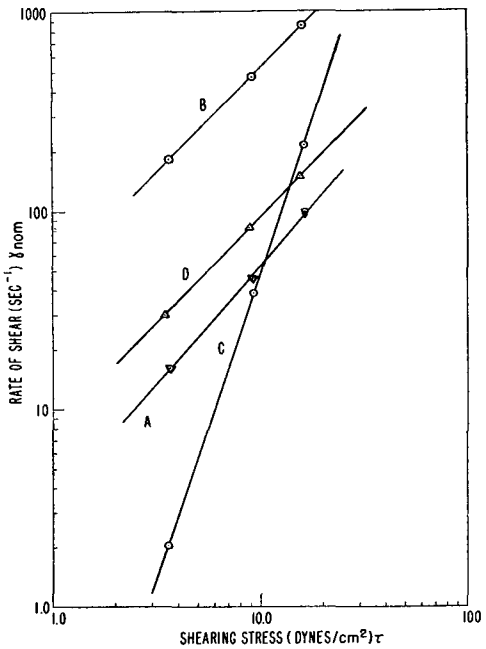

Figure 4. Determination of Index of Non-Newtonian Flow for a 1.7% Soap Solution in Benzene

A. **0.1 mole of water per mole of soap**
B. **1.5 moles of water per mole of soap**
C. **3.3 moles of water per mole of soap**
D. **Newtonian viscosity oil**

The differences between systems A and C, which show nearly equal flow times from the middle viscometer bulb, is strikingly shown when either their viscosities at unit shearing stress or their indices, n, of non-Newtonian behavior are examined. The data in this case have been interpreted (*10*) as indicating the presence of very large but shear-stable linear aggregates in solution A, and of more compact and less assymmetrical soap micelles in solution B. In solution C the high values for $\eta_{\tau=1}$ and n are taken to indicate the presence of extensive but loosely bonded and shear-sensitive structures.

A number of other equations have been reported which can be fitted to data for non-Newtonian flow in capillaries by the adjustment of two constants which are often obtainable graphically (*2-4, 6, 7, 9, 11, 13, 14, 17-19*). For some of these equations (*7, 14, 17, 18*) one constant will reflect the viscosity of the system at zero shearing stress (or rate) instead of at unit shearing stress (or rate); this may be an advantage if the extrapolation implied is justifiable. Most of these equations are applicable to a more limited range of systems than Equation 10, and their validity must be scrutinized carefully before applying them to a new situation.

Table II. Rheological Constants for Sodium Phenylstearate Solutions in Benzene with Successive Additions of Water[a]

System	Water, Moles per Mole of Soap	η_r for Middle Bulb	$\eta_{\tau=1}$	n
A	0.1	33.04	28.2	1.20
B	1.5	3.169	1.98	1.02
C	3.0	38.22	1520	3.00

[a] Soap concentration 1.7%.

ACKNOWLEDGMENT

The x-ray photographs used in this work were furnished by Walter Sadler of the Metallurgy Division of this laboratory, whose assistance is gratefully acknowledged.

SYMBOLS USED

A, B	=	instrument constants
a, b	=	constants in flow equations
g	=	gravitational constant
h	=	hydrostatic head, cm.
l	=	length of the capillary tube, cm.
n	=	index of deviation from Newtonian flow (Ostwald-deWaele)
P	=	hydrostatic pressure
r	=	radius of capillary tube, cm.
t	=	flow time, seconds
V	=	volume, cc.
γ_{nom}	=	nominal rate of shear at wall of capillary
γ_w	=	actual maximum shear rate at wall of capillary
ζ	=	viscosity counterpart (Krieble and Whitwell)
η	=	viscosity (poises)
$\eta_{\tau=1}$	=	viscosity at unit shearing stress
η_{nom}	=	nominal viscosity
ρ	=	density of solution
τ_w	=	shearing stress at wall of capillary

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Reaction between Zinc and Salicylaldoxime

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The reaction between zinc(II) and salicylaldoxime yields an insoluble product, the composition of which varies with the conditions of precipitation. This investigation was undertaken to study the reaction more completely. It was found that the composition of the precipitate varies with the pH of the solution from which it was precipitated. At pH 6.8, the precipitate had the composition of zinc disalicylaldoximate; at pH 8.5, the precipitate had the composition of zinc monosalicylaldoximate; and at the intermediate pH, the precipitate was a mixture of the two. Digestion at 90° to 100° C. converted the precipitate into the monosalicylaldoximate, regardless of the pH of the solution from which it was precipitated. When precipitated from a solution of pH 7.5 at a temperature of 10° C., pure monosalicylaldoximate was obtained; whereas when precipitated from a solution of the same pH at room temperature, a mixture was obtained. The presence of neutral salts in the solution affected not only the completeness of precipitation, as previously reported, but also the composition of the precipitate. If the reaction between zinc(II) and salicylaldoxime is to be used as the basis for the gravimetric determination of zinc, the conditions of precipitation must be rigorously controlled.

THE formation of an insoluble complex of zinc with salicylaldoxime was first reported by Ephraim (*2*). Later, Pearson (*4*) made a more thorough investigation of the properties of zinc salicylaldoximate and concluded that it was not suitable for the gravimetric determination of zinc because the pH range for complete precipitation was too limited, the precipitate was appreciably soluble in various neutral salt solutions, and the precipitate slowly decomposed above 80° C. Precipitated from solutions of pH 7 to 8, the compound corresponded to the formula $Zn(C_7H_6O_2N)_2$, which contains 19.36% zinc. Attempts to determine zinc gravimetrically in this form gave extremely variable results, depending upon such factors as the time of standing before filtration and pH of solution from which precipitate was formed.

Flagg and Furman (*3*) studied the reaction more completely and found that if the freshly precipitated zinc salicylaldoximate was allowed to digest for 10 minutes at 90° to 100° C. a significant transformation took place. The original voluminous precipitate became dense and curdy, and could, after filtering and washing, be dried for several hours at 110° C. without loss of weight. This product contained 32.50% zinc, corresponding to the formula $ZnC_7H_5O_2N$. The first turbidity appeared in the range pH 6.2 to 6.8 and the precipitate redissolved at pH 8.8 to 9.4. Precipitation was complete between pH 7 and 8. Good analytical results were obtained on synthetic mixtures and National Bureau of Standards brass samples.

Biefeld and Ligett (*1*) also investigated the feasibility of the reaction for gravimetric determination of zinc and their results confirmed the work of Flagg and Furman.

The present investigation was undertaken in an attempt to learn more about the conditions under which the two forms, zinc mono- and disalicylaldoximate, are formed.

EXPERIMENTAL

Reagents and Apparatus. A 1% solution of salicylaldoxime was prepared by dissolving 1 gram of salicylaldoxime (Eastman, No. 2956) in 5 ml. of ethyl alcohol and then diluting to 100 ml. with warm water. The solution was stored in an amber bottle in a refrigerator to avoid possible decomposition.

A standard zinc solution was prepared from reagent grade zinc nitrate hexahydrate to contain 2 to 3 mg. of zinc per ml. It was standardized gravimetrically by the zinc ammonium phosphate method and found to contain 2.38 mg. of zinc per ml.

All other reagents used were of reagent grade.

A Beckman Model G pH meter with a glass electrode assembly, standardized frequently against a buffer solution of pH 7.00, was used for all pH measurements.

A Hayes x-ray diffraction unit and a Spectron spectrometer with filtered copper radiation were used to record the diffraction maxima of precipitates prepared under different conditions.

Procedures and Results. COMPARISON OF UNDIGESTED AND DIGESTED PRECIPITATES. Several sets of precipitates were prepared by mixing 60 ml. of 1% salicylaldoxime solution with 50 ml. of standard zinc solution and adjusting the pH to 8.50 by the slow addition of dilute ammonia solution from a buret. After thorough stirring, one set of precipitates was filtered and washed with water immediately after precipitation, whereas another set was heated for 10 minutes at 90° to 100° C. before filtration. A 1% ferric chloride solution was used to test for completeness of washing.

Both sets of precipitates were dried to constant weight at 80° C. and then analyzed for zinc by ignition of the precipitate to zinc oxide and for nitrogen by the micro-Dumas method. The ignition of the precipitate was carefully carried out by slow heating in a porcelain crucible to avoid loss of precipitate (the compound burns very easily with a vigorous evolution of heavy smoke); after the initial heating the residue was ignited to constant weight at 900° C. in an electric muffle furnace. The results of the analyses are given in Table I.

The theoretical composition of the zinc monosalcylaldoximate is 32.61% zinc and 6.95% nitrogen.

The x-ray diffraction recordings of both sets of precipitates were identical except that the one of the undigested precipitate gave broadened maxima and many of the weak lines were absent. This indicated a very small particle size.

Table I. Composition of Undigested and Digested Precipitates Prepared at pH 8.50

	Undigested		Digested	
	Zn, %	N, %	Zn, %	N, %
	32.74	6.89	32.12	6.91
	32.43	..	32.79	..
Av.	32.59		32.46	

Table II. Effect of pH on Composition of Precipitate

Undigested		Digested	
Final pH	Zn, %	Final pH	Zn, %
7.20	28.23	7.00	32.61
7.50	29.30	7.23	32.43
8.00	31.20	8.00	32.59
8.50	32.48	8.50	32.61

EFFECT OF pH ON COMPOSITION OF PRECIPITATE. Precipitations were carried out by the procedure described except that the pH of the final solution was varied. The initial pH of all solutions was between 4.7 and 5.0 and the pH was adjusted by the slow addition with thorough stirring of dilute ammonia solution from a buret. Completeness of precipitation was not considered.

Two sets of precipitates were prepared, one was filtered immediately after formation and the other was digested for 10 minutes at 90° to 100° C. The precipitates were dried to constant weight at 80° C. and analyzed for zinc by ignition to zinc oxide. The results are given in Table II.

It was observed that the higher the final pH of the solution,

the whiter the color of the precipitate. At lower pH values, the precipitate was yellowish.

In order to avoid a localized region of high hydroxyl ion concentration, sodium acetate was used to adjust the pH of the solution containing the zinc and salicylaldoxime. Standard solutions of zinc and salicylaldoxime were mixed thoroughly and 50 ml. of 2.5*M* sodium acetate was added slowly from a buret. The first turbidity occurred in all cases at a pH of about 5.8. The final pH was from 6.85 to 6.90. One set of precipitates was filtered and washed immediately after filtration; another set was digested for 10 minutes at 90° to 100° C. before filtration. All precipitates were dried to constant weight at 80° C. and analyzed for zinc. The results obtained are given in Table III.

X-ray diffraction recordings were made of both sets of precipitates. The principal lines are given in Table IV.

Table III. Composition of Precipitates Obtained by Adjusting pH with Sodium Acetate

Zn, %	
Undigested	Digested
19.31	32.81
19.81	32.39
Av. 19.56	32.60

Table IV. Principal Lines of Zinc Mono- and Disalicylaldoximates

Zinc Monosalicylaldoximate, Digested		Zinc Disalicylaldoximate, Undigested	
d	Intensity[a]	*d*	Intensity[a]
13.5	VS	13.2	VS
10.64	M	10.37	W
6.40	S	6.47	M
5.83	M	4.81	W
5.01	M	4.65	M
4.75	M	4.30	M
4.46	W	4.11	S
4.07	VW	4.03	S
3.93	W	3.82	W
3.80	W	3.35	W
3.48	S	2.86	M
3.41	S	2.21	W
3.15	W	2.16	W
3.02	W		
2.65	M		
2.45	VW		
2.17	M		
2.01	VW		
1.88	W		

[a] VS, very strong; S, strong; M, medium; W, weak; VW, very weak.

Effect of Low Temperature on Composition of Precipitate. Solutions of zinc and salicylaldoxime were thoroughly mixed and placed in an ice bath. When the temperature of the solutions had reached 9° to 11° C. the pH was adjusted by the slow addition of dilute ammonia solution. The first turbidity appeared at pH 5.3 to 6.0, just as in the cases when the precipitation was carried out at room temperature. The precipitate was filtered and washed immediately after precipitation. Filtration and washing were difficult because the precipitate was very fine and passed through the filter. Complete removal of the excess reagent was finally accomplished by washing with a solution containing 20% alcohol. The precipitate was dried to constant weight at 80° C. and analyzed for zinc. The results are given in Table V.

Table V. Composition of Precipitates Obtained by Precipitation at 10° C.

Final pH	Temp., ° C.	Zn, %
7.50	11	32.69
7.54	10	32.46
7.60	9	32.79

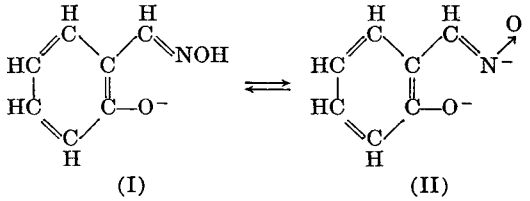
Effect of pH on Completeness of Precipitation. Precipitations were carried out by mixing the standard solutions of zinc and salicylaldoxime thoroughly and regulating the pH by slow addition of dilute ammonia solution. The precipitates were digested for 10 minutes at 90° to 100° C. before filtration, filtered and washed, and dried at 110° C. to constant weight. The precipitates were weighed and analyzed for zinc. In each case the composition of the precipitate corresponded to that of the zinc monosalicylaldoxime. The results are given in Table VI.

Table VI. Effect of pH on Completeness of Precipitation

pH	Zn Recovered, %
Orig. Zn Content of Soln., 173.92 Mg. Zn/100 Ml.	
6.60	61.69
7.00	73.36
7.64	96.97
8.03	99.26
8.72	99.97
Orig. Zn Content of Soln., 86.96 Mg. Zn/100 Ml.	
6.48	61.17
7.00	82.53
7.63	95.53
8.05	99.63
8.50	99.89
8.72	96.83

DISCUSSION

The composition of the product of the reaction between zinc and salicylaldoxime depends upon the pH of the solution in which the precipitate is formed and upon the temperature of digestion. Depending upon the conditions of the precipitation, zinc monosalicylaldoxime, zinc disalicylaldoxime, or a mixture of the two is formed. The monosalicylaldoxime is evidently the more stable because digestion of the precipitate at 90° to 100° C. always transforms the disalicylaldoxime into the monosalicylaldoxime, regardless of the pH at which the precipitate was formed. This is shown by the data in Table II. In fact, Pearson's (*4*) table showing the loss of weight during heating of the precipitate at various temperatures shows that the transformation occurs in the dry, solid state, being complete at 140° C. When precipitated from solution having a pH 8.50, the monosalicylaldoxime is always obtained; below pH 8.50 a mixture of the monosalicylaldoxime and disalicylaldoxime is obtained. This is probably due to an equilibrium between two ionic species of the oxime:



(I) (II) (1)

The oxime group is a very weak acid (*5*), so that in solutions of lower pH, form I is present in appreciable quantities and the disalicylaldoxime is formed; in solutions of higher pH, form II predominates and the monosalicylaldoxime is formed exclusively; and in solutions of intermediate pH, mixtures are formed. From the data in Table II the amounts of each compound formed at the different pH values can be calculated by the following relationships:

$$\% \text{ Zn} = f_m \times \% \text{ Zn}_m + f_d \times \% \text{ Zn}_d \quad (2)$$

$$f_m + f_d = 1 \quad (3)$$

where % Zn is the percentage zinc in the mixture; % Zn_m and % Zn_d are the percentages of zinc in the monosalicylaldoxime and the disalicylaldoxime, respectively; and f_m and f_d are the fractions of the mono- and disalicylaldoximates, respectively, in the mixture. The results of such calculations are given in Table VII.

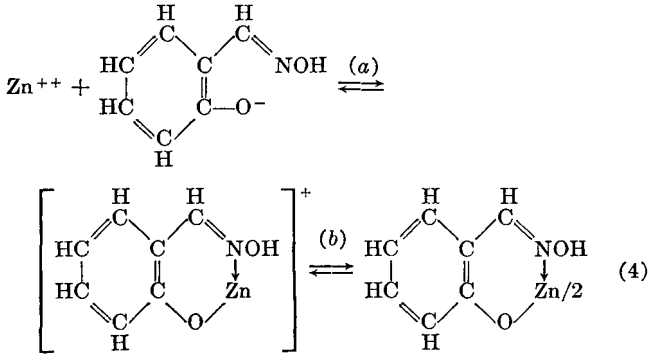
When the dilute ammonia solution is added to the solution of zinc and salicylaldoxime, there is a localized area at the point of addition where the pH is higher than that of the bulk of the so-

Table VII. Zinc Monosalicylaldoximate Content of Precipitates as a Function of pH

pH	Zinc Monosalicylaldoximate, %
7.20	66.9
7.50	75.0
8.00	89.4
8.50	99.0

lution. Thus, some monosalicylaldoximate is formed even when the final pH of the solution is kept low. This localized, high pH area is minimized when the pH of the solution is adjusted by the addition of a sodium acetate solution, so that in this case a precipitate of pure zinc disalicylaldoximate can be obtained.

When precipitated from a solution of pH 7.50 at a temperature of 10° C. pure monosalicylaldoximate was obtained, whereas when precipitated from a solution of the same pH at room temperature a mixture was obtained. An explanation for this is possible by considering the formation of the disalicylaldoximate as taking place in two steps with the formation of a soluble intermediate.



In an experiment investigating the feasibility of the reaction for the determination of zinc amperometrically (in a sodium acetate–buffered solution) it was found that 15 to 20 minutes was required to reach a steady current state after each increment of salicylaldoxime had been added. This indicates a slow rate-determining step, which could be step *b*. If the temperature were decreased, the rate could be slowed down to such an extent that the formation of the monosalicylaldoximate predominates, because of the equilibrium shown by Equation 1.

The range of complete precipitation was found to be between pH 8.1 and 8.7, the range changing slightly with the original concentration of the zinc. This is essentially in agreement with Flagg and Furman (*3*) and Biefeld and Ligett (*1*) who found precipitation complete between pH 7 and 8. The difference is probably due to the slightly different methods used; in this investigation the pH measurements were made on the supernatant liquid prior to digestion, whereas the pH measurements made by Biefeld and Ligett were on the filtrate obtained after digestion of the precipitate. Undoubtedly, some ammonia was lost during the digestion of 10 minutes at 90° to 100° C.

ACKNOWLEDGMENT

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Determination of Small Amounts of Niobium in Pure Tantalum and Its Oxide

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A sensitive chemical method was needed for the analysis of pure tantalum metal. The spectrophotometric method for the determination of niobium by measuring the intensity of the ether extract of the yellow thiocyanate complex of niobium has been reported but there has been no extension of the method to a material containing a preponderance of tantalum which reduces the intensity of the color. Details of concentration, manipulation, and timing must be strictly observed. A method is presented for the determination of niobium in pure tantalum metal in the range of 0.01 to 0.30% niobium with good reproducibility. No separations are necessary except for the extraction of the thiocyanate complex of niobium with ether. Contamination from large amounts of reagents is avoided.

OF THE minor constituents known to be present in pure tantalum metal (99.8% tantalum), niobium was shown to be present to the extent of 0.1% or less from qualitative spectrographic analysis.

There are over 30 references in the literature to the determination of niobium and tantalum. Most of them are concerned with the analysis of ores, minerals, and steels and a few refer to pure salts. None of the methods are directly applicable to the determination of niobium in the presence of a preponderance of tantalum. The spectrophotometric determination of the yellow thiocyanate complex of niobium in solution appeared to offer the best solution to the problem. The previous work of Alimarin (*1*) in Russia, Hume and his coworkers (*3*), and Freund and Levitt (*2*) all furnished valuable information on the problem. The details of the method as presented here had to be worked out, in some cases as the investigation proceeded.

GENERAL PRINCIPLES

The tantalum metal is dissolved in hydrofluoric acid and a solution of potassium bisulfate–oxalic acid is added to compensate for that present in the solutions used in preparing the calibration curve. After evaporation to a moist salt, hydrochloric acid is added and finally, in quick succession and in precise amounts, solutions of boric acid, stannous chloride, and ammonium thiocyanate are added. The thiocyanate forms a yellow complex with niobium which is extracted with ethyl ether, and the absorb-

ancy of the ether extract is measured on a Beckman DU spectrophotometer at 386 mμ (Figure 1) in 1-cm. Corex cells with ether used as a reference.

DISCUSSION

A common method for preparing a solution of tantalum or niobium is by fusion of the oxide with potassium bisulfate. The presence of niobium in moderate amounts has a marked effect on the properties of tantalum, one of which is that the mixed oxide fuses readily with potassium bisulfate. With pure tantalum oxide, fusion requires time and attention.

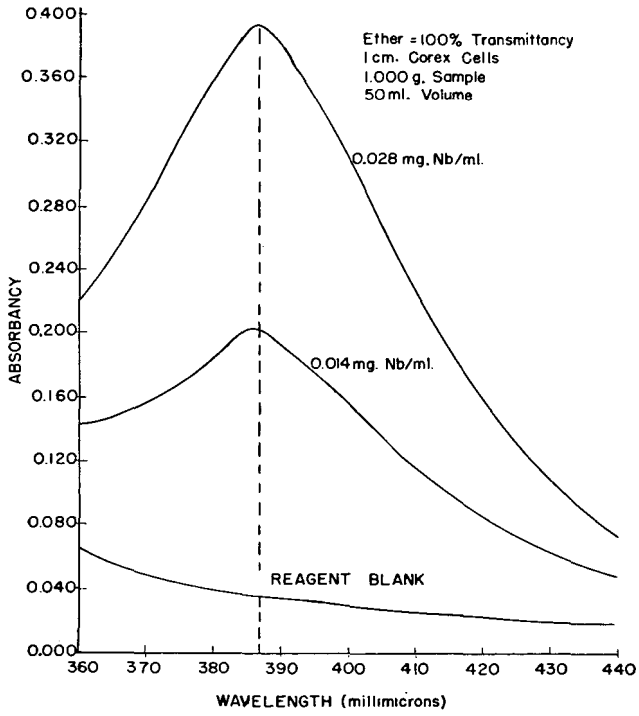

Figure 1. Absorption Curve for Niobium-Thiocyanate Complex

Sulfates should be kept at a minimum for best results in the use of the thiocyanate method. Ordinarily, the bisulfate melt is dissolved in a solution of oxalate or tartrate, both of which interfere with the intensity of the thiocyanate complex. It therefore appeared that an attack of the metal by acid was preferable. The use of concentrated sulfuric acid was not advisable because of the interference of sulfate and also because of previous difficulty with hydrolysis of tantalum in dilute sulfuric acid.

A mixture of hydrofluoric and nitric acids is very satisfactory for dissolving tantalum but both interfere with the color development. However, the best compromise appeared to be the use of hydrofluoric acid and subsequent fixation of it with boric acid if any were present after evaporation.

Other complications made it necessary to adhere rigorously to the conditions of manipulation and timing as given in the procedures described.

The concentrations of ammonium thiocyanate, hydrochloric acid, and boric acid all affect the intensity of the color adversely. The solutions must be prepared accurately and consistently the same.

The intensity of the color changes irregularly with time between the addition of the reagents and the extraction. This random effect was attributed to the hydrolysis of tantalum when the remaining fluoride ions were removed with boric acid.

The polymerization of thiocyanate in acid solution makes it necessary to work rapidly.

In investigating the extraction of the thiocyanate complex of niobium, it was found that carbon tetrachloride, chloroform, and petroleum ether were unsatisfactory. *Isopropyl ether* and dichlorodiethyl ether extracted a small amount (10 to 15%) of the complex. Diethyl ether produces an intensely colored extract and was used.

There were no reference standards available. Therefore, samples from the same lot of tantalum were used for preparing the calibration curve and as references with each series of determinations.

INTERFERENCES

Iron. Iron was known to be present to the extent of 0.005% or less. The addition of stannous chloride would reduce the iron and there should be no interference. The addition of 0.05% of iron to a sample produced no interference in the method.

Titanium. Titanium was known to be present in the range of 0.01% but was not expected to interfere. The addition of 0.05% of titanium caused no interference.

Molybdenum. Molybdenum was not shown to be present qualitatively in any of the metal which had been received but was known to interfere if present (*5*, *6*).

Upon adding molybdenum to a solution of the tantalum, it was found that the extract of thiocyanate absorbed strongly at 468 mμ and weakly at 386 mμ. If molybdenum is present, a correction may be applied in the determination of niobium by measuring the absorbancy at both wave lengths and solving an equation for a two-component system (*4*).

Tantalum. Tantalum inhibits the development of color and thus limits the flexibility of the method. Once a calibration curve has been prepared based on 1-gram samples of tantalum and increments of niobium in the expected range, it is not possible to change the ratio of niobium to tantalum. A new calibration curve must be prepared.

Potassium. Potassium thiocyanate was used by previous investigators. A precipitate formed which was thought to be potassium fluotantalate. Since there was danger of adsorption and loss of niobium if the material was removed by filtration, a change was made to ammonium thiocyanate; this reagent proved satisfactory.

SPECIAL REAGENTS

All reagents were A.C.S. specification grade unless no specification existed.

Hydrofluoric Acid, 48%.

Potassium Bisulfate, fused and powdered.

Oxalic Acid. $H_2C_2O_4.2H_2O$.

Potassium Bisulfate–Oxalic Acid Solution. Dissolve 5 grams of potassium bisulfate and 1.5 grams of oxalic acid in 1 liter of water.

Oxalic Acid Solution. Dissolve 1.5 grams of oxalic acid in 75 ml. of water.

Boric Acid Solution (4%). Dissolve 40 grams of boric acid in 1 liter of water.

Stannous Chloride Solution (20%). Dissolve 100 grams of stannous chloride, $SnCl_2.2H_2O$, in 500 ml. of hydrochloric acid (1 to 1).

Ammonium Thiocyanate Solution (23%). Dissolve 230 grams of ammonium thiocyanate in 1 liter of water.

Diethyl Ether.

Standard Niobium Solution (1 ml. = 0.20 mg. of niobium). Fuse 0.290 gram of pure niobium oxide (spectrographic standard grade) with 5.00 grams of potassium bisulfate in a Vycor crucible of 30-ml. capacity. When a clear, fused mass is obtained, cool and dissolve in 75 ml. of hot oxalic acid solution (2%). Dilute to 1 liter with water.

CALIBRATION CURVE

Prepare solutions for a calibration curve by adding 0, 1, 2, 3, 4, and 5 ml. of the standard niobium solution to 1.000-gram samples of tantalum metal in platinum dishes. Add 5, 4, 3, 2, 1, and 0 ml. of the potassium bisulfate–oxalic acid solution so that each standard will contain the same quantity of potassium bisulfate and oxalic acid. Carry the samples through the procedure given below. Subtract the absorbancy reading of the solution to

which no niobium has been added from that of each of the standard solutions and plot the values against the concentration of niobium.

Figure 1 shows the absorption curves for two of the standard niobium-tantalum solutions with a maximum in each case at 386 mμ. Beer's law was followed.

PROCEDURE

Transfer a 1.000-gram sample of tantalum to a 50-ml. platinum dish. Add 5 ml. of potassium bisulfate–oxalic acid solution. This step is necessary in order to have the salt concentration the same as that of the standard niobium solution. Add 10 ml. of hydrofluoric acid and place on a steam bath. Avoid overheating until dissolution of the metal is complete. After the tantalum has dissolved, evaporate the solution until crystals can be seen when the dish is swirled. Add 10 ml. of water and evaporate again to incipient crystallization and repeat this step. Care must be taken in the evaporation so that the salts do not become dry at any time.

Remove the dishes from the steam bath and add, by means of a pipet, 25 ml. of hydrochloric acid (1 to 1). After the addition of hydrochloric acid, each sample must be treated individually. Timing is critical and manipulations should be carried out rapidly so that all of the conditions are constant for each sample.

Add, by means of a pipet, 25 ml. of boric acid solution (4%) and transfer the solution to a 250-ml. separatory funnel. Rinse the dish with water. Immediately, add in quick succession 10 ml. of stannous chloride solution (20%), 25 ml. of ammonium thiocyanate solution (23%), and 25 ml. of ethyl ether from burets. Shake the mixture for 1 minute and allow the aqueous and ether layers to separate. Draw off the aqueous layer and drain the ether layer through a dry filter paper into a dry 50-ml. volumetric flask. Extract the aqueous layer twice more with 15 and 10 ml. of ether, respectively, shaking the mixture 30 seconds for each extraction. Combine the ether extracts and dilute to 50 ml. with ether if the volume is not correct.

Immediately transfer a portion of the extract to a 1-cm. Corex cell and read the absorbancy on a Beckman Model DU spectrophotometer at 386 mμ and a slit width of 0.10 mm. Compare the solution with ether at 100% transmittance for reference.

A blank must be carried through the procedure and a correction applied for the blank.

If molybdenum is present, the absorbancy should be read at both 386 and 468 mμ and a correction applied for the molybdenum (*4*).

REPRODUCIBILITY

The precision of the method was established by determining the niobium in one sample of tantalum on separate days. The results are shown in Table I.

Table I. Determination of Niobium in Tantalum

(σ = standard deviation, x = individual value, and $\bar{x}$ = average value $\sigma = \pm\sqrt{\frac{\Sigma(x-\bar{x})^2}{n-1}}$, $\sigma = \pm 0.001\%$ niobium)

Niobium, %
0.028
0.029
0.029
0.026
0.028
0.027
0.029
0.028
0.028
Av. 0.028

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Tracer Method for Sulfur Solubility and Diffusivity in Rubber

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Sulfur solubility determinations for rubber have heretofore been limited almost entirely to specimens of reasonable optical clarity. They have depended on the observation of the occurrence of sulfur crystals. A method which could be used with opaque compounds was required to study the effect of compounding ingredients on sulfur solubility. A new method was devised for measuring sulfur solubility which employed the radioactive sulfur-35 isotope. The solubility was deduced from the equilibrium counting rate and an appropriate calibration curve of the counts for rubber containing known concentrations of the radiosulfur. The effect of a number of compounding ingredients, including carbon black, on apparent sulfur solubility was measured. The diffusivity of sulfur in rubber can be determined by suitable application of these procedures. Migration of sulfur to the surface, or blooming, was followed by changes in the counting rate during storage of a specimen at a lower temperature after the solubility determination. These methods should be applicable for measuring the solubility, diffusivity, and migration of compounds tagged with sulfur-35 or carbon-14.

PROBLEMS in the rubber industry connected with the solubility of compounding ingredients and especially sulfur have a history as old as the industry itself. They are still current. Bloom—i.e., migration of an ingredient to the surface of the rubber because of supersaturation—is usually very objectionable on a finished product. When it occurs on raw stock during processing, it may lead to troublesome difficulties in fabrication. Despite the ubiquity of these problems, there has been no general laboratory method of sufficient scope to secure the necessary solubility, diffusivity, and migration data to deal with them. Tracer techniques can be applied for this purpose in ways which are illustrated here for sulfur.

Sulfur solubilities in various types of rubber have been determined by a number of investigators using different methods. The literature on the subject has been amply covered by Kemp, Malm, Winspear, and Stiratelli (*8*) and by Williams (*4*). A brief comparison of experimental procedures and the principles involved is sufficient here.

Previous experimental methods have proved to be of limited value. Thus, when rubber samples are enclosed in a sulfur pack there is a tendency for the sulfur to crystallize within the rubber, thereby increasing the apparent solubility (*8*). Visual methods have been developed in which temperatures are noted at

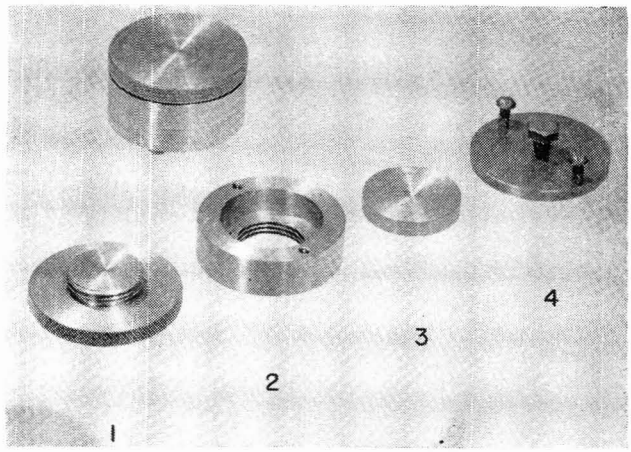

Figure 1. Cell Used for Solubility Measurements

1. Cover
2. Cell body
3. Piston
4. Pressure adjusting component

the onset of crystallization for fixed sulfur concentrations in rubber. The methods, of course, are limited to transparent rubbers. The method developed by Morris (*10*) which involves microscopic observation of a rubber specimen held at a constant temperature was considered by Kemp *et al.* (*8*) to be subject to errors due to possible supersaturation because the sample is not agitated. Although this may be a potential source of error, there is no indication from the present work that it actually occurred. This problem was not involved in the methods of Williams (*11*) and Kemp *et al.* (*7*, *8*), who banded the rubber on a mill and gradually lowered the temperature. Difficulties in determining exact temperatures for crystallization are noted by the authors. These difficulties are eliminated with the present method which employs the radioactive sulfur-35 isotope. Since the beta radiation from carbon-14 is so similar to that from sulfur-35, the method should apply as well for measuring the solubility of compounds tagged with this isotope.

EXPERIMENTAL

A rubber specimen is prepared in the form of a small disk which is clamped in a stainless steel cell over a layer of sulfur powder tagged with sulfur-35. The rubber is thick enough to absorb all of the beta radiation, so that there is no count above background when the cell is brought under a Geiger-Müller end window counting tube. The cell is then placed in a constant-temperature oven. Sulfur diffuses into the rubber until it is saturated, a condition indicated by a constant counting rate over an extended time period. The sulfur solubility is then determined from the equilibrium counting rate by means of a suitable calibration curve.

The component parts as well as an assembled unit of the stainless steel cell used for the solubility measurements are shown in Figures 1 and 2. The rubber specimen, secured by molding in a laboratory press is a $1^3/_8$-inch diameter disk about 0.03 inch thick, which is evenly covered with a layer of sulfur powder tagged with sulfur-35. An aluminum disk of the same diameter and 0.004 inch thick is placed over the sulfur. The assembly is then inverted so that the disk acts as a support for the rubber. The rubber and aluminum disk is then placed on a piece of aluminum foil (0.001-inch gage) $1^3/_4$ inches in diameter so that both pieces of aluminum are in contact. The overlapping edge of the foil is then folded over the edge of the rubber. Sulfur is thereby prevented from scattering when the rubber is placed in or removed from the cell. The overlapping border of the foil also allows a minimum of contact between the rubber and the cell, thereby preventing its contamination.

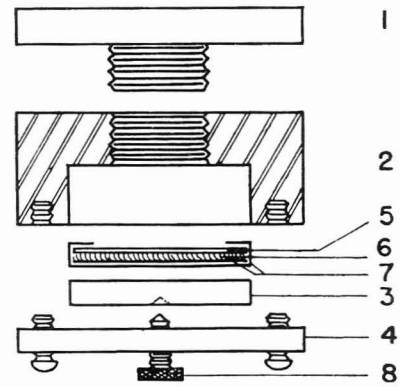

Figure 2. Cell Used for Solubility Measurements (Schematic)

1. Cover
2. Cell body
3. Piston
4. Bottom plate
5. Rubber
6. Sulfur
7. Aluminum foil
8. Pressure adjusting screw

The specimen is then placed in the well of the cell body which is $1^3/_8$ inches in diameter (Figures 1 and 2) so that the rubber surface is exposed through the 1-inch opening. The specimen is held in place with component 3. Intimate contact between sulfur and rubber is obtained with the pressure adjusting screw of component 4. Activity measurements are made by removing the threaded cover, component 1, and placing the exposed rubber surface under the window of a Geiger-Müller tube. A piece of Teflon film is inserted between the cover and rubber to avoid sticking. This is removed for counting.

Samples were counted twice daily for periods of 3 to 8 days. The counting rates were corrected for any uncontrolled

Table I. Sulfur Solubilities and Calculated Heats of Solution

(Grams sulfur/100 grams rubber or mixture)

	Temp., ° C.								ΔH,
	30	40	50	60	70	80	90	100	Kcal./Mole
Base rubbers									
Air-dried Hevea latex	..	1.07	1.38	1.76	..	4.11	5.68	...	7.90
Polyisobutylene	..	0.045	0.31	0.76	1.06	1.70	2.25	...	12.1
GR-S-1500	1.01	1.37	1.94	..	..	..	..	...	6.76
GR-I-18 (2.5% isoprene)	..	0.056	0.35	0.79	1.13	1.68	..	...	11.9
Smoked sheet	..	1.19	1.55	2.06	..	..	..	...	5.67
GR-S-1006, 76.5–23.5 butadiene/styrene	1.28	1.80	2.52	3.45	4.60	6.13	8.03	10.15	7.32
Polybutadiene	..	1.38	..	..	..	..	..	...	...
GR-S-1023, 88–12 butadiene/styrene	..	1.66	..	..	..	..	..	...	...
Polystyrene	..	0.050	..	..	..	..	..	...	...
Pale crepe (unmilled)	..	1.55	..	..	..	..	..	...	...
Pale crepe (milled 45 min.)	..	1.56	..	..	..	..	..	...	...
Pale crepe (milled 65 min.)	..	1.44	..	..	..	..	..	...	...
Rubbers compounded with blacks									
Smoked sheet + 25 parts MPC	0.76	0.97	1.36	2.13	..	..	..	...	6.95
Smoked sheet + 50 parts MPC	0.61	0.87	1.19	1.84	..	..	..	...	7.40
Oil polymer (GR-S-1801) + 62.5 parts HAF	0.88	1.28	1.63	2.19	..	..	..	...	4.89
GR-S-1006 -- 50 parts SAF (Statex 160)	..	1.19	1.72	2.28	3.01	4.02	..	...	5.79
GR-S-1006 + 50 parts MT	..	..	1.49	1.89	2.62	3.50	..	...	7.32
GR-S-1000 + 25 parts HMF	0.81	1.05	1.55	..	..	..	..	...	6.22
GR-S-1000 + 25 parts MPC	0.68	1.07	1.50	..	..	..	..	...	7.68
Rubbers compounded with other ingredients									
Smoked sheet + 5 parts yellow-dip rosin oil	0.92	1.15	1.59	2.44	..	..	..	...	5.94
Smoked sheet + 5 parts rubber processing oil	0.80	1.09	1.51	2.19	..	..	..	...	6.45
Smoked sheet + 2 parts stearic acid	0.81	1.19	1.65	2.58	..	..	..	...	7.78
Oil polymer (GR-S-1705) + 3 parts stearic acid	1.04	1.62	2.07	2.69	..	..	..	...	6.49
GR-S-1006 -- 5 parts Paraflux	0.93	1.40	1.79	2.38	..	..	..	...	6.48
Polyisobutylene + 20 parts TMTD[a]	..	0.086	0.42	0.88	1.29	1.74	..	...	11.0

[a] Tetramethylthiuram disulfide.

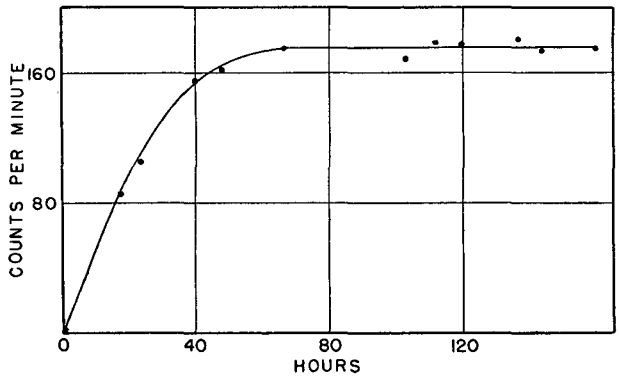

Figure 3. Illustration of Equilibrium Condition Attained from Diffusion of S^{35} into a GR-S-1000 + 50 Parts HMF Mixture, 30° C.

fluctuations in daily counting rates by reference to a standard carbon-14 source in the usual way. In no case with sulfur was there any indication, exceeding possible experimental error, of an increase in solubility with time during the equilibrium period. This is graphically illustrated in Figure 3 where activity is plotted against time for a representative sample.

Standard deviations from the average equilibrium value were determined for most of the solubilities listed in Table I. The coefficient of variation was determined from these values and an over-all average of 3.69% was obtained. Standard deviations were also determined from the totalized counts of individual sample and background activity measurements. The over-all average for the coefficients of variation determined from these standard deviations was 3.57%. This information indicates that the accuracy of these solubility measurements was largely a function of the statistical counting error rather than experimental techniques. Greater accuracy could therefore be accomplished by simply using sulfur of a higher specific activity. The initial specific activity of the sulfur used for these measurements was 11,400 counts per minute per mg.

The calibration curve was prepared by dissolving weighed quantities of rubber and tagged sulfur in benzene, evaporating the benzene, and then milling the rubber. Disks were prepared similar to the other specimens and the activity was determined. The activity was independent of the rubber composition. Thus, the activity per gram of tagged sulfur was the same for black stocks, etc. as for the base rubbers. A typical calibration curve is shown in Figure 4.

RESULTS AND DISCUSSION

The solubilities which were measured are listed in Table I. They are grouped as base rubbers, rubbers compounded with blacks, and rubbers compounded with other ingredients. They are expressed as grams of sulfur per 100 grams of base or compounded rubber.

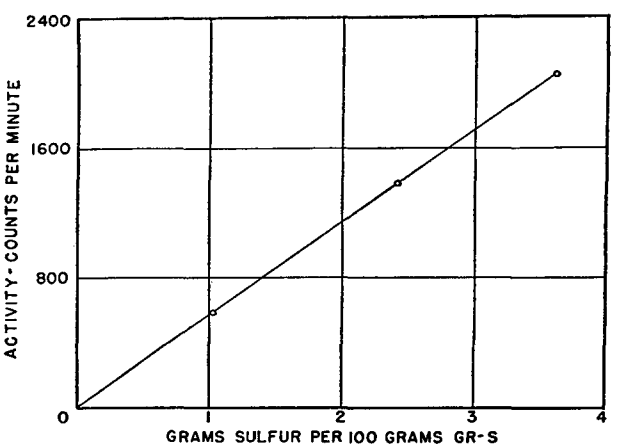

Figure 4. Calibration Curve for Converting Activity to Sulfur Solubility

Kemp *et al.* (*7*) had noted that the sulfur solubility increased with mill breakdown. This relationship was not substantiated here. Pale crepe samples which had been milled for 45 and 65 minutes on equipment similar to that described by Kemp *et al.* showed about the same sulfur solubility as an unmilled sample (Table I). These values are comparable with that obtained by Morris (*10*). The data for GR-S-1006 compares well with the data of Kemp *et al.* (*7*) for Buna S, as shown in Figure 5.

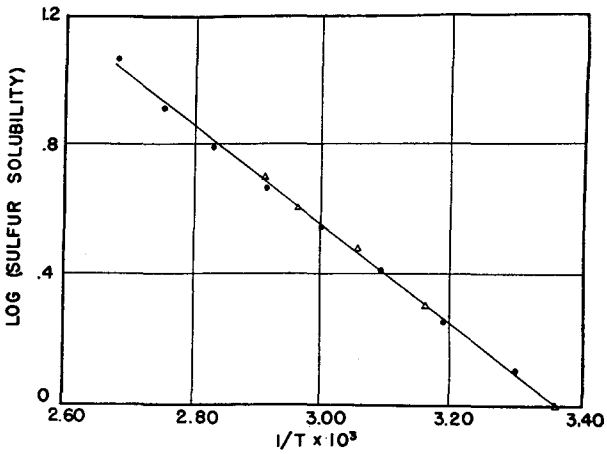

Figure 5. Effect of Temperature on the Sulfur Solubility in GR-S-1006

● **Data from Table I**
△ **Data from Kemp *et al.* (7)**

Carbon blacks vary in particle size and surface roughness. It would be anticipated, therefore, that a rubber compounded with a large surface area black might possess an apparently higher sulfur solubility than the same rubber with a lower surface area black because of surface adsorption of the sulfur by the black. This was found to be true when SAF and MT blacks were milled into GR-S-1006. SAF black whose surface area and roughness factor are larger than MT black gave a 15 to 20% greater apparent sulfur solubility.

It has been suggested that tetramethylthiuram disulfide (TMTD) forms an unstable trisulfide under vulcanization conditions (*3*). It should, therefore, increase the sulfur solubility of the medium in which it is dissolved or dispersed. To illustrate the broad application of the techniques being described and to test this hypothesis, 20 parts were milled into polyisobutylene, to avoid vulcanization side reactions, and the solubility of the mixture was measured. The data in Table I indicate that the solubility did increase; however, the differences were too small for making further calculations as to the amount of trisulfide formed.

Sulfur solubilities in hot polymerized styrene and butadiene polymers and copolymers were determined to see what effect the styrene content has on the solubility. The data are given in Table I and are shown graphically in Figure 6. They are expressed in terms of bound butadiene-styrene content. A maximum in the sulfur solubility is indicated at about 25% styrene content for this series of polymers.

Heats of solution were calculated from plots of the solubility data using the following relationship.

$$\log S = \frac{-\Delta H}{2.303\,R\,T} + I$$

where S = sulfur solubility
ΔH = heat of solution
R = gas constant
T = absolute temperature
I = integration constant

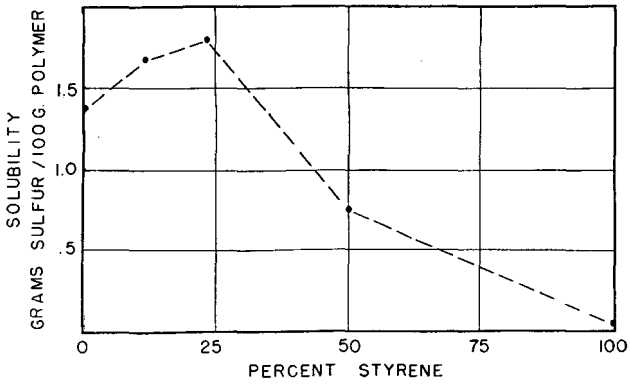

Figure 6. Sulfur Solubilities of Butadiene and Styrene Polymers and Copolymers, 40° C.

The heat of solution is the product of the slope of the line and 2.303 R. A typical plot is shown in Figure 5.

The heats of solution are listed in Table I. They vary over the range of 5 to 8 kcal. per mole of sulfur for the highly unsaturated polymers and mixtures. This range is in general agreement with the range calculated from data collected by Hildebrand and Scott (*6*). ΔH is about 12 kcal. for polyisobutylene and GR-I-18. The difference in the heats of solution of the two polymer groups indicates stronger attractive forces between the sulfur and the unsaturated polymers. The addition of tetramethylthiuram disulfide to polyisobutylene lowered the heat of solution to 11 kcal., which again suggests that association or reaction takes place between the sulfur and tetramethylthiuram disulfide.

An attempt was made to determine the solubility of mercaptobenzothiazole in GR-S using mercaptobenzothiazole in which the mercapto sulfur was radioactive. A saturated equilibrium condition was not attained, however, even after 14 days at 35° C. Instead mercaptobenzothiazole continued to be absorbed in a linear manner. This suggested that the mercaptobenzothiazole was reacting with the GR-S. Extraction of the GR-S samples with alcohol removed all but 12% of the activity. This presumably represented reacted mercaptobenzothiazole.

The solubility of mercaptobenzothiazole in polyisobutylene was determined. Polyisobutylene being saturated did not react and equilibrium conditions were readily obtained. The solubilities over a limited temperature range are given in Table II.

Table II. Solubility of Mercaptobenzothiazole in Polyisobutylene

Temp., ° C.	Solubility, G. Mercaptobenzothiazole/100 G. Polymer
80	0.037
90	0.047
100	0.096
110	0.183

DIFFUSIVITY OF SULFUR

A method for determining the diffusivity of sulfur and sulfur-35 or carbon-14 tagged compounds in rubber should be a useful supplement to the solubility method which has been described. A relatively simple and accurate method for measuring diffusivities in rubber is desirable for investigations of the rate of crystallization and migration of compounds in rubber. For example, the protective action of certain waxes and antioxidants may depend on the way in which they migrate to the surface of the rubber. Furthermore, diffusivity data have been shown to be applicable for making deductions in regard to the internal mobility of rubber (*2*, *5*).

In the solubility determinations, the rate at which the counts increase as the specimen is held at constant temperature depends upon the diffusivity constant at that temperature. Hence, the diffusivity can be calculated from experimental data obtained in the course of a solubility determination.

The mathematical solution to the problem is analogous to the solution for heat flow through a slab of infinite area. One surface of the slab is held at constant temperature and the other surface is insulated. The initial temperature in the slab is zero. The condition for the insulated surface is met by the following considerations. For a slab of twice the thickness with both surfaces held at the constant temperature there will be no heat flow across the midsection. Hence the midsection corresponds to an insulated surface. The temperature distribution in one half of the double thickness slab will correspond to that of the case in question. By analogy, the diffusion equation which applies follows:

$$\frac{C_s - C}{C_s} = \frac{4}{\pi}\left[e^{-\frac{D\pi^2 t}{4d^2}} \sin\frac{\pi x}{2d} + \frac{1}{3}e^{-\frac{9D\pi^2 t}{4d^2}} \sin\frac{3\pi x}{2d} + \ldots\right] \quad (1)$$

where C_s = concentration for saturation—i.e., concentration at the bottom of the rubber specimen
C = concentration at distance x from the bottom of the rubber specimen at time t
D = diffusivity constant
d = thickness of the rubber specimen

The second term is usually negligible except for very small values of t.

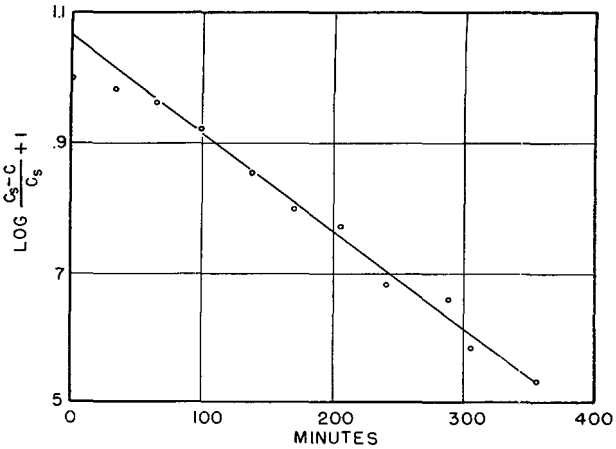

Figure 7. Sulfur Diffusion in Pale Crepe, 50° C.

In the experimental work, the counting rate is determined by the concentration of radioactive sulfur in a thin layer at the upper surface of the rubber so that x is approximately equal to d. Making these simplifications, the following equation may be used to determine D from the experimental data:

$$\frac{C_s - C}{C_s} = \frac{4}{\pi}\left[e^{-\frac{D\pi^2 t}{4d^2}}\right] \quad (2)$$

The error involved in the assumption that the counting rate gives the concentration at d, whereas actually there may be a contribution to the counting rate from a thin layer near the top of the specimen, can stand closer examination. The range for the radiation from sulfur-35 is 15 mg. per sq. cm. (*9*). The surface density required to absorb half of the radiation is 1.9 mg. per sq. cm. Translated into rubber thickness, these figures are, respectively, 0.0064 and 0.00081 inch. Since the specimen thickness was in the range 0.02 to 0.09 inch, it is apparent that the observed counting rate is determined by the concentration in a surface layer which is relatively thin compared to the thickness of the specimen. Furthermore, any importance of the error can be reduced by increasing the thickness of the specimen. There is

another consideration which mitigates this effect. It can be realized from the heat flow analogy previously discussed, in which there was no heat flow across the insulated surface, that the temperature gradient at the insulated surface is zero. Similarly, the concentration gradient at the top of the specimen is at all times zero. The concentration is essentially constant for a small depth below the surface. This can be shown, of course, by differentiating Equation 1 with respect to x.

When Equation 2 is changed into logarithmic form, Equation 3 is obtained. This assumes the form of a straight-line equation. D is, therefore, readily calculated from the slope of this line. A typical plot is shown in Figure 7.

$$\log \frac{C_s - C}{C_s} = -\frac{D\pi^2 t}{4\,d^2} + \log \frac{4}{\pi} \qquad (3)$$

Diffusivity constants for sulfur in rubber were determined for pale crepe and GR-S at several temperatures and thicknesses. The constants are given in Table III.

Table III. Diffusivity Constants

	Pale Crepe		GR-S-1006	
Temp., ° C.	d, cm.	D, cm.^{2} sec.$^{-1}$	d, cm.	D, cm.^{2} sec.$^{-1}$
40	0.053	0.507×10^{-7}	...	...
50	0.064	0.925	0.114	1.47×10^{-7}
60	0.102	2.50	0.102	3.16
60	0.238	2.57	...	...

The activation energy, as calculated from the Arrhenius equation, was 17 kcal. per gram-atom for both pale crepe and GR-S. This is of the same order of magnitude as activation energy values obtained by others for the diffusion of various gases in para rubber (*1*).

BLOOMING CHARACTERIZATION

The rubber industry from its inception has been plagued with the problem of sulfur bloom. Difficulties in alleviating blooming conditions have been enhanced by lack of solubility data and methods for evaluating various additives which might either increase the solubility or slow down the diffusion rate to the surface.

The experimental procedures described here lend themselves well for evaluating blooming tendencies. Thus, if specimens which have been used for solubility determinations at elevated temperatures are brought down to room temperature, sulfur may bloom and the change in surface activity with time will provide a measure of the blooming characteristics of the rubber compound.

Blooming can take place on both surfaces of the rubber specimen but occurs most probably on the undersurface since it is already seeded with sulfur. To standardize the method, the top surface was covered with a polyethylene terephthalate film $^1/_4$-mil thick which reduced the counting rate by 24%. This reduced the tendency for bloom on the top surface but allowed sufficient activity to penetrate for measurement. Typical results are shown in Figures 8 and 9.

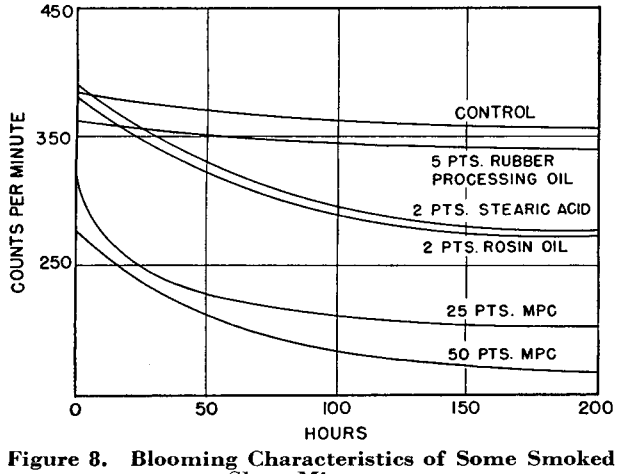

Figure 8. Blooming Characteristics of Some Smoked Sheet Mixtures

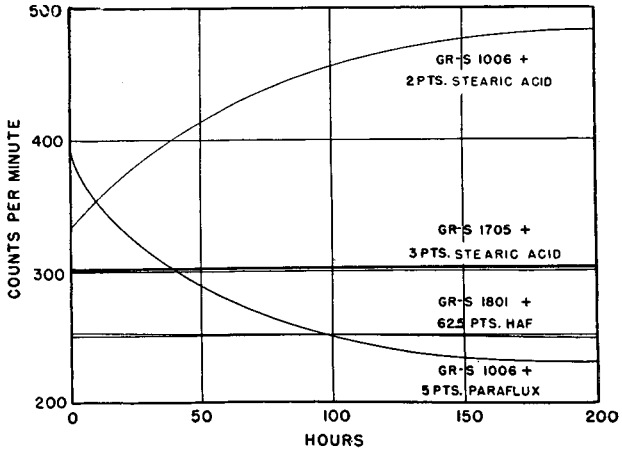

Figure 9. Blooming Characteristics of Some GR-S Mixtures

In Figure 8 a number of smoked sheet mixtures are compared. Of these, the control and the mixture containing the rubber processing oil show the greatest resistance toward bloom. In Figure 9, several GR-S mixtures are shown. GR-S-1801 and 1705, which are oil polymers, show almost no tendency to bloom. They were done in duplicate to substantiate this property. The other GR-S mixtures showed a marked tendency toward blooming. The tendency of the stearic acid mixture to bloom was so pronounced that the polyethylene terephthalate film failed to prevent bloom on the top surface. It should be emphasized that bloom characterization by this simple procedure does not necessarily indicate what might happen under factory conditions. There not only are sulfur nuclei for seeding prevalent but the stock is subjected to temperature fluctuations, temperature gradients, and mechanical working. The tracer technique could also be applied for a more sophisticated blooming test which would include these factors.

CONCLUSIONS

A new method has been devised for measuring sulfur solubility in rubber. It consists of bringing sulfur tagged with sulfur-35 in intimate contact with rubber. The sulfur diffuses into the rubber until it is saturated. The activity of the rubber on the opposite side is measured and converted to sulfur concentration from a calibration curve.

The procedures described can be adapted for measuring the diffusivity of sulfur in rubber and rubber compounds. In this case the data obtained previous to saturation are used to determine the diffusivity constant.

The blooming characteristics of various rubbers and mixtures can be determined by saturating rubber specimens with sulfur at elevated temperatures and then allowing them to bloom at room temperature. The increase or decrease in activity with time provides a measure of the blooming characteristics of the rubber.

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Rectification of Nonlinear Beer's Law Plots

Application to Alkaline Chromate and *p*-Nitrophenolate Solutions

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Two colored solutions that nominally obey Beer's law, alkaline potassium chromate and alkaline *p*-nitrophenol, yield nonlinear absorbance, *A*, *vs.* concentration, *C*, plots with filter photometers and wide-bandwidth spectrophotometers. These systems have been studied to determine whether linear relations may be established by an appropriate choice of axes. Plots of *A/C vs. A* are shown to be linear for chromate solutions in a Coleman junior spectrophotometer at 400 mμ and in a Klett-Summerson colorimeter using a No. 42 filter. The nonlinear *A-C* data for the *p*-nitrophenolate system are likewise rectified by an *A/C vs. A* plot for the Klett colorimeter and for the Coleman instrument at 430 to 440 mμ. The adherence to linearity is sufficiently rigid to permit establishment of the relationship with as few as two to four points. For purposes of calculation without reference to a graph, concentrations are computed directly from the observed absorbances by means of the formula $C = \frac{A}{K - A} \times \frac{1}{m}$, where *K* and *m* are constants.

COLORED solutions which adhere to Beer's law in tests with a sensitive spectrophotometer are occasionally observed to deviate widely with filter photometers or the less expensive spectrophotometers in general use (*1*, *4*, *6*). The difficulty is characteristic of instruments possessing a low degree of monochromaticity and arises when the absorption of the solution changes rapidly through the spectral band transmitted by the monochromator. This is particularly the case where the transmittance curves of the solution and of the monochromator are not inversely symmetrical.

Under these circumstances a calibration curve relating absorbance to chromogen concentration cannot be established with one or two standards. Instead a sufficiently large number of standards must be processed to fix the curve throughout the entire range of values apt to be encountered in the analysis. The accuracy of such a procedure is limited by the analyst's skill in tracing a curve to fit the experimental points. Furthermore, it becomes necessary to repeat all the standard determinations at intervals to test the fidelity of the plot, especially when new batches of reagents are employed.

The need for a practical solution to this problem in the clinical laboratory has long been apparent, particularly in dealing with yellow-colored solutions. Two such systems are considered: alkaline potassium chromate, commonly employed as a spectrophotometric standard (*3*); and alkaline solutions of *p*-nitrophenol, an indicator whose liberation by the enzymic hydrolysis of colorless ester conjugates (as *p*-nitrophenyl sulfate and *p*-nitrophenyl phosphate) is used as a direct colorimetric index of enzyme activity.

EXPERIMENTAL

p-Nitrophenol (Eastman grade) was recrystallized twice from water and dried over sulfuric acid in vacuo. Stock aqueous solutions were prepared containing 0.025 to 0.5 micromole per 2 ml. The colored (or blank) solutions consisted of 2-ml. portions of the standard *p*-nitrophenol solutions (or water), 5 ml. of tungstic acid (*7*), and 0.2 ml. of saturated potassium carbonate solution to bring the final pH in the neighborhood of 10.

The potassium chromate standards, prepared directly from the C.P. grade without further purification, contained 0.5 to 10 mg. per 100 ml. of solution. Potassium hydroxide, 0.05*N*, served both as the solvent and color blank.

Absorption measurements were made in a Model DU Beckman spectrophotometer at 400 mμ using 1-cm. Corex cells and a tungsten lamp; in a Model 6B Coleman junior spectrophotometer at 400 to 440 mμ with matched Kahn tubes (12 × 75 mm.) selected from the serology stock supply; and in several Klett-Summerson photoelectric colorimeters with No. 42 filters using flat-bottomed (micro) test tubes. The Klett readings were converted to absorbances by multiplying by 0.002 (*5*).

RESULTS

Absorption studies of both colored systems, conducted at 400 to 440 mμ, disclosed in each case a curvilinear response by the Klett-Summerson colorimeter as well as by the Coleman junior spectrophotometer, in contrast to the completely linear response of the Beckman spectrophotometer (Figures 1 and 2). These findings are consistent with the steep absorption spectra of the solutions. Attempts to rectify the aberrant Beer's law curves by plotting the data on semilog and log-log graph paper were unsuccessful, although in the latter case linearity was obtained over several experimental points in the lower absorbance ranges. Subsequent treatment of the data, described below, has been more successful in eliciting a simple and appropriate choice of axes.

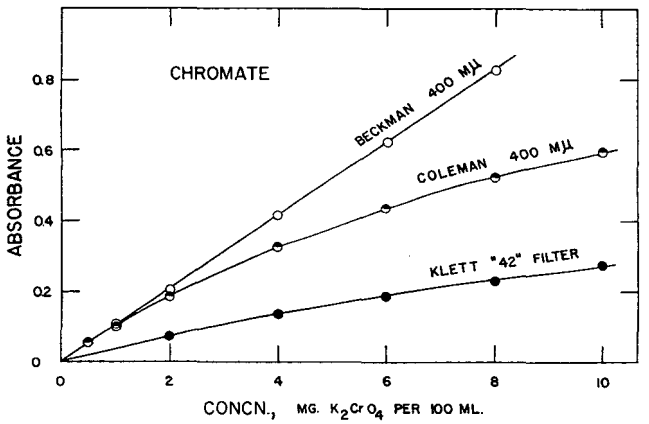

Figure 1. Conventional *A vs. C* Plots for Alkaline Potassium Chromate Solutions

The nonlinear relationship between chromogen concentration, C, and absorbance, A, may be represented with any desired degree of accuracy by assigning a sufficient number of terms to the general series

$$C = aA + bA^2 + cA^3 + dA^4 + eA^5 + \ldots \quad (1)$$

where the coefficients $a,b,c,d,e,\ldots$ are constants. When Beer's law is obeyed, $b = c = d = e = \ldots = 0$, and $C = aA$. As a first approximation to the nonlinear plots we may retain the first and second power A terms and tentatively drop the others, yielding

$$C = aA + bA^2 = A(a + bA) \quad (2)$$

and

$$C/A = a + bA \quad (3)$$

whence C/A would expectedly be a linear function of A. Actually, of all the data tested in this way, a linear C/A *vs.* A plot was noted only for the Klett chromate system. From this it can be deduced that the higher order terms in Equation 1 have considerable weighting value, and consequently cannot be ignored. A more satisfactory treatment is possible if additional terms are adopted in Equation 1 beyond the second and their ratios are assumed to be relatively constant and equal to the ratio of the first two terms. Then

$$C = aA + bA^2 + \frac{b^2}{a}A^3 + \frac{b^3}{a^2}A^4 + \ldots\ldots = \frac{A}{\frac{1}{a} - \frac{b}{a^2}A} \quad (4)$$

By this procedure the properties of a geometric progression are imputed to Equation 1, which seems to find justification in that the equations derived therefrom are in general accord with the data. Setting $1/a = k$ and $b/a^2 = m$, the expression

$$C = \frac{A}{k - mA} \quad (5)$$

is obtained. Its form is suggestive of the Beer relation, with the term mA a correction factor on the coefficient, k.

Equation 5 may be rearranged to give

$$A/C = k - mA \quad (6)$$

or

$$1/C = k/A - m \quad (7)$$

According to Equations 6 and 7, straight lines should be obtained on plotting A/C *vs.* A (Figure 3) or $1/C$ *vs.* $1/A$. To test these relationships, the chromate absorbance and concentration data used to construct the curves in Figure 1 have been replotted in the appropriate forms (Figure 4). The curves are entirely linear. With the A/C *vs.* A plot, the Beckman results fall on a line parallel to the A axis, since the A/C values are constant according to Beer's law: $A/C = k$, and the slope, $-m$, of Equation 6 is 0. On the other hand, because of the lag in increase of A with increasing C, the Klett and Coleman data yield straight lines which regress with A.

An example of the type of graph corresponding to Equation 7 is given in the inset to Figure 4. The nature of the reciprocal plot is such as to spread out the low absorbance-concentration points and cluster the high points along the line in the direction of the axes. Equation 7 therefore offers greatest sensitivity in the lower, rather than the higher, concentration-absorbance ranges, but does not permit interpolations down to zero absorbance. This is possible with Equation 6, which has the further advantage of giving a more uniform point spread and sensitivity over the entire range of absorbances. On this basis Equation 6 is to be preferred to Equation 7 in practice.

Equation 6 has also been found to be applicable to the Klett *p*-nitrophenolate data (Figure 5). The results obtained with the Coleman spectrophotometer are more involved and have been studied in greater detail in the range 400 to 440 mμ. With this instrument there is initial adherence to Beer's law at 400, 420, and 430 mμ as indicated by the horizontal lines in Figure 5.

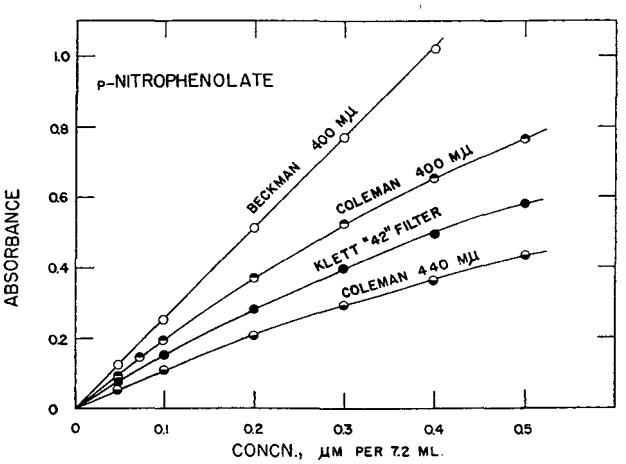

Figure 2. Conventional *A vs. C* Plots for Solutions of *p*-Nitrophenol in Carbonate Buffer

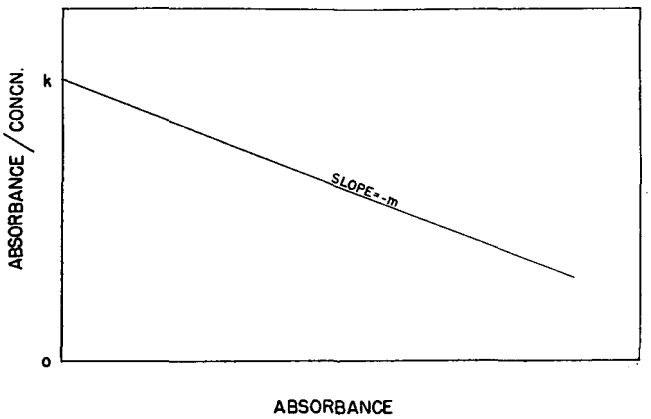

Figure 3. *A/C vs. A* Plot for Rectification of Nonlinear Beer's Law Curves

Extended line intercepts the *A* axis at *k/m*

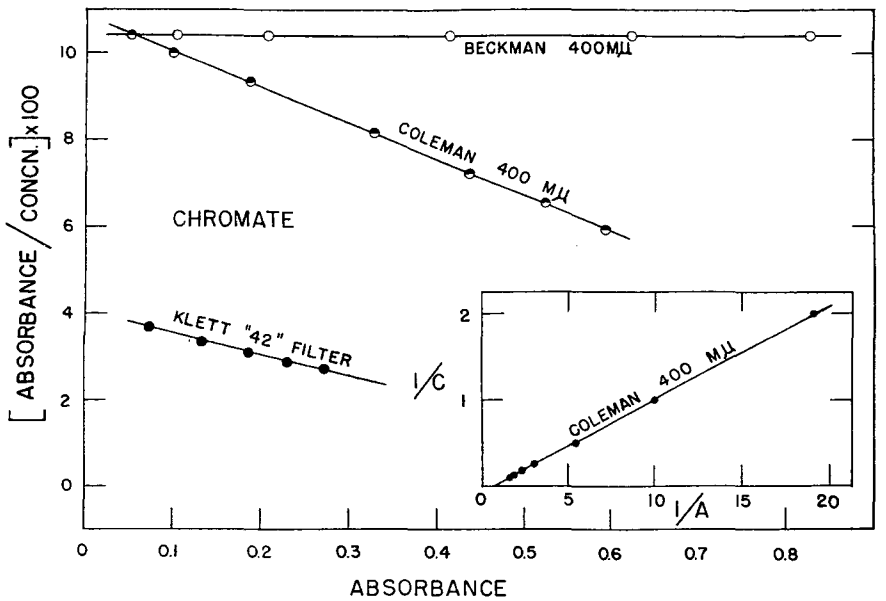

Figure 4. *A/C vs. A* Plots of Alkaline Chromate Data in Figure 1

Inset. Reciprocal plot of Coleman response at 400 mμ

As the concentration is increased, two breaks appear in the plots at 400 and 420 mμ, while only one is evident at 430 mμ. At 440 mμ the *A/C vs. A* plot is entirely linear. In short, as the wave-length setting recedes from the absorption maximum at 400 mμ, a shift occurs which is marked by a foreshortening of the incipient horizontal segment with a transition to the "normal" *A/C vs. A* plot at 440 mμ.

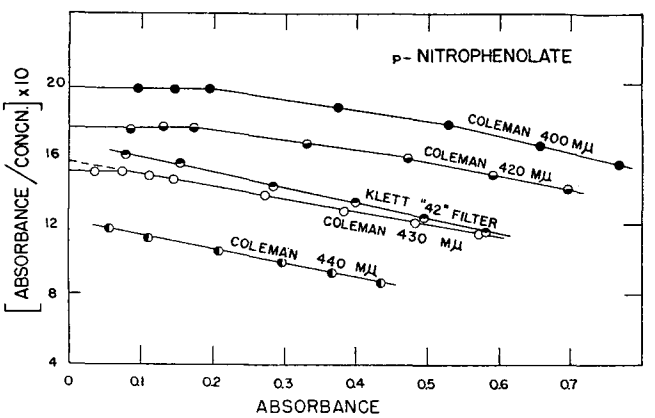

Figure 5. *A/C vs. A* Plots of *p*-Nitrophenolate Data in Figure 2

Additional Coleman data included at 420 and 430 mμ

Although the Coleman setting at 440 mμ affords a straight *A/C vs. A* line which can be established with a minimum number of points, the use of this wave length limits the sensitivity of the measurements, since the *p*-nitrophenolate absorbances at 440 mμ are only 56 to 59% of the maximum values at 400 mμ. At 430 mμ, however, the absorbances rise to 73 to 75% of the maximum; further, there is an exact adherence to a single linear *A/C vs. A* plot over at least a sevenfold range of concentrations—i.e., from under 0.075 to over 0.5 micromole of *p*-nitrophenolate ions per 7.2 ml. of solution, corresponding to absorbances of 0.09 to over 0.575 under the given experimental conditions.

The concentration errors incurred by extrapolating this plot down to zero absorbance, indicated by the broken line in Figure 5, are 0.7, 2.0, and 3.3% at absorbances of 0.075, 0.050, and 0.025, respectively, which are equivalent to absorbance errors of ≤ 0.001, the limit of reproducibility of the instrument. The choice of the 430 mμ setting would therefore appear to give maximum color sensitivity consistent with simplicity of graphical construction and calculations.

As to the practical use of Equations 5 and 6, if the linear *A/C vs. A* plot is shown to hold satisfactorily through the desired concentration range, it may be used as such in interpolating the concentrations of "unknowns." *C* is then equal to *A* divided by the corresponding ordinate value. Or one may alternatively ascertain the values of *k* and *m* from the graph (Figure 3) or by direct calculation from the experimental data (described below), and use Equation 5 to determine the concentrations of unknowns from their corresponding absorbances. In this case the calculation is somewhat expedited by putting Equation 5 in the form

$$C = \frac{A}{K - A} \times \frac{1}{m} \tag{8}$$

where $K = k/m$. It is then only necessary to subtract *A* from *K* and complete the calculation on a slide rule.

The constants *k*, *m*, and *K* can be computed directly from the absorbances, A_1 and A_2, of two standard solutions of concentrations C_1 and C_2 with the formulas

$$k = \frac{C_2 - C_1}{C_1 C_2} \times \frac{A_1 A_2}{A_2 - A_1} \tag{9}$$

$$m = \frac{\frac{A_1}{C_1} - \frac{A_2}{C_2}}{A_2 - A_1} \tag{10}$$

$$K = \frac{C_2 - C_1}{\frac{C_2}{A_2} - \frac{C_1}{A_1}} \tag{11}$$

These relations were derived by solving the simultaneous equations resulting from the substitution of C_1, A_1 and C_2, A_2 for *C* and *A* in Equation 5.

DISCUSSION

Although the *A/C vs. A* relationship is by no means a universal linear function, it may very likely hold for a number of solutions which absorb in regions of the spectrum other than the violet. For example, preliminary studies indicate its applicability to the divergent data obtained with the ferrous-phenanthroline system using a Klett colorimeter and a No. 52 filter. No information is available, however, on its significance relative to colored solutions whose deviations from Beer's law are of chemical origin.

The results of the *p*-nitrophenolate studies with the Klett and Coleman instruments suggest that linear *A/C vs. A* plots may be obtained more generally with filter photometers than with wide-band-width spectrophotometers at the wave length of maximum absorption. In the latter case, polyphasic plots may arise when there is initial adherence to Beer's law at low chromogen levels followed by deviations at higher concentrations.

Applications Outside the Field of Colorimetry. The expressions presented herewith are not limited to colorimetry. Completely analogous relations have been discerned in several protein adsorption phenomena and in the quantitative treatment of enzyme-substrate systems which do not show strict adherence to zero-order kinetics (*2*). Indeed, by appropriate approximations with suitable geometric progressions, a number of linear equations may be derived for enzyme systems acting in the zone of transition kinetics (*2*).

ACKNOWLEDGMENT

Readings on the Klett-Summerson colorimeters were kindly taken by Morris Goldberg.

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Spectrophotometric Determination of Cobalt with 2-Nitroso-1-naphthol-4-sulfonic Acid

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The investigation was undertaken to ascertain whether the color of the water-soluble red complex which is formed when cobalt(II) reacts with 2-nitroso-1-naphthol-4-sulfonic acid could be employed as the basis for a spectrophotometric method for the quantitative determination of the metal. The system was found to obey Beer's law between the concentration limits of 4.00×10^{-6} to 1.25×10^{-4} *M* cobalt(II) and remain stable with respect to time and temperature. The effects of pH, reagent concentration, and diverse ions—chiefly iron(III), copper(II), and nickel(II)—were studied. Procedures for effectively removing nickel(II) and preventing the interferences of concentrations of iron(III) or copper(II) up to 1.00×10^{-3} *M* were developed. The method is convenient, sensitive, reproducible, accurate, and precise.

THE most popular analytical procedure that exists for determining minute amounts of cobalt is based on the spectrophotometric measurement of the amount of color which is produced when cobalt(II) reacts with nitroso R salt (*4*). This method has been applied to many types of materials, including soils, grasses, steels, and carbides (*7*). However, if reproducible results are desired, appreciable quantities of iron(III) and copper(II) must first be removed (*3*). Also, the amount of time the solution is boiled after the reagent and nitric acid are added and the final concentration of the acid are important factors which can affect the intensity of the color (*3*).

Since 2-nitroso-1-naphthol-4-sulfonic acid has a chelating system which is almost identical with the one possessed by the nitroso R salt, it seemed desirable to investigate the known color reaction of the former with cobalt(II). The reaction was first mentioned by Hoffman (*2*). Some 50 years later Sarver (*5*) described the color reactions of the reagent with iron(III), iron(II), cobalt(II), nickel(II), and copper(II). These experiments were conducted to develop qualitative spot tests only, and no effort was made to adapt them for use as spectrophotometric procedures. Consequently, an investigation was undertaken to determine whether the color reaction of cobalt(II) with the reagent could be utilized as the basis for a convenient, sensitive, and quantitative spectrophotometric method.

APPARATUS AND REAGENTS

A General Electric automatic recording spectrophotometer operating on a band width of 10 mμ and equipped with two matched 1-cm. cells was used for all spectrophotometric measurements. A Beckman Model H-2 pH meter was utilized to indicate pH values. During the investigation the precipitates which were formed, because of the presence of diverse ions, were separated from the solutions with the aid of a centrifuge.

The reagent, 2-nitroso-1-naphthol-4-sulfonic acid, was prepared and purified from 1-naphthol-4-sulfonic acid (National Aniline), sodium nitrite, and hydrochloric acid according to published techniques (*8*). The required amount of purified 2-nitroso-1-naphthol-4-sulfonic acid was dissolved in distilled water so that the reagent concentration was 1.00×10^{-2} *M*. All other solutions were prepared from reagent grade compounds and distilled water. Citric acid was always utilized as the solid when it was used to complex diverse ions.

Table I. Effect of Ammonium Ion Concentration on Absorbance of the System

[Cobalt(II) = 5.00×10^{-5} *M*; reagent = 6.00×10^{-4} *M*; pH = 7.0]

Molar Concn. of $(NH_4)^+$	Absorbance of System at 525 Mμ
0.00	0.720
0.01	0.660
0.10	0.610
1.00	0.600

EXPERIMENTAL

Effect of pH on System. Cobalt(II) will react with 2-nitroso-1-naphthol-4-sulfonic acid to produce a water-soluble red complex. Figure 1 shows that at 525 mμ the absorbance of an aqueous solution of cobalt(II) and reagent, when measured against a reagent blank, increases as the pH is increased from 4.5 to 6.0; it then remains constant between 6.0 and 10.0. Figure 2 exhibits the effect of pH on the spectrophotometric properties of an aqueous solution of the reagent. In the latter case a distilled water blank was employed. Examination of Figures 1 and 2 revealed that pH 7.0 is most suitable. At this value the absorbance at 525 mμ which is due to the cobalt complex is developed to a maximum and that of the reagent is a minimum. Dilute sodium hydroxide instead of ammonium hydroxide was chosen for increasing the pH, for an increase in the concentration of the ammonium ion at constant pH was found to cause a decrease in the absorbance of the system at 525 mμ (Table I). This effect can be attributed to the formation of complexes of cobalt and ammonia.

Effect of Reagent Concentration. A study was undertaken to examine the effect of the concentration of the reagent on the

absorbance of the system. It was found that if enough reagent is present to complex all of the cobalt(II), a further increase in the concentration of the reagent will not produce a significant change in the absorbance value at 525 mμ (Table II). On the basis of the results of this study the conclusion was reached that at pH 7.0 a reagent concentration of $6.00 \times 10^{-4}M$ is sufficient to complex any concentration of cobalt(II), up to $1.25 \times 10^{-4}\ M$.

Stability of System with Respect to Time and Temperature. An examination of the stability of the system with respect to time was conducted by allowing the sample and its blank to stand in the laboratory, and it was found that the absorbance at 525 mμ remained constant for at least 3 months. The solution used contained $1.00 \times 10^{-5}M$ cobalt(II) and $6.00 \times 10^{-4}M$ reagent at pH 7.0.

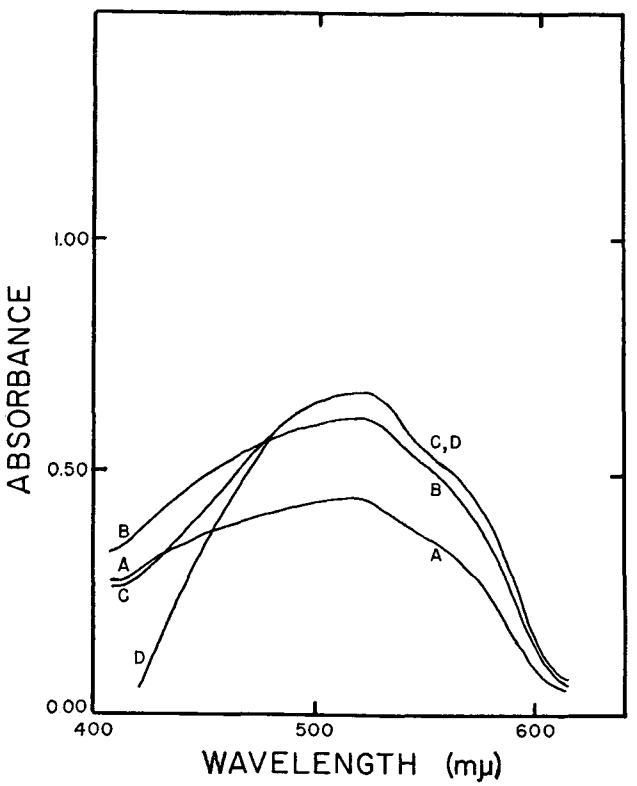

Figure 1. Effect of pH on Color of Cobalt Complex

Sample, $5.00 \times 10^{-5}M$ cobalt(II) and $2.00 \times 10^{-4}M$ reagent
Blank, $2.00 \times 10^{-4}M$ reagent
A. pH 4.5
B. pH 5.0
C. pH 6.0
D. pH 7.0–10.0

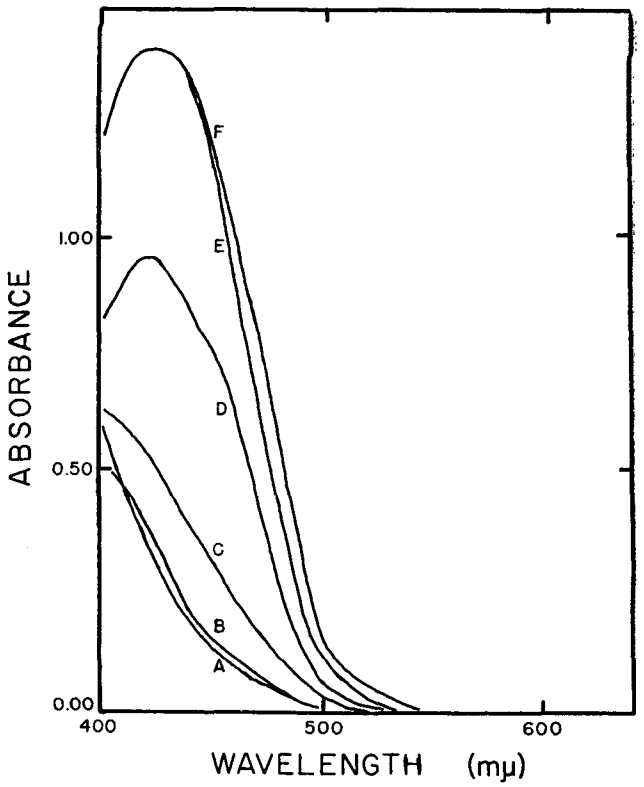

Figure 2. Effect of pH on Color of Reagent

Sample, $2.00 \times 10^{-4}M$ reagent
Blank, distilled water
A. pH 4.5
B. pH 5.0
C. pH 6.0
D. pH 7.0
E. pH 8.0
F. pH 9.0–10.0

The temperature of the cobalt(II) solution when the reagent is added and the pH adjusted is not a factor which will alter the absorbance of the system at 525 mμ so long as the temperatures of the solutions are brought to the same value before the respective absorbance values are measured. The reaction temperature range between the limits of 10° and 95° C. was investigated, and this variation did not affect the spectrophotometric properties of the system.

Preparation of a Calibration Curve. In order to determine whether the system obeys Beer's law, a calibration curve was prepared. It was found that in the absence of interfering ions the system conforms to Beer's law between the concentration limits of 4.00×10^{-6} and $1.25 \times 10^{-4}M$ cobalt(II) (0.24 to 7.5 p.p.m. cobalt).

Table II. Effect of Reagent Concentration on Absorbance of System

Molar Concn. of Cobalt(II) $\times 10^5$	Molar Concn. of Reagent $\times 10^4$	Moles of Reagent per Mole Cobalt(II)	Absorbance of System at 525 Mμ
1.00	6.00	60.0	0.160
1.00	14.0	140	0.160
2.50	3.00	12.0	0.375
2.50	6.00	24.0	0.380
2.50	14.0	56.0	0.370
5.00	3.00	6.00	0.715
5.00	6.00	12.0	0.725
5.00	14.0	28.0	0.720
7.50	6.00	8.00	1.055
7.50	14.0	18.7	1.060
10.0	6.00	6.00	1.375
10.0	14.0	14.0	1.370
12.5	6.00	6.80	1.680
12.5	14.0	11.2	1.690

SUGGESTED METHOD FOR DETERMINING COBALT(II) IN ABSENCE OF INTERFERING IONS

Pipet 3.00 ml. of $1.00 \times 10^{-2}M$ reagent to the solution which contains cobalt(II).

Dilute to almost 50 ml. with distilled water and adjust the pH to 7.0 with $0.01M$ sodium hydroxide.

Finish diluting the sample to exactly 50 ml.

Prepare a blank by diluting 3.00 ml. of $1.00 \times 10^{-2}M$ reagent to 50 ml. with distilled water, and adjust the pH of the solution to 7.0 with $0.01M$ sodium hydroxide.

Measure the absorbance of the system at 525 mμ with a spectrophotometer and convert absorbance to cobalt(II) concentration with the aid of a previously prepared calibration curve.

Sensitivity and Applicability of Method. At

Table III. Results of Several Determinations

(Reagent = 6.00×10^{-4} M; pH = 7.0)

Molar Concn. of Cobalt(II) $\times 10^6$		
Taken	Found	Error, %
1.00	0.80	−20
2.00	1.85	−7.5
4.00	4.00	...
6.00	6.10	+1.7
8.00	7.85	−1.9
10.0	10.0	...
20.0	20.0	...
40.0	40.0	...
60.0	60.5	+0.8
80.0	80.0	...
100	101	+1.0
125	127	+1.6

525 mμ the molar absorptivity of the system is 1.44×10^4 liter-mole^{-1}-cm.$^{-1}$. Such a large value permits this method to be used for determining minute amounts of cobalt.

Table III contains the results of a series of twelve determinations which was undertaken to investigate the applicability of the method. On the basis of the data in Table III, it can be assumed that if the cobalt(II) concentration is between 4.00×10^{-6} and $1.25 \times 10^{-4}M$ and if no interfering ions are present, the method is accurate to ±2%. However, under the same circumstances cobalt(II) concentrations as low as $1.00 \times 10^{-6}M$ (0.06 p.p.m.) can be determined with an accuracy of ±20%. Using this method systems containing concentrations of cobalt(II) greater than $1.25 \times 10^{-4}M$ would have transmittances which are too small for spectrophotometric measurement in 1.00-cm. cells.

Accuracy and Precision of Method. Upon investigating the data in Table III it is evident that the ideal concentration range for this method is 1.00×10^{-5} to $1.00 \times 10^{-4}M$ cobalt(II) (0.6 to 6.0 p.p.m. cobalt). In order to demonstrate the accuracy and precision which can be obtained within these limits, determinations were conducted on ten solutions containing $1.00 \times 10^{-5}M$ cobalt(II) and ten solutions which contained $1.00 \times 10^{-4}M$ cobalt(II). The results are tabulated in Table IV. They show that the standard deviation (σ) is 0.005 of an absorbance unit at both of these concentrations. This corresponds to 0.02 p.p.m. cobalt.

Table IV. Results of Precision and Accuracy Determinations

(Reagent concn. = $6.00 \times 10^{-4}M$; pH = 7.0)

Expected Absorbance Value at 525 Mμ	
For system with $1.00 \times 10^{-5}M$ cobalt(II) = 0.160, obsvd. values	For system with $1.00 \times 10^{-4}M$ cobalt(II) = 1.370, obsvd. values
0.155	1.365
0.160	1.360
0.160	1.370
0.165	1.365
0.160	1.365
0.160	1.375
0.150	1.370
0.165	1.365
0.160	1.365
0.155	1.370
Std. deviation 0.005	0.005

Effects of Diverse Ions. A study was undertaken to determine which of the more common ions will interfere with this method. The procedure that was employed to examine these effects was the same as the one outlined earlier except that the diverse ion was added to the original cobalt(II) solution before carrying out the procedure. If a precipitate formed during this process it was settled by centrifuging. After the supernatant liquid was removed distilled water was added to the precipitate, and the precipitate was thoroughly dispersed by shaking. The mixture was again centrifuged and the liquid was decanted and added to the main solution. This practice was repeated until the supernatant liquid was void of any color. Then the final pH and volume adjustments were made and the absorbance of the system was measured at 525 mμ. Sometimes such precipitates will cause low results by adsorbing the red-colored cobalt-2-nitroso-1-naphthol-4-sulfonic acid complex, and repeated shakings with distilled water and subsequent centrifugings will not remove this adsorbed color. Aluminum(III), cadmium(II), and lead(II) hydroxides are very prone to do this. Table V lists the effects of some of the more common ions. An interference is defined as an alteration of at least ±2% in the absorbance value of a solution

Table V. Results of Investigation of Effects of Diverse Ions

No Interferences at Concentrations $10^{-2}M$[a] or Smaller	Interferences at Concentrations $10^{-3}M$[b] or Larger
F^-	Ce^{++++}[c]
Cl^-	Fe^{++}[c]
Br^-	Fe^{+++}[c]
I^-	Ni^{++}[c]
BO_3^-	Cu^{++}[c]
CO_3^{--}	Pb^{++}[c]
HPO_4^{--}	Al^{+++}[c]
NO_2^-	Cd^{++}[c]
NO_3^-	Hg^{++}[c]
SCN^-	Bi^{+++}[c]
SO_4^{--}	Sn^{++++}[c]
SO_3^{--}	Sb^{+++}[c]
VO_3^-	As^{+++}[c]
WO_4^{--}	UO_2^{++}
$Oxalate^{--}$	CrO_4^{--}
$Citrate^{--}$	$Cr_2O_7^{--}$
$Tartrate^{--}$	CN^-
Mg^{++}	Mn^{++}[d]
Ca^{++}	
Sr^{++}	
Ba^{++}	
Zn^{++}[c]	

[a] Highest limit investigated.
[b] Lowest limit investigated.
[c] Indicates the formation of a precipitate.
[d] Mn^{++} interferes if its concentration is $10^{-2}M$, but does not if its concentration is $10^{-3}M$.

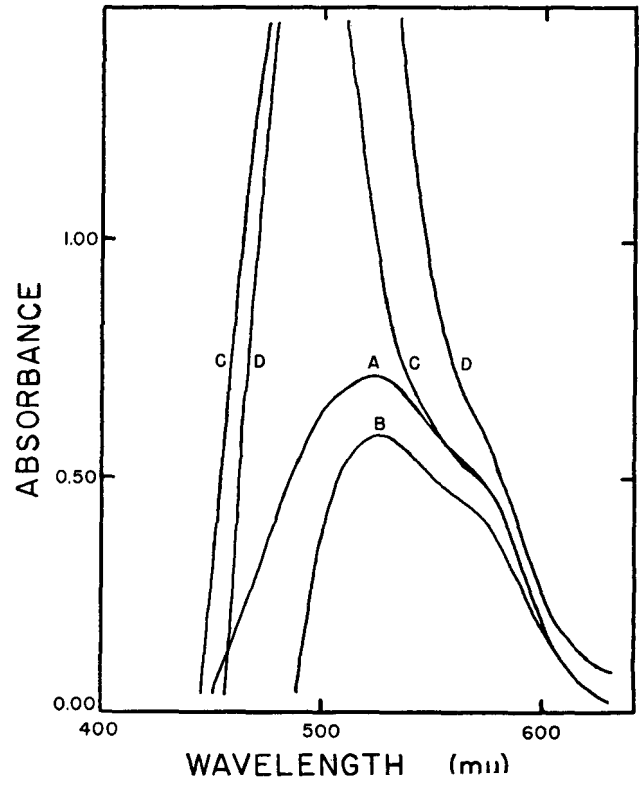

Figure 3. Interferences Caused by Iron(III), Nickel(II), and Copper(II)

A. Cobalt(II), no interfering ions
B. Interference caused by iron(III)
C. Interference caused by nickel(II)
D. Interference caused by copper(II)

at pH 7.0 containing $5.00 \times 10^{-5}M$ cobalt(II) and $6.00 \times 10^{-4}M$ reagent.

Figure 3 illustrates the interfering effects caused by $1.00 \times 10^{-3}M$ iron(III), copper(II), or nickel(II) upon a system containing $5.00 \times 10^{-5}M$ cobalt(II) and $6.00 \times 10^{-4}M$ reagent. Since the iron(III) and copper(II) distort the entire spectrophotometric curve of the cobalt-2-nitroso-1-naphthol-4-sulfonic acid complex, methods of complexing or removing these ions had to be found to determine satisfactorily the amount of cobalt(II) present.

SUGGESTED METHOD FOR MASKING CONCENTRATIONS OF COPPER(II) OR IRON(III) LESS THAN $10^{-3}M$

Attempts were made to complex iron(III) or copper(II) with fluoride, oxalate, tartrate, or citrate ions, and then determine the amount of cobalt(II).

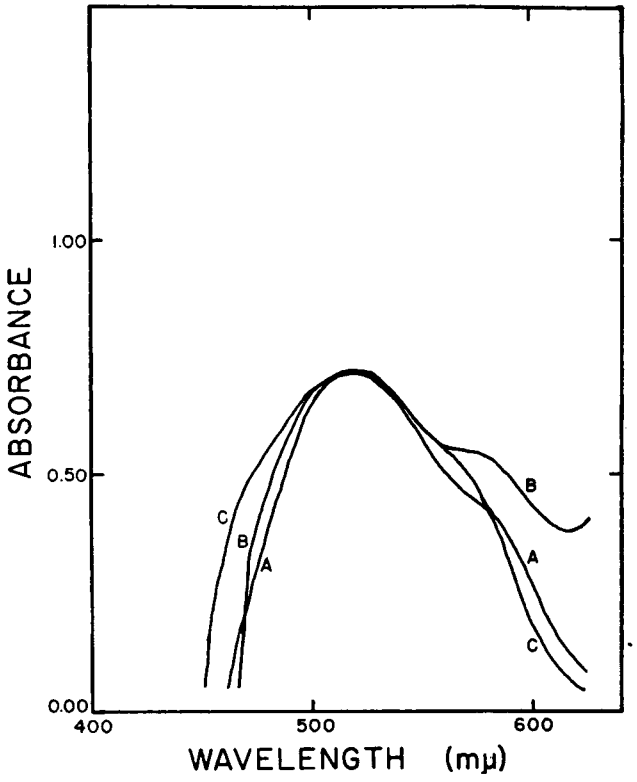

Figure 4. Removal of Interfering Effects of Iron(III) and Copper(II) with Citrate Ion

A. Cobalt(II), no interfering ions
B. Iron(III) complexed with citrate ion
C. Copper(II) complexed with citrate ion

The citrate ion at a concentration of $0.1M$ appears to be the most efficient agent for complexing either $10^{-3}M$ iron(III) or $10^{-3}M$ copper(II); it will permit accurate absorbance measurements at 525 mμ for a system containing $6.00 \times 10^{-4}M$ reagent and $5.00 \times 10^{-5}M$ cobalt(II) (Figure 4). However, it was found that if the cobalt(II) concentration is increased to $1.00 \times 10^{-4}M$ in the presence of $10^{-3}M$ iron(III) or $10^{-3}M$ copper(II), the reagent concentration must be increased to $1.00 \times 10^{-3}M$ in order to obtain the calibration curve value for the absorbance corresponding to $1.00 \times 10^{-4}M$ cobalt(II). This is attributed to the fact that in spite of the citrate ion the iron(III) or copper(II) can react with the 2-nitroso-1-naphthol-4-sulfonic acid and not enough reagent remains to complex all of the cobalt(II) and develop the color.

Removal of Iron(III) and Copper(II). If the concentration of iron(III) or copper(II) is greater than $1.00 \times 10^{-3}M$, $0.1M$ citrate ion will not serve as an efficient agent for completely alleviating the undesirable effects caused by these ions. Consequently, they must be removed before the reagent solution is added if accurate results are desired for the determination of cobalt(II). Iron(III) may be extracted from a $7.5N$ hydrochloric acid solution with the aid of isopropyl ether (*1*), and copper(II) is precipitated from an acidic solution with hydrogen sulfide. The hydrogen sulfide is then removed by boiling the acidic solution before the reagent is added and the pH increased. After these procedures the pH must be adjusted to approximately 3 by boiling or by adding base to prevent the destruction of the reagent when it is introduced into the solution containing the cobalt(II).

Removal of Nickel(II). None of the previously mentioned complexing agents were found to be satisfactory for preventing the interference of nickel(II). The only method which was found for this is to remove it. The procedure used to accomplish this is based on the facts that both nickel(II) and cobalt(II) form complexes with dimethylglyoxime, but the nickel complex is extremely insoluble in basic solutions while the corresponding cobalt complex is very soluble.

Nickel(II) is removed by precipitating it with an excess of dimethylglyoxime in the presence of ammonium hydroxide and filtering the mixture through a medium-pored sintered-glass crucible. The cobalt complex and excess dimethylglyoxime contained in the filtrate are then destroyed by adding concentrated sulfuric acid, evaporating to fumes of sulfur trioxide, and heating the fuming mixture until no evidence of any undestroyed carbon remains. More sulfuric acid is added when necessary. The solution is allowed to cool, diluted to a suitable volume, and the pH adjusted to about 3. The reagent is added and the usual procedure of developing and measuring the color is followed. During this process two important sources of error occur. A sufficient excess of dimethylglyoxime must be used to complex all of the cobalt(II) before it can be assumed that all of the nickel(II) has been precipitated (*6*); and if both cobalt(II) and iron(III) are present, a brown complex with the composition $FeCoC_{12}H_{19}N_6O_6$ will be precipitated. The latter can be prevented by removing the iron, as previously mentioned, or by reducing it with sulfur dioxide and carrying out the precipitation of the nickel(II) in the presence of tartrate ion (*6*).

SUGGESTED METHOD FOR DETERMINING COBALT(II) IN PRESENCE OF SMALL QUANTITIES OF NICKEL(II)

Figure 3 shows that the presence of nickel(II) does not cause the spectrophotometric curve of the cobalt-2-nitroso-1-naphthol-4-sulfonic acid complex to become distorted in the vicinity of 560 mμ. Consequently, if a molar ratio of nickel(II) to cobalt(II) of only 20 to 1 exists, a new procedure for determining cobalt could be developed by measuring the absorbance of the system at 560 mμ. The sensitivity of this spectrophotometric method for cobalt(II) would be about 20% smaller than if the absorbance measurements were taken at 525 mμ, but this sacrifice would be very insignificant in comparison to the advantages which would be gained by eliminating the time-consuming procedure of removing the nickel(II).

CONCLUSIONS

The results of this investigation reveal that the reaction of cobalt(II) with 2-nitroso-1-naphthol-4-sulfonic acid produces a water-soluble red complex which has an absorbance maximum at 525 mμ and provides a useful method for the quantitative spectrophotometric determination of the element. Since the normal eye has a maximum sensitivity at about 550 mμ, this color could be used as the basis for a visual comparison method. The procedure given can be used to determine cobalt(II) in the

presence of small quantities of iron(III) or copper(II) after these foreign ions have been complexed with citrate ion. However, large quantities of iron(III), copper(II), and nickel(II) must be removed. The system is stable, independent of reagent concentration, and obeys Beer's law. The method is sensitive, reproducible, accurate, and precise. Consequently, its advantages render it very useful for determining minute amounts of cobalt.

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Measuring Wet Gel Strength of Coagulant-Dipped Films

Paper Dip Method

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A property of latex which is considered of fundamental importance in the latex industry is the so-called wet gel strength. This term connotes the tensile strength of the freshly set film, but hitherto there has been no adequate method of measurement of this property, since the film is so weak that it cannot readily be removed from the surface on which it is deposited. The present method is based upon the use of absorbent paper of low wet strength, impregnated with calcium nitrate, as a base for the deposition of a latex film. The strip of paper, which may be in a dumbbell shape, is dipped for 30 seconds and then removed from the latex, together with the adhering coagulant dipped film. This film is rinsed in water and then mounted on a special tensile testing machine designed for high elongation and low tensile. Elongation and tensile are measured at a standard rate of jaw separation of 20 inches per minute. These properties have been studied using natural and various synthetic latices. The effects of prevulcanization, compounding, and dilution of these latices have been determined. Tensile properties of the film from a given latex have also been measured as a function of the time and conditions of drying of the film after deposition.

IN THE majority of applications of latex, such as dip goods, foam rubber, and castings, the first step is the formation of a continuous film of rubber in the desired shape. Some form of treatment is used—for example, chemical coagulation, heating or evaporation—whereby the individual rubber particles of the latex are brought in contact with one another, resulting in the establishment of a continuous latticelike phase of rubber suspended in, or permeated by, a continuous phase of water or serum. This system of two continuous phases is termed a wet gel. The tensile properties of this wet gel are far inferior to those of the dried polymer, and it is universally recognized in the latex industry (*3*) that the weakness of the wet gel imposes a severe limitation on the applicability of latex.

Despite the interest of the latex industry in the so-called wet gel strength, no adequate method has hitherto appeared by which this property can be measured and characterized. This fact is due primarily to the inherent weakness of the wet gel, which makes it difficult to remove a freshly dipped or coagulated film from the form on which it is cast or dipped—for example, a strip may be coagulant-dipped on a glass slide, but distortion of the film usually takes place when the film is removed from the slide. The film may be cast on mercury, but it is difficult to obtain a film of definite shape in this manner.

In the present method, a latex film is deposited directly on a strip of paper of low wet strength by a coagulant dip process. The film assumes the shape of the paper, which can be made in a dumbbell shape for tensile testing. The moist strip of paper contained between the two layers of wet gel tears readily and so does not affect the measurement of the tensile properties. Owing to the low tensile strength of the wet gel, a testing machine of much greater sensitivity than that ordinarily employed in rubber testing must be used.

By this procedure, it is possible to study the tensile properties of fresh coagulant-dipped latex films. These films can also be carried through various procedures such as leaching and drying, and the tensile properties can be measured at any stage. When these properties are known it should be possible for the engineer

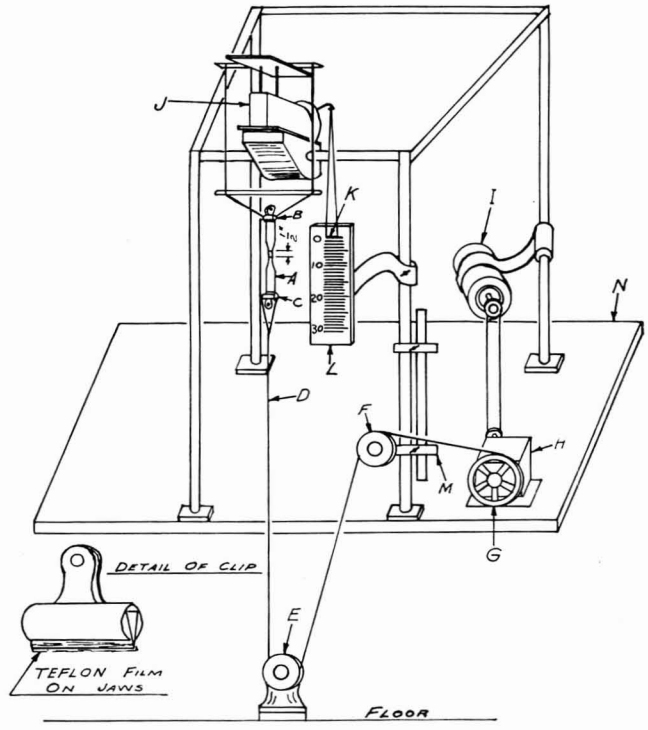

Figure 1. Tensile Test Apparatus

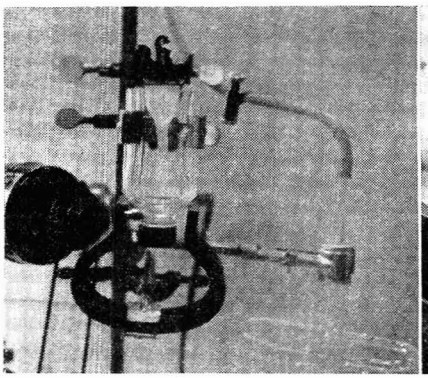

Figure 2

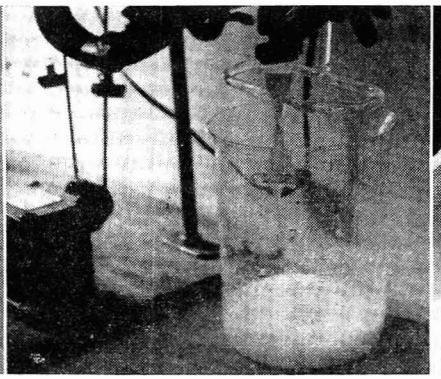

Figure 3

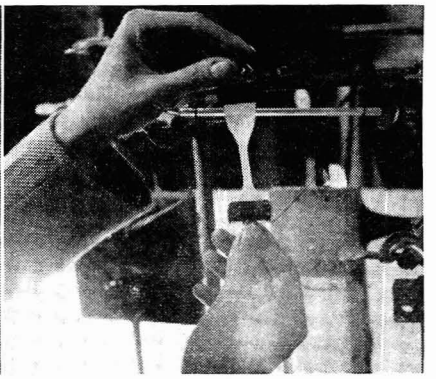

Figure 4

Figures 2 to 4. Procedure for Dipping, Rinsing, and Mounting Test Specimen

to treat latex films as materials of construction of known properties, which can be handled on a scientific rather than an empirical basis.

APPARATUS

Many of the tensile tests were performed on a simple homemade apparatus sketched in Figure 1. The dumbbell-shaped strip, *A*, is clamped between two spring clips, *B* and *C*, and the lower clip is pulled by a nylon cord, *D*, which passes around the pulleys, *E* and *F*, and is attached to the wheel, *G*. The wheel is mounted on the output shaft of a 600 to 1 reduction gear, *H*, which is driven by a governor-controlled motor, *I*.

A standard rate of pull of 20 inches per minute has been used. The force is measured by means of a 2-pound postage scale, *J*, with an attached pointer, *K*, in front of a scale, *L*, in a position directly behind the strip, *A*. The elongation is measured in the conventional manner by holding a ruler behind the bench marks on strip *A*. The elongation and force at the moment of rupture are noted and recorded. After each strip has been pulled, the position of pulley *F* is adjusted by moving the multiclutch connector, *M* (Fisher Scientific Co., No. 14-666-22); after several strips have been run cord *D* is unwound and *L* is repositioned. The entire apparatus is mounted on a base plate, *N*.

Other tests were performed on an Instron tensile testing machine (Model TTB, manufactured by the Instron Co., Quincy, Mass.). In this machine, the specimen is pulled by a screw mechanism, and the load is measured with a strain gage connected to a recording potentiometer. In this way complete stress-strain curves are recorded automatically. A ruler is held behind the specimen and when the bench marks are stretched to a certain length—for example, every inch—a button is pressed which makes a small "pip" on the curve. The Instron machine gives results of much greater sensitivity, precision, and completeness than the homemade instrument. Nevertheless, for laboratories which are unable to purchase an Instron machine, useful results may be obtained with a homemade apparatus.

MATERIALS

The paper employed for this test is Scott toilet tissue, 15 to 20 sheets of which are folded together and cut with a standard dumb-bell-shaped die (die C of the American Society for Testing Materials Method D 412–51T). The coagulant mixture consisted of 40 parts of calcium nitrate pentahydrate dissolved in 60 parts of methanol. The samples of latex were obtained from the General Latex and Chemical Corp. A nonionic surface-active agent (Igepal CA-633), an alkyl phenoxypolyoxyethylene ethanol, was obtained from the Antara Chemical Co.

PROCEDURE

About 0.25 inch is cut off one end of the paper strip (previously cut to shape with the die), and an ordinary paper clip is slipped onto that end. The other end is held in a spring clip similar to clip *B* of Figure 1. The strip is immersed in the coagulant solution for 3 or 4 seconds (until the strip appears saturated), removed slowly while excess solution on the lip of the container is drained off, and allowed to dry for 15 or 20 seconds. It is then hung inside an inverted 4-ounce prescription bottle from which the bottom has been cut off (Figure 2).

The paper clip at the bottom of the strip is held in place by a horseshoe magnet beneath the bottle, and the spring clip is clamped in the desired position. The sample of latex is poured into the bottle and the strip is left in place for the desired time (generally 30 seconds). At the end of this time the magnet is lowered and the paper strip is removed. The strip is then washed from both sides simultaneously with a stream of distilled water (Figure 3).

Table I. Deposition of Latex Films

Sample	Solids, %	Igepal, %	Gel Characteristics	Gel Thickness, Mils[b]	Elongation at Break, %	Max. Tensile, Lb./Sq. Inch
Tensiles Measured on Apparatus in Figure 1[a]						
GR-S-2003	62	...	Good	28	100	25
	62	1	Good	26	1500	22
	40	...	Very soft	...	...	...
	40	1	No film	...	...	...
GR-S-2000	60[c]	...	Soft	...	...	...
	40	...	Good	23	850	21
GR-S-X-667	54[c]	...	Soft, leggy	...	...	...
	54[c]	1	Soft, leggy	...	...	...
	40	...	Good	26	700	15
G-4580[d]	60[c]	...	Good	20	700	45
G-4580[d]	60[c]	1	Good	27	1500	21
G-4794[d]	40	...	Poor	...	...	...
G-4794[d]	40	1	Good	25	2200	15
GR-S-X-710	60	...	No film	...	...	...
	40	...	Good but leggy	21	450	18
Natural (H&C)	62	...	Good	28	900	130
	50	...	Good	26	750	65
	43	...	Good	21	900	60
	62	1	No film	...	...	...
	50	1	No film	...	...	...
	43	1	No film	...	...	...
Tensiles Measured with Instron Machine						
Natural (H&C)	62	...	Good	25	850	180
	45	...	Good	24	750	57
	32	...	Good	22	720	50
	62[e]	...	Good	19	770	200
	62[f]	...	Good	52	750	200
GR-S-2000 (A)	40	...	Good	15	1500	20
	23	...	Good	18	1400	14

[a] All values are averages. [b] Thickness given is that of the double film of wet gel, corrected for the thickness of paper.
[c] Heat-concentrated.
[d] Experimental low-temperature GR-S latex.
[e] Ten-second dip time.
[f] Three-minute dip time.

The strip is then cut with scissors about 0.25 inch above the paper clip; this severed portion of the strip is saved for a thickness measurement with a thickness gage graduated in 0.001 inch (Randall and Stickney). The cut end of the dumbbell paper strip is placed between the jaws of spring clip *B* (Figure 1). In order to avoid handling of the strip, the strip is held by means of the spring clip with which it was originally suspended in the latex, and clip *B* is held open in an inverted position while the end of the strip is lowered into it (Figure 4). The other end of the strip is then cut off at the edge of the wet gel (marking the depth to which the strip was immersed in the latex) and this end is similarly lowered into clamp *C*.

The 0.5-inch bench marks are stamped on the center portion of the strip, using two rubber stamps mounted on tongs so that the lines are marked on the front and back of the strip simultaneously; this is necessary because the strip sometimes turns as it is being pulled so that the front lines may no longer be visible. The motor is then started and the tensile and elongation are noted as described above and calculated in the conventional manner—i.e., based on the original dimensions of the center portion of the strip.

An alternative dipping procedure is simply to lower the paper strip into a jar of latex. However, the weight of the paper clip is not sufficient to pull the strip down through a fairly viscous latex; and furthermore a larger jar and hence a larger sample of latex (8 *vs.* 3.5 ounces) is required than in the above method where the strip is held in place in a flat bottle.

Table II. Effect of Rate of Pull on Wet Gel Measurements[a]

Sample	Solids, %	Gel Thickness, Mils[b]	Rate of Pull, Inches/Min.	Type of Curve[c,d]	Elongation, % Max.	Elongation, % Break	Tensile, Lb./Sq. Inch
Natural (H and C)	62	26	20	S	...	850	180
	62	25	5	S	...	950	180
GR-S-2000 (B)	40	18	20	U	200	530	17
	40	17	5	U	100	290	11
	40	17	1	U	90	150	8.5
GR-S-2003 (B)	62	26	20	N	...	80	24
	62	24	5	N	...	35	19
	62	25	1	N	...	40	16
Prevulcanized	60	27	20	N	...	260	36
Natural	60	27	5	N	...	150	22
Prevulcanized	40	18	20	U	170	260	20
GR-S-2000	40	22	5	U	120	160	12
Chemigum 235 HS	42	23	20	U	...	250	18
	42	23	5	U	...	140	13

[a] All values are averages of three or more runs on the Instron machine.
[b] Double film without paper.
[c] See discussion of rate of pull.
[d] For U curves, elongation given at point of maximum tensile as well as at break point. Tensile given only at its maximum value.

PROCEDURE FOR DRY FILMS

For the preparation of dry films, a 3 × 8 inch glass slide was dipped in a commercially available calcium nitrate coagulant solution. After partially drying, the slides were dipped for 3 minutes in the latex and then withdrawn. The films were air-dried for 1 hour and then dried for 1 hour in an oven at 58° C. The films were stripped carefully from the slides and lightly dusted with talc. Dumbbell specimens were cut with the die from these films, using the same die as in the wet gel test. These specimens were desiccated 24 hours and were then pulled on either a Scott testing machine or on the Instron machine.

RESULTS OF ANALYTICAL SIGNIFICANCE

Film Deposition. In order to be able to carry out a meaningful test, it is first of all necessary to deposit a good film on the paper. Film deposition on paper appears to be affected by various conditions in much the same way as film deposition on glass or on a metal mold. It is well known in latex technology that many types of latex do not give satisfactory films under any conditions; others require proper adjustment of total solids concentration, or addition of compounding ingredients, to obtain coherent films. The present test serves only to measure the tensile properties of films which can be satisfactorily formed by the coagulant dip process. No standard procedure can be given for the treatment of the latex prior to film deposition; rather, it is necessary to adjust the concentration and compounding ingredients in the light of experience, in order to obtain a suitable film.

Some factors influencing the deposition of GR-S films are illustrated in Table I. A poor film may be obtained if the latex is too dilute; in this case concentration of the latex—for example, by evaporation—is recommended. On the other hand, if the latex is of high concentration (50 to 60% solids) but is viscous, a soft, incompletely coagulated film may be obtained; in this case the latex should be diluted.

If the latex is of a very fine particle size, a very thin film may be obtained which resists penetration by calcium nitrate and so prevents build-up of a film of reasonable thickness; with such a latex the rate of coagulation can be controlled by addition of a nonionic surface active agent such as Igepal CA-633. However, addition of Igepal to a latex of large particle size (GR-S-2003) which is capable of depositing a good film in the absence of Igepal, results in weakening of the wet gel.

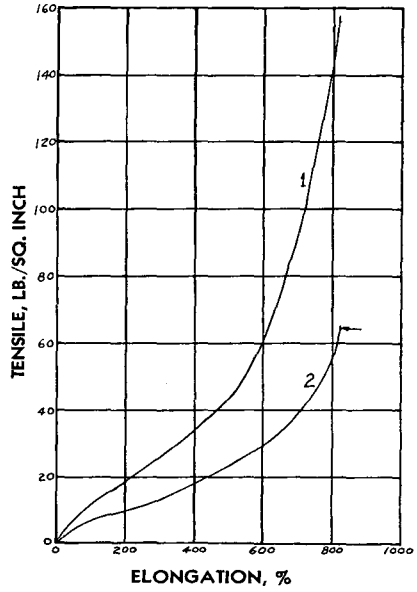

Figure 5. Stress-Strain Curves of Natural Latex

Arrows indicate point of rupture of specimen

The behavior of natural latex, also illustrated in Table I, is somewhat different from that of the various GR-S samples, in that good films can be obtained from natural latex over a range of the total solids concentrations from 40 to 62% and also in that Igepal prevents deposition of a good film from natural latex. Results obtained with natural latex films at 62 and 40% solids, using the Instron machine, are shown in Figures 5 and 6, in which the tensile is plotted against elongation and jaw separation, respectively. The curves for the 40% solids latex are of similar shape to those of the 62% solids latex, but the tensile values are lower throughout.

Significant results can be obtained only if due care is given to such details as the elimination of bubbles and removal of floc. It is also essential that the calcium nitrate–soaked paper strip be somewhat moist before dipping in the latex; if the salt is allowed to dry out, a poor deposit will result. In practice the desired moistness is obtained by blowing or breathing on the strip.

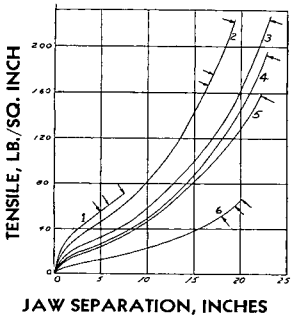

Figure 6. 1. Neoprene Type 571 (triplicate). 2. Neoprene Type 572 (triplicate). 3, 4, 5. Natural (H & C, 62% solids). 6. Natural (H & C, 40% solids)

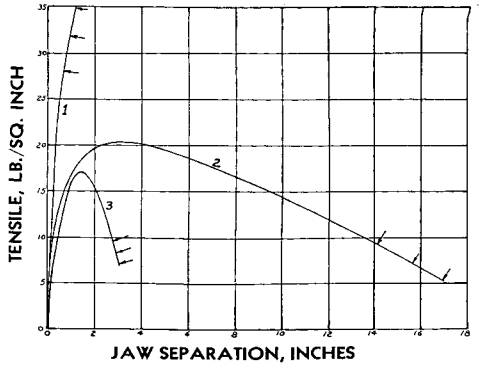

Figure 7. 1. GR-S 2003 (triplicate). 2. GR-S 2000 (triplicate). 3. Chemigum 235 HS (triplicate)

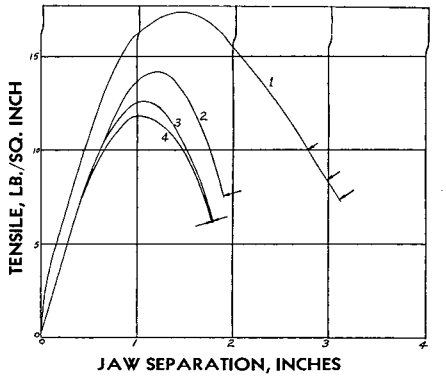

Figure 8. Chemigum 235 HS at different rates of jaw separation. 1. 20 inches per minute (triplicate). 2, 3, 4. 5 inches per minute

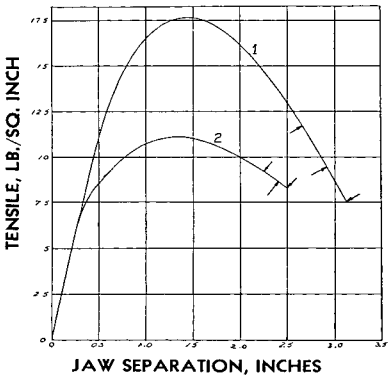

Figure 9. 1. Chemigum 245 HS. 2. Prevulcanized Chemigum 245 HS

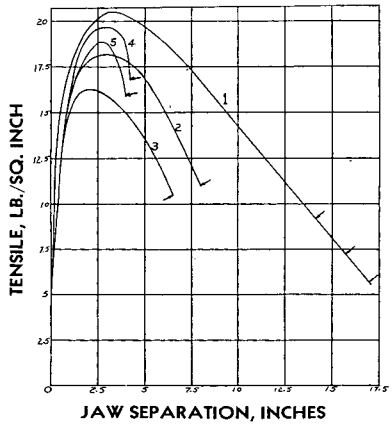

Figure 10. 1. GR-S-2000(A) (triplicate). 2, 3. GR-S-2000(B). 4, 5. Prevulcanized GR-S-2000

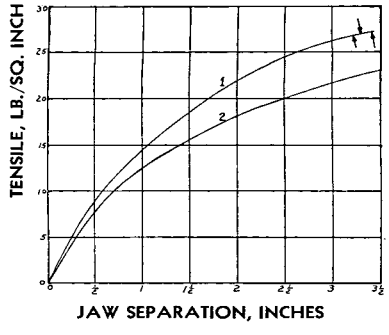

Figure 11. Natural latex. 1. Prevulcanized (Type C) (triplicate). 2. Raw (initial portion of curve)

Figures 6 to 11. Tensile Stress (Modulus) *vs.* Jaw Separation of Various Wet Gel Samples

Arrows indicate points of rupture of individual specimens. Several arrows on a single curve indicate that the several specimens gave virtually identical curves up to the points of rupture

Since the moist calcium nitrate tends to run down the strip and collect on the paper clip, this clip may be blotted before using this strip. Hanging the strip in a hygrostat before use has been tried, but satisfactory results were not obtained.

With latex films deposited and rinsed according to the above standard procedure, the thickness at the bottom of the dumbbell-shaped strip is generally within 0.001 or 0.002 inch of that at the top.

The latex film does not adhere to the wet paper, except by the capillary action of water. Consequently it seems reasonable to assume that the properties of the film are not influenced by the paper. This assumption is difficult to check experimentally, owing to the difficulty of preparing a free latex film.

Rate of Pull. The effect of the rate of pull is shown in Table II. It is important here to distinguish among the different types of stress-strain curves found with wet gels. Natural latex characteristically gives a reverse S-shaped curve with a steep initial portion, followed by a relatively flat portion, followed finally by a more steeply rising portion. Many synthetics give a curve in which the slope decreases continually up to the break point, with the tensile stress increasing up to the moment of rupture. Other synthetics give a curve in which the tensile stress rises to a maximum and then decreases until the break point. These three types of curves are designated as S, N, and U, respectively. Examples of such curves, as determined with the Instron machine are given in Figures 5, 8, and 11, respectively.

The rate of pull has only a negligible effect on the tensile strength and ultimate elongation of the natural latex gel (S curve). With GR-S-2003 (N curve) there is a slight effect on the tensile and a large effect on the elongation. The elongation of this latex is, in any case, very low and not easily measured. With specimens which give a U-type curve, there is a large effect on the tensile and particularly on the elongation. These specimens form "legs" during the pulling (presumably at or somewhat before the point of maximum tensile stress, or "yield" point); during the subsequent pulling the polymer flows out of the legs into nodules or into the bulk of the specimen.

It has been confirmed experimentally that if such a sample is pulled past the yield point and then held at a fixed jaw separation, the specimen will eventually rupture. Accordingly, the elongation and modulus at the break point of such samples are of little significance but merely reflect the relative rates of jaw separation and polymer flow. For such samples, it is recommended that the maximum modulus be taken as the tensile strength, and the elongation at the point of maximum modulus be considered as the true ultimate elongation.

It is of interest to speculate on the reason for the lower tensile strength found at the lower rate of pull. Possibly small tears or breaks are formed at a relatively low tensile stress. With the lower rate of pull these tears develop into legs at a low elongation and tensile stress, while at the higher rate of pull, the rate of stretching exceeds the rate of tear growth.

For ordinary work a rate of pull of 20 inches per minute is recommended in standard testing. This is about as fast a rate as will permit accurate measurement of the elongation. A slower rate is undesirable from the standpoint of tearing, as well as from the practical consideration that an unduly long time would be required to rupture a specimen of high elongation at a slow rate of pull.

RESULTS OF PRACTICAL SIGNIFICANCE

Wet Gel Strength of Raw Latices. Several commercially available latices have been evaluated by the procedure given above. These latices were produced in nature or in a reactor, and concentrated and stabilized by various means, but not otherwise compounded. Results are given in Table III and Figures 5 to 10.

The data of Table III show the great superiority of natural latex over the butadiene-based copolymers in the tensile strength of the wet gel. Neoprene Types 571 and 735 are intermediate between these two extremes, while Neoprene Type 572 is slightly higher than the natural latex. Neoprene Type 572 is known to crystallize more readily than Neoprene Type 571. The extremely high elongation of Neoprene Type 735 is worth noting; this is not a false effect caused by "legginess" since the load continued to increase up to the break point.

Most of the butadiene-based copolymers, on the other hand, gave U type stress-strain curves—i.e., curves which rose to a maximum (the yield point) and then decreased gradually before the final rupture. Among these copolymers only the GR-S-2003 exhibits a stress-strain curve of "normal" (N) appearance—i.e., rising with continually decreasing slope to a maximum value at the break point—and only this latex gives a tensile strength superior to the other butadiene-based copolymers. However, on the basis of the "tensile product," or tensile strength based on the cross-sectional area at the moment of measurement (*1*, *2*), the GR-S-2003 appears comparable to the GR-S-2000. There is little to choose between the remaining GR-S latices and the butadiene-acrylonitrile latices (Chemigum 245 HS and 235 HS), regarding tensile strength of the wet gel.

The tensile of the natural latex wet gel is about 7% of that of the dry film; for the GR-S and Chemigums the ratio is about 12%. Evidently the low tensiles of the latter stocks are to be blamed on the polymer properties rather than on colloidal properties of the wet gel, or else upon colloidal properties which persist in the dry coagulant-dipped film.

The tensile strengths of the various raw latices are in the same general order as the utilization experience with these latices, particularly as regards dipping properties. It is therefore proposed that the term "wet gel strength" be defined as the tensile strength of a latex film as determined by the above method, or alternatively, that the term "wet gel strength" remain undefined and the term "wet gel tensile" be used for the tensile as determined above.

Many samples gave films which were unsatisfactory for testing; these included GR-S-X-667 and X-633 (soft and leggy) and two high styrene latices (Pliolite 160 and Koppers KB-900-A) as well as a polybutadiene latex (GR-S-X-653), all of which were crumbly.

Wet Gel Strength of Prevulcanized Latices. For various applications it is common to use prevulcanized latex, either natural or synthetic. Wet gel properties of several prevulcanized latices are shown in Table IV and Figures 9 to 11.

It is seen that the tensiles and elongations of the prevulcanized natural latex wet gels are considerably lower than those of the natural latex from which they were prepared. Both tensile and elongation decrease with increasing degree of cure. Evidently

Table III. Wet Gel Strengths of Raw Latex Films[a]

		Wet Gel Properties						Dry Film Properties		
					Elongation, %					
Sample	Method of Concn.	Solids, %	Gel thickness, mils[b]	Type of curve[c]	Max.[d]	Break	Tensile, lb./sq. inch[d]	800% modulus	Elongation at break, %	Tensile strength, lb./sq. inch
Natural (H and C)	Centrifuged	62	25	S	...	850	180	1350	1200	2650
Natural (NC-401)	Creamed	63	25	S	...	850	160	500	1175	2100
Neoprene Type 571	...	40	21	N	...	450	72	100	1075	1175
Neoprene Type 571	Heat	51	21	N	...	350	75	...	...	...
Neoprene Type 572	...	53	23	S	...	800	190	100	1200	1550
Neoprene Type 735	...	37	19	S	...	2600[e]	110[e]	...	2000[g]	320[g]
GR-S-2000 (A)[f]	...	40	15	U	400	1500	20	...	...	...
GR-S-2000 (B)[f]	...	40	18	U	200	530	17	170	880	180
GR-S-2000	Creamed	53	15	U	90	200	19	...	...	...
GR-S-2001	...	39	11	U	80	2200	13	Film too soft	...	...
GR-S-2003 (A)	...	62	23	N	...	105	36	Film tore too readily	...	...
GR-S-X-710	...	40	21	U	40	1000	18	...	2900[g]	140[g]
GR-S-X-736[h]	...	35	21	U	30	700	14	...	...	...
Chemigum 245HS	Creamed	37	18	U	75	200	19	70	1400	110
Chemigum 235HS	Creamed	42	23	U	50	250	18	...	...	...

[a] All wet gel values are averages of three or more runs on Instron Machine at a rate of pull of 20 inches per minute.
[b] Double film without paper.
[c] S refers to curves similar to that of Figure 5, N to Figure 11, and U to Figure 8.
[d] For U curves, elongation is given at point of maximum tensile as well as at break point. Tensile is given only at its maximum value.
[e] Elongation of sample too great to permit measurement of conventional dumbbell specimen in Instron machine; therefore straight strips 0.25 × 1 inch were used.
[f] Two different lots.
[g] Owing to extremely high elongation, samples were pulled by hand at approximately 50 inches per minute.
[h] A high-modulus cold GR-S latex, normally oil-extended and coagulated and processed; however, this sample obtained without added oil.

Table IV. Wet Gel Strength of Prevulcanized Latex Films[a]

			Wet Gel Properties					Dry Film Properties			
					Elongation, %						
Sample	Base Stock	Solids, %	Gel thickness, mils[b]	Type of curve	Max.	Break	Tensile, lb./sq. inch	T-50, °C.	600% modulus	Elongation at break, %	Tensile strength, lb./sq. inch
A	Natural	62	23	N-S	...	550	30	13.5	300	1070	3600
B	Natural	62	23	N	...	250	45	12.2	600	1040	5700
C	Natural	62	26	N	...	310	51	12.0	650	960	4600
D	Natural	62	26	N	...	200	28	9.0	1100	880	5175
E	Natural	62	27	N	...	100	22	7.0	875	870	4575
F	GR-S-2000	40	18	U	170	260	20	...	800	710	1400
G	Chemigum 245	43	19	U	75	200	11	...	...	1150	<100

[a] All wet gel values are averages of three or more runs on Instron machine at a rate of pull of 20 inches per minute.
[b] Double film, without paper.

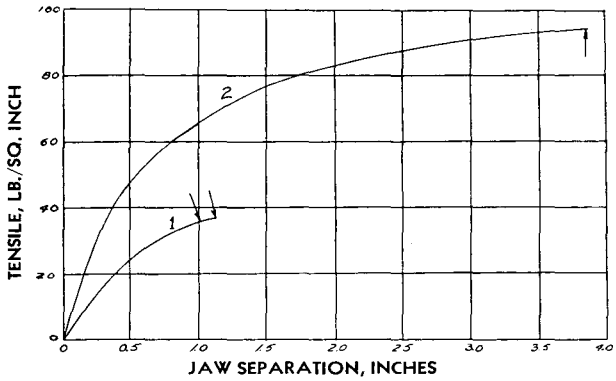

Figure 12. Comparison of Wet Gel and Partially Dried GR-S-2003 Film

1. GR-S-2003 wet gel
2. GR-S-2003, dried 10 minutes at 105° C.

as the rubber within each polymer particle becomes more cross-linked, the individual polymer particles become less cohesive.

It is of particular interest to compare the shapes of the stress-strain curves obtained with the raw and prevulcanized latex samples. Prevulcanization of natural rubber latex causes little change in the initial portion of the curve, but the final rising portion obtained with raw natural latex is completely absent in the prevulcanized stock. This final rising portion is presumably due to alignment of molecules to form crystallites. In order for this alignment to take place before rupture of the specimen, it would seem essential that molecules from adjacent latex particles come in contact with one another and share in crystallite formation. Prevulcanization introduces cross links within each particle and restricts the freedom of motion of the molecules within each particle, so that molecules from adjacent particles may not be able to align with one another.

In the dry film, on the other hand, some cross-linking has taken place between adjacent polymer particles, thus forming a continuous polymer network with a high tensile strength. There is no apparent correlation between the wet gel tensile and the degree of cure, as indicated by the $T - 50$ value. However, these latices were prevulcanized according to different types of formulas.

The raw synthetic latices which gave U curves showed comparatively little change in both the shape of the curves and the actual tensile and elongation values on prevulcanization.

From the practical standpoint, several of the prevulcanized natural latices show a lower tensile than GR-S-2003 (sample A, Table III). It is well known that the dip properties of prevulcanized natural latex are superior to those of GR-S-2003. For example, a dipped doll's foot prepared from the former can be removed from the mold, but not if GR-S-2003 is used as the dip stock. This is due to the extremely low elongation of the GR-S-2003 at a low rate of pull (Table II), reflecting the ease with which this sample tears rather than ruptures.

Drying of Latex Films. Profound changes in the structure and properties of a latex film take place as the film is dried. Accompanying the loss of moisture there is necessarily a reduction in volume corresponding to the volume percentage of water lost. If the film is constrained to remain constant in one dimension—as, for example, by the shape of the form or mold—then a certain stress is set up in this dimension; this may be designated as the "set modulus." During drying there also takes place an increase in the tensile strength of the film, perhaps by several hundredfold. An important objective of the present study has been to establish the relationships between several of the changes which take place on drying under various conditions. Some of the results which have been obtained up to the present time are shown in Figures 12 to 14.

Figures 12 and 13 illustrate the change in tensile properties of GR-S-2003 on drying in an air oven (noncirculating). The ultimate tensile and elongation values here plotted were obtained with the dumbbell-shaped strips used in the standard procedure given above; after dipping, these strips were dried for the indicated times, then cooled to room temperature and pulled.

To measure the shrinkage of the films on drying, straight strips of toilet paper, 0.5 × 4 inches, were coagulant-dipped by the above procedure, and then one edge of each strip was cut off to permit subsequent removal of the paper. Bench marks were

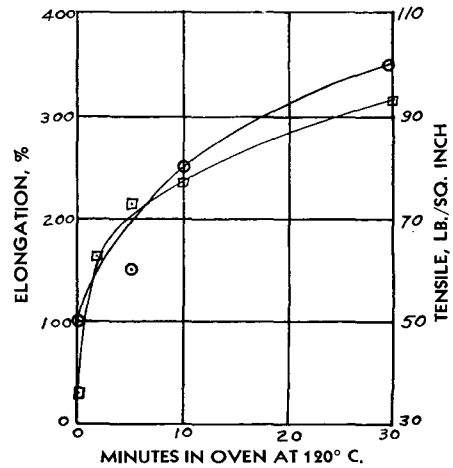

Figure 13. Elongation and Tensile Strengths of GR-S-2003 Films Dried for Various Lengths of Time

○. Elongation
□. Tensile

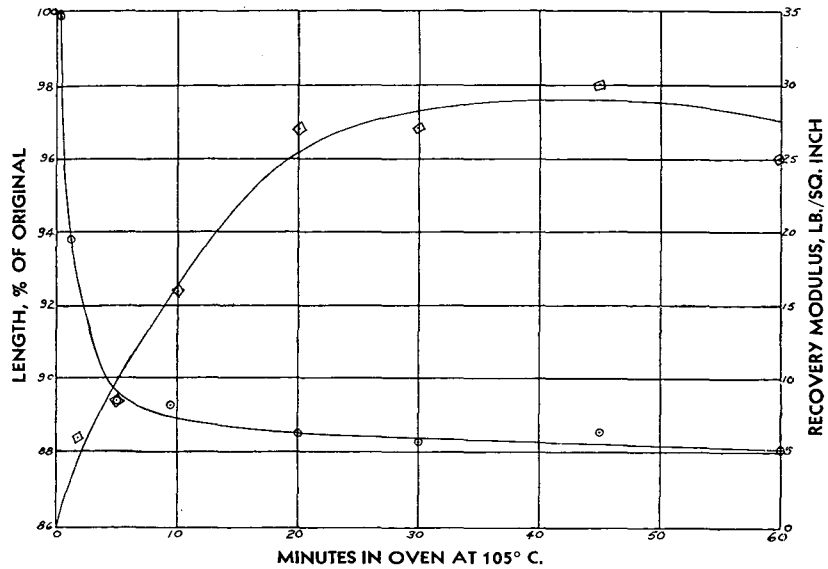

Figure 14. Shrinkage and "Recovery Modulus" of Prevulcanized Natural Latex (Type C) Films Dried for Various Lengths of Time

⊙. Length
⊡. Recovery modulus

made with India ink at a spacing of 6.50 cm. These strips were hung in the oven for various lengths of time, then cooled, pressed between glass slides, and remeasured. Each strip so prepared was then stretched to its original length (between bench marks); the tensile stress thus produced, which may be called the "recovery modulus," was measured. As a first approximation, the recovery modulus should be equal to the set modulus, defined above, although the latter should be somewhat the smaller owing to creep during drying.

Values of shrinkage and recovery modulus with a prevulcanized natural latex (sample D of Table IV) are plotted in Figure 14. It is significant that while the shrinkage, or loss of water, is virtually complete in 4 minutes, the recovery modulus has reached only one third of its final value at this stage. In other words, during the heating subsequent to driving off the water, the tension set up in a latex film on a mold would continue to increase.

The present results are only preliminary. It would appear that the tensile strength, ultimate elongation, shrinkage, and recovery modulus are the four most important factors whose interrelated change during drying and heating determines the tendency of a given latex film to break on a form or mold of a particular shape.

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Colorimetric Determination of Fluoride

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The bleaching effect of low concentrations of fluoride upon 18 organoferric colored complexes in acid solution was investigated to determine if any were sufficiently sensitive to be useful for the determination of fluoride. It was found that the iron(III) complexes of three reagents, resorcylaldoxime, 5-phenylsalicylic acid, and resacetophenone, gave approximately a 4% change in percentage transmittancy per 1 p.p.m. of fluoride at a pH of 2 to 3 and the proper concentration of iron(III). However, the colored complex of resorcylaldoxime is not stable on standing for an appreciable period of time. The latter two complexes were found to be stable over long periods of time and to give reproducible and sensitive results for fluoride in concentrations from 0 to 6 p.p.m. Investigation of the effect of the presence of 13 foreign ions showed that those which form stable complexes with iron, such as citrate and tartrate, and also a high concentration of aluminum, interfere with the determination.

THE determination of fluoride ion has long been a subject of concern to analytical chemists. Stevens (*17*) in 1936 and McKenna (*11*) in 1951 reviewed the history of this determination and discussed the gravimetric, volumetric, nephelometric, and colorimetric methods available. In 1936 the American Waterworks Association set up a committee to study the known methods for the determination of fluoride ion in many types of waters. They selected (*1, 3, 9*) the Scott (*16*) modification of the Sanchis (*15*) method which uses a zirconium-alizarin reagent that is decolorized by fluoride and the color compared with standards of known concentration.

The method is simple and fairly accurate, but has some disadvantages. The yellow color of the uncombined dye causes a change in hue when the zirconium-alizarin lake decreases in intensity as a result of increasing fluoride concentration, and up to 1.4 p.p.m. of fluoride the standards are unstable. Since then, other colorimetric methods (*5, 9, 12*) have been investigated.

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In recent years the fluoridation of community water supplies to reduce dental caries has become fairly widespread. The fluoride ion is added by means of various compounds, generally in the range of 0.6 to 1.5 p.p.m. Therefore, a simple, rapid, colorimetric method for the determination of fluoride ion in water supplies is desirable.

The bleaching effect of the fluoride ion in the colorimetric methods for determining iron(III) in acid solution, caused by formation of the colorless fluoroferric complexes, is well known. This bleaching effect of low concentrations of fluoride ion upon various organoferric colored complexes in acid solution was studied to see if any were sensitive enough to be satisfactory for the determination of very small amounts of fluoride ion.

A survey of the literature disclosed numerous organic reagents which produce color reactions with iron(III) in acid solution. Eighteen of these were selected and, where possible, the organoferric complexes were produced according to the directions in the literature. The wave length of maximum absorption was determined, and then a quantitative study was made of the effect of both pH and ferric ion concentration upon the ability of the fluoride ion to cause a fading effect. The fading effect was determined by measuring the increase in percentage transmittancy of radiant energy by the colored complex at constant pH and constant ferric ion concentration as the fluoride ion concentration was increased.

EXPERIMENTAL

A Lumetron filter photometer Model 402E with 2-cm. cells and filters of approximately 30 mμ band width was used to measure the transmittancy. The experimental data were confined to results between 20 and 60% transmittancies to decrease the absolute errors, as recommended by Ayres (*2*) and Ringbom (*13*). A Macbeth Model A pH meter was used to adjust the acetate buffer solutions. The standard iron(III) solution of 100 p.p.m. was prepared from reagent-grade ferrous ammonium sulfate by oxidation with bromine, and the standard fluoride solution of 2.04 p.p.m. of fluoride ion was prepared from reagent grade sodium fluoride.

Buffer solutions of pH 1, 2, and 3 were prepared according to Britton (*4*) and were adjusted to ±0.02 pH unit at 25° C. with a pH meter. These buffers had an acetate content of about 0.2*M*.

The bleaching effect of the fluoride ion in the region of low concentrations (0 to 10 p.p.m.) was of primary interest. This was studied in two ways:

By plotting the log percentage transmittancy against the volume of fluoride solution added to the colored organoferric complex to determine whether the change in percentage transmittancy obeyed the Lambert-Beer law.

By plotting $\%\ T_v - \%\ T_o$ *vs.* the volume of fluoride solution added, where T_v is the transmittancy with fluoride present and T_o is the transmittancy with no fluoride present. The slope of this plot gives a value of $\Delta\%T/\Delta V$ or the change in percentage transmittancy per 1 p.p.m. fluoride. This value gives a comparison of the sensitivity of an organoferric complex to fluoride under various conditions and between various complexes.

RESULTS

The first reagent studied was ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid) which Swank and Mellon (*18*) have used for the colorimetric determination of iron. They found that with an iron(III) concentration of 1 p.p.m. and at a pH of 3 using a 5-cm. cell, the presence of 10 p.p.m. of fluoride caused a 10% change in the color intensity. Fahey (*8*) and Urech (*20*) have investigated this color change as a colorimetric method for fluoride. This reagent was chosen to compare the bleaching effect with that obtained by Swank and Mellon and to see if greater sensitivity could be obtained at any other pH or iron(III) concentration.

Table I. Sensitivity of Organoferric Complexes to Fluoride

Organic Reagent	Filter, mμ	pH	Fe(III), P.P.M.	$\frac{\Delta\%T}{1\ P.P.M.\ F}$
Ferron	620	2	5	0.7
Salicylic acid	515	2.7	10	0.8
Tiferron	640	2	5	1.2
Sulfosalicylic acid	515	2	10	2.1
Kojic acid	490	2	10	1.1
Acetylacetone	490	2	15	2.1
β-Resorcylic acid	515	2	10	2.5
Resacetophenone	465	2	10	2.9
5-Phenylsalicylic acid	575	2	5	3.3
β-Resorcylaldoxime	515	3	15	3.6

It was found that the greatest sensitivity was obtained at an iron(III) concentration of 5 p.p.m., a pH of 2, and with a 620-mμ filter and 2-cm. cell. Since the percentage change depends upon the iron(III) concentration and buffer capacity of the solution, calculations showed only that at a pH of 3 and 2 p.p.m. of iron(III) the percentage change was of the same order of magnitude as obtained by Swank and Mellon.

The 17 other reagents were then investigated in a similar manner. Aminopyrine, chromotropic acid (4,5-dihydroxy-2,7-naphthalenedisulfonic acid), dinitrosoresorcinol, hematoxylin, isonitrosodimethyldihydroresorcinol, salicylaldoxime, *sym*-diphenylcarbazide, and tannic acid gave unstable colors or showed no bleaching effect with fluoride ion, so they were not investigated further. For the other 10 the results showing the optimum pH and iron(III) concentration giving the greatest change in percentage transmittancy per 1 p.p.m. of fluoride ion are shown in Table I. The last three reagents have the greatest sensitivity to fluoride, and these were investigated further with respect to reproducibility of results, stability, and the effect of other ions.

β-Resorcylaldoxime. The complex of ferric iron and β-resorcylaldoxime (2,4-dihydroxybenzaldoxime) was investigated by Chien and Shih (*6*).

One gram of the reagent was dissolved in 25 ml. of 95% ethyl alcohol and diluted to 500 ml. with water. Two milliliters of reagent, iron(III), fluoride solutions, and buffer to total 100 ml. were used for the various iron(III) concentrations and pH values tried. Measuring the transmittance at 515 mμ, the best results were obtained at a pH of 3 and 15 p.p.m. of iron over the range of 0 to 10 p.p.m. of fluoride.

Repetition of these experiments showed that the results varied with the acetate content, confirming the results of Thoms and Gantz (*19*) that the ferric acetate complex is more stable than the ferric fluoride complex. From Figure 1 it can be seen that the best results were obtained with a diluted (1 to 4) buffer where the pH varied from 3.2 to 2.6 on addition of the iron(III) solution. However, it was found that these solutions showed a 2 to 3% change in transmittancy after standing in daylight for 1 hour. Because this was unsatisfactory for a colorimetric method, this reagent was not investigated further.

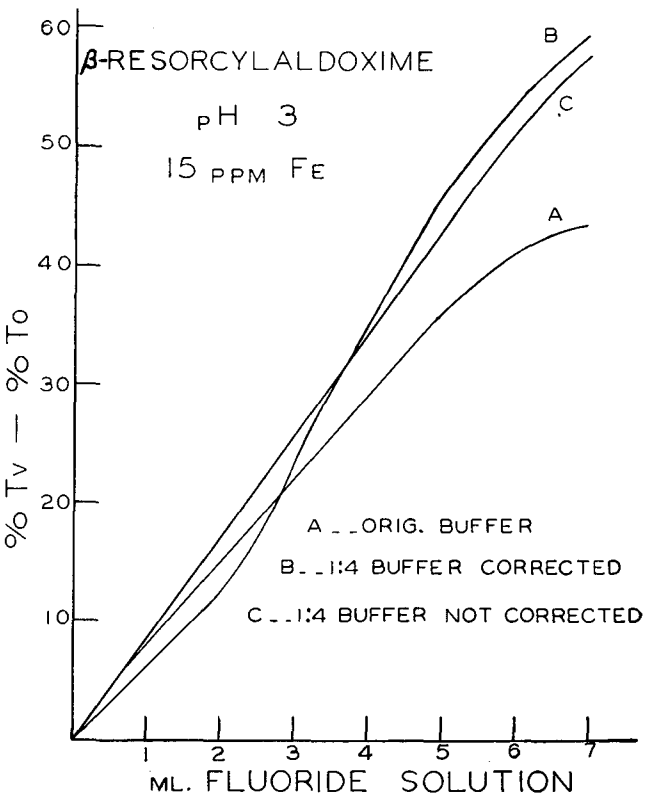

Figure 1. Effect of Buffer Concentration on Transmittancy

Table II. Effect of Fluoride on 5-Phenylsalicylic Acid–Iron(III) Complex

Volume NaF Solution, Ml.	Percentage Transmittancy	Average	Average Deviation
0	47.4, 47.4, 47.3, 47.3	47.4	±0.05
1	54.6, 54.4, 54.7, 54.7	54.6	±0.1
2	61.2, 61.0, 61.0, 61.1	61.1	±0.1
3	66.8, 67.0, 67.8, 66.8	67.1	±0.4
4	71.6, 71.8, 72.2, 71.5	71.8	±0.2
5	75.7, 75.7, 76.7, 75.3	75.8	±0.4
7	82.7, 82.3, 82.3, 82.3	82.4	±0.2

5-Phenylsalicylic Acid. The complex of iron(III) and 5-phenylsalicylic acid has been studied by Yoe and Harvey (*21*).

One gram of 5-phenylsalicylic acid was dissolved in 100 ml. of 95% ethyl alcohol, since the reagent precipitates in aqueous solution at a pH of 3.3 or below. One milliliter of the reagent solution, 40 ml. of ethyl alcohol, iron(III) solution, and fluoride solution, and buffer to total 100 ml. were used for each iron(III) concentration and pH studied. The best conditions for fluoride sensitivity were at pH 2 using 5 p.p.m. of iron(III) and 1 ml. of reagent; a bright blue color was obtained which was almost completely decolorized by 14 p.p.m. of fluoride.

At 575 mμ the percentage transmittancy was linear from 0 to 6 p.p.m. of fluoride, with a sensitivity of 3.3 per 1 p.p.m. of fluoride, and nonlinear at higher concentrations. The results of four runs are given in Table II. The colors were stable over a long period of time.

The effect of the presence of various foreign ions on the color intensity of the solutions is given in Figures 2 and 3. The chief interference in water supplies would be due to aluminum and sulfate which is allowable in drinking water up to 250 p.p.m. (*10*). In addition it was found that the presence of 100 p.p.m. of calcium, 50 p.p.m. of magnesium, 5 p.p.m. of cobalt(II), or 10 p.p.m. of nickel(II) ions does not have an appreciable effect upon the sensitivity.

Resacetophenone. A 10% acetone solution of resacetophenone (2,4-dihydroxyacetophenone) was used, because the reagent precipitated on standing from a 10% ethyl alcohol solution, as used by Cooper (*7*), at a pH of 3 or below.

The red color systems were developed by using 1 ml. of reagent, iron(III), and fluoride solutions and diluting to 100 ml. with buffer solution the same as with 5-phenylsalicylic acid. The best conditions for fluoride sensitivity were at pH 2 using 10 p.p.m. of iron(III), 1 ml. of reagent, and a 0.1*M* buffer.

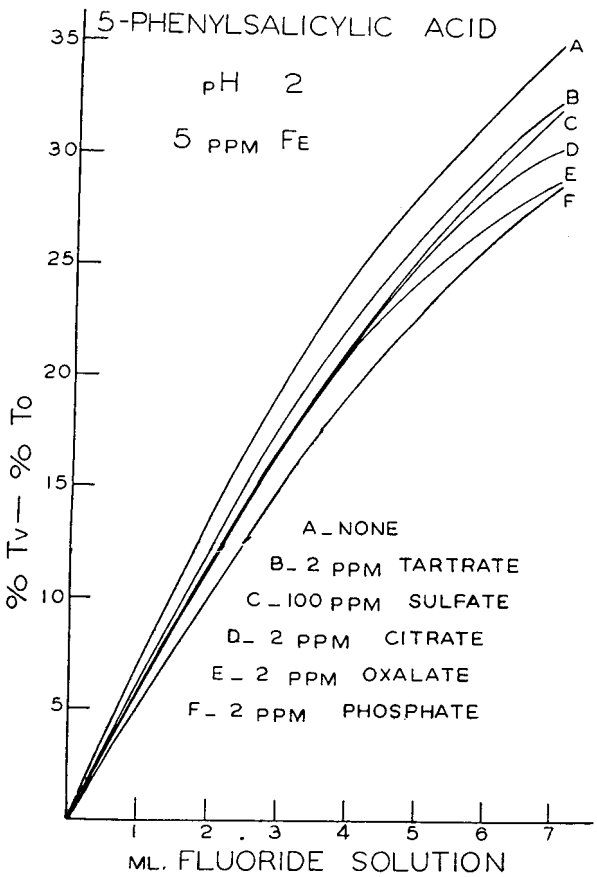

Figure 2. Effect of Foreign Ions on Transmittancy

Using a 465 mμ filter, the percentage transmittancy was linear from 0 to 6 p.p.m. of fluoride with a sensitivity of 3.9 per 1 p.p.m. of fluoride and nonlinear up to 14 p.p.m. The results of four runs are given in Table III and Figure 4. The colors were stable in daylight for 6 hours. In all cases, 100 ml. containing only 1 ml. of reagent and buffer was used for 100% transmittance.

The effect of the presence of various foreign ions on the color intensity of the solutions is given in Figure 5. In addition it was found that the presence of 100 p.p.m. of sulfate, 10 p.p.m. of tetraborate, 100 p.p.m. of bromide and calcium, 50 p.p.m. of magnesium, 5 p.p.m. of copper and cobalt, and 10 p.p.m. of nickel have no adverse effect. As in the previous case, the interference of aluminum is the most serious.

As most water supplies are treated with alum, the effect of smaller amounts of aluminum was investigated.

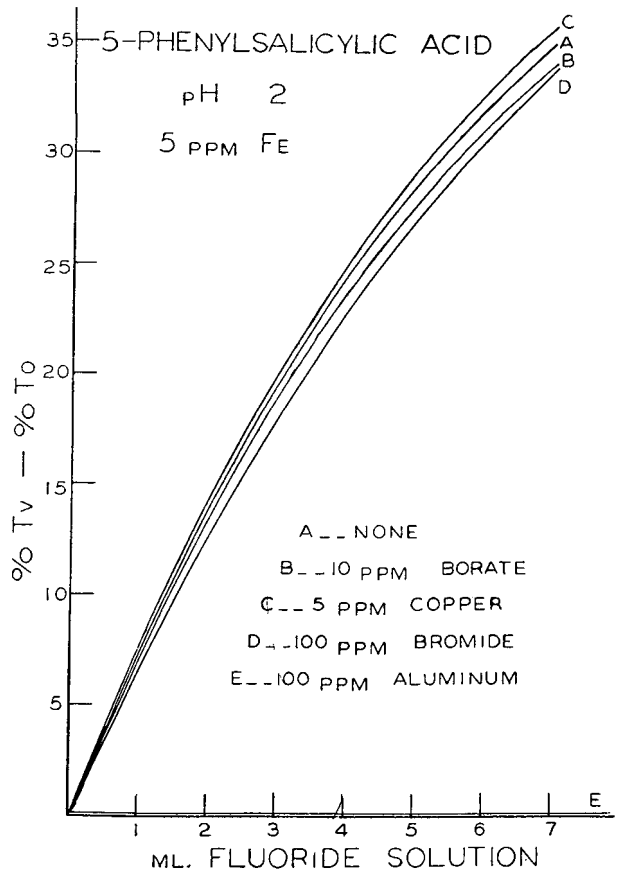

Figure 3. Effect of Foreign Ions on Transmittancy

Ten parts per million of iron, 5 p.p.m. of fluoride, various amounts of aluminum as aluminum sulfate, and 1 ml. of reagent were placed in flasks and diluted to 100 ml. with the 0.1*M* buffer solution of pH 2. The percentage transmittancy was determined at 10 minutes, 1 hour, and 8 hours after mixing.

The results (Table IV) show that the destruction of the ferric fluoride complex is a reasonably slow reaction at higher concentrations. For the readings at 10 minutes, there is an almost linear relationship between the change in percentage transmittancy and parts per million of aluminum. With 5 p.p.m. of aluminum there is a change of 2.5% in the $\%T_v - \%T_o$ values.

Table III. Effect of Fluoride on Resacetophenone–Iron(III) Complex

Volume NAF Solution, Ml.	Percentage Transmittancy	Average	Average Deviation
0	38.2, 38.2, 38.6, 38.4	38.4	±0.2
1	47.2, 47.2, 47.3, ...	47.2	±0.1
2	55.6, 55.4, 55.7, 55.8	55.6	±0.1
3	63.8, 63.9, 63.3, 63.3	63.6	±0.3
4	69.1, 68.8, 68.8, 69.0	68.9	±0.1
5	73.7, 73.5, 73.8, 73.8	73.7	±0.1
7	80.2, 80.3, 80.4, 80.3	80.3	±0.1

Table IV. Effect of Aluminum on Determination of Fluoride with Resacetophenone

Solution, P.P.M.			10 Minutes		1 Hour		8 Hours	
Fe(III)	Al(III)	F	%T	Δ%T	%T	Δ%T	%T	Δ%T
10	...	...	38.7	...	37.7	...	39.5	...
10	...	5	71.0	...	70.5	...	72.0	...
10	1	5	70.6	0.4	70.3	0.2	71.8	0.2
10	5	5	70.2	0.8	67.9	2.6	69.9	2.1
10	10	5	68.3	2.7	66.4	4.2	64.8	7.2
10	20	5	66.4	4.6	63.1	7.4	61.0	11.0
10	25	5	65.0	6.0	60.7	9.8	58.5	13.5
10	50	5	57.6	13.4	44.4	26.1	41.7	30.3

Since in the previous experiments the $\%T_o$ was obtained with only iron present, which might account for the change in $\%T_v - \%T_o$ values, the experiments were repeated, with readings at 10 minutes, obtaining the $\%T_o$ values with both iron and the same amount of aluminum present as is present with the fluoride. The results in Table V indicate that if the $\%T_o$ values are obtained with aluminum present, correct $\%T_v - \%T_o$ values are obtained for fluoride.

Table V. Effect of Aluminum on Determination of Fluoride with Resacetophenone

Solution, P.P.M.			$\%T$	$\%T_v - \%T_o$
Fe(III)	Al(III)	F		
10	...	...	38.5	...
10	...	5	71.3	32.8
10	1	...	38.3	...
10	1	5	71.0	32.7
10	5	...	37.8	...
10	5	5	70.6	32.8

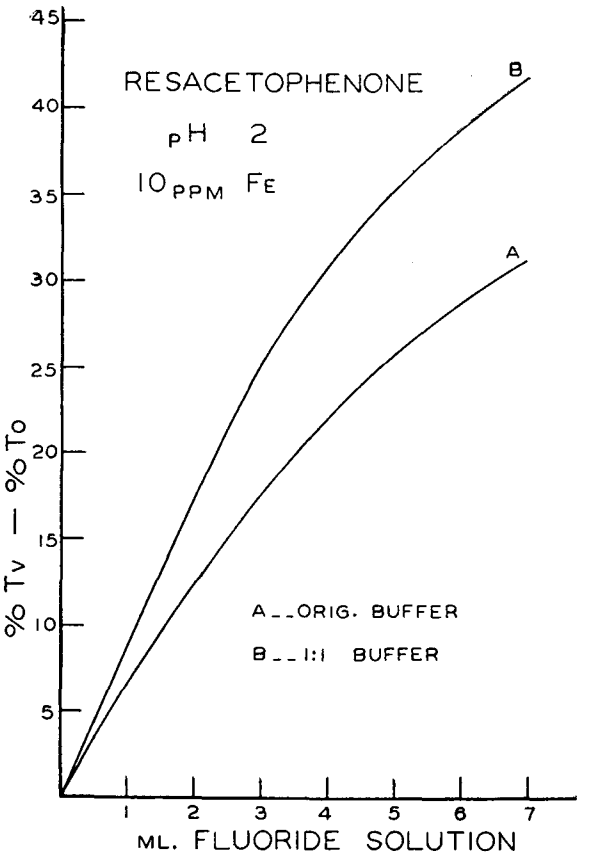

Figure 4. Effect of Buffer Concentration on Transmittancy

Since the sensitivity to fluoride is approximately the same with both 5-phenylsalicylic acid and resacetophenone and the interference of foreign ions is less with the latter, the determination of fluoride was tried on the Cornell University water supply. This water contains no fluoride, but has been treated with alum. Fifty milliliters of the water was analyzed for total aluminum and iron with aluminon (*14*). No positive test could be obtained, and since the reagent is sensitive to 10^{-4} mg. of aluminum, the aluminum content is apparently less than 0.1 p.p.m.

The determination was made by first preparing standards; sodium fluoride was added to 1 liter of the tap water to which 2 ml. of hydrochloric acid had been added to prevent the precipitation of calcium fluoride. One to 5 ml. of each of these standards was mixed with enough iron(III) solution to give a concentration of 10 p.p.m. and was diluted to 99 ml. with the 0.1*M* buffer of pH 2. Then 1 ml. of a 10% acetone solution of resacetophenone was added and the percentage transmittancy determined at 465 mμ.

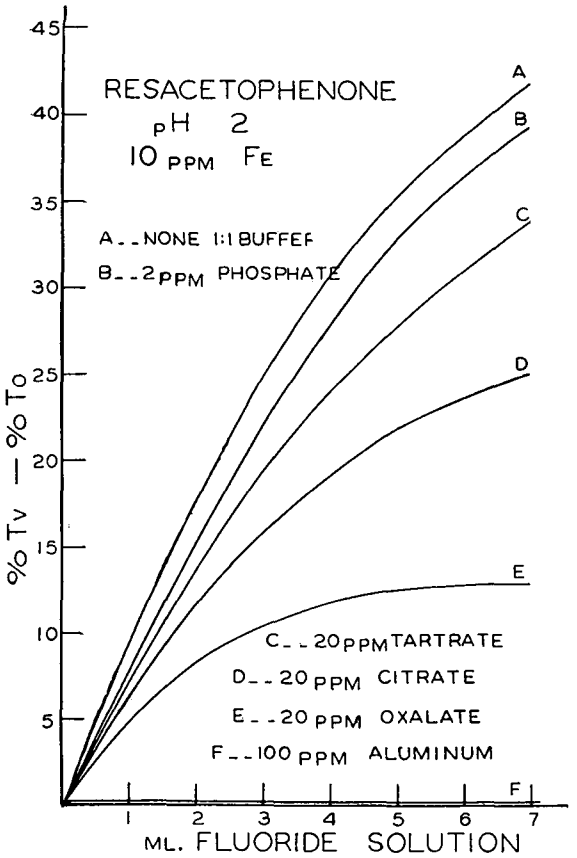

Figure 5. Effect of Foreign Ions on Transmittancy

The values obtained in Table VI were plotted as $\%T_v - \%T_o$ *vs.* parts per million of fluoride and showed a sensitivity of 3.1 over the range of 0 to 6 p.p.m. of fluoride. Two unknown solutions were measured and the fluoride concentration was determined from this curve (Table VI).

These results with resacetophenone indicate that the percentage transmittancy values vary with different batches of reagents. If the $\%T_o$ and $\%T_v$ values for the standards are determined with the same amount of aluminum present as in the water to be

Table VI. Determination of Fluoride in Water Samples with Resacetophenone

Standards

Fluoride, p.p.m.	Percentage transmittance	$\%T_v - \%T_o$
0	45.0	...
1	50.2	5.2
2	53.5	8.5
3	56.0	11.0
4	58.5	13.5
5	61.2	16.2
6	63.8	18.8
8	70.8	25.8
10	74.2	29.2

Unknowns

Present	Percentage transmittance	$\%T_v - \%T_o$	Found
0	45.0	...	...
2	53.2	8.2	1.95
6	64.3	19.3	6.2

analyzed and the readings taken after 10 minutes, the method will determine fluoride content correctly even in the presence of up to 5 p.p.m. of aluminum. Similar modifications may be necessary in the presence of appreciable concentrations of some of the other interfering ions which are not so common in water supplies.

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Testing a Quick-Weighing Balance

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The increasing use of quick-weighing balances necessitated the development of test procedures suited to such balances. Two tests have been developed, one for determining the linearity of the direct-reading scale, the other for calibrating the dial-operated weights. Estimates of the performance of the balance are obtained from each test. The computation form for the second test provides for the rapid and systematic least squares adjustment of the observed corrections of the weights. The test procedure, which is presented through the use of a numerical example and the discussion of statistical tests and estimates, provides for the calibration of the dial-operated weights and the estimation of the performance of a quick-weighing balance.

HOW good are modern quick-weighing balances? How much of the accuracy is sacrificed for the convenience and speed of a quick-weighing attachment? Such a device as a rider, chain, projected direct-reading scale, or set of built-in weights may contribute not only to the convenience or speed of operation of the balance but also to the variability of the balance. The test of a balance with projected direct-reading scale (capacity 100 mg.) and a set of built-in weights (capacity 99.9 grams) for a total capacity of 100 grams is considered in this paper. The rider, chain, and other quick-weighing devices will be considered in another paper. The tests described are designed specifically for the 100-gram Mettler Gram-atic balance, but could be adapted to other quick-weighing balances of similar design by taking into account the particular arrangement of the built-in weights. These special tests for the Mettler balance were devised because the built-in weights of this balance cannot be easily removed for testing and hence must be tested along with the balance.

DESCRIPTION OF BALANCE

Only those features of the balance related to the tests of the quick-weighing devices are described here. Built into the Gram-atic balance are three sets of dial-controlled weights arranged in decades, each set controlled by a separate dial. The "tenths" dial controls four weights: one each of nominal values 0.5 and 0.2 gram, and two of nominal value 0.1 gram. The weights used for each dial setting are shown in the following table, where the two 0.1-gram weights are distinguished by subscripts.

Dial Setting	Combination of Weights Used
0.1	$(0.1)_1$
0.2	(0.2)
0.3	(0.2) + $(0.1)_1$
0.4	(0.2) + $(0.1)_1$ + $(0.1)_2$
0.5	(0.5)
0.6	(0.5) + $(0.1)_1$
0.7	(0.5) + (0.2)
0.8	(0.5) + (0.2) + $(0.1)_1$
0.9	(0.5) + (0.2) + $(0.1)_1$ + $(0.1)_2$

Similarly, the "units" dial controls the four weights: 5 grams, 2 grams, 1 $gram_1$, and 1 $gram_2$. The "tens" dial is also similar, except that the weights come in pairs: (25 + 25 grams), (10 + 10 grams), $(5 + 5\ grams)_1$, and $(5 + 5\ grams)_2$. This is because it is necessary to balance the larger weights on the weight hanger. Thus the 50-gram dial setting removes two 25-gram weights symmetrically located on the hanger. Since, however, the two weights of a pair are always used together, they may be considered as one weight, and therefore the tens dial may be treated in the same manner as the units and tenths dials.

A fourth dial controls a 50-mg. weight used in differential weighing which, briefly, is a weighing performed within the range of the optical scale—i.e., without changing the dial settings. When the method of differential weighing is used, errors in the values of the dial-controlled weights do not enter into the results of a weighing. Only the variability of the balance and any error in the adjustment of the sensitivity will affect the results.

The balance has only one pan and stirrup and two knife-edges. A counterpoise on the beam replaces the second pan and stirrup and the third knife-edge. This feature eliminates the variability which would arise from the third knife-edge.

The dial-controlled weights normally hang from the weight hanger which is attached to the stirrup. All weighing is by substitution—that is, with the unknown on the pan of the balance the dial-controlled weights are removed by the dial controls until equilibrium is achieved. The total load on the stirrup is always 99.9 grams (plus the weight of pan and weight hanger and the amount indicated by the projection scale and the 50-mg. weight).

Because of the high magnification of the optical system, the balance is particularly sensitive to tilt. The balance should therefore be mounted on a sturdy support.

Table I. Determination of Correction for 0.1-Gram Dial Weight and Determination of Sensibility Reciprocal

Step	Operation	Observation, Mg.	Corr. for Std.[a], Mg.	Computations: For 0.1-g. wt.	Computations: For 100 divisions
1	Adjust zero and read	a_1	...	...	...
2	Place a 100-mg. standard on pan, set dial at 0.1 g.; read	a_2	s_1	$s_1 + a_1 - a_2 = x_1$	...
3	With standard still on pan, set dial at 0.0 g.; read	a_3	s_1	...	$s_1 + a_4 - a_3 = y_1$
4	Remove standard from pan and make zero reading (but do not readjust zero)	a_4	...	...	...
5	Arrest balance; reset zero (arbitrarily, need not read exactly zero); read	a_5	...	...	...
6	Place a different 100-mg. standard on pan; set dial at 0.1 g.; read	a_6	s_2	$s_2 + a_5 - a_6 = x_2$	...
7	With the second standard still on pan, set dial at 0.0 g.; read	a_7	s_2	...	$s_2 + a_6 - a_7 = y$
8	Remove standard from pan and make zero reading (do not readjust zero)	a_8	...	...	...
9	Repeat steps 1 through 8, using same standards, until a total of five sets of observations are obtained	b_1	...	...	...
		b_2	s_1	$s_1 + b_1 - b_2 = x_3$	...
		b_3	s_1	...	$s_1 + b_4 - b_3 = y_3$
		b_4	...	...	...
		b_5	...	...	...
		b_6	s_2	$s_2 + b_5 - b_6 = x_4$	...
		b_7	s_2	...	$s_2 + b_8 - b_7 = y_4$
		b_8	...	...	...
		etc.	...	...	...
Average value of correction for 0.1-g. weight, $=\bar{x}$				$\bar{x}$	
Average value of correction for 100 divisions, $=\bar{y}$					$\bar{y}$

[a] Correction for standard is quantity which must be added to nominal value to give actual mass of the standard.

If it is assumed that the values of the standards are known very much better than the balance reproduces its readings, then the standard deviation from their average of the ten values for the 0.1-gram dial weight may be used as a measure of the variability of the balance. (Weights having a National Bureau of Standards Class S certificate will meet this condition with most projection-reading balances. If better accuracy is required, a Class M set of weights may be used.) If $x_i = x_1, x_2 \ldots\ldots x_{10}$ are the ten values and $\bar{x}$ is their average Table (I), then the standard deviation is computed by the formula:

$$\text{Standard deviation } (S_1) = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{9}} = \frac{1}{3}\sqrt{\Sigma(x_i - \bar{x})^2}$$

The standard deviation from their average of the ten values of the correction for 100 divisions may also be used as a measure of the variability of the balance at readings near full scale of the projected scale.

$$\text{Standard deviation } (S_2) = \sqrt{\frac{\Sigma(y_i - \bar{y})^2}{9}} = \frac{1}{3}\sqrt{\Sigma(y_i - \bar{y})^2}$$

If the variability of the balance when the balance is used near the zero end of the projected scale and when it is used near the other end is the same, then the data may be combined to form a

SENSITIVITY

The manufacturer recommends that the 0.1-gram dial weight be used as the standard for adjusting the sensitivity of the balance. If this weight is in error, then the sensitivity will be incorrectly adjusted and the optical scale will not be direct reading in milligrams. The first step in testing the balance after leveling it and making sure that it is otherwise in working order is to adjust the sensitivity by comparing full scale deflection against standard weights.

After the sensitivity is adjusted as closely as possible, the sensibility reciprocal, SR, may be accurately determined by repeated weighings against standards. The sensibility reciprocal is a measure of the sensitivity of the balance and is defined as the number of milligrams which must be added to the load on the balance pan to cause a one-division change in the rest point. At the same time that the sensibility reciprocal is determined it is convenient to determine the value of the 0.1-gram dial weight. The sequence of weighings shown in Table I may be used, in which all readings are estimated to 0.01 mg.

The correction for the 0.1-gram dial weight is given by $\bar{x}$. The sensibility reciprocal can be computed from the average value of the correction for 100 divisions, $\bar{y}$, by the following equation:

$$SR = \frac{100 \text{ mg.} + \bar{y} \text{ mg.}}{100 \text{ divisions}} = \left(1 + \frac{\bar{y}}{100}\right) \frac{\text{mg.}}{\text{division}}$$

Table II. Computation Form for Balance Test and Calibration of Dial-Controlled Weights

Dial Setting		Obsvd.[a]	Computed	Residuals, Obs.-Comp.	Residuals, (Residuals)^2
1 =	$(1)_1$	a =			
2 =	(2)	b =			
3 =	(2) + $(1)_1$	c =			
4 =	(2) + $(1)_1$ + $(1)_2$	d =			
5 =	(5)	e =			
6 =	(5) + $(1)_1$	f =			
7 =	(5) + (2)	g =			
8 =	(5) + (2) + $(1)_1$	h =			
9 =	(5) + (2) + $(1)_1$ + $(1)_2$	i =			

Sum of Squares =

A +	A −	B +	B −	C +	C −	D +	D −
$-2a$		$0a$		$+2a$			$-3a$
$-2b$		$+2b$		$0b$			$-3b$
$-4c$		$+2c$		$+2c$			$-6c$
$-3d$		$+1d$		$+1d$			$-3d$
$+6e$		$-2e$		$-2e$			$+8e$
$+4f$		$-2f$		$0f$			$+5f$
$+4g$		$0g$		$-2g$			$+5g$
$+2h$		$0h$		$0h$			$+2h$
$+3i$		$-1i$		$-1i$			$+5i$

Check on Computations of A, B, C, and D

+	−
$-3a$	
$-3b$	
$-6c$	
$-4d$	
$+10e$	
$+7f$	
$+7g$	
$+4h$	
$+6i$	

(5) $+\frac{1}{19}$ A

$+\frac{1}{19}$ A

A
B
C
D

=

(2)	$(1)_1$	$(1)_2$
$+10(5)$	$+10(5)$	$-100(5)$
$+2B$	$+2C$	$+4D$
Sum	Sum	Sum
$\frac{1}{8}$ Sum	$\frac{1}{8}$ sum	$\frac{1}{8}$ Sum

Checks on Computations (Add residuals as follows)

$r_4 + r_8$
$r_2 + r_3 + r_7 + r_8$
$r_5 + r_6 + r_7 + r_8 + r_9$
$r_1 + r_3 + r_8 + r_8$

Summary of Tests of Three Dials

Dial	Sum of Squares
Tenths	
Units	
Tens	
Sum	

$\frac{1}{15}$ Sum

Standard deviation = $\sqrt{\frac{1}{15} \text{ Sum}}$

[a] To the observed difference, zero reading minus standard reading, add correction for standard weights.

single measure of the variability. The test to determine whether the two estimates of the variability, S_1 and S_2, are estimates of the same thing (*4*) is as follows:

$$\left(\frac{S_1}{S_2}\right)^2 < 3.18 \quad \text{or} \quad \left(\frac{S_2}{S_1}\right)^2 < 3.18 \qquad 9 \text{ times in } 10$$

where the larger value is used in the numerator. If the above test is satisfied, the data may be combined to form the single measure of variability:

$$\text{Standard deviation } (S_3) = \sqrt{\frac{\Sigma(x_i - \bar{x})^2 + \Sigma(y_i - \bar{y})^2}{9 + 9}}$$

DIAL-CONTROLLED WEIGHTS

The corrections for the dial-controlled weights may be determined by comparing each dial setting against suitable standards. This introduces errors which are due to the variability of the balance. It would be better if the dial weights could be removed from the balance and calibrated against standards on a more precise equal-arm balance. However, the weights cannot be removed from the Mettler balance with ease or without danger of putting the dial mechanism out of alignment. Hence, the following scheme has been devised.

The following weighings are made, in which all scale readings are estimated to 0.01 mg:

Load on Pan, G.	Observations: Dials, g.	Observations: Scale, mg.	Corr. for Std., Mg.	Corrected Observations for Dial Wt., Mg.
Set 0	00.0	a_0	...	...
0.1	00.1	a_1	s_1	$a = s_1 + a_0 - a_1$
0.2	00.2	b_1	s_2	$b = s_2 + b_0 - b_1$
0	00.0	b_0	...	...
Reset 0	00.0	c_0	...	...
0.3	00.3	c_1	s_3	$c = s_3 + c_0 - c_1$
0.4	00.4	d_1	s_4	$d = s_4 + d_0 - d_1$
0	00.0	d_0	...	...
Reset 0	00.0	e_0	...	...
0.5	00.5	e_1	s_5	$e = s_5 + e_0 - e_1$
0.6	00.6	f_1	s_6	$f = s_6 + f_0 - f_1$
0	00.0	f_0	...	...
Reset 0	00.0	g_0	...	...
0.7	00.7	g_1	s_7	$g = s_7 + g_0 - g_1$
0.8	00.8	h_1	s_8	$h = s_8 + h_0 - h_1$
0	00.0	h_0	...	...
Reset 0	00.0	i_0	...	...
0.9	00.9	i_1	s_9	$i = s_9 + i_0 - i_1$
1	01.0	etc.	etc.	etc.
0	00.0			
Reset 0	00.0			
2	02.0			
3	03.0			
0	00.0			
etc.	etc.			

And so forth through the remainder of the units dial and through the tens dial. If the weighings are made in the order shown, and the corrected observations (a through i for each dial) are computed from adjacent zeros as shown, most of the effect of a uniform zero shift will be cancelled out of the final values for the weights. A zero shift will, however, increase the residuals as discussed below.

Nine values (a through i) are now known for as many combinations of the four weights 0.5, 0.2, 0.1_1, and 0.1_2 gram. Thus the observation equations are:

$$\begin{aligned}
&(0.1)_1 && && - 0.1 = a\\
&(0.2) && && - 0.2 = b\\
&(0.2) && + (0.1)_1 && - 0.3 = c\\
&(0.2) && + (0.1)_1 && + (0.1)_2 - 0.4 = d\\
(0.5) && && && - 0.5 = e\\
(0.5) && && + (0.1)_1 && - 0.6 = f\\
(0.5) && + (0.2) && && - 0.7 = g\\
(0.5) && + (0.2) && + (0.1)_1 && - 0.8 = h\\
(0.5) && + (0.2) && + (0.1)_1 && + (0.1)_2 - 0.9 = i
\end{aligned}$$

It will be noted that there are more observation equations than unknowns. The least squares method of solution is appropriate (*3*). If the observation equations are given equal weight, the normal equations are:

$$\begin{aligned}
5(0.5) + 3(0.2) + 3(0.1)_1 + (0.1)_2 &= && && +e + f + g + h +\\
3(0.5) + 6(0.2) + 4(0.1)_1 + 2(0.1)_2 &= && +b + c + d && + g + h + i\\
3(0.5) + 4(0.2) + 6(0.1)_1 + 2(0.1)_2 &= +a && + c + d && + f + h + i\\
(0.5) + 2(0.2) + 2(0.1)_1 + 2(0.1)_2 &= && + d && && + i
\end{aligned}$$

In the above equations, the constants 0.1 through 0.9 have been eliminated by assuming that the weight symbols (0.5), (0.2), $(0.1)_1$, and $(0.1)_2$ now stand for the corrections for the weights rather than their actual values. For example, correction (0.5) = actual value (0.5) − 0.5 gram.

The solution of the normal equations is

$$\begin{aligned}
(0.5) &= \tfrac{1}{19}(-2a - 2b - 4c - 3d + 6e + 4f + 4g + 2h + 3i)\\
(0.2) &= \tfrac{1}{38}(-5a + 14b + 9c + 2d - 4e - 9f + 10g + 5h - 2i)\\
(0.1)_1 &= \tfrac{1}{38}(+14a - 5b + 9c + 2d - 4e + 10f - 9g + 5h - 2i)\\
(0.1)_2 &= \tfrac{1}{38}(-7a - 7b - 14c + 18d + 2e - 5f - 5g - 12h + 20i)
\end{aligned}$$

The necessary computations may be simplified by arranging them according to the computation form illustrated in Table II. First the corrected observations (a through i) are recorded. These are then multiplied by the appropriate factors and added to obtain the quantities A, B, C, and D. The computations of A, B, C, and D are now checked for accuracy as shown on the form.

As indicated, the correction for the weight (5), in this case (0.5), is $\frac{1}{19}A$. The corrections for the weights (0.2), $(0.1)_1$, and $(0.1)_2$ are then obtained from this value for (0.5) and the quantities B, C, and D, respectively. Thus

$$\begin{aligned}
(0.5) &= +\tfrac{1}{19}A\\
(0.2) &= \tfrac{1}{8}[+10\,(5) + 2\,B]\\
(0.1)_1 &= \tfrac{1}{8}[+10\,(5) + 2\,C]\\
(0.1)_2 &= \tfrac{1}{8}[-100(5) + 4\,D]
\end{aligned}$$

By using the computation form shown only one division by 19 need be made longhand (or using a machine). All of the remaining calculations may be made mentally.

The same computation form may also be used for the units and tens weights.

After the values of the corrections for the four weights controlled by each dial have been computed in the manner described, the corrections for the individual dial settings may be computed from them and recorded on the computation form in the column headed "computed." These values which have been computed by the method of least squares are the best values to use in allowing for the errors in the dial-controlled weights.

Agreement with the value previously determined for the 0.1-gram dial weight may be used as a check on the computations involved in the least squares adjustment of the values for the corrections of the tenths dial weights. The computations may also be checked at each step, as described below.

VARIABILITY

A measure of the variability of the balance may be computed from the residuals obtained when computing the corrections for the dial-controlled weights. The residuals (Table II) are the differences between the corrected observed values for each dial setting and the least-squares adjusted values. If the residuals are squared and the sum of the squares found for the tenths, units, and tens dials, and if the sum of these three sums is divided by 15 and the square root found, the result is the standard deviation.

$$\text{Standard deviation } (S_4) = \sqrt{\frac{\Sigma r_{0.1}^2 + \Sigma r_1^2 + \Sigma r_{10}^2}{15}}$$

Table III. Balance Test and Calibration of Dial-Controlled Weights for Tenths Dial

Dial Setting		Obsvd.[a]	Computed	Residuals, Obs.-Comp.	(Residuals)²
0.1 =	$(1)_1$	a = −0.025 mg.	−0.026 mg.	+0.001 r_1	0.000001
0.2 =	(2)	b = +0.038	+0.044	−0.006 r_2	0.000036
0.3 =	(2) + $(1)_1$	c = +0.026	+0.018	+0.008 r_3	0.000064
0.4 =	(2) + $(1)_1$ + $(1)_2$	d = +0.039	+0.037	+0.002 r_4	0.000004
0.5 = (5)		e = +0.028	+0.011	+0.017 r_5	0.000289
0.6 = (5)	+ $(1)_1$	f = −0.027	−0.015	−0.012 r_6	0.000144
0.7 = (5) + (2)		g = +0.049	+0.055	−0.006 r_7	0.000036
0.8 = (5) + (2) + $(1)_1$		h = +0.033	+0.029	+0.004 r_8	0.000016
0.9 = (5) + (2) + $(1)_1$ + $(1)_2$		i = +0.047	+0.048	−0.001 r_9	0.000001
				Sum of squares =	0.000591

A			B			C			D		
	+	−		+	−		+	−		+	−
−2 a	0.050		0 a			+2 a		0.050	−3 a	0.075	
−2 b		0.076	+2 b	0.076		0 b			−3 b		0.114
−4 c		0.104	+2 c	0.052		+2 c	0.052		−6 c		0.156
−3 d		0.117	+1 d	0.039		+1 d	0.039		−3 d		0.117
+6 e	0.168		−2 e		0.056	−2 e		0.056	+8 e	0.224	
+4 f		0.108	−2 f	0.054		0 f			+5 f		0.135
+4 g	0.196		0 g			−2 g		0.098	+5 g	0.245	
+2 h	0.066		0 h			0 h			+2 h	0.066	
+3 i	0.141		−1 i		0.047	−1 i		0.047	+5 i	0.235	
	+0.621	−0.405		+0.221	−0.103		+0.091	−0.251		+0.845	−0.522
	−0.405			−0.103				+0.091		−0.522	
	+0.216			+0.118				−0.160		+0.323	

Check on Computations of A, B, C, and D			(0.5)	(0.2)	(0.1)₁	(0.1)₂
	+	−	$+\frac{1}{19}$ A +0.01137	+10(5) +0.114	+10(5) +0.114	−100(5) −1.137
				+2 B +0.236	+2 C −0.320	+4 D +1.292
−3 a	0.075			Sum +0.350	Sum −0.206	Sum +0.155
−3 b		0.114				
−6 c		0.156	$+\frac{1}{19}$ A +0.011	$\frac{1}{8}$ Sum +0.044	$\frac{1}{8}$ Sum −0.026	$\frac{1}{8}$ Sum +0.019
−4 d		0.156				
+10 e	0.280		+ −			
+7 f		0.189	A 0.216			
+7 g	0.343		B 0.118			
+4 h	0.132		C 0.160			
+6 i	0.282		D 0.323			

Checks on Computations (Add residuals as follows)

$r_4 + r_9$	+0.001
$r_2 + r_3 + r_7 + r_8$	0.000
$r_5 + r_6 + r_7 + r_8 + r_9$	+0.002
$r_1 + r_3 + r_6 + r_8$	+0.001

Note that sums vanish

+1.112	−0.615	+0.657	−0.160
−0.615		−0.160	
+0.497	=	+0.497[b]	

[a] Note. To the observed difference, zero reading minus standard reading, add the correction for the standard weights.
[b] Note agreement.

The reason for dividing by 15 is that although 27 observations are made (9 observations for each dial) 12 unknowns are found (4 weights for each dial), leaving only 15 degrees of freedom (*4*).

This value of the standard deviation may be compared with that previously computed, S_3, and should be in good agreement with it (see the section on checks). When in good agreement, the two values may be combined according to the formula:

$$\text{Standard deviation } (S_5) = \sqrt{\frac{\Sigma(x_i - \bar{x})^2 + \Sigma(y_i - \bar{y})^2 + \Sigma r_{0.1}^2 + \Sigma r_1^2 + \Sigma r_{10}^2}{9 + 9 + 15}}$$

S_5 or some multiple of S_5 may be used as a measure of the variability of the balance and therefore of the suitability of the balance for a particular application. S_1, S_2, or S_4 and therefore S_3 or finally S_5 is the standard deviation not of a single observation but of the difference between a pair of observations. It takes a pair of observations to make a weighing: The mass of an object is determined from the difference between the balance readings with the object on the pan and with the pan empty. The mass of a sample is determined from the difference between the balance reading for the container and the balance reading for the container plus sample. (The latter is called a differential weighing whenever the two balance readings are made without changing the setting of the dials.) Since a weighing involves the determination of the difference between two observations, S_5 is the standard deviation of a weighing.

CHECKS ON OBSERVATIONS AND COMPUTATIONS

The computation sheet illustrated in Table II contains various checks on observations and computations.

An intermediate check on the computations is provided by computing the sum of A, B, C, and D:

$$A + B + C + D = -3a - 3b - 6c - 4d + 10e + 7f + 7g + 4h + 6i$$

These sums should be in exact numerical agreement.

The calculations involved in the least squares adjustment may be checked by observing whether or not the following sums of residuals add to zero within the error of rounding off.

$$\begin{aligned} r_4 + r_9 &= 0 \\ r_2 + r_3 + r_7 + r_8 &= 0 \\ r_5 + r_6 + r_7 + r_8 + r_9 &= 0 \\ r_1 + r_3 + r_6 + r_8 &= 0 \end{aligned}$$

The uniformity of the residuals serves as a check against gross errors in the observations.

The following additional statistical checks may be made:

There is only one chance in twenty according to statistical theory that the ratio of the largest of the three sums $\Sigma r_{0.1}^2$, Σr_1^2, or Σr_{10}^2 to the sum of the three will be greater than 0.7071 (Cochran's test) (*1*).

$$\frac{(\Sigma r^2)\text{ max.}}{\Sigma r_{0.1}^2 + \Sigma r_1^2 + \Sigma r_{10}^2} < 0.7071$$

19 times in 20

This statement is true only if the three sums are measures of the same thing—i.e., only if there is reason to expect the same variability when using the different dials. As the balance is always operated at the same total load, the variability of the balance should probably be independent of the dial used. Hence, the inequality may be considered a rough check on the observations.

In comparing the standard deviations, S_3 and S_4, it is necessary to divide the larger of these two values by the smaller. This ratio will be greater than the values given below only one time in ten, provided that the two standard deviations are measures of the same thing (*2*, *5*).

$$\left(\frac{S_3}{S_4}\right)^2 < 2.36 \quad \text{or} \quad \left(\frac{S_4}{S_3}\right)^2 < 2.27 \qquad 9 \text{ times in } 10$$

NUMERICAL EXAMPLE

The following is a sample of the observations from which the sensibility reciprocal and the correction for the 0.1-gram dial weight are computed:

Load on Pan, Mg.		Observations: Dials, g.	Observations: Scale, mg.	Corr. for Std., Mg.	Computations: 0.1-G. wt., mg.	Computations: 100 divisions, mg.
Set	0	00.0	0.00	...	...	...
	L 100_1	00.1	+0.04	−0.015	−0.055	...
	L 100_1	00.0	99.96	−0.015	...	+0.005
	0	00.0	−0.02	...	...	...
Reset	0	00.0	0.00	...	...	...
	L 100_2	00.1	+0.03	−0.007	−0.037	...
	L 100_2	00.0	99.99	−0.007	...	+0.003
	0	00.0	0.00	...	...	...
Reset	0	etc.	...	...	...	...
Average values					$\bar{x}$ = −0.036 mg.	$\bar{y}$ = +0.009 mg.
$\Sigma(x_i - \bar{x})^2$ or $(y_i - \bar{y})^2$					0.003650	0.001970
Standard deviation					s_1 = 0.020 mg.	s_2 = 0.015 mg.

Table IV. Balance Test and Calibration of Dial-Controlled Weights for Units Dial

Dial Setting		Obsvd.[a]	Computed	Residuals, Obs.-Comp.	(Residuals)^2
1 =	$(1)_1$	a = −0.015 mg.	−0.018 mg.	+0.003 r_1	0.000009
2 =	(2)	b = +0.084	+0.064	+0.020 r_2	0.000400
3 =	(2) + $(1)_1$	c = +0.029	+0.046	−0.017 r_3	0.000289
4 =	(2) + $(1)_1$ + $(1)_2$	d = −0.042	−0.032	−0.010 r_4	0.000100
5 = (5)		e = +0.043	+0.065	−0.022 r_5	0.000484
6 = (5)	+ $(1)_1$	f = +0.063	+0.047	+0.016 r_6	0.000256
7 = (5) + (2)		g = +0.128	+0.129	−0.001 r_7	0.000001
8 = (5) + (2) + $(1)_1$		h = +0.107	+0.111	−0.004 r_8	0.000016
9 = (5) + (2) + $(1)_1$ + $(1)_2$		i = +0.042	+0.033	+0.009 r_9	0.000081
				Sum of Squares =	0.001636

A				B				C				D			
	+		−		+		−		+		−		+		−
−2 a	0.030			0 a				+2 a			0.030	−3 a	0.045		
−2 b			0.168	+2 b	0.168			0 b				−3 b			0.252
−4 c			0.116	+2 c	0.058			+2 c	0.058			−6 c			0.174
−3 d	0.126			+1 d			0.042	+1 d			0.042	−3 d	0.126		
+6 e	0.258			−2 e			0.086	−2 e			0.086	+8 e	0.344		
+4 f	0.252			−2 f			0.126	0 f				+5 f	0.315		
+4 g	0.512			0 g				−2 g			0.256	+5 g	0.640		
+2 h	0.214			0 h				0 h				+2 h	0.214		
+3 i	0.126			−1 i			0.042	−1 i			0.042	+5 i	0.210		
	+1.518		−0.284		+0.226		−0.296		+0.058		−0.456		+1.894		−0.426
	−0.284						+0.226				+0.058		−0.426		
	+1.234						−0.070				−0.398		+1.468		

Check on Computations of A, B, C, and D

+		−
−3 a	0.045	
−3 b		0.252
−6 c		0.174
−4 d	0.168	
+10 e	0.430	
+7 f	0.441	
+7 g	0.896	
+4 h	0.428	
+6 i	0.252	
	+2.660	−0.426
	−0.426	
	+2.234	

	(5)	(2)	$(1)_1$	$(1)_2$
$+\frac{1}{19}$ A	+0.06495	+10(5) +0.649	+10(5) +0.649	−100(5) −6.495
		+2 B −0.140	+2 C −0.796	+4 D +5.872
		Sum +0.509	Sum −0.147	Sum −0.623
$+\frac{1}{19}$ A	+0.065	$\frac{1}{8}$ Sum +0.064	$\frac{1}{8}$ Sum −0.018	$\frac{1}{8}$ Sum −0.078

	+	−
A	1.234	
B		0.070
C		0.398
D	1.468	
	+2.702	−0.468
	−0.468	
=	+2.234[b]	

Checks on Computations (Add residuals as follows)

$r_4 + r_9$	−0.001
$r_2 + r_3 + r_7 + r_8$	−0.002
$r_5 + r_6 + r_7 + r_8 + r_9$	−0.002
$r_1 + r_3 + r_6 + r_8$	−0.002

Note that sums vanish

[a] Note. To the observed difference, zero reading minus standard reading, add the correction for the standard weights.
[b] Note agreement.

The computations for the dial-controlled weights are given in Tables III, IV, and V.

From the summary at the end of Table V, it is seen that

$$\frac{(\Sigma r^2)\ \text{max.}}{\Sigma r^2_{0.1} + \Sigma r_1^2 + \Sigma r^2_{10}} = \frac{0.001636}{0.002736} = 0.60 < 0.7071$$

The ratio 0.60 is large, but not so large as to create doubt that the standard deviations for the three dials may be considered to be measures of the same thing. Hence, the standard deviations for the separate dials may be combined to form a single estimate of the variability of the balance.

$$S_4 = \sqrt{\frac{0.002736}{15}} = 0.014 \text{ mg.}$$

If the appropriate inequality is applied, it is seen that S_3 and S_4 are measures of the same thing, and hence a single measure of the variability of the balance (S_5) may be computed:

$$\left(\frac{S_3}{S_4}\right)^2 = \left(\frac{0.018}{0.014}\right)^2 = 1.7 < 2.36$$

$$S_5 = \sqrt{\frac{0.003650 + 0.001970 + 0.002736}{9 + 9 + 15}} = \sqrt{\frac{0.008356}{33}} = 0.016 \text{ mg.}$$

The $L100_1$ and $L100_2$ are two 100-mg. standards of the L set, and are marked with one and two dots, respectively. Although the weighings are estimated to only 0.01 mg., the computations are made to 0.001 mg. in order not to lose any precision by rounding off the known values of the standards.

From this it is seen that

$$SR = \frac{100 + 0.009}{100} = 1.00009 \text{ mg./division}$$

$$S_1 = \sqrt{\frac{0.003650}{9}} = 0.020 \text{ mg.}$$

$$S_2 = \sqrt{\frac{0.001970}{9}} = 0.015 \text{ mg.} \qquad \left(\frac{S_1}{S_2}\right)^2 = \frac{3650}{1970} = 1.85 < 3.18$$

Hence, these two estimates of the variability of the balance may be combined.

$$S_3 = \sqrt{\frac{0.003650 + 0.001970}{9 + 9}} = 0.018 \text{ mg.}$$

To show how the corrected observations are obtained, the first few observations for the tenths dial are shown:

Load on Pan, Mg.	Observations: Dials, g.	Observations: Scale, mg.	Adjacent Zero Minus Observation, Mg.	Corr. for Std., Mg.	Corrected Observations, Mg.
0	00.0	+0.04	...	...	...
$L100_1$	00.1	+0.05	−0.01	−0.015	−0.025
$L100_1 + 100_2$	00.2	0.00	+0.06	−0.022	+0.038
0	00.0	+0.06	...	...	...
0	00.0	+0.04	...	...	...
$L200 + 100_1$	00.3	+0.01	+0.03	−0.004	+0.026
$L200 + 100_1 + 100_2$	00.4	0.00	+0.05	−0.011	+0.039
0	00.0	+0.05	...	...	...
0	00.0	+0.01	...	...	...
$L500$	00.5	+0.01	0.00	+0.028	+0.028
etc.					

This is the standard deviation to be expected in the weighing of a sample on this balance.

CONCLUSIONS

Four 100-gram Mettler Gram-atic balances were tested in the Mass Laboratory of the National Bureau of Standards. The standard deviations to be expected in the differential weighing of samples on these balances were found to be 0.016, 0.017, 0.016, and 0.034 mg., respectively.

The first three of these are the standard deviation S_5—that is, all of the other standard deviations satisfied the various tests for combination into the single standard deviation S_5. The last value shown is the value of S_4 for the fourth balance. The value of S_3 for the fourth balance was found to be 0.015 mg. Thus

$$\left(\frac{S_4}{S_3}\right)^2 = \left(\frac{0.034}{0.015}\right)^2 = 5.1 > 2.27$$

Since this ratio is greater than 2.27, the two standard deviations are not likely to be measures of the same thing. The zero shift during the course of the test was considerably larger for this fourth balance than for the other three. Recomputing S_4 for this balance using interpolated zeros rather than adjacent zeros, however, resulted in only a slight decrease in S_4 (to 0.032 mg.). Without further investigation, the best that can be said is that the large zero shift and the large value for S_4 are possibly results of the same constructional defects.

An accuracy of 0.02 mg. is claimed by the manufacturer for samples measured by differential weigh-

Table V. Balance Test and Calibration of Dial-Controlled Weights for Tens Dial

Dial Setting		Obsvd.[a]	Computed	Residuals Obs.-Comp.	(Residuals)^2
10 =	$(1)_1$	a = +0.042 mg.	+0.047 mg.	−0.005 r_1	0.000025
20 =	(2)	b = +0.014	+0.024	−0.010 r_2	0.000100
30 =	(2) + $(1)_1$	c = +0.066	+0.071	−0.005 r_3	0.000025
40 =	(2) + $(1)_1$ + $(1)_2$	d = −0.104	−0.102	−0.002 r_4	0.000004
50 = (5)		e = −0.112	−0.096	−0.016 r_5	0.000256
60 = (5)	+ $(1)_1$	f = −0.050	−0.049	−0.001 r_6	0.000001
70 = (5) + (2)		g = −0.068	−0.072	+0.004 r_7	0.000016
80 = (5) + (2) + $(1)_1$		h = −0.016	−0.025	+0.009 r_8	0.000081
90 = (5) + (2) + $(1)_1$ + $(1)_2$		i = −0.197	−0.198	+0.001 r_9	0.000001
				Sum of squares =	0.000509

A			B			C			D		
	+	−		+	−		+	−		+	−
−2 a		0.084	0 a			+2 a	0.084		−3 a		0.126
−2 b		0.028	+2 b	0.028		0 b			−3 b		0.042
−4 c		0.264	+2 c	0.132		+2 c	0.132		−6 c		0.396
−3 d	0.312		+1 d		0.104	+1 d		0.104	−3 d	0.312	
+6 e		0.672	−2 e	0.224		−2 e	0.224		+8 e		0.896
+4 f		0.200	−2 f	0.100		0 f			+5 f		0.250
+4 g		0.272	0 g			−2 g	0.136		+5 g		0.340
+2 h		0.032	0 h			0 h			+2 h		0.032
+3 i		0.591	−1 i	0.197		−1 i	0.197		+5 i		0.985
	+0.312	−2.143		+0.681	−0.104		+0.773	−0.104		+0.312	−3.067
		+0.312		−0.104			−0.104				+0.312
		−1.831		+0.577			+0.669				−2.755

Check on Computations A, B, C, and D

+	−
−3 a	0.126
−3 b	0.042
−6 c	0.396
−4 d 0.416	
+10 e	1.120
+7 f	0.350
+7 g	0.476
+4 h	0.064
+6 i	1.182
+0.416	−3.756
	+0.416
	−3.340

	+	−
A		1.831
B	0.577	
C	0.669	
D		2.755
	+1.246	−4.586
		+1.246
=		−3.340[b]

(50)	(20)	$(10)_1$	$(10)_2$
$+\frac{1}{19}$ A −0.09636	+10(5) −0.964	+10(5) −0.964	−100(5) +9.636
	+2 B +1.154	+2 C +1.338	+4 D −11.020
	Sum +0.190	Sum +0.374	Sum −1.384
$+\frac{1}{19}$ A −0.096	$\frac{1}{8}$ Sum +0.024	$\frac{1}{8}$ Sum +0.047	$\frac{1}{8}$ Sum −0.173

Checks on Computations (Add residuals as follows)

$r_4 + r_9$	−0.001
$r_2 + r_3 + r_7 + r_8$	−0.002
$r_5 + r_6 + r_7 + r_8 + r_9$	−0.003
$r_1 + r_2 + r_6 - r_3$	−0.002

Note that sums vanish

Summary of Tests of Three Dials

Dial	Sum of Squares
Tenths	0.000591
Units	0.001636
Tens	0.000509
Sum	0.002736
$\frac{1}{15}$ Sum	0.0001825
Standard Deviation = $\sqrt{\frac{1}{15}\text{ sum}}$	0.0135 mg.

[a] Note. To the observed difference, zero reading minus standard reading, add the correction for the standard weights.
[b] Note agreement.

ing with balances of this model. The differential method of weighing eliminates the errors of the dial weights from the result of a weighing. If it is assumed that a differential weighing is also free from other systematic errors, it follows that the uncertainty present in a differential weighing will be determined entirely by the precision with which the balance repeats its indications. Therefore, the standard deviation or the probable error could be used as the measure of the accuracy of a differential weighing; however, the concept accuracy usually carries with it the connotation that an actual error greater than the stated accuracy will rarely occur. There is no generally accepted definition of a rare occurrence—one time in ten or hundred or otherwise is used depending on the purpose. One time in twenty has been chosen as being fairly rare and yet not too unfavorable to the manufacturer.

If therefore by the accuracy of a differential weighing is meant that 95% of the time any two differential weighings of the same sample will agree with each other to within a given value, it may be stated that the values of accuracy for the balances tested are 0.044, 0.047, 0.044, and 0.09 mg., respectively. (The quantities given in the text are for agreement between two weighings. Agreement between two weighings is the same as the error of an analysis involving two weighings. The standard deviation for the difference between two quantities each of standard deviation S is $S' = \sqrt{2}\,S$. Ninety-five per cent of the area under the normal curve lies between limits of $\pm 1.960\,S'$.) In order to have an accuracy of 0.02 mg. in this sense it is necessary that the standard deviation be 0.007 mg. Alternatively, it could be said that each of the first three of the foregoing balances has an accuracy of 0.02 mg. if instead of requiring this agreement in 95% of the cases it is required in two thirds of the cases only.

It will be observed from the data given in the numerical example that, if other than differential weighing is used and if the corrections for the dial-controlled weights are neglected, a maximum positive error of +0.255 mg. is obtained at a dial setting of 37.7 grams, and a maximum negative error of −0.256 mg. is obtained at 94.1 grams. Corresponding figures for the other balances tested are +0.210 and −0.221 mg.; +0.22 and −0.06 mg.; and +0.095 and −0.258 mg. The maximum possible error in the difference between two dial settings is approximately 0.5 mg.

ACKNOWLEDGMENT

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Analytical Problems in the Determination of Evans Blue

Caused by Absorption on Glass and Protein Surfaces

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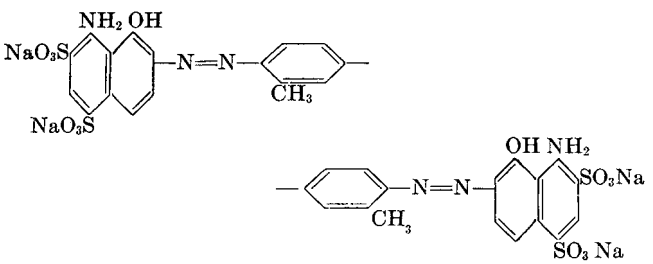
So many difficulties were encountered in adapting Evans Blue methods to the microliter scale that a systematic study of error was undertaken. The major problems were due to the tendency for this dye to be adsorbed on glass and protein surfaces. In protein-free solutions as much as 20 to 50% of the dye was adsorbed upon the wall of the cuvette. This percentage could be even higher under varying conditions of pH and salt concentration. In solutions containing protein, the dye was adsorbed upon protein surfaces. In all cases low spectrophotometric results were obtained. A variety of analytical problems were observed as a direct result of adsorption errors. These problems are described and discussed. High concentrations of Zephiran prevented the adsorption of Evans Blue on glass surfaces, removed it from protein, and thus eliminated these adsorption errors.

EVANS Blue, or Tolidine-1824, is a blue dye with the absorption curve shown in Figure 1 and the structural formula:



Its synthesis and purification have been described (*11*).

Because it is rapidly and tenaciously bound to plasma albumin, this dye is commonly used in physiology for the determination of plasma volume. In essence, this procedure involves injecting a known amount of Evans Blue into the blood stream, and, after a suitable mixing period, withdrawing a sample of blood, removing the red cells by centrifugation, and determining the Evans Blue concentration in the plasma. From a knowledge of the amount of dye injected and the final dye concentration in the plasma, it is possible to estimate the volume in which the dye is distributed—i.e., the plasma volume of the animal. The physiological factors involved have recently been reviewed (*16*).

Table I. Demonstration of Dye Adsorption by Elution of Adsorbed Dye from the Walls of a 1 × 1 Cm. Cuvette

Cell No.	Absorbance at 620 Mμ (5 γ Dye/Ml. H_2O)				Absorbance at 620 Mμ after Rinsing and Refilling Cuvettes with Water	
	5 min.	20 min.	30 min.	2 hours	5 min.	24 hours
2	0.366	0.350	0.342	0.341	0.005	0.023
3	0.356	0.351	0.338	0.337	0.008	0.011
4	0.362	0.357	0.353	0.352	0.006	0.012

EXPERIMENTAL

The dye used in this work was obtained from Eastman Kodak Co. and checked for purity by the method of Hartwell and Fieser (*11*). The spectrophotometric values were determined with a Beckman DU quartz spectrophotometer using either the standard 1 × 1 cm. macrocells with a 3-ml. liquid volume or 0.3 × 1 cm. microcells with a 150-μl. liquid volume.

ADSORPTION ON GLASS

The adsorption of Evans Blue on the walls of the 1 × 1 cm. quartz-faced cuvette and its slow elution with distilled water are demonstrated in Table I. Both the rates and absolute amounts of these absorbance changes are variable from cell to cell and were found to change from day to day within the same cell. The rate of adsorption is affected by small differences in the character and cleaning on the glass surfaces. Scratches or cracks may have a marked effect (*8*).

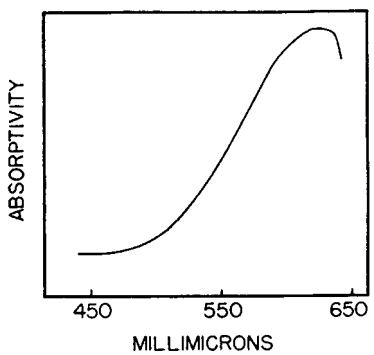


Figure 1. Evans Blue Absorption Curve

In Table II are shown the absorbance readings obtained when three different concentrations of dye were read in microcells and in macrocells. In all cases, there were substantial deviations from Beer's law, which became even larger with time. The column of expected results given in Table II are the values obtained when Zephiran was added to the dye solutions to prevent the adsorption of the dye onto glass and quartz surfaces. The reason for using Zephiran is discussed shortly. Using these expected values as a basis for comparison, errors of 2 to 20% were encountered within the first minute after the solution was placed in the cuvette. Over a period of 24 hours these adsorption errors became as large as 49%.

In the last four lines of Table II are given comparable data for volumetric flasks and Desicoted Erlenmeyer flasks. In these cases, larger concentrations of dye solution were allowed to stand in contact with the flask surfaces. At the specified times, aliquots were rapidly pipetted into Zephiran solution (to prevent further adsorption) and spectrophotometric readings were made at 620 mμ. The changes caused by adsorption were very small in all cases, indicating that only trivial adsorption errors are involved in the storage of high concentrations of dye. In the case of the Desicoted flasks, consistent increases were noted with time. The absorbance values continued to increase for a few days and then progressively decreased. The increase was apparently due to a turbidity set up in the solution as the Desicote film disintegrated and became suspended in the solution. As the Desicote left the glass surface, adsorption of the dye onto the glass progressed and the dye concentration decreased.

Adsorption errors were frequently greater in microcells than in macrocells and much greater in these cells than in flasks. In part, this is due to the higher dye concentrations in the flasks. In addition, however, the shape of the containers (surface area per unit of liquid volume) had a marked effect. The adsorption is dependent upon the surface area involved. When compared in

Table II. Direct Estimation of Extent of Dye Adsorption on Surfaces of Containers Commonly Used in Analytical Work

Container in Which Soln. Was Stored	Dye Concn., γ/Ml.		Absorbance at 620 Mμ			Expected Results	Difference betw. Obsvd. and Expected, %		
	Stored	Read	1 min.	30 min.	24 hr.		1 min.	30 min.	24 hr.
Microcell (quartz faced)	4	4	0.205	0.184	0.130	0.256	−20	−28	−49
	6	6	0.323	0.297	...	0.384	−16	−23	...
	8	8	0.482	0.472	0.428	0.512	−6	−8	−16
Macrocell (Corex glass)	4	4	0.205	0.184	0.173	0.256	−20	−28	−32
	6	6	0.348	0.326	0.301	0.384	−9	−15	−22
	8	8	0.500	0.460	0.433	0.512	−2	−10	−15
Volumetric flask (borosilicate glass)	12	6	0.386	0.373	0.375	0.384	+1	−3	−2
	100	6	0.382	0.386	0.384	0.384	−1	+1	0
Desicoted Erlenmeyer flask	12	6	0.381	0.384	0.407	0.384	−1	0	+6
	100	6	0.376	0.383	0.408	0.384	−2	0	+6

Table III. Effect of pH on Tendency for Evans Blue to Be Adsorbed and on Shape of Its Absorption Curve

Wave Lengths, Mμ	pH 2	4	6	7	8	10	12
	Absorption						
480	0.057	0.055	0.057	0.056	0.054	0.061	0.110
540	0.191	0.186	0.188	0.182	0.179	0.190	0.254
620	0.385	0.377	0.394	0.381	0.375	0.346	0.143
	24 Hours Later						
480	0.025	0.039	0.047	0.053	0.051	0.054	0.107
540	0.090	0.141	0.161	0.173	0.174	0.180	0.248
620	0.180	0.292	0.340	0.356	0.361	0.354	0.153

terms of square centimeters of glass surface per milliliters of liquid, ratios of 10 to 5 to 3 are found for microcells, macrocells, and flasks, respectively. Thus, each unit of liquid in a microcell is exposed to twice as much glass surface as if it were in a macrocell and three times as much as if it were in a flask. In all containers the adsorption is similar when expressed in terms of dye adsorption per unit of glass surface. In this basis, the average adsorption in Table II amounted to 0.06γ of Evans Blue per sq. cm. of glass surface at 1 minute and 0.16γ of Evans Blue per sq. cm. of glass surface at 24 hours.

In Table III is seen the effect of pH upon the tendency of Evans Blue to be adsorbed on the glass surface. The more acidic the solution, the greater is the adsorption on glass. At a pH of 8 there is a substantial reduction in the tendency for the dye to be adsorbed on glass, but little change in the extent of its binding to plasma protein (Table IV). At pH's more alkaline than pH 8 the shape of the absorption curve of this dye changed and the absorption maximum moves progressively toward shorter wave lengths as the pH increases. From the point of view of this analytical procedure such a shift would be undesirable. Greater difficulty would be encountered in correcting the values for the presence of hemoglobin and the exact shape of the curve would be dependent upon pH.

Table IV. Effect of Diluent on the Discrepancy between Protein-Containing and Protein-Free Dye Solutions

Dye Soln. Containing	Concn., γ Dye/Ml.	Diluent: Saline (0.9%)	Buffer (pH 8)	Zephiran (12%)
Plasma	4	0.219	0.221	0.266
	6	0.322	0.332	0.377
	8	0.426	0.438	0.507
5% serum albumin	4	0.237	0.232	0.255
	8	0.458	0.465	0.525
10% serum albumin	4	0.239	0.236	0.263
	8	0.484	0.479	0.509
Distilled water (protein-free)	4	0.218	0.262	0.266
	6	0.340	0.391	0.395
	8	0.465	0.508	0.493

ADSORPTION ON PROTEIN

The absorptivity of Evans Blue is lower in plasma or protein-containing solutions because of the adsorption of this dye upon the surface of protein particles. The absorptivity varies from one plasma sample to the next, is not directly proportional to protein level (Table IV), and is reported to vary with dilution (*2*). Any procedure which would eliminate these problems would give this method wider applicability.

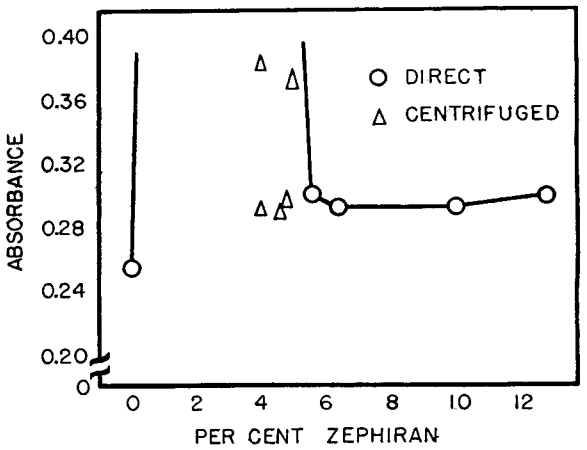


Figure 2. Effect of Adding Various Concentrations of Zephiran to a Dyed Plasma Solution

At concentrations below 6%, turbidity prevented useful readings; attempts to remove this turbidity by centrifugation were not consistently successful

The authors have found that high concentrations of a cationic detergent will remove the dye from its protein binding and hold it in true solution. Zephiran, an alkyldimethylbenzylammonium chloride (available in 12.8% aqueous solution from Winthrop-Stearns Co., New York 13, N. Y.) is very satisfactory for this purpose. In the presence of Zephiran, protein-free Evans Blue solutions obey Beer's law and give absorbance readings which are constant with time, and there is no difference in absorptivity between aqueous standards and dyed plasmas. This eliminates the problem of variable absorptivity normally encountered in work with protein-containing solutions and allows dyed plasma to be compared directly with protein-free dye standards.

It is necessary to use high concentrations of Zephiran because of its effect upon protein. The addition of low concentrations of Zephiran to dyed plasma samples resulted in a marked turbidity attributable to the precipitation of protein. This may account for a previous failure (*6*) to obtain a useful result with cationic detergents. As seen in Figure 2, this turbidity can be eliminated by the addition of higher concentrations of Zephiran. It is also to be noted in Figure 2 that the absorbance at 620 mμ was greater after adding Zephiran than it was in the absence of Zephiran, indicating that the Zephiran had broken the dye-protein binding and had brought the dye into true solution.

In Table IV is seen a direct comparison of results obtained when saline, pH 8 buffer, or Zephiran was used to dilute aqueous dye standards and dyed protein solutions. In saline solution all of the values are low because of adsorption errors. When pH 8 phosphate buffer was used as the diluent, the samples containing plasma and serum protein gave low results, but the standard solutions of dye in water gave higher results which obeyed Beer's law

fairly well. With Zephiran as a diluent all of the values agreed with the predicted values within the manipulative variation of this procedure.

In preparing all of the solutions in Table IV it was necessary at some point in the procedure to pipet and work with Evans Blue standards made up in distilled water. The larger reading variations observed with the saline solutions were associated with a difficulty in repeating spectrophotometric readings on rapidly changing solutions. When all manipulations were carried out in Zephiran-containing solution, duplicate dilutions prepared and read on different days agreed within $\sigma = 0.003$ absorbance, or 0.7% relative error, and all values showed excellent agreement with Beer's law.

DISCUSSION

Many of the problems and anomalies in the Evans Blue literature (*1, 2, 7–10, 18*) may be the direct result of a failure to appreciate the analytical significance of these adsorption effects. This may not be surprising, for in most other cases in analytical chemistry (*4, 12–14, 17*) adsorption errors have proved to be negligibly small.

Gregersen *et al.* report that Evans Blue is unstable in physiological saline solution (*9, 10*) and that its absorbance decreases progressively with increasing salt concentrations (*8*). Allen (*1*) criticizes Morris' (*15*) method on the basis that Evans Blue is unstable in acid solutions. The present work also confirms that lower results are obtained in solutions containing salt (Table IV) and acid (Table III). Recovery experiments have demonstrated, however, that these effects are due to increased adsorption rather than to a destruction of the dye.

Contrary to the views expressed by Ayres (*3*), the fact that a standard curve does not obey Beer's law indicates that there is an uncontrolled and usually an unknown factor operating in the analytical system which may be a source of analytical error. This factor may be chemical, physical, or instrumental (*5*). In the present case this deviation from Beer's law was one of the most marked and easily measured indicators of this adsorption effect.

Vierheller (*18*) reported the dependence of absorption values upon the shape of the spectrophotometer cell. It seems possible that these results are analogous to those in Table II and are explainable in the same fashion. Errors of 30 to 40% were occasionally observed by Gregersen (*7*) in his work with a visual color comparator. If one compares dyed plasma with a protein-free dye solution in a Duboscq-type colorimeter, adsorption effects might conceivably account for errors of this size because of the relatively large glass surface involved. Allen and Gregersen (*2*) report that when dyed plasma is diluted the absorptivity of the dye changes. Wherever deviations from Beer's law are observed in Evans Blue work, adsorption effects should be studied for the possible cause.

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Microscopic Identification of Wustite

In Presence of Other Oxides of Iron

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In the microscopic examination of partly reduced iron ores, wustite is often overlooked because of its resemblance to magnetite. Microscopic methods of identifying wustite, hematite, and magnetite are described. An etch solution of saturated alcoholic stannous chloride will attack wustite in 1 or 2 minutes, but it does not affect the other oxides. Wustite is easily scratched with a steel needle, but magnetite is scratched with difficulty or not at all. Wustite has a Knoop hardness of 155; magnetite, 361. Powdered wustite is black, isotropic, and nonmagnetic. Powdered magnetite is black, isotropic, and magnetic. Hematite has a greater reflectivity than the other oxides; it is anisotropic, and forms a red nonmagnetic powder when scratched. The described techniques used with reflected-light microscopy of partly reduced iron ores offer simple and accurate means of determining the types and amounts of the oxides present.

IN STUDYING the reducibility of iron ores, it is desirable to know which of the three forms of iron oxide—wustite (FeO), hematite (Fe_2O_3), and magnetite (Fe_3O_4)—are present in partly reduced ore or sinter. Chemical analysis will show whether the iron is ferrous or ferric, but will not reveal which of the oxide phases are present. X-ray diffraction analysis will show the major constituents present, but will not detect oxide phases below certain concentration thresholds. Microscopic methods are the easiest, cheapest, and quickest; with these methods, it is possible not only to identify the oxide phases but also to determine the quantity and distribution of each phase in a given specimen.

However, in a microscopic examination of partly reduced iron ores or sinters, wustite is often overlooked because of its resemblance to magnetite. Methods by which wustite can be distinguished from magnetite microscopically are described in the present paper.

Table I. Iron Oxides Identified in Reduced Iron Ores

Stage of Examination	Phases Identified: By x-ray methods	Phases Identified: By microscopic methods
	Group 13 Ore	
As received	Fe_2O_3, $Fe_2O_3.H_2O$	Fe_2O_3, $Fe_2O_3.H_2O$
0.5-minute treatment[a]	Fe_2O_3, Fe_3O_4	Fe_2O_3, Fe_3O_4
5-minute treatment[a]	Fe_3O_4, FeO, Fe_2O_3	Fe_3O_4, FeO, Fe_2O_3
10-minute treatment[a]	Fe, FeO	Fe, FeO, Fe_2O_4
After 15-minute treatment[a]	Fe	Fe, FeO
	Fontana Ore	
As received	Fe_2O_3	Fe_2O_3, Fe_3O_4
5-minute treatment[b]	FeO, Fe_3O_4	FeO, Fe_3O_4, Fe_2O_3
10-minute treatment[b]	FeO, Fe_2O_3, Fe_3O_4, Fe	FeO, Fe_2O_3, Fe_3O_4, Fe
15-minute treatment[b]	Fe	Fe, FeO
7-hour treatment[b]	Fe	Fe, FeO

[a] Heated at 800° C. in hydrogen for specified time, then water quenched.
[b] Heated at 800° C. in hydrogen for specified time, then furnace-cooled in nitrogen.

EXPERIMENTAL

Specimens of Group 13 iron ore (a hematite ore) were heated in hydrogen at 800° C. (1475° F.) for 0.5, 5, 10, and 15 minutes. At the end of each period, a specimen was removed from the furnace and quenched in water. Each of these partly reduced specimens, as well as an unheated ore specimen, was cut in half. Half of each specimen was pulverized so as to pass a 100-mesh screen and was analyzed by x-ray diffraction; the other half was mounted in Bakelite and polished for microscopic examination under reflected light.

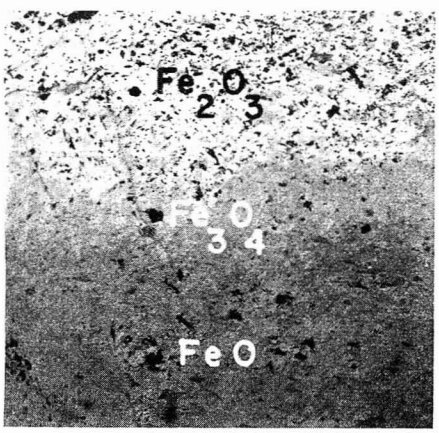

Figure 1. Ore Specimen (Originally Fe_2O_3) after Heating for 10 Minutes in Hydrogen at 800° C. Followed by Quenching in Water

Area illustrated shows all three forms of iron oxide in the unetched condition. Original magnification ×125, reduced 3/4 in reproduction

Specimens of Fontana ore (an ore containing both hematite and magnetite) were treated in the same manner as the Group 13 ore specimens, except that the heating times were 5, 10, and 15 minutes, and 7 hours. The specimens heated for 5 and for 10 minutes were quenched in water; those heated for 15 minutes and for 7 hours were cooled in a nitrogen atmosphere in the furnace.

ETCH METHODS

The properties ordinarily used in identifying iron-ore constituents by reflected-light microscopy are reflectivity, form anisotropy, reaction to etchants, hardness, and magnetism. However, the reflectivity, form, and anisotropy of wustite are so nearly identical with the corresponding properties of magnetite that they cannot be used in differentiating the two phases. Consequently, reaction to etchants, hardness, and magnetism were the properties employed in distinguishing between wustite and magnetite.

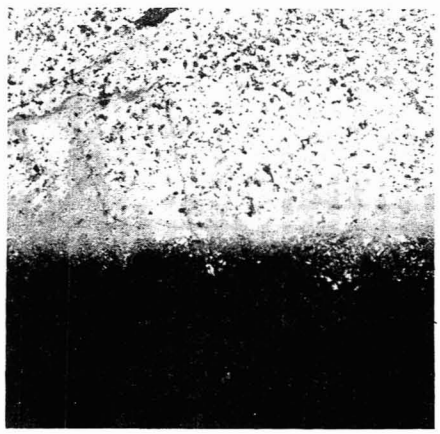

Figure 2. Same Ore Specimen after Etching in Saturated Alcoholic Stannous Chloride for 1 Minute

FeO is well etched but Fe_3O_4 and Fe_2O_3 are unaffected. Original magnification ×125, reduced 3/4 in reproduction

Several etchants were tried, but the one that gave the best results was ethyl alcohol saturated with stannous chloride. Cooke (*2*) suggests a mixture of stannous chloride in hydrochloric acid to distinguish wustite from magnetite. It is believed, however, that alcoholic stannous chloride is preferable because the reaction is slower and more easily controlled. This etchant cannot be stored; it must be mixed fresh for each use. The etching operation was usually carried out by placing a drop of the etchant upon a selected area of the specimen by means of a small wire loop made of platinum. The length of time that the etchant should remain upon the specimen was determined experimentally and depended upon the severity of etch desired. After being etched, the surface of the specimen was wiped with a dry lens tissue. With the alcoholic stannous chloride etchant, 1 to 2 minutes seemed to be optimum for etching wustite; magnetite was not affected by as much as 5 minutes in the etchant (Figures 1 and 2).

HARDNESS METHODS

The hardness of magnetite is given by (*3*) as $5\frac{1}{2}$ to $6\frac{1}{2}$ on the Mohs scale of hardness. No information could be found concerning the hardness of wustite. However, experience in preparing metallographic specimens containing wustite inclusions has indicated that the hardness of wustite is less than that reported for magnetite. To test this observation, a steel needle was drawn under moderate pressure across a field containing both wustite and magnetite. The surface of the magnetite was not scratched, only slightly marked. The wustite, however, was scratched readily (Figure 3). To obtain quantitative evidence of the difference in hardness between the two phases, a series of Knoop diamond indentations, 100-gram load, was made across a field containing both wustite and magnetite (Figures 4 and 5). The procedure was repeated on a number of different fields each containing both wustite and magnetite. Wustite had an average Knoop hardness of 155; magnetite an average hardness of 361.

MAGNETIC METHODS

Under certain conditions, the magnetic property of magnetite may be used in distinguishing it from the other two oxides. When the point of a magnetized needle is pushed along the surface of ore specimens, a powder is formed. Hematite powder is red and nonmagnetic. Magnetite powder is black and clings to the point of the needle. Wustite powder is also black but nonmagnetic. Often, however, the magnetite is intermingled with

the other oxides to such an extent that this method is not applicable; identification made with other methods should then be confirmed by using the etching techniques.

EFFECT OF VARIABLE OXYGEN CONTENT ON REFLECTIVITY

Hematite can usually be identified by its relatively great reflectivity; in partly reduced ores, metallic iron is the only commonly encountered phase that has a reflectivity greater than that

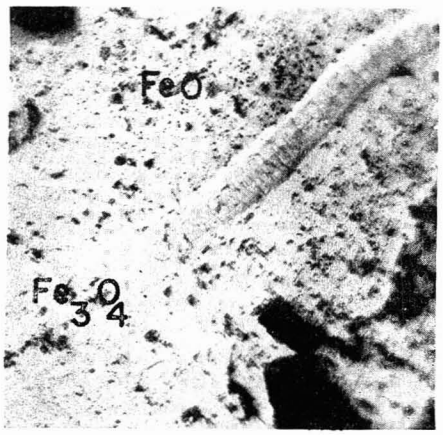

Figure 3. Same Ore Specimen after Scratching

Scratch produced by drawing sharp-pointed steel needle across unetched specimen at the FeO-Fe_3O_4 interface. Shows difference in hardness of the two phases. Original magnification ×500, reduced 3/4 in reproduction

of hematite. The reflectivity of magnetite is usually less than that of hematite. However, it is possible for magnetite to contain oxygen in excess of its stoichiometrical composition, which results in a proportionate increase in reflectivity. Such an excess of oxygen is most likely to occur in ores that have been wholly or partly fused and rapidly cooled; all or part of the excess oxygen in the magnetite is retained in solution during fast cooling and makes the reflectivity of the magnetite similar to that of hematite.

A close examination of rapidly-cooled ore will usually show hematite arranged in a Widmanstatten pattern within the magnetite grains. If the fused ore has been slowly cooled, hematite will be prevalent, and the reflectivity of the magnetite will be less than that of the hematite. Wustite usually has slightly less reflectivity than does magnetite; however, the difference cannot always be detected by eye. In polarized light, hematite exhibits anisotropy, but magnetite and wustite are isotropic.

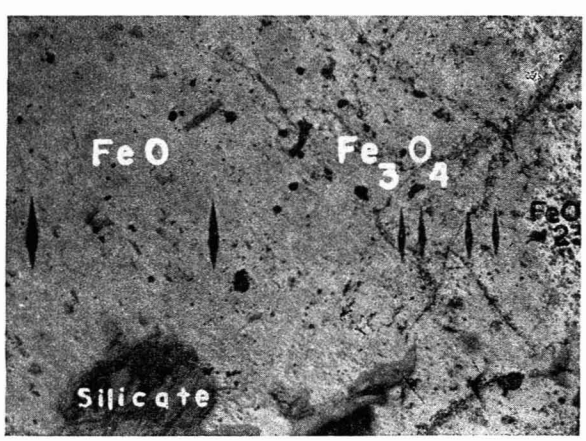

Figure 4. Same Ore Specimen with Diamond Hardness Indentations

Indentations made across FeO and Fe_3O_4 areas. Original magnification ×125, reduced 3/4 in reproduction

After the phases have been identified, their concentrations may be determined by the point-count method (*1*).

COMPARISON OF MICROSCOPIC AND X-RAY METHODS

The use of x-ray diffraction techniques for identifying iron oxide phases is limited because each phase has a concentration threshold below which it cannot be detected by x-ray methods. Furthermore, silicate phases in the ore gangue may mask small concentrations of iron oxide when x-ray methods are used.

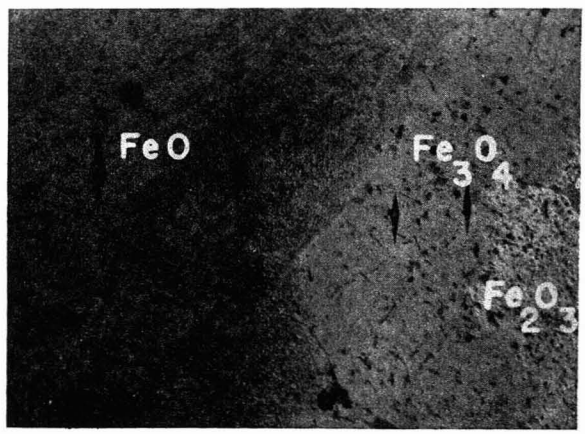

Figure 5. Same Ore Specimen after Light Etching with Saturated Solution of Alcoholic Stannous Chloride

Light etching accentuates FeO area. Original magnification ×125, reduced 3/4 in reproduction

In this laboratory, reducibility studies on iron ores have shown that some iron oxide remains even after 7 hours of reduction in hydrogen at 800° C. Microscopic examinations, Table I, confirmed this finding, although x-ray analysis did not show the presence of iron oxide after only 15 minutes of hydrogen reduction at 800° C.

Occasionally, when the grain size of the phases is extremely small and the phases are intermingled, microscopic methods may not be adequate and x-ray analysis or chemical analysis must be used. Usually, microscopic methods will provide the desired information.

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Determination of Calcium and Magnesium in Lake Waters—Correction

In the article on "Determination of Calcium and Magnesium in Lake Waters" [ANAL. CHEM., **26**, 347 (1954)] the formula at the bottom of Table I, page 348, should read:

$$\%s = \frac{100}{\bar{c}} \sqrt{\frac{\sum_{1}^{4} (\bar{c} - c)^2}{n - 1}}$$

V. W. MELOCHE

Some Aspects of Microscopy in Cellulose Research

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The gross and fine morphology of native cellulose fibers has been studied microscopically in a wide variety of physical and chemical environments. Recent technical developments in image formation and in methods of fiber dissection point to the filling of several gaps in existing knowledge. Heretofore, microscopy of the fiber has been limited to staining and swelling methods, together with the use of polarized light. Such examinations, including observations of birefringence, have contributed much to the present understanding of cellulose morphology, but the picture is still incomplete. Phase contrast microscopy, which can eliminate the necessity for staining, has not yet been fully explored, and infrared and ultraviolet microscopy have scarcely been applied at all to cellulose studies. Such methods, aimed at overcoming lack of contrast and of resolution, the main shortcomings of optical microscopy, deserve careful evaluation. The necessity of preparing suitably thin specimens for electron microscopy has led to useful advances in manipulative and microscopical techniques. The development of methods for isolation of individual components of the cell wall for purposes of electron microscopy has permitted interesting observations with the light microscope. Quantitative measurements of shrinkage in the isolated primary wall of the cotton fiber confirm its restrictive influence on fiber swelling. The location and orientation of the cellulosic "winding layer" is thought to account for its nonreactivity in certain substitution reactions.

THE ordinary microscope, despite its well-known limitations attributable to the finite wave length of light, has been responsible for providing most of the present knowledge of fiber morphology. Although useful magnifications are limited to about 1500 and the size of the smallest particle that can adequately be resolved is about 0.2 micron, the microscope has been effectively used for the study of both gross and fine features of fiber organization in its natural state and after a wide variety of physical and chemical treatments.

Newer instruments now available are capable of revealing much more about fiber structure, but the light microscope is indispensable in making these newer techniques useful. In spite of the great magnifications possible with the electron microscope, scientists are confronted with almost insurmountable difficulties because of the absorption of electrons by cellulose. Only with extremely thin sections is it possible to obtain images of fine detail and the procurement and handling of such thin fragments of whole fibers tax the ingenuity of the laboratory technician while the interpretation of structural relationships in torn specimens is inevitably open to question. The problem is to reduce the natural cellulose fiber to a condition suitable to meet the limitations of the electron microscope without destroying the natural architectural pattern; in attempts to solve this problem the light microscope is beginning to be used as an accessory tool to aid in dissection of investigating the microchemistry of raw materials.

This rebirth of light microscopy in cellulose research is the subject of the present discussion, which includes various adaptations such as polarized light and phase microscopy, the possibilities of infrared and ultraviolet light in microscopical investigations of cellulose fibers, and such advances in instrumentation and manipulative techniques as are tied in with the essential contribution of light microscopy as the handmaiden of the electron microscope.

POLARIZED LIGHT

Light microscopy of vegetable fibers has been limited for the most part to studies of microtome sections and to conventional staining and swelling techniques. With the polarizing microscope additional information may be gained from optical properties which are entirely independent of any morphological features but are indicative of internal molecular structure. Refractive index, degree of birefringence, and angle of crystallite orientation are all fiber characteristics which require polarized light for observation. Cellulose crystallites are doubly refractive; this property leads to the production of color effects in cellulose specimens when observed in polarized light, depending on the retardation and interference of light by the crystallites within the specimen. By use of selective retardation in the form of a selenite plate in the optical path, these colors may be changed and intensified to give increased contrast in the color effects (*40*).

Refractive index of a textile fiber is determined microscopically in polarized light by the Becke immersion method. The difference between the refractive index along the fiber axis and that across it is known as birefringence; in natural cellulose fibers birefringence is positive, indicating that the greater refractive index lies in the direction of the fiber axis and the lesser index in the lateral direction.

According to Hermans (*24*) the optical properties of cellulose fibers are due to superposition of the optical effects of the elementary structural glucose units in the cellulose molecular chains. When the longitudinal axes of all chain molecules or crystalline regions in the fiber are parallel to the fiber axis, the fiber would have maximum orientation and would exhibit maximum birefringence in polarized light. Under this concept, the state of orientation in a fiber can be described by comparing its measured birefringence with that of an ideal fiber of perfect orientation and of the same density. There are some native cellulose fibers whose orientation is almost ideal: typical examples are flax and ramie, in which the cellulose molecules are arranged almost entirely parallel to the fiber axis. For practical purposes, therefore, it is sufficient to compare the refractive indices of an unknown fiber with those of one of these highly oriented fibers to determine an approximate orientation figure. The results may be expressed as a ratio of the measured birefringence of the unknown to that of the chosen standard, but it is more instructive to convert the results into a figure for the average angle of inclination to the fiber axis, by substituting the measured refractive index values in the formula for an ellipse (*39*). The angle of orientation for cotton, in which certain structural elements are known to have a spiral arrangement, has been found to be approximately 30 degrees to the fiber axis.

These measurements which serve to indicate the arrangement of the longitudinal axes of monomeric residues offer means for comparing the orientation of any location along an individual fiber and of different fibers in a sample. Birefringence measurements can be conveniently used to follow changes of orientation which accompany chemical or mechanical treatments of cellulose fibers. The significance of such observations in research is illustrated by the fact that both major and minor refractive indices of mercerized fibers are lower than those of the corresponding indices of the unmercerized control; the birefringence of

regenerated cellulose fibers is nearer that of mercerized cellulose than to that of native cellulose. In regenerated cellulose fibers birefringence increases as the fiber becomes progressively better oriented during extension (*38*) in both drawing and testing, so that microscopical measurements of fiber birefringence furnish clues as to the extensibility and, correspondingly, the strength of the fiber.

In laboratory practice, birefringence is also used as a clue to thickness of specimen. In samples which are known to be of the same substance and to have the same orientation, brilliance of birefringence is taken as indicative of thickness, thinner specimens being less bright. Conversely, in specimens of the same known thickness, brilliance of birefringence is interpreted as indicative of degree of orientation.

ULTRAVIOLET MICROSCOPY

In ultraviolet microscopy the shorter wave lengths of the incident radiation allow approximately twice the resolving power that can be obtained with visible light but the equipment is relatively expensive, for since glass is opaque to ultraviolet wave lengths the optics of both microscope and illuminating unit must be of high grade quartz, as must also the microscope slides and coverslips. Sources of radiation are high pressure mercury arc lamps or cadmium arcs. Only a few of the solutions used for mounting media are transparent to ultraviolet light, so that choice of mountant is restricted to sandalwood oil or to specially purified synthetic oils.

The poor transmission of glass objectives has been partially overcome by achromatic objectives in which quartz and fluorite have been combined and corrected for spherical and chromatic aberration over the region 2650 to 2750 A. (*21*). A further step in making ultraviolet light feasible as a microscopic research tool is the reflecting microscope, in which the usual difficulties of refracting lenses are obviated by aluminum reflecting surfaces in a two-mirror objective (*11*, *14*, *15*). A recent application of this reflecting-type objective is the color translating ultraviolet microscope originally developed by Brumberg (*13*) and now being perfected by Land and others at the Polaroid Corp. (*29*). At present the technique consists of taking photographs at three different wave lengths in the ultraviolet. The negatives are then reproduced on color film through three visual color filters. Though the colors of the resulting image are purely arbitrary, they serve to demonstrate, conveniently and vividly, differences in ultraviolet transmission of different parts of the specimen. The fact that various biochemicals demonstrate marked selective absorption at various wave lengths throughout the ultraviolet has been used very successfully in the examination of fresh biological material (*17*, *30*), particularly in the study of subtle changes in the balance of certain biochemicals within the living cell linked with specific conditions of disease.

In the field of cellulose, however, the ultraviolet microscope still has not been used either as a microscopic or a spectroscopic tool. The absorption curve for cellulose is practically constant throughout, both the visible and the near ultraviolet regions of the spectrum to the far ultraviolet (*19*) turning upward sharply at 2700 A. until at about 2200 A. absorption of the radiation by cellulose is roughly five times what it was at 2700 A. It might be possible to get useful differential absorption in the wave lengths below 2500 A. but the difficulty is to find sources of radiation which produce those shorter wave lengths in sufficient intensity and microscopic equipment which can utilize this type of illumination.

Some information could doubtless be obtained with ultraviolet light by use of fluorescent dyes on the fiber in much the same way that biological stains are used in visible light, but it is hardly likely that selective absorption of the cellulose for these substances would offer any new advantages worth the trouble and expense of using ultraviolet light. No investigations have been reported of the impregnation of the cellulose fiber with barium salts or other materials opaque to shorter wave lengths.

INFRARED MICROSCOPY

Microscopical investigations with infrared light have been made possible by the adaptation of the electronic converter tube used in World War II Snooperscope and Sniperscope devices (*5*, *32*). Some natural reddish materials and red-stained specimens reveal considerable detail with infrared microscopy (*48*). Thicker sections may be used than with visual rays and the implication is that such a device would be useful in the study of heavily discolored sections of lignified woody tissues or of very heavily dyed dark-colored textile fibers. Too little infrared microscopy has been done to permit critical evaluation, but cellulose exhibits such high transmission in that region of the spectrum (with the first group of absorption bands appearing at about 30,000 A, *18*) that the infrared technique offers little advantage except through differential absorption of such infrared-opaque dyes as Naphthol green. The use of reflecting microscope objectives in infrared work has permitted some microscopic spectroscopy, but this has not been applied to cellulose.

OTHER SPECIAL TECHNIQUES

Interference methods can also be used in microscopy for the measurement of surface irregularities and inhomogeneities in transparent materials, but according to Merton (*33*) the method is limited to specimens a few microns thick. No specific measurements on cellulose have been reported.

Spectrographic attachments are available for the microscope and both absorption spectra and fluorescence may be determined with such devices. Their application to cellulosic materials probably will depend on selective absorption of some ultraviolet-sensitive substances by the cellulose; no specific work of this sort has been reported.

PHASE MICROSCOPY

None of the special adaptations of microscopy mentioned so far have been exploited in the study of cellulose and few have ever been adequately explored.

The phase microscope, on the other hand, seems to have peculiar adaptation to the study of specimens too transparent to be seen in bright field microscopy. A diffraction plate or coating added within the objective and an annular diaphragm below the condenser of the bright field microscope have the purpose of converting slight and invisible alterations of light passing through the specimen into visible differences in image intensity which may be seen and photographed (*12*). As pointed out by Barer (*10*), the use of polarized light with the phase microscope increases the contrast obtainable in many cases.

In the field of cellulose the phase microscope has found its greatest usefulness in the examination of rayon fibers (*44*). In cross sections of viscose rayon the skin effect can be seen readily without any staining and the distribution of solid pigment particles or of gas bubbles or foreign inclusions in the body of the fiber can be studied and recorded easily.

In the case of cotton it has been found that isolated cell wall fragments can be examined without any mounting medium, thus making it possible to observe specimens in the same desiccated condition in which they are photographed in the electron microscope, for better correlation between observations made with the two different instruments.

EXPERIMENTAL RESULTS WITH COTTON FIBERS

Microscopical approaches have been variously applied in fundamental investigations of cellulose fibers for approximately a century. The extensive work on the cotton fiber in the first quarter of the 20th Century by Balls (*6*, *7*) served to stimulate

the contributions of Anderson (*4*), Kerr (*27, 28*), Hock (*26*), Mangenot (*31*), and many others, so that by 1950 the generally accepted concept of cotton fiber morphology as summarized by Flint (*30*) was supported by considerable evidence from many independent investigators. Tripp's (*47*) schematic diagram of fiber architecture represents the cell wall as a lamellate structure composed of outer membrane or primary wall, winding layer, secondary wall, and lumen or central canal. From electron microscope studies the primary wall and cuticle have been estimated to be about 0.1 micron in thickness and the winding layer of the secondary wall not more than about 0.2 micron. The main body of the secondary wall is probably between 4 and 5 microns in thickness and is composed of many layers whose thickness varies with many factors of growth. Each layer is believed to be made up of microfibrils of cellulose branching and rebranching, but roughly parallel and arranged in a more or less spiral fashion about the main axis of the fiber. In the first layer of secondary thickening (the winding layer) the spirals are much coarser and spiral in a direction opposite to those of all the various layers of the main body of the secondary wall. At the center is the collapsed tubular central canal containing the remains of cell protoplasm.

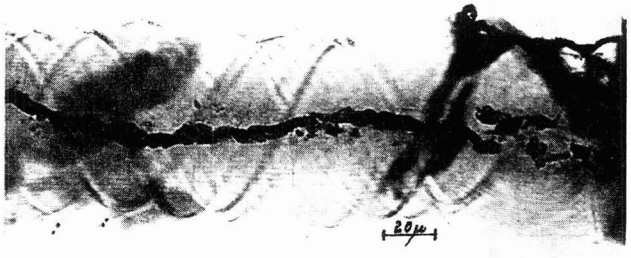


Figure 1. Cotton Fiber Stained with Nile Blue Sulfate and Swelled with Cupriethylenediamine Hydroxide

In general, this picture of the layered morphology of the cotton fiber cell wall is confirmed for various other types of plant cell walls by the observations of Van Iterson (*49*), Aldaba (*1*), Bailey (*8, 9*), Anderson (*3*), Ritter (*41*), Rollins (*42*), and others.

None of these features is visible in raw, unswollen fibers, even under high magnifications. Swelling in such agents as 70% sulfuric acid or the cupritetrammine bases is necessary to reveal structural details in native fibers; the pattern which can be observed in the swelling of chemically modified cottons in appropriate solvents is very similar. Because of its pectic content the primary wall may be stained with an aqueous solution of ruthenium red, methylene blue, or Nile blue sulfate, the basic dyestuffs reacting with the carboxyl groups present; they also stain the proteinaceous lumen contents for the same reason (*35*). The wax complexes of the cuticle can be colored with such fat stains as Sudan black and oil red but satisfactory intensity is achieved only after the fibers have been treated briefly with boiling ethyl alcohol (*35, 47*). By such conventional swelling and staining techniques the gross morphology of the fiber can be demonstrated in longitudinal view, as in Figure 1, which shows a mature cotton fiber, swelled with cupriethylenediamine hydroxide to show the various fiber components. The primary wall, stained with Nile blue sulfate, can be seen disappearing at the outside edge of the fiber in the form of ruptured fragments, and the winding layer with flecks of primary wall clinging to it, wraps around the fiber. Within the winding layer may be seen some of the

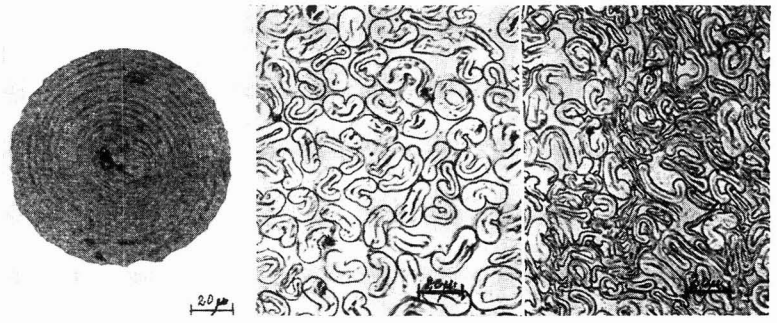


Figure 2. Cross Sections of Cotton Fibers

A. **Single fiber swollen to show growth layers**
B. **Bundle of mature fibers**
C. **Bundle of immature fibers**

layers of the secondary wall, and at the center the dark-stained lumen and protoplasmic residue.

In the greatly swollen cross section at the left in Figure 2 the growth layers can be plainly seen, while at the right are illustrated collapsed cross sections of dried fibers. The full-bodied mature fibers, at the center, which received their full complement of cellulose during growth, are contrasted with the collapsed sections of the undernourished, immature fibers at the right.

One of the simplest laboratory tests for this cell wall maturity is the ASTM method (*2*) using polarized light, in which the criterion of cell wall thickness is the amount of retardation of the light upon passing through the fiber. This test is illustrated in Figure 3 in which the lower fiber is mature and thick-walled, the upper, thin-walled and immature. When placed in the proper position in the field of a microscope equipped with crossed Nicols and a first-order red selenite plate, the brilliantly birefringent thick-walled fiber transmits a green or yellow color and the thin-walled fiber a purple or deep blue color. The picture also illustrates an interesting phenomenon of crystallite orientation in cotton fibers. Although the microfibrils in cotton lie roughly parallel to the main axis of the fiber, they spiral around the axis in a helical manner. The direction of the helix reverses many times along the length of the fiber and when the fiber is observed under the microscope in polarized light these points of fibril reversal appear as dark extinction bands in the brilliantly birefringent fiber. Wakeham (*50*) has concluded from statistical considerations of the frequency of rupture at reversal points during tensile breaks that these are probably areas where the fiber is more brittle, and therefore more crystalline, than along the main body of the fiber.

STUDIES OF THE PRIMARY WALL

A technique which has improved the usefulness of light microscopy in investigations of fiber morphology is based on the isolation of fiber parts by beating (*35, 47*). It has been found (Figure 4) that when cotton fibers are beaten very briefly in water in a Waring Blendor fairly large sheets of primary wall will float off,

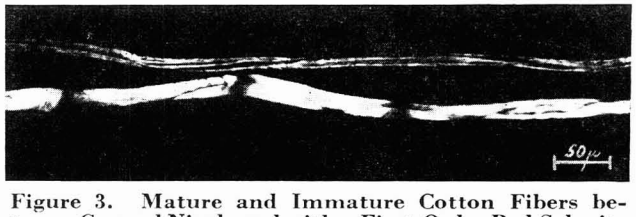


Figure 3. Mature and Immature Cotton Fibers between Crossed Nicols and with a First-Order Red Selenite Plate

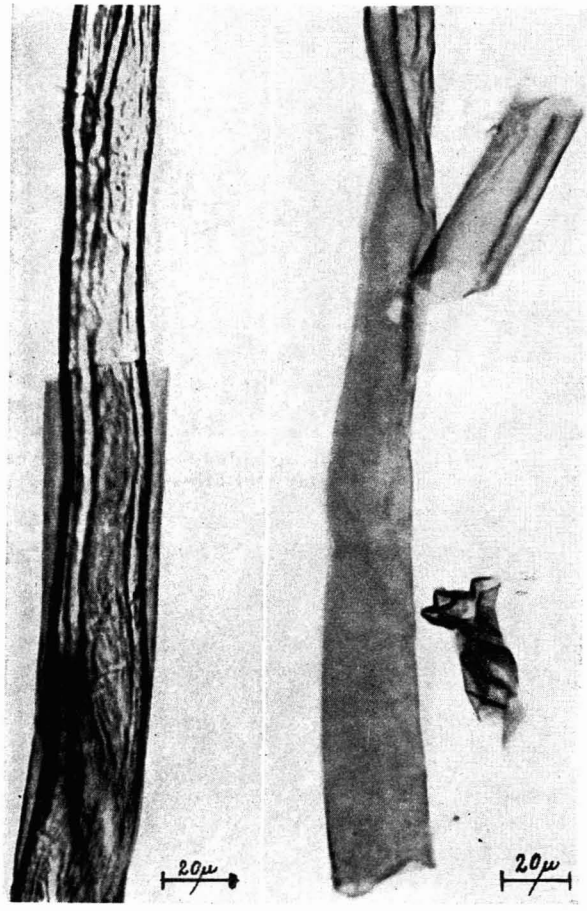


Figure 4. Primary Wall Freed from Cotton Fiber by Beating in Water

usually in the form of sleeves which when released from the fiber expand to a width much greater than that of the fiber itself, probably returning to the size and shape of the primary wall in the growing state. By careful manipulation these fragments can be collected in milligram quantities for further study. Under the microscope the typical staining reactions and characteristically faint birefringence aid in determining that the primary wall samples are free from contamination with other portions of cell wall. By chemical analyses reliable estimates have been obtained for the first time of the constituents of the cotton fiber primary wall (Table I). The interpretation of the nitrogen content as protein has been confirmed by paper chromatograms which showed various amino acids in the hydrolyzate; similar chromatographic techniques permitted identification of the pentose sugars xylose and arabinose, in addition to glucose and galactose, two hexoses normally expected in cellulosic materials.

In the electron microscope these raw primary wall specimens showed little or no structure (Figure 5*A*) but after extraction with 2% sodium hydroxide had the random arrangement of microfibrils (Figure 5*B*), shown by Mühlethaler (*36*) to be typical of primary walls in vegetable fibers. Samples of such purified cellulose, obtained by prolonged digestion of isolated primary wall in ethanolamine, have proved to be remarkably resistant to hydrolysis. Electron micrographs of sheets of this material after 300 hours in 6*N* hydrochloric acid at room temperature showed no discernible difference in appearance of fibrils from those of freshly extracted material; and after 6 hours in 6*N* hydrochloric acid at 100° C. the sleeve though weakened still maintained its morphological integrity. Figure 6 shows light microscope pictures illustrating the shrinkage of a purified primary wall sleeve in the process of alkali treatment equivalent to mercerization. On the left the primary wall specimen is in water; on the right the identical fragment is in 18% sodium hydroxide. Table II shows actual measurements of such specimens as these. The results are the means of 30 measurements of ribbon width. In purified primary wall material extracted free of noncellulosic substances, the shrinkage is approximately 40% in the lengthwise direction and nearly 60% in the crosswise direction; in raw, untreated primary wall the shrinkage in lengthwise direction is only 3% while that of the crosswise direction is 10 times as great. These measurements would imply a directional pattern of encrustation favoring transverse shrinkage.

Table I. Chemical Composition of Cotton Fiber and Primary Wall (*47*)

Constituent	Per Cent of Dry Weight	
	Entire fiber (*22*)	Primary wall
Cellulose	95.3	52
Protein (N × 6.25)	1.0	12
Pectic substances	1.0	12
Wax	0.8	7
Ash	0.9	3
Cutin (?)	..	3
Other (organic acids, sugars)	1.0	11

Table II. Dimensional Changes of Short Lengths of Primary Wall and Whole Fiber upon Transfer from Water to 18% Sodium Hydroxide

Condition	Change, %	
	Length	Width
Primary wall		
No treatment (control)	− 3 ± 1	−32 ± 2
Wax-free (alcohol extracted)	−11 ± 1	−38 ± 2
Wax- and pectin-free (ethanolamine extracted)	−41 ± 2	−57 ± 2
Fiber		
No treatment (control)	−13 ± 1	20 ± 4
Primary wall removed mechanically	−20 ± 3	65 ± 9
Wax- and pectin-free (by extraction)	−13 ± 1	43 ± 4
Commercially purified (by kiering)	−10 ± 1	28 ± 5

Further indication of the restricting influence of the primary wall on the swelling of the cotton fiber is shown in the figures for swelling of untreated fibers and fibers from which the primary wall has been removed. Untreated whole fibers swell only about 20% in ribbon width when passed from water into 18% sodium hydroxide, the swelling increasing when noncellulosic encrusting substances are removed by purification treatments. But the 66% swelling of the mechanically stripped fiber shows how much

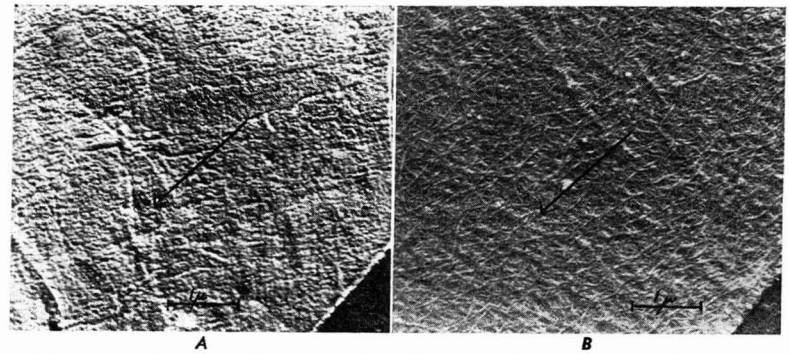


Figure 5. Electron Micrograph of Primary Wall Freed by Beating

***A.* Raw**
***B.* Purified by extraction**
Arrow indicates direction of fiber axis

the secondary wall cellulose could swell in mercerization if it were not for the restricting influence of the primary wall.

WINDING LAYER

Immediately beneath the primary wall lies the first layer of secondary thickening, called the winding by Hock (*26*) because of its characteristic behavior in certain swelling reactions. This first layer of secondary thickening has recently been isolated from untreated, native cotton fibers by beating in water in the Waring Blendor (Figure 7). It can readily be distinguished from the primary wall fragments which cling to it by its failure to stain with any of the reagents which color noncellulosic materials and by its higher birefringence in polarized light. The winding appears to be composed of a single layer of fibril bundles oriented at an angle to the fiber axis. In certain regions of the specimens obtained the reversal of direction of some of the fibril bundles could be observed.

In Figure 8 the banded pattern observed in the light microscope is revealed by the electron microscope to have a complex structure of alternating bands of closely aligned and openly woven fibril bundles. This arrangement is obviously very different from that in the layers of the main body of the secondary wall as illustrated in Figure 9.

Under the light microscope the winding gives with iodine–zinc chloride the typical dark staining reaction of cellulose, and the membrane is completely dispersed by cuprammonium or cupriethylenediamine hydroxide, apparently without residue. None of the usual staining tests for pectic or nitrogenous materials was positive and the phloroglucinol reaction for lignin was likewise negative. It has not yet been possible to obtain sufficient material for hydrolysis and chromatography but so far the isolated winding layer gives no evidence of being other than cellulose.

Figure 8. Electron Micrograph of Winding Layer from 17-Day-Old Fiber

Figure 9. Electron Micrograph of Portion of Secondary Wall

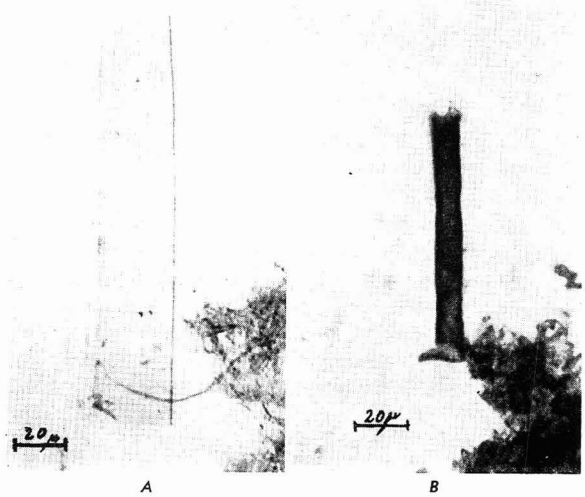


Figure 6. Shrinkage of Primary Wall in Mercerization

A. In water
B. In 18% sodium hydroxide

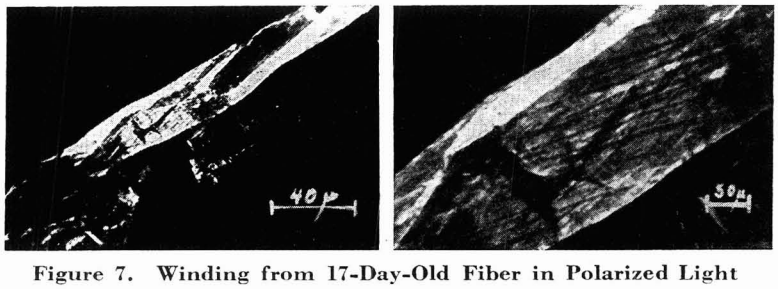


Figure 7. Winding from 17-Day-Old Fiber in Polarized Light

With this picture of the winding layer clearly in mind a brief look is given its behavior in the swelling of fibers. Figure 10 shows the pattern of the winding in a cotton fiber after oxidation in nitrogen dioxide gas (*43*) and swollen only slightly in alkali. The primary wall is still present on the fiber but the effect of the winding on it is in evidence and gives the impression of a helical tape about the fiber. Figure 11 shows the characteristic behavior of the winding in a carboxymethylated cotton fiber in 40% ethyl alcohol and in water.

This helical tape structure has been often noted in swollen fibers and is frequently referred to in the literature, especially that dealing with cellulose derivatives. It is not unlike the illustrations shown by Hock (*26*) for the swelling of depectinized cotton in cuprammonium hydroxide and by Mangenot (*31*) for the swelling of nitrated cotton in cyclopentanone. It also strongly resembles a lignin formation demonstrated by Mitchell (*34*) in nitrated spruce wood and is similar in appearance to figures shown

by Haas and coworkers (*23*) in the swelling of xanthated beech wood pulp and by Carpenter and Lewis (*16*) in studies on unbleached raw-cook Jack pine kraft fibers.

The failure of the winding layer to become completely soluble when chemically substituted cotton fibers are immersed in appropriate solvents can possibly be explained on the basis of its physical structure. In the course of these chemical reactions there is usually enormous swelling of the secondary wall, and the winding layer at the outer area of the fiber is thus put under considerable tension by the enlargement of the cellulose cylinder beneath it. It has been stated by Sisson (*45*) that cellulose under tension tends to resist intramicellar swelling; thus the degree of substitution of the winding layers may be somewhat less in any given length of reaction time than that of the rest of the secondary walls. In solvents which disperse the fully substituted cellulose of the main body of the fiber, the winding layer persists as a more slowly soluble skeleton. This may in part explain the original source of the cloudy residues of some solutions of cellulose derivatives.

OTHER USES OF MICROSCOPY

In addition to such studies of fiber morphology many degradative processes and chemical treatments can be evaluated effectively with the microscope.

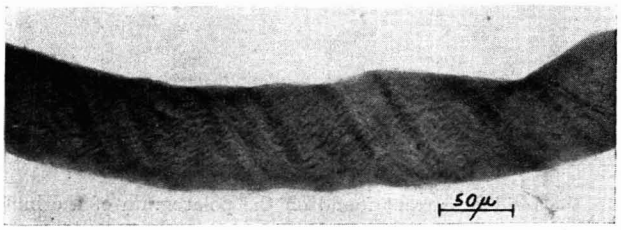
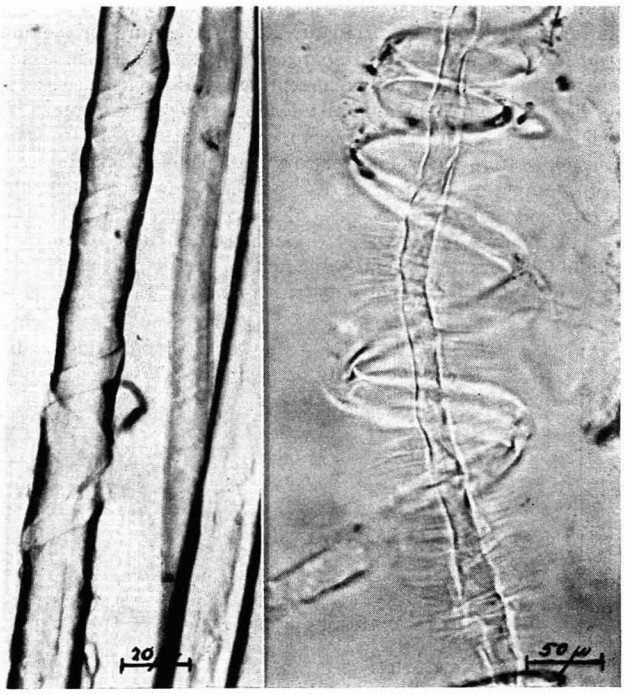


Figure 10. Nitrogen Dioxide–Oxidized Cotton Fiber Stained with Methylene Blue and Slightly Swollen to Show Winding



A B

Figure 11. Progressive Swelling of Carboxymethylated Cotton Fiber

A. In 40% ethyl alcohol
B. In water

Microscopical examinations of large numbers of fibers damaged by microbial decomposition strongly indicate that the enzymatic attack of either bacteria or fungi on the cellulose fiber is highly localized (*25*, *46*). Most mechanical damage, such as abrasion, tensile rupture, or beating in paper manufacturing processes, results in longitudinal fraying and fibrillation; the typical pattern of acid degradation is a transverse fissuring of the fiber which is increased by mounting the fiber in strong hydroxide for observation.

Patel and Frey-Wyssling (*37*) in comparisons of oxycelluloses produced by periodate, dichromate, and hypobromite oxidations showed characteristic fragmentation patterns which the authors associated with the types of oxidation; but in every case, when a sufficient degree of oxidation was reached, transverse disintegration of the microfibrils occurred.

CONCLUSION

The continued use of the light microscope as an accessory tool in the new science of electron microscopy is inevitable. The application of the two techniques in investigations of the chemistry of vegetable materials will open new avenues of usefulness to light microscopy. The significance of such developments in cellulose research is well presented by Preston (*38*).

Before a chemical reaction can take place the reacting molecules must come together and the more intimately the reacting molecules are mixed the more rapidly can the reaction take place. In reactions with fibers the process is generally heterogeneous, since in most cases the fiber is not first dissolved in some solvent. Although compared to matter in mass the available surface of fibers is large and may easily be a thousandfold greater; still, compared with the surface which would be exposed by the same chain molecules in solution it is about a thousandfold less. These quantitative differences are so great that they can produce apparent qualitative differences in behavior. It is not surprising, therefore, that there are differences of behavior between cellulose fibers and free cellulose molecules. The structural and architectural characteristics of fibers control the accessibility of the internal fiber substance to chemical reactants with different sizes of molecules and electric charge. Therefore considerations of pure chemistry must always be modified by considerations of structure.

Cellulose has not yet been synthesized in vitro. Therefore, the only sources of the raw material are those provided by nature. What will be accomplished either industrially and economically or theoretically will depend in some measure on how well the natural forms of these raw materials are understood. It is on this frontier that light microscopy will continue to make its contribution to cellulose research.

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Polarography of Thiourea

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THIOUREA is known to form complexes with a number of metals and salts (*1*). Although it is not reducible at the dropping mercury electrode, it was thought that at an anodic mercury electrode some reaction might take place with the mercurous ions. Experimentally it was found that an insoluble mercurous complex was formed.

APPARATUS

An automatic and recording polarograph described earlier (*2*) was used in this work.

The dropping mercury electrode when disconnected from the polarograph had a drop rate of T = 6.90 seconds in water. Under these conditions the mass of mercury delivered was m = 0.948 mg. per second.

All polarograms were obtained using the cell described earlier (*2*) and at a temperature of 29.5° C.

A saturated calomel half cell with a saturated potassium chloride bridge (*2*) was used as a reference electrode in these experiments.

REAGENTS

Thiourea was recrystallized at room temperature from a solution in ethyl alcohol by adding petroleum ether. Analysis of this product gave C = 15.87% and H = 5.34%; theory is C = 15.78% and H = 5.30%.

Buffer solutions, pH 4 and 6, were Clark and Lub buffer mixtures containing sodium hydroxide and potassium biphthalate.

PROCEDURE

A cell containing 25 ml. of buffer solution was deoxygenated by a stream of nitrogen and then polarographed from −0.2 to +0.3 volt. An aliquot of a standard aqueous thiourea solution was then added, and the polarogram was repeated. The half-wave potential becomes more negative with increasing concentration, so measurements of limiting current cannot be made between set potentials. Each limiting current measured was corrected for the residual current found on the polarogram of the buffer alone.

DISCUSSION

In buffer solution of pH 4 a definite polarographic wave is exhibited (Figure 1). When i_d is plotted against concentration, a linear relationship results (Figure 2). A procedure for the quantitative determination of thiourea is now being used in which a measure of the diffusion current represents thiourea concentration.

The reaction of thiourea at the anodic dropping mercury electrode could be an oxidation or a reaction with mercurous or mercuric ions to form insoluble or very stable complex products. In an attempt to identify this reaction the following polarographic evidence was obtained.

Polarograms of the same thiourea concentration run at pH 4 and 6 have the same half-wave potentials. This eliminates any reaction that might involve hydrogen ions.

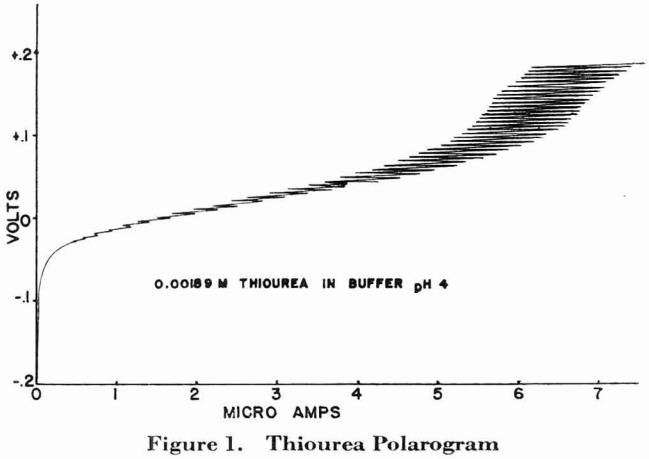

Figure 1. Thiourea Polarogram

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The half-wave potentials of polarograms run on various concentrations of thiourea were found to shift to more negative values with increasing concentration. In order to measure these potentials as accurately as possible, the IR drop across the cell must be considered. The resistance of the system, from the mercury reservoir through the cell of buffer pH 4, potassium chloride bridge, and saturated calomel electrode, was measured as 2300 ohms with a General Radio Co. impedance bridge Type 650-A. Using the expression $E = IR$ and the i_d values measured, the voltage drop at each concentration was calculated. These corrections were subtracted from the measured half-wave potentials to get the true half-wave potentials.

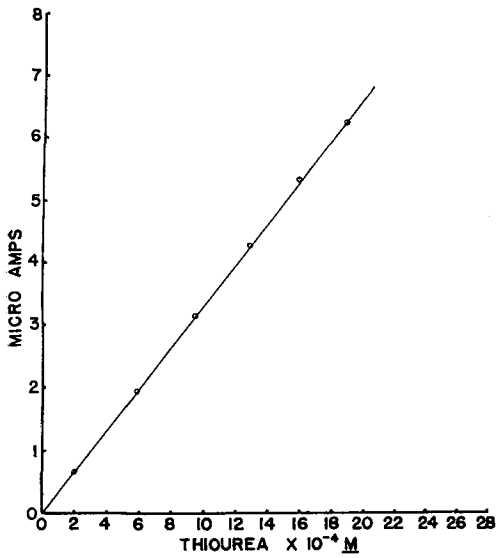


Figure 2. Linearity Check

The shifting $E_{1/2}$ and pH independence suggests a complex or insoluble reaction product with mercury rather than an oxidation. If the zwitterion form of thiourea is accepted (4), the reaction may be represented as follows.

$$a\ \mathrm{NH_2C(=NH_2^+)S^-} + b\ \mathrm{Hg_2^{++}} \rightleftharpoons \left(\mathrm{NH_2C(=NH_2^+)S}\right)_a \mathrm{Hg_{2b}} \qquad (1)$$

Since the mercurous ions are furnished by an anodic oxidation from the dropping mercury electrode, the electrode reaction will be

$$2\mathrm{Hg} \rightarrow \mathrm{Hg_2^{++}} + 2e \qquad (2)$$

The equation for the polarographic wave will then be

$$E_{de} = E^\circ_{red} + \frac{0.06}{2} \log [\mathrm{Hg_2^{++}}] \text{ at } 30^\circ \text{ C.} \qquad (3)$$

if activities and activity coefficients are neglected.

The free mercurous ions at the electrode will be present in a concentration governed by the solubility product or equilibrium constant of the product from Reaction 1.

$$[\mathrm{Hg_2^{++}}] = \sqrt[b]{\frac{K\left[\left(\mathrm{NH_2C(=NH_2^+)S}\right)_a \mathrm{Hg_{2b}}\right]}{\left[\mathrm{NH_2C(=NH_2^+)S^-}\right]^a}} \qquad (4)$$

Assuming an insoluble reaction product

$$[\mathrm{Hg_2^{++}}] = \sqrt[b]{\frac{K_s}{\left[\mathrm{NH_2C(=NH_2^+)S^-}\right]^a}} \qquad (5)$$

Substituting this concentration in Equation 3 describes the polarographic wave in terms of thiourea concentrations.

$$E_{de} = E^1 - \frac{0.03}{b} \log \left[\mathrm{NH_2C(=NH_2^+)S^-}\right]^a \qquad (6)$$

At any point E_{de} on the polarographic wave in the concentration of thiourea at the electrode would be proportional to $(i_d - i)$.

$$E_{de} = E'' - \frac{0.03}{b} \log (i_d - i)^a \qquad (7)$$

At the half-wave potential $i_d = 2i$.

$$E_{1/2} = E''' - 0.03 \frac{a}{b} \log (i_d) \qquad (8)$$

If Equation 8 is a true expression of the reaction, a plot of log (i_d) versus $E_{1/2}$ must produce a straight line with a slope of $\frac{0.03}{b} a$. Figure 3 represents the correct half-wave potentials plotted against the log i_d. A slope of 0.0516 was found, indicating a ratio of $\frac{a}{b} = 1.72$. The experimental value of $a = 1.72$ checks fairly well with the theoretical value of 2.

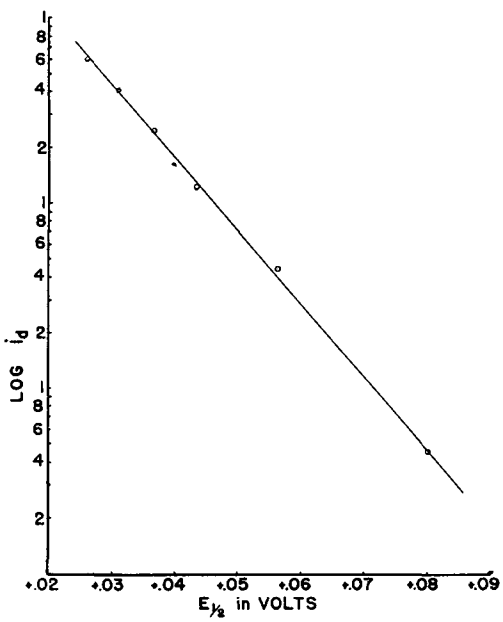


Figure 3. $E^1/_2$ Change with Concentration

A plot of log $(i_d - i)^a$ versus E_{de} as in Equation 7 should produce a straight line if the reaction is reversible. Diffusion currents at various potentials on the wave were carefully measured from the polarogram illustrated in Figure 1. Each potential was corrected for the IR drop as described earlier. These values when plotted as in Figure 4 show that no straight line results, indicating an irreversible reaction.

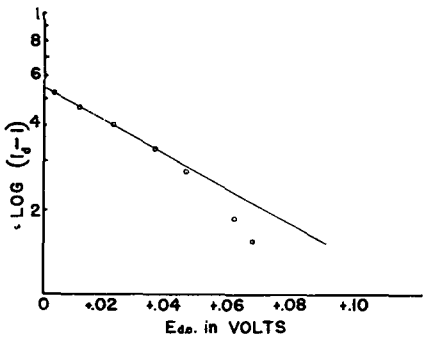
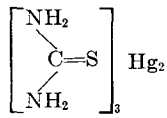
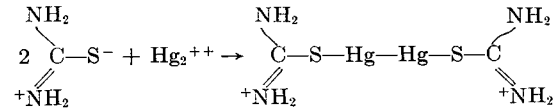


Figure 4. Reversibility Check

The only other possibility that seems to fit the experimental data is that a soluble complex is formed having the composition



Judging from known complexes and reactions of thiourea, the first assumption is more reasonable, and the reaction is probably as indicated herewith.



Sartori and Liberti (*3*) have also described the reaction of thiourea at the dropping mercury electrode as being a complex or insoluble compound formation rather than an oxidation. They did not, however, give any details of the reaction or enough experimental evidence to allow a derivation of possible reactions.

ACKNOWLEDGMENT

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Comparison of pK_a' Values Determined by Electrometric Titration and Ultraviolet Absorption Methods

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THE dissociation constants of organic compounds are receiving increased attention as the possibilities of practical application to problems of structure and identity and to the determination of absorption spectra, are more generally appreciated. In view of this importance, it is of interest to compare pK_a' values obtained by two methods of determination, electrometric titration and spectrum absorption, as a partial evaluation of the relative quality of data and the merits of the two methods in routine laboratory operations.

DISSOCIATION CONSTANT VALUES

Methods. In connection with extensive observations of the absorption spectra of purified benzenoid compounds (*6*, *7*), the pK_a' values of those derivatives with ionizable groups were determined by the absorption technique of Sager, Schooley, Carr, and Acree (*14*). The potentiometric values of these compounds were obtained subsequently, using the method of Parke and Davis (*13*) and equipment identical with theirs.

Results. Table I summarizes pK′ values obtained in routine application of the two methods to substituted phenols, anilines, and benzoic acids, at a room temperature of 25° C. The absorption figures given are the means of values from all the intermediate curves obtained for each ionization; the titration figures are to the nearest 0.05 unit read off the plotted curve through the transparent plastic overlay (*13*).

Agreement with Literature Values. It is of course important that values obtained by both absorption and titration methods, in addition to agreeing with each other, be of acceptable accuracy. A comparison with representative constants available in the literature shows that either method gives satisfactory values.

The pK_a' of phenol, for example, is reported as 9.94 (*8*) and 9.95 (*9*); aniline as 4.60 (*11*) and 4.636 (*10*); benzoic acid as 4.18 (*2*), 4.21 (*4*), 4.30 (*1*), and 4.198 (*10*). Values for disubstituted compounds are equally successful: *p*-Hydroxybenzoic acid, first anion, is given as 4.53 (*4*) and 4.54 (*2*); second anion, as 9.33 (*14*) and 9.39 (at 20° C.) (*12*); *p*-toluidine, as 5.12 (*11*), 5.17 (*3*), and 5.098 (*10*); *m*-toluidine as 4.77 (*10*); *o*-toluidine, as 4.46 (*10*); *p*-anisic acid, as 4.43 (*4*), 4.44 (*2*) and 4.47 (*5*).

A number of the pK'_a values of the compounds in Table I have not been reported heretofore; some are given in mixed solvents or at temperatures different from that used in this study. In general, the values by absorption and titration are in good agreement with literature values obtained under comparable conditions.

DISCUSSION

It is evident from inspection of the table that values obtained by the two methods are in good agreement. Comparison would indicate that either is satisfactory, and that, in results obtained, there is little advantage in one over the other. However, titration is usually a bit more rapid than the absorption method if the equipment is conveniently set up and manipulative experience has been acquired. This arises from the automatic nature of the procedure; it is not necessary to know or discover from consecutive curves the solution pH of the limiting species, nor to learn by trial the intermediate pH at which ionization takes place.

The titration method has a great advantage when there are two or more ionizable groups in a molecule. Usually time is prohibitive, and execution is fairly difficult, to run a sufficient number of curves to establish adequately the limiting species when

several groups are modified by pH change. If the ionizations happen to take place at adjoining pH units, the individual species may be impossibly difficult to recognize and distinguish.

The absorption method is sometimes handicapped with ionizations of minimum electron-displacing effect, as in the case of some of the carboxyl derivatives. With these the spectrum changes are not large, and the difference in absorbance between the mole and ionic forms is so small as to reduce precision in measurement to some extent. On the other hand, ionizations with relatively great electron-displacing effect, including most of the hydroxyl and amino derivatives, result in spectrum changes adequate for precise determinations.

At relatively low pH values, in the neighborhood of unity or less, the titration method may be uncertain; in this situation the absorption method would be preferable. The absorption method was also used conveniently with some samples of low relative solubility, the titrations of which were rendered unsatisfactory in aqueous solvent by precipitation at the neutralization point.

Table I. Comparison of pK_a' Values by Ultraviolet Absorption and Electrometric Titration Methods

Substituted Phenols			Substituted Anilines			Substituted Benzoic Acids		
	pK_a'			pK_a'			pK_a'	
Substituent group	Absorption	Titration	Substituent group	Absorption	Titration	Substituent group	Absorption	Titration
Para			Para			Para		
H	9.87	9.8	H	4.67	4.5	H	4.16	4.15
CH_3	9.81	9.65	CH_3	5.15	5.1	CH_3	4.36	(6.2)[a]
Cl	9.02	9.05	Cl	4.05	4.05	Cl	4.00	(5.3)[a]
Br	9.27	(10.25)[a]	Br	3.95	3.8	Br	3.93	(5.4)[a]
NH_2	[b]	9.4	I	3.84	3.75	I	3.98	(5.55)[a]
CO_2^-	9.31	9.15	OH	5.65	5.55	OH	4.48	4.5
$COCH_3$	7.84	7.75	OCH_3	5.40	5.3	OCH_3	4.41	4.55
COC_2H_5	7.95	8.05	NH_2	6.2	6.2	NH_2	4.82	4.85
CHO	7.41	7.35	NH_3^+	2.7	2.8	COOH	3.2	(4.85)[a]
NO_2	7.00	6.85	SO_3H	3.18	3.2	CO_2^-	4.3	4.5
			CN	1.75	..			(6.2)[a]
			COOH	2.40	2.5	NO_2	3.4	3.5[a]
			$COCH_3$	2.19	2.2			
			CHO	1.76	..			
			NO_2	1.13	..			
Meta			Meta			Meta		
CH_3	9.86	9.7	CH_3	4.81	4.7	CH_3	4.24	4.35
Cl	8.84	8.8	Cl	3.52	3.4	Cl	3.70	(5.25)[a]
OH	[b]	9.3	Br	3.54	3.55	Br	3.78	(5.2)[a]
OCH_3	9.20	9.25	I	3.68	3.5	I	3.79	(5.5)[a]
NH_2	9.83	9.9	OH	4.3	4.25	OH	3.94	4.1
CO_2^-	9.74	9.9	NH_2	5.0	5.0	OCH_3	3.92	4.0
$COCH_3$	9.18	9.0	NH_3^+	2.3	2.4	NH_2	4.60	4.65
COC_2H_5	9.21	9.05	SO_2NH_2	2.84	2.9	COOH	..	(5.1)[a]
CHO	8.82	8.75	CN	2.81	2.7	CO_2^-	4.6	4.5
NO_2	8.21	8.15	COOH	3.01	3.1			(6.4)[a]
			$COCH_3$	3.59	3.6	NO_2	3.4	3.35
			NO_2	2.52	2.5			
Ortho			Ortho			Ortho		
CH_3	10.06	10.2	CH_3	4.53	4.4	CH_3	3.81	3.9
Cl	8.32	8.5	Cl	2.71	2.6	Cl	3.01	(5.1)[a]
Br	8.29	8.2	Br	2.55	2.45	Br	2.81	(4.9)[a]
I	8.34	8.4	I	4.74	4.65	I	2.84	(5.2)[a]
NH_2	9.66	9.75	OH	4.59	4.45	OH	2.85	2.95
CN	6.9	..	OCH_3	4.74	4.6	OCH_3	4.02	4.0
$COCH_3$	10.17	10.3	NH_2	0.6	..	NH_2	4.90	4.8
CHO	8.10	8.25	NH_3^+	1.0	..	COOH	2.90	2.95
NO_2	7.04	7.0	SO_2NH_2	0.95	..	CO_2	5.25	5.3
			CN	2.12	2.2	NO_2	2.14	2.3
			COOH	2.22	2.4			
			$COCH_3$	−0.05	..			
			NO_2					

[a] Solvent, 50% dimethylacetamide.
[b] Sample not sufficiently stable in alkali for dependable spectrum determination.

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Modified Amdur's Dipicrylaminate Method

Applied to the Study of Potassium Contents of Maple Sirups

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LITHIUM dipicrylaminate precipitates potassium from its solutions and can thus be used for the determination of this element (*2*). The potassium content may be obtained directly by the study of the potassium dipicrylaminate (*2*) or indirectly by the use of the partially decolored lithium dipicrylaminate (*1*). While the direct method calls for washing the precipitate without any loss, the indirect method requires the separation of the mother liquors for the crystals by a special technique. Both involve dissolving the crystals or diluting the mother liquor.

This paper presents a modification of the indirect method, which makes it more suitable for routine potassium determinations. This modification replaces the pipetting and subsequent dilution of the indirect method by decantation, centrifugation, and measurement of the light transmittance through a thin layer of the mother liquor.

Both Kolthoff's (*4*) and Amdur's (*1*) methods use solutions from ashes. In order to eliminate the necessity for ashing samples of sirup, a study was made of the influence of sugars, in the

proportions met in maple products, upon the precipitation of potassium dipicrylaminate.

This investigation on potassium was made to find a more reliable method for the study and control of adulteration of maple products with white sugar.

It was shown by one of the authors (*3*) that the two conditions required for a better method are that it rest on an element that is plentiful and that the amount present be as constant as possible in pure maple products. The latter condition requires that the element be water-soluble.

It was felt that potassium would fulfill these conditions, since it is widely distributed in a water-soluble form in the vegetable kingdom.

The potassium content in maple products was established by analyzing authentically pure samples from the experimental sugarbush at Plessisville, Quebec, Canada, and also samples secured from many other sugarbushes in the province of Quebec.

Potassium contents of maple sirups are plotted against soluble ash and conductivity to demonstrate the relative abundance of potassium in maple sirups.

EXPERIMENTAL

Modification of Amdur's Method. ELIMINATION OF DILUTION. In the application of Amdur's method, the small volume of the solution, which is only 2 ml., prevents the use, without diluting the solution, of the usual cuvettes of the Coleman spectrophotometer (Model 14).

This difficulty was eliminated by the use of smaller cuvettes and special adapters to fit into the Coleman cuvette carrier. Test tubes, 11 mm. in diameter (Kahn tubes), were chosen such that their percentages of light transmittance, which agree to within 1%, were constant no matter what the setting of the tube. The adapter, made of wood, had external dimensions (16 × 16 × 120 mm.) equal to those of the square cuvettes commonly used with the Coleman spectrophotometer. It provided one opening in the center for the introduction of the Kahn tubes. In the lower end, two rectangular slots (2 × 20 mm.) were made on opposite walls of the adapter and along the length.

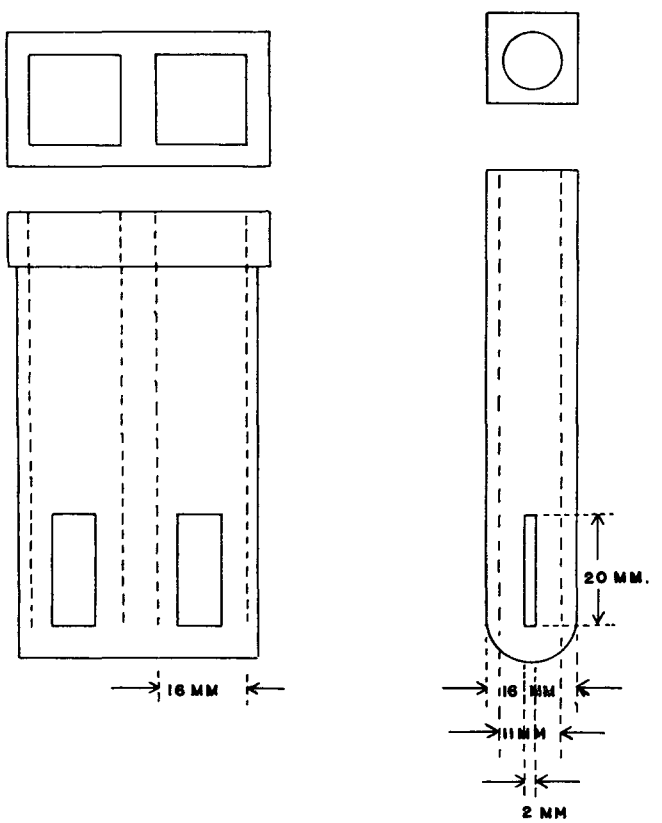

Figure 1. Apparatus

Left. Coleman support
Right. Adaptor

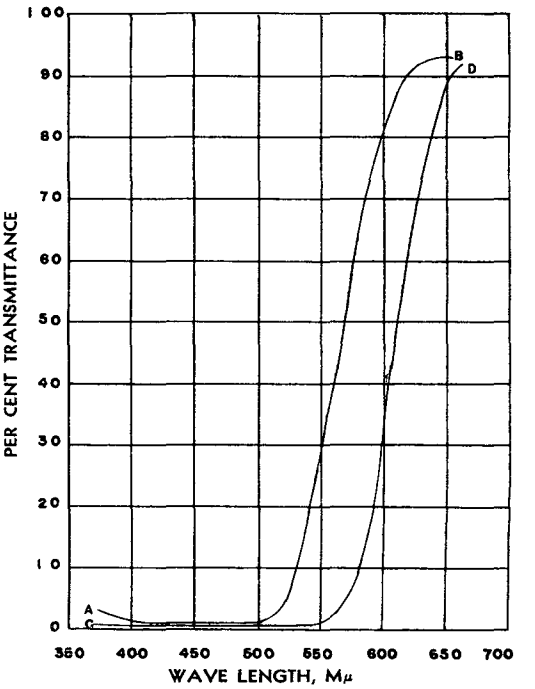

Figure 2. Transmittance Curves for Solutions Containing Potassium Oxide

AB contains 1.0 mg. of K_2O
CD contains 0.0 mg. of K_2O

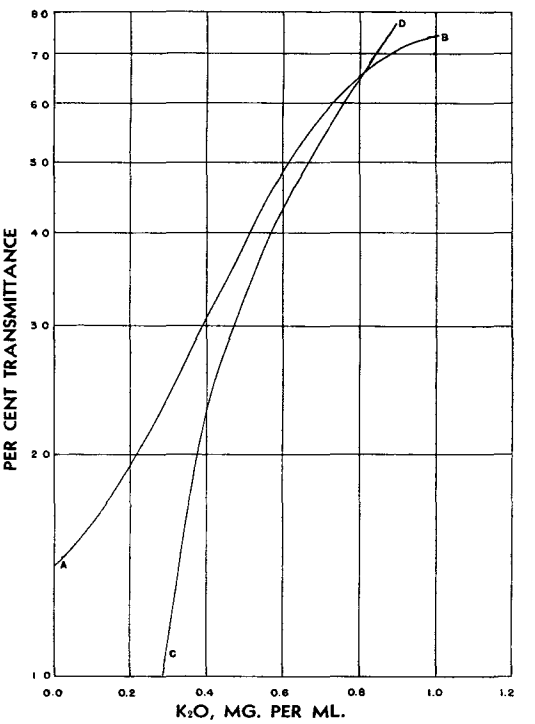

Figure 3. Transmittance Curves for Solutions Allowed to Stand at Different Temperatures

AB. Solutions crystallized at room temperature
CD. Solutions crystallized at about 5° C.

When in position, the adapter is such that the lower end of the slots is about 17 mm. above the bottom of the Coleman cuvette carrier.

Figure 1 shows drawings of the adapter and of the Coleman carrier.

ELIMINATION OF CRYSTALS. The crystallization of potassium dipicrylaminate is such that crystals stick to the inner side of the tubes and cannot be moved down to the bottom even by centrifugation at 30,000 r.p.m. Since the crystals interfere with the amount of light transmitted, it is impossible to complete the determination with the tubes in which crystallization has taken place. The contents are then poured into another tube and centrifuged. The crystals carried over with the solution at the time of pouring are then deposited easily on the bottom of the tube. The reading of light transmittance can now be made without interference.

Using the above modification, the reagents can thus be mixed in any tube, allowing crystallization to take place, and only from then on are the standardized tubes used.

CHOICE OF OPTIMUM WAVE LENGTH. Figure 2 gives transmittance curves for solutions containing, respectively, the equivalent of 0.0 and 1.0 mg. of potassium oxide. A study of these curves shows that the optimum wave length lies around 595 mμ.

Preparation of Standard Curve. From a potassium chloride solution, 1 ml. of which contains the equivalent of 1 mg. of potassium oxide, one prepares a series of tubes containing the equivalent of 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 mg. of potassium oxide. By the addition of a suitable amount of water, the volume of these solutions is brought to 1 ml.

To each of these tubes, 1 ml. of lithium dipicrylaminate is added and the solution is thoroughly mixed by agitation and set aside overnight at room temperature.

The following day, the contents of the tubes are poured into standardized Kahn tubes. After centrifugation, the spectrophotometer reading is taken.

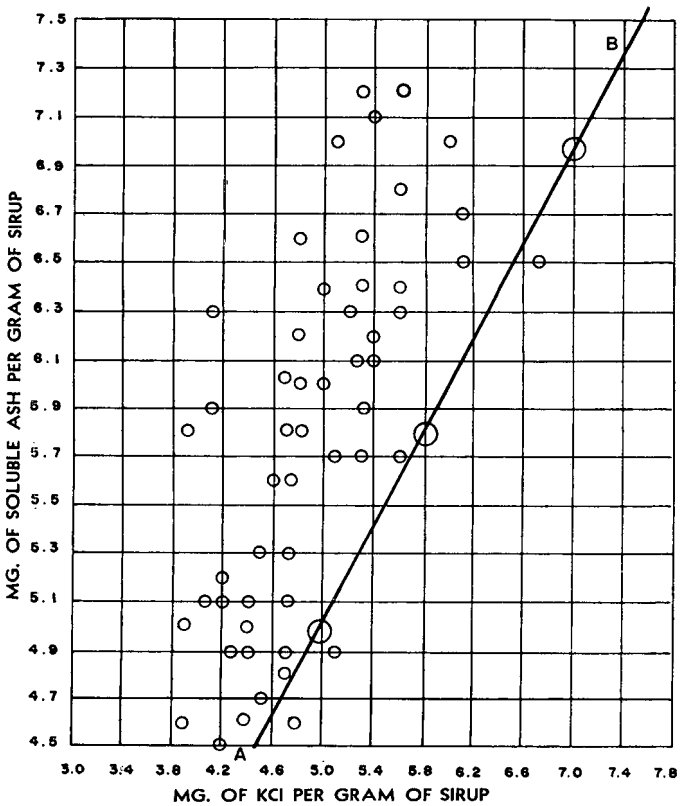

Figure 4. Soluble Ash Content of Some Maple Sirups *vs.* Their Potassium Value as KCl

AB **Theoretical curve where only KCl is present in soluble ash**

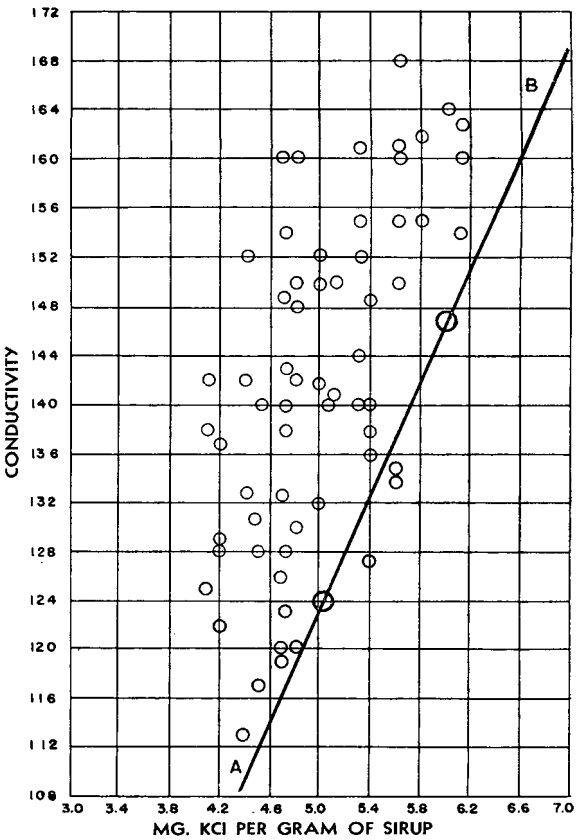

Figure 5. Conductivity Values of Some Maple Sirups *vs.* Their Potassium Values as KCl

AB. **Conductivity of KCl in solutions containing 25% of sucrose**

Figure 3 shows curves obtained from solutions allowed to stand at different temperatures. Curve *AB* resulted from solutions crystallized at room temperature and curve *CD* was the result of crystallization at temperatures around 5° C. The temperature for curve *AB* is optimum, since a wider range of potassium oxide values can be determined between 20 and 70% transmittance, approximately 0.2 to 0.9 mg. per ml.

Influence of Sugars. This study has been made with sirups containing 1.0 mg. of potassium chloride per milliliter and the quantities of sucrose and invert sugar shown in Table I. The varying percentages of light transmittance obtained from different sirups containing the same amount of potassium demonstrate that potassium dipicrylaminate cannot be quantitatively precipitated in a maple sirup without ashing.

PROCEDURE

Five grams of sirup, of a known percentage of solids, are introduced into a platinum dish. The dish and its contents are left overnight in an oven at a temperature of about 100° C. The next morning, a drop of olive oil is added to the hardened sirup and the dish is heated under an infrared lamp. Half an hour later the dish is introduced into a furnace at a temperature of about 550° C.

When the ashes are whitish, the dish is allowed to cool, 1 or 2 ml. of water are added to wet all the ashes, and the dish is placed back under an infrared lamp until dry. The calcination is then completed in the same furnace. The ashes are taken up with water at 100° C. and the solution is poured into a graduated flask of 25 ml. After cooling, the solution is brought to volume. This solution is then poured into a test tube, about 0.1 gram of magnesium oxide is

Table I. Influence of Sugars Found in Maple Sirups upon Precipitation of Potassium Dipicrylaminate

Composition of Sample, %		Transmittance, %
Sucrose	Invert sugar	
0	0	71.0
65	0	65.0
0	65	21.0
60	5	35.5
55	10	51.0
50	15	54.0
45	20	35.0

Table II. Precision of Method

Determination	Transmittance, %	K_2O, Mg.	K_2O, Dry Basis, %
1	34.8	0.448	0.328
2	35.0	0.45	0.330
3	34.8	0.448	0.328
4	34.5	0.445	0.326

added, and the solution is heated to incipient boiling. Using 1 ml. of this cooled and filtered solution, one proceeds as in the preparation of the standard curve.

PRECISION OF THE METHOD

The precision of the method has been checked by making four different determinations on the same sirup containing 68.3% of solids. The results are given in Table II.

RESULTS

Using the above method, the authors have analyzed genuine maple syrups grouped according to their origin. The 25 sirups from the Plessisville, Quebec, experimental sugarbush have shown potassium contents varying from 0.29 to 0.42% as potassium oxide, the mean value being 0.32%.

The other sirups, 80 in all, originating from different sugarbushes of Quebec province, had potassium contents ranging from 0.26 to 0.39% as potassium oxide with a mean value of 0.32%, the same as that mentioned above.

In Figure 4, the soluble ash content of some maple sirups has been plotted against their potassium value expressed as potassium chloride. The straight line, *AB*, is the theoretical curve that would be obtained if only potassium chloride were present in the soluble ash.

In Figure 5, the conductivity values of some maple sirups have been plotted against their potassium values. The straight line, *AB*, gives the conductivity of potassium chloride in solutions containing 25% of sucrose.

CONCLUSION

The modification of Amdur's method outlined above is very suitable for routine determinations of potassium in maple sirups. The percentages of potassium thus found and expressed on a dry basis are reproducible to 0.01%.

All the authentic maple sirups analyzed to date showed potassium contents, expressed as potassium oxide, which varied from 0.26 to 0.42%, the mean value being 0.32%.

Potassium salts constitute the bulk of soluble ash in maple products. They are also the main electrolyte.

Assuming that these limits of variation are representative of the potassium contents of all pure maple sirups, it has been shown (*3*) through calculation that, theoretically, this potassium index is twice as sensitive as the conductivity value which, of all the common tests (*2*) in use, is the most reliable (*3*) for the study of adulteration of maple products with white sugar alone.

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Determination of Micro Amounts of Phosphorus in High-Purity Iron

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THE preparation of high purity iron has been a fascinating challenge to metallurgists for many years. Valuable information concerning the basic physical properties of iron has been obtained. The point has been reached, however, where further study will prove inconclusive unless methods are developed to establish the percentage content of those impurities which heretofore have been reported as being less than some given figure or nondetectable. To keep pace with the increasing interest in the effect of trace impurities on the properties of metals, it has become necessary to extend the range of accurate analysis. A method has been developed to determine 0.0001% phosphorus on a 4-gram sample of high-purity iron. Lower percentages may be determined by increasing the sample weight. The bulk of the iron is separated from the phosphorus by electrolysis with a mercury cathode; further purification is effected by precipitating the acid sulfide group. The phosphorus is determined colorimetrically in the filtrate by the phosphomolybdenum blue technique.

BACKGROUND

The most recent studies of the wet chemical analysis of high purity iron were reported by Bright (*2*) and by Short (*7*). Bright detected "less than" 0.0005% phosphorus in two of 19 ingots tested with the conventional alkali molybdate technique; there were no figures reported for the remaining 17 ingots. Short, by colorimetric analysis, reported an average phosphorus content of "less than" 0.001% with the vanadophosphomolybdate technique followed by the extraction of the yellow complex with organic solvents.

The mercury cathode (*5*, *6*), generally employed to separate iron from 0.2 to 0.5-gram samples in solutions containing a slight excess of sulfuric acid, may also be used to separate iron from much larger samples even without careful control of acidity. The author has found it possible to remove the bulk of the iron from a 4-gram sample in 1 hour with a water-cooled Melaven cell (*5*) with air stirring and a current of 15 amperes. Neutralization of excess acid as electrolysis progresses is unnecessary. Thus the accumulation of salts is avoided.

The molybdenum blue reaction (*1*, *4*) has been used for many years to determine low percentage phosphorus. Hague and Bright (*3*) have made a detailed study of its use for determining phosphorus in iron and steel. They used hydrofluoric acid and hydrobromic acid to eliminate errors due to silicon and arsenic, respectively. After separating the phosphorus from the iron

and acid sulfides which consist largely of mercury, the author has applied their technique to determine micro amounts of phosphorus in high purity iron.

REQUIREMENTS

The determination of as little as 0.0001% phosphorus in high purity iron by wet chemical methods poses the following considerations:

1. The bulk of the iron should be separated.
2. Salt concentrations should be kept at a minimum.
3. Reagents and distilled water must be sufficiently phosphorus-free to cause little or no color development in the blank.

APPARATUS

Assorted laboratory borosilicate glassware. Water-cooled Melaven cell or its equivalent. Filter photometer or spectrophotometer. A source of direct current electricity.

REAGENTS

Perchloric, nitric, hydrofluoric, and hydrobromic acids.

Potassium thiocyanate, 5% solution.

Sodium sulfite. Dissolve 100 grams of anhydrous sodium sulfite in 500 ml. of water, dilute to 1000 ml., and filter.

Hydrazine sulfate. Dissolve 1.5 grams of hydrazine sulfate in 1000 ml. of water.

Ammonium molybdate. Add 300 ml. of concentrated sulfuric acid to 500 ml. of water and cool; add 20 grams of ammonium molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$] to the cooled sulfuric acid and dilute to 1000 ml.

Ammonium molybdate–hydrazine sulfate. Dilute 25 ml. of the ammonium molybdate solution to 80 ml. with water. Add 10 ml. of hydrazine sulfate solution, and dilute to 100 ml. with water. This solution is unstable; prepare only as needed.

PROCEDURE

Transfer a 4-gram sample of high purity iron to a 600-ml. beaker and cover with a watch glass. Dissolve the sample with 50 ml. of (1 to 1) nitric acid. Add a few drops of hydrofluoric acid to volatilize the silicon and 28 ml. of perchloric acid. Evaporate to fumes of perchloric acid. Continue to fume until salts of perchloric acid separate out and very little excess acid remains in the beaker. Do not allow the samples to remain on the hot plate until the white ferric perchlorate salts break down to brown ferric oxide. Cool, rinse, and dilute with 75 ml. of water. Boil 1 minute to expel chlorine. Cool and transfer to the Melaven cell. Adjust the leveling bulb so that the cell contains about 35 ml. of mercury.

Into the plating solution insert the anode, a platinum gauze electrode, or heavy platinum wires. Place a stemless funnel across the top of the cell to reduce loss of sample as spray during the electrolysis. Through the hole in the funnel pass a glass tube of sufficient length to extend about 1 inch into the mercury in the bottom of the cell. Pass air through the mercury at the rate of 1 bubble per second. Electrolyze for 1 hour with a current of 15 amperes. The potential drop across the cell is usually 12 or 14 volts during the electrolysis. Separate the mercury from the electrolyte by manipulating the leveling bulb while the current is still flowing. Return the solution to the original beaker and evaporate to fumes of perchloric acid. Continue to fume until salts separate out again in the bottom of the beaker. Cool, dilute to 75 ml., boil 1 minute, and cool to room temperature. Transfer the solution to a clean Melaven cell and continue the electrolysis at 4 amperes until spot plate tests with potassium thiocyanide show only a trace of ferric iron. The second electrolysis does not require a water-cooled cell.

Again separate the mercury from the electrolyte without interrupting the current. Return the electrolyte to the original beaker and evaporate to fumes of perchloric acid. To expel excess acid, fume until about 3 ml. of perchloric acid remain in the beaker. Cool, dilute with 75 ml. of water, and boil for 1 minute. Pass in hydrogen sulfide for 10 minutes to precipitate the acid sulfides. Filter into a 250-ml. beaker through a 9-cm. Whatman No. 30 filter paper containing pulp. Wash twice with saturated hydrogen sulfide water. Evaporate the filtrate to perchloric acid fumes. Cool, add 5 ml. of (1 to 4) hydrobromic acid to volatilize the arsenic, and evaporate gently just to dryness. To attain the acidity recommended by Hague and Bright, which is a critical factor, add exactly 3 ml. of perchloric acid and fume for 2 minutes. Cool, add 10 ml. of water, and boil 1 minute. Cool somewhat and add 15 ml. of sodium sulfite solution. Boil gently for 30 seconds. Add 20 ml. of ammonium molybdate–hydrazine sulfate solution, and heat until the solution just begins to boil. Transfer to a steam bath for 30 minutes. Remove and cool in a water bath, then transfer to a 50-ml. volumetric flask. Dilute to the mark with 1 to 4 ammonium molybdate–hydrazine sulfate, mix well, and read the percentage transmission. The instrument should first be adjusted to 100% transmittance with a blank carried throughout the analysis. The phosphomolybdenum blue complex shows maximum absorption at 830 mμ; however, the author used a 650 mμ filter because it was incorporated in the instrument used for routine photometric determinations.

Table I shows the phosphorus recovery obtained directly from a high purity iron sample, FeA. Recovery results are also shown when phosphorus additions were made to the same sample. All samples, including the aliquots of a standard solution used to prepare the phosphorus curve, were electrolyzed in the mercury cathode and further purified with hydrogen sulfide. The standard phosphorus solution, used to make the above additions, was prepared from the National Bureau of Standards sample 8g.

Table I. Phosphorus Recovery from High-Purity Iron (FeA)

Wt. of Sample, Grams	Phosphorus Added, γ	Total Phosphorus Recovered, γ	% Phosphorus in Sample	Deviation from Average, %
4	..	5.5	0.00014	+0.00002
4	8	12.0	0.00010	−0.00002
4	40	45.0	0.00012	0.00000
4	..	3.0	0.00008	−0.00004
4	40	43.0	0.00008	−0.00004
2	..	3.0	0.00015	+0.00003
4	..	6.5	0.00016	+0.00004
6	..	8.0	0.00013	+0.00001
4	..	6.5	0.00016	+0.00004
4	..	5.5	0.00014	+0.00002
4	..	2.0	0.00005	−0.00007
4	..	6.0	0.00015	+0.00003
4	..	6.0	0.00015	+0.00003
4	..	4.0	0.00010	−0.00002
			Av. 0.00012	

A 2.1505-gram sample of 8g was dissolved in dilute nitric acid in an Erlenmeyer flask. After solution, the sample was treated with a few drops of hydrofluoric acid and 20 ml. of perchloric acid, and evaporated to perchloric fumes. The solution was cooled slightly, diluted with 50 ml. of water, boiled 1 minute, and cooled to room temperature. It was then transferred to 200-ml. volumetric flask and diluted to the mark. This solution contained 10γ of phosphorus per ml.

Table II shows phosphorus recovery from aliquots of standard solutions of both N.B.S. 8g and diammonium hydrogen phosphate by the mercury cathode–hydrogen sulfide procedure as compared with the recovery from similar aliquots analyzed directly according to the Hague and Bright procedure. The reference curve was prepared from a diammonium hydrogen phosphate stock solution which contained 0.001 gram of phosphorus per milliliter. The phosphorus value of the stock solution was established by

Table II. Comparison of Methods

Source of Phosphorus	Phosphorus Taken, γ	Phosphorus Recovered, γ Set 1	Set 2	Set 3
1. NBS 8g. (0.01075 gram)	10.0	12.0	10.0	12.0
2. NBS 8g. (0.05375 gram)	50.0	48.0	47.0	51.0
3. $(NH_4)_2HPO_4$ soln.	20.0	20.0	21.0	23.0
4. $(NH_4)_2HPO_4$ soln.	100.0	99.0	100.0	103.0
5. $(NH_4)_2HPO_4$ soln.	100.0	100.0	100.0	103.0
6. Blank on reagents	...	...	...	2.5

Reference curve prepared from transmittancies of 3, 5, and 6, of set 1.

Set 1 treated with 3 ml. of perchloric acid and treated as directed by Hague and Bright (*3*).

Set 2 treated with 25 ml. of perchloric acid and 10 ml. of nitric acid to determine blank on reagents required for 4-gram sample. It was taken to perchloric fumes and fumed to volume of approximately 3 ml. Molybdenum blue complex developed as directed by Hague and Bright.

Set 3 treated with 25 ml. of perchloric acid and 10 ml. of nitric acid. Mercury cathode–hydrogen sulfide procedure was followed before development of molybdenum blue complex.

precipitating the phosphate with magnesia mixture and igniting to magnesium pyrophosphate. The results in set 3 indicate a slight pickup of phosphorus when the proposed mercury cathode–hydrogen sulfide procedure is used. The resulting error caused by this apparent pickup of phosphorus approaches insignificance when a 4-gram sample is used. This error is overcome when the photometer is set at 100% transmittance with the reagent blank.

Table III shows typical values of the effect of silicon and arsenic additions on the recovery of phosphorus from the high purity iron sample. The presence of small amounts of silicon can be tolerated without the use of hydrofluoric acid, but large amounts make its use mandatory.

The addition of 5 ml. of hydrobromic acid (1 to 4) prior to the final perchloric acid fuming will eliminate errors caused by the presence of arsenic.

Table III. Effect of Silicon and Arsenic on Phosphorus Recovery

Sample (FeA), Grams	Arsenic Added, γ	Silicon Added, γ	HF Added	HBr Added, ml.	Apparent Phosphorus Recovery, γ
4	...	55	..	..	5.5
4	...	137	..	..	7.5
4	...	548	..	..	43.0
4	...	548	2 drops	..	6.5
4	400	...	..	..	16.5
4	400	...	..	..	11.5
4	400	...	..	5	5.0

COMMENTS

With little or no change in technique the method should be applicable to phosphorus microdeterminations in any high-purity element or material that forms soluble perchlorate salts and that may be separated by electrolysis with the mercury cathode.

While greater sensitivity may be had by measuring the transmittancies at 830 mμ, the sensitivity is great enough to permit the determination of 0.0001% phosphorus on a 4-gram sample with a 650 mμ filter, which is still used by many laboratories to measure the molybdenum blue complex photometrically.

No attempt was made to determine phosphorus in the electrolyte after the first electrolysis with the mercury cathode. Sufficient iron may be removed at this stage to cause no difficulty with the subsequent development of the color complex.

The removal of mercury by hydrogen sulfide is necessary because its presence causes turbidity which leads to erroneous transmittancy readings; it is not sufficient merely to remove the metallic mercury by filtration since there are always small amounts of soluble mercury salts found in the electrolyte.

As it is not necessary to remove the iron completely, it should be possible to conduct the electrolysis satisfactorily in a water-cooled beaker in the event a water-cooled Melaven cell is not available.

The use of perchloric acid for conducting mercury cathode electrolyses is far from new. In spite of this, the trend seems to favor the use of sulfuric acid. While sulfuric acid may be preferable for some analyses, perchloric acid offers certain advantages with iron and steel samples. Dehydration of steel sample solutions with perchloric acid proceeds rapidly and smoothly with no danger of bumping and spitting, which is not true in the case of sulfuric acid. A thoroughly dehydrated sample of ferric sulfate is extremely hard to redissolve upon dilution, while ferric perchlorate dissolves very readily.

ACKNOWLEDGMENT

Grateful acknowledgment is made to C. M. Bible, Analytical Chemistry Section, for advice and suggestions during the investigation, and for making available water-cooled mercury cathode cells of his design.

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Molar Absorptivity of Dithizone in Chloroform

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IT IS possible to prepare pure dithizone solutions of known concentrations by utilizing the extraction procedure of Cooper and Sullivan (*2*), thus eliminating the necessity of obtaining the solid dithizone in a highly purified form.

This purification is accomplished by stripping the dithizone-chloroform solution twice with dilute ammonium hydroxide (1 to 100) with volumes equivalent to 10 times the volume of dithizone solution. After removal of the chloroform layer, the aqueous dithizone phase is filtered through a pledget of cotton inserted in the stem of a Squibb funnel into another Squibb. The filtrate is carefully neutralized with metal-free 1 to 1 hydrochloric acid to precipitate dithizone, which is then re-extracted into chloroform purified according to Bambach and Burkey (*1*). The concentration of dithizone in moles per liter may be obtained by dividing the observed absorbancy, A_s at 606 mμ by the molar absorptivity at this wave length, using a cell of 1.0-cm. light path.

As the result of 25 replicate determinations, the molar absorptivity of dithizone in chloroform, ϵ_{606}, has been found to be 40.6 $\pm$ 0.5 $\times$ 10^3. This was obtained by shaking 25.0 ml. of a dithizone-chloroform solution (4.99 mg. per liter) with an equal volume of an aqueous solution, buffered at pH 3.4 with potassium acid phthalate, of known but deficient mercuric content (0.498 $\times$ $10^{-5}M$). Since mercuric dithizonate does not absorb at 606 mμ, the absorbancy of the mixed-color, A_{sm}, is equal to the absorbancy of the excess dithizone, A_{se}. The latter value when subtracted from the absorbancy of the original dithizone solution, A_{so}, gives the change in absorbancy, ΔA_s. Dividing the molar concentration of dithizone entering the complex into this change in absorbancy gives the molar absorptivity, or

$$\epsilon_{606} = \frac{\Delta A_s}{2(Hg^{++})}$$

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A further advantage may be obtained from this procedure in the preparation of dithizone solutions of reproducible concentrations. This is readily accomplished through the use of a stock solution prepared by purifying 100 mg. of solid dithizone, dissolving in 100 ml. of chloroform, extracting as indicated with the exception that the ammonia concentration is increased tenfold (1 to 10), and re-extracting into 500 ml. of chloroform at 20.0° C.

Utilizing 25.0- and 40.0-ml. portions of the stock (and 1 to 100 ammonia) produced standard dithizone solutions of 4.4 and 7.1 mg. per liter, respectively, when the final volume was 1.0 liter at 20.0° C. These doubly purified solutions were stable, not easily oxidized, had a very narrow range of variation in concentration, and proved to be highly satisfactory for use in the determination of cadmium, lead, and mercury.

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Determination of Carbon in Tantalum

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THE low pressure combustion method for the determination of carbon in steel has been adapted for the analysis of tantalum. Apparatus described by Murray and Niedrach (*2*) has been used. The present report describes a sample holder suitable for nonmagnetic samples. A 19/38 standard-taper joint allows this holder and the steel sample holder to be interchangeable. Apiezon W wax is used for sealing this joint.

PROCEDURE

Half-gram samples are placed in Kovar cans, *E*, Figure 1, 0.5 inch in diameter and 0.75 inch high. These are placed in the 6-inch arm of the holder. After evacuation and blanking out, the entire group of cans is moved toward the dumping area with a magnet. The side arm, *D*, contains a pointed glass rod attached to a piece of Kovar, *B*. It is moved forward with a magnet to separate one can from the rest. This can is then carried by a second magnet to the dumping area, *C*, and turned over until the sample has fallen into the crucible. The empty can is finally transferred to *A* for storage.

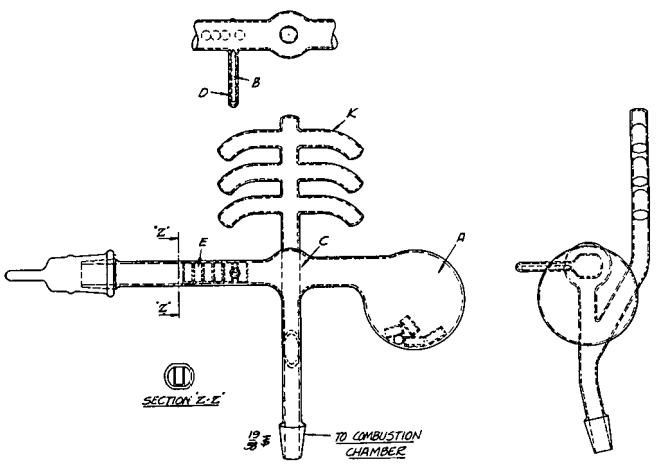

Figure 1. Sample Holder

If only a few samples are to be analyzed, a platinum crucible without a ceramic liner may be used. The tantalum oxide does not alloy with the platinum, and the crucible is easily cleaned.

However, if more than three or four samples are to be analyzed, the above method must be modified. Tantalum oxide does not fuse at the operating temperature, and consequently is not in good thermal contact with the crucible. This, coupled with a large surface area, introduces serious difficulties in degassing when a large amount of oxide has accumulated. To circumvent this difficulty, a loading arm, *K*, for magnetic samples was built into the holder. With this arrangement, a steel sample can be burned after every two or three tantalum samples. The iron oxide fuses along with the tantalum oxide, resulting in a slag with low surface area which does not offer degassing trouble. This procedure necessitated the use of an aluminum oxide crucible within the platinum to avoid injury to the latter.

RESULTS

Operating Conditions. Reproducible results were obtained over a range of crucible temperatures from 800° to 1400° C., and over a range of sample weights from 0.200 to 0.500 gram.

Combustion takes place quickly and completely when the sample is dropped into the crucible. Reproducible results were obtained over a range of combustion times from 5 to 20 minutes.

Precision and Accuracy. Conditions were standardized at: 1100° C. crucible temperature; 0.500-gram sample weight; and 5-minute combustion time.

Multiple determinations have been performed on a large number of samples ranging from 0.002 to 0.007% carbon. Standard deviation is usually about 0.0006%, which is approximately as good as is obtained in the analysis of steel.

One sample of 0.5-mil foil has been analyzed by the present method and also with the Leco conductometric carbon determinator, Model CD-10 [adapted from the method of Bennet, Harley, and Fowler (*1*)].

	Carbon, %	
	Low pressure method	Leco method
	0.0035	0.0044
	0.0027	0.0046
	0.0039	0.0044
	0.0035	0.0043
	0.0036	0.0043
Average	0.0034	0.0044
Std. deviation	0.0004	0.0001

Results obtained by the low pressure method have not been corrected for the average blank of 0.0005%. This is in accordance with previous practice in this laboratory (*2*). The Leco method (using a 1-gram sample) required the use of 1 gram of low carbon steel plus 0.5 gram of tin as flux. Results are corrected for 0.0021% carbon in the steel flux. Blank corrections are unnecessary, as results are obtained from a calibration curve in which net per cent carbon in standard samples is plotted against ohms resistance change. National Bureau of Standards samples 131 and 55c were used for calibration.

DISCUSSION

For the conductometric method, the large flux of steel and tin was required because induction heating was used—i.e., the tan-

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talum when heated alone ignited instantaneously (but only partially) to form an oxide which was discontinuous with respect to the one-turn secondary current. Residual unburned tantalum remained. Use of the flux resulted in a smooth slag of completely burned sample.

The results obtained by the conductometric method unfortunately involved a large correction for carbon in the steel flux. The slight discrepancy between the two methods is probably attributable to this cause, and also to an uncertainty in the blank in the conductometric method—that is, a new freshly fired crucible is used for each analysis. If standards and unknowns are of the same material, the temperature acquired during the combustion is probably reproducible, and any carbon dioxide evolved by the crucible does not introduce an error by virtue of the method of calibration. However, tantalum burns to a higher temperature than the steels used for calibration. Consequently, in so far as this liberates more carbon dioxide from the crucible, the results for tantalum may be slightly high.

The latter source of error is not inherent in the low pressure combustion method, in which a single crucible, never exposed to the atmosphere, is used for a series of analyses. The results presented indicate that high precision can be obtained by either method. The absolute accuracy of the low pressure combustion method is probably within 0.001% of carbon, and perhaps even better if the discussion of the comparison of methods is valid.

ACKNOWLEDGMENT

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An Explicit Function for Specific Surface Area

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IT IS the purpose of this paper to show that an explicit function for the specific surface area of an adsorbent may be obtained as a consequence of the Brunauer, Emmett, Teller theory (*1*). It has been the writer's experience that this has been largely overlooked by investigators in the field. For example, Harkins and Jura (*3*) observed that "... no single equation of state is capable of transforming these data [i.e., experimental parameters such as pressures, volumes, and weights of adsorbed vapors] into a correct area for a solid in every case." As a result, numerous investigations have been directed toward developing new equations, graphical methods of solution, and new principles of surface area measurement (*2, 4–6*).

It is not the intention, here, to analyze these principles and techniques. It is considered, however, that the present treatment offers, for many purposes, a simpler and more expeditious method. In the usual procedure, adsorption data are plotted according to the equation.

$$\frac{P}{N_a(P_0 - P)} = \frac{1}{N_m C} + \frac{C - 1}{N_m C} \times \frac{P}{P_0} \qquad (1)$$

where

N_a = number of moles adsorbed per gram of adsorbent
N_m = number of moles needed to form a monolayer
p = pressure at which adsorption is measured
P_0 = saturation vapor pressure of the adsorbate at the temperature of measurement
C = a constant defined by the equation $E_1 - E_2 \cong RT \log C$

where E_1 is the average heat of adsorption in the first layer and E_2 is the heat of liquefaction of the adsorbate. This plot gives a straight line, the slope of which is $\frac{C - 1}{N_m C}$ and the intercept, $\frac{1}{N_m C}$. Equating these quantities to the experimentally determined slope and intercept of the straight line gives two equations which may be solved for N_m. From this value and the cross-sectional area of the adsorbate molecule, the specific surface area of the absorbent may be calculated directly. In order to perform the indicated calculation it is necessary to make an extensive tabulation of data involving rather time-consuming computations. Because the slopes obtained are large numbers, even for materials with large surface areas, one must have at least five or six adsorption points in the relative pressure range 0.05 to 0.35 to determine the intercept accurately. The raw data may be handled in many ways. In some laboratories, for example, the "point B" method is used—i.e., graphical deduction of the point of monolayer formation. However, this and other similar methods involve enough computation to make an analytical solution preferable, in the opinion of the writer.

The method for surface area measurement that is now described has been applied to a wide variety of adsorbents in the writer's laboratory. It depends essentially on the fact that the quantity $E_1 - E_2$ is appreciable. Therefore C is large and $\frac{1}{N_m C}$ is a small number. In fact, it may be assumed that the straight line passes through the origin or that $\frac{1}{N_m C} = 0$. Furthermore, C is large with respect to unity, so that we may write $C >> 1$ and

$$S = \frac{C - 1}{N_m C} \cong \frac{1}{N_m} \qquad (2)$$

Now the quantity of gas in the dead spade may be estimated by assuming the relationship

$$q = p_2 b \qquad (3)$$

where q is the number of moles of gas in the dead space at equilibrium pressure p_2 and b is a constant which is a function of the size of the sample bulb. Let p_1 be the initial pressure and so chosen that upon exposing the sample to the adsorbate (without changing the volume of the measuring system) an equilibrium pressure p_2 is obtained within the relative pressure range 0.15 to 0.35. Then the number of moles of gas adsorbed per gram of adsorbent $(N)_a$ is given by

$$N_a = \frac{a(p_1 - p_2) - bp_2}{g} \qquad (4)$$

where

g = weight of sample

a = constant = $\frac{v}{RT}$

v being the volume of the measuring system, T is the absolute temperature, and R is the gas constant. If nitrogen is the adsorbate at 78° K, $p_0 \cong 760$. Assuming liquidlike packing leads to a value for a molecular area of 16.2 sq. A. or 9.85×10^4 square meters per mole. From Equations 1 and 2,

$$N_m = \frac{1}{S} = \frac{p_2/p_0}{p_2/N_a(p_0 - p_2)} = \frac{N_a(p_0 - p_2)}{p_0} \quad (5)$$

Combining Equations 5, 4, and 2 and inserting the constants for nitrogen gives, for the specific surface area,

$$\Sigma = \frac{[a(p_1 - p_2) - bp_2]\,[760 - p_2] \times 9.85 \times 10^4}{760\,g} \quad (6)$$

Thus, if the constants a and b for a particular system have been determined, one equilibrium point suffices for a surface area measurement.

By comparison of Equation 1 with Equation 5 it may be seen that

$$\frac{\Sigma\ (\text{BET})}{\Sigma\ (\text{Equation 6})} = \frac{p_0/p + C - 1}{C} \quad (7)$$

Thus for $p/p_0 = 0.2$ and $C = 100$, one obtains an error of 4% assuming the BET value to be correct. It is apparent, however, from an examination of Equation 7 that one may not apply the method in cases with much smaller C values without introducing an appreciable error.

It is evident also, that the value of p/p_0 should be high (at least 0.15) to minimize any discrepancy which might result from a low C value. In any case, it is recommended that the method be applied only after some experience with a particular adsorbate-adsorbent system. With these reservations understood, the method may be used in any system which follows the BET equation. Some typical results are given below:

Sample	Specific Surface Area Square Meters/Gram, BET	Equation 6
Silica gel	490	479
African MnO_2	15.0	15.1
Synthetic MnO_2	95.0	99.0
Experimental carbon black	482	465
Shawinigan carbon black	65.2	64.4
$MnCO_3$	26.6	26.3

The object of this work was to underscore an aspect of the BET theory which has not received sufficient attention. It is not suggested, of course, that the technique here described should be used in lieu of the BET theory, which has been very valuable in understanding the mechanism of adsorption. The present concern was with the use of the theory essentially as a surface-measuring device. It is believed that the method described offers a very simple and expeditious means of measuring specific surface area and at the same time gives very satisfactory agreement with the results obtained from a complete adsorption isotherm.

ACKNOWLEDGMENT

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Determination of Small Amounts of Tin with Dithiol

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OF THE organic reagents for the colorimetric determination of tin, dithiol (*2, 3, 6*) appears to be the most promising. Even the dithiol method has been unsatisfactory, however, principally because it has been necessary to compare visually the depth of color (with those of standards) by means of reflected light; therefore the highest precision was not obtainable. Until recently (*4, 5, 7*), the method was not studied photometrically. In a record of the Manhattan Project (*5*), it is reported that, in the absence of a dispersant, the red color of the tin-dithiol complex, in the range of 10 to 60 γ of tin in a volume of 10 ml., remains clear for 15 minutes; thus the transmittancy can be read at 540 mμ. An alternative procedure using agar-agar is also mentioned in (*5*). This solution, however, is unsuitable for absorptiometric measurement. Kenyon and Ovenston (*4*) used Belloid T.D. to disperse the tin-dithiol complex and measured the color spectrometrically. They state that solutions with up to 10 γ of tin per ml. are stable from 1 to 2 hours. Williams and Whitehead (*7*) report Teepol X to be a suitable dispersing agent for the tin-dithiol complex. Using this dispersant, they report that the transmittance of light through the solutions obeys Beer's law up to 16 γ of tin per ml. and that the color is stable for at least 3 hours.

EXPERIMENTAL

The authors obtained some Belloid T.D. but did not have much success with the initial experiments. Teepol X was unobtainable; the authors therefore turned to dispersants easily available in America. A very suitable dispersing agent was found, Santomerse S (30%), made by the Monsanto Chemical Co. This reagent, when used as recommended below, renders the tin-dithiol complex entirely suitable for absorptiometric measurements. It is recommended that the transmittance be read at 530 mμ, since absorption curves (Figure 1) transmit the least at that wave length. A calibration curve prepared from standard solutions as described below, shows that the relationship between the percentage transmittance and the tin concentration, up to 16 γ of tin per ml., is linear; thus, Beer's law is obeyed. Solutions were checked also for stability and found to be stable for at least 3 hours. While a concentration of 1.5 ml. of sulfuric acid in the

final volume of 50 ml. is recommended in the procedure below, this amount can be varied by as much as ± 0.25 ml. of the concentrated acid with no effect on the absorbancy of the solutions. In addition, it was found that 0.30 ml. of hydrochloric acid may be present without any effect. Calibration curves were prepared in the absence of this acid and also in the presence of 0.20 ml. of hydrochloric acid as in the procedure below and were found to be identical. All the work described was done on a Model DU Beckman sprectrophotometer, but the method is suitable for use with other instruments as well.

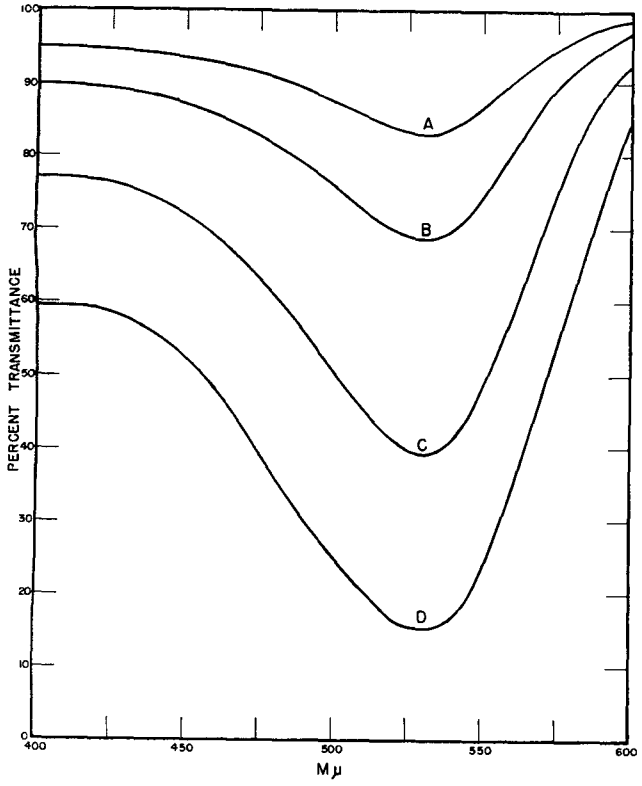

Figure 1. Transmittance Curves for Tin-Dithiol Complex

A. 1.6 γ Sn per ml.
B. 3.2 γ Sn per ml.
C. 8 γ Sn per ml.
D. 16 γ Sn per ml.

Although satisfactorily stable colors can be prepared, a number of the heavy metals (bismuth, copper, iron, nickel, cobalt, silver, mercury, lead, cadmium, arsenic, antimony, molybdenum, etc.) react with dithiol and direct application of the reagent is not feasible without first isolating the tin. While a number of methods are available for isolating tin from various elements, distillation is very effective, since certain elements such as arsenic, antimony, etc., can first be distilled over as the chloride. Tin can then be distilled with a hydrobromic acid–hydrochloric acid mixture which leaves behind the remaining nonvolatile interfering metals.

Briefly, the method consists of destroying organic matter, if present, first distilling over arsenic, antimony, etc., as chloride and then distilling over the tin. The resulting tin solution which is free from interfering elements is treated with sulfuric acid and hydrogen peroxide to remove bromides, the tin is reduced with thioglycolic acid, and the color is developed with dithiol in the presence of Santomerse S as a dispersing agent. The red color is measured at 530 mμ. The effectiveness of the distillation is shown in Table I. Results obtained with Bureau of Standards samples are shown in Table II. Details of the method are as follows.

Table I. Effectiveness of Distillation in Removing Interfering Elements

Tin Added[a], Mg.	Tin Found, Mg.
0.040	0.041
0.080	0.081
0.200	0.200
0.400	0.400
0.800	0.800

[a] In each case tin was added to 5 mg. each of Bi, Fe, Cu, Ni, Co, Hg, Ag, Pb, Cd, As, Sb, and Mo.

Table II. Analysis of Bureau of Standards Samples for Tin

Sample	Tin Reported, Mg.	Tin Found, Mg.
NBS 21d steel	0.077	0.076
NBS 87aluminum-silicon alloy	0.063	0.063
NBS 37d sheet brass	0.97	0.95
NBS 55a open-hearth iron	{0.006[a] 0.007	0.006

[a] Only two values are given for this sample.

Preparation of Calibration Curve for Tin. Standard Tin Solution. Strong, 1 ml. = 0.4 mg. of tin. Weigh and transfer 0.2000 gram of pure tin to a 500-ml. volumetric flask and add 50 ml. of hydrochloric acid. When solution is complete, dilute with water, cool, make up to volume, and mix well. This solution is stable for at least 1 month.

Standard Tin Solution. Weak, 1 ml. = 0.04 mg. of tin. Pipet 25 ml. of the strong standard tin solution into a 250-ml. volumetric flask, dilute to volume, and mix well. This solution is not stable and should be prepared just before use.

Sulfuric Acid Solution (3 to 7). Add 75 ml. of sulfuric acid to 100 ml. of water, cool, transfer to a 250-ml. volumetric flask, dilute to volume, and mix well.

Thioglycolic Acid. Use as received from the Matheson Co.

Dithiol Reagent (0.30%). Weigh 0.15 gram of dithiol (A.D. Mackay, New York) into a 100-ml. beaker, add 8 drops of thioglycolic acid, and then add 50 ml. of sodium hydroxide solution (2%). Stir until the dithiol is completely dissolved. If the solution is not perfectly clear, filter through a dry, very fine-grained filter paper into a clean, dry, glass-stoppered bottle and store in a refrigerator. The solution is stable for 1 week.

Santomerse *S* (30%). Use as received from the Monsanto Chemical Co.

Calibration Solutions. Into four 50-ml. volumetric flasks pipet 5 ml. of sulfuric acid solution (3 to 7), add 5 ml. of water to each, and cool. Pipet 2, 5, 10, and 20 ml. of the standard tin solution (1 ml. = 0.04 mg. of tin) into the four 50-ml. volumetric flasks and then immediately add 5 drops of thioglycolic acid to each and swirl to mix. Dilute to about 45 ml. with water and swirl to mix. Proceed as described below.

Blank Solution. Pipet 5 ml. of sulfuric acid solution (3 to 7) into a 50-ml. volumetric flask, add 5 ml. of water, cool, add 5 drops of thioglycolic acid, and swirl to mix. Dilute to about 45 ml., swirl to mix, and proceed as described below.

Color Development. To the first flask add 2 drops of Santomerse S (30%) and swirl for about 0.5 minute to mix. The flask should be swirled gently to avoid foaming. Proceed in a like manner with the remaining solutions. Pipet 1 ml. of dithiol reagent (0.30%) into the first flask and immediately swirl solution (gently to avoid excess foaming) for 1 minute. Add 8 drops more of Santomerse S and swirl gently for 1 minute. Proceed in a like manner with the remaining solutions. Dilute each solution to volume with water, stopper, invert, and shake for about 5 seconds. Repeat this mixing twice.

The solution may become turbid after the addition of the dithiol reagent or after the addition of the 8 drops of Santomerse S later on. There is no need for concern should this occur, as the solution will become clear after being made up to volume and mixed.

Photometry. Transfer suitable portions of the solutions to absorption cells (1 cm.) and, with the blank solution set at 100% transmittancy, measure the transmittance of the solution at 530 mμ. The color is stable for at least 3 hours.

Calibration Curve. Plot the photometric readings of the calibration solutions against milligrams of tin per 50 ml. of solution.

Determination of Tin. If the material is of a biological or other organic nature, add 25 ml. of sulfuric acid and destroy the organic matter through repeated additions of nitric acid and evaporation to fumes of sulfur trioxide. When the organic matter has been destroyed, cool, wash down sides of beaker with

water, and evaporate to fumes of sulfur trioxide. Repeat twice to ensure complete removal of nitric acid and then cool.

If the material does not contain organic matter, dissolve in hydrochloric acid or sulfuric acid. If nitric acid is required to effect solution, this then must be removed as described in the paragraph above. Tin, especially in the oxidized condition, hydrolyzes readily from a sulfuric acid medium. Hydrolysis of tin will also occur, though not so readily, from a hydrochloric acid medium, if the acid concentration becomes too low. In the event that an aliquot of the sample is to be used for analysis, it is recommended that the entire sample be at least 1 to 9 in hydrochloric acid, even if sulfuric acid is present. With both organic and inorganic materials, a blank should be carried through the entire procedure with the sample.

Introduce 2 grams of hydrazine sulfate (powdered solid) with the aid of a minimum amount of water to the distillation apparatus [see Figure 7 in (*1*)]. Transfer the sulfuric or hydrochloric acid solution of the sample, containing not less than 0.04 mg. and not more than 0.8 mg. of tin, to the distillation apparatus with the aid of not more than 20 ml. of water. Add 10 ml. of phosphoric acid, 20 ml. of hydrochloric acid and increase the sulfuric acid content to a total of 25 ml., if this amount is not already present.

Add 50 ml. of water to a 400-ml. beaker and place under the condenser so that the tip is submerged at least 0.25 inch. The apparatus should be so arranged that the distillate can be removed at any time. Place 150 ml. of hydrochloric acid in the acid bulb, start a slow stream of carbon dioxide through the solution, bring to a boil, and boil gently. When the temperature has reached 165° C., introduce the hydrochloric acid from the bulb into the flask at such a rate that the temperature remains between 155° to 170° C. (about 40 drops per minute). When about 125 ml. of hydrochloric acid has been introduced into the flask, allow the distillation to continue but remove distillate, wash down stem of condenser, and replace the first beaker with a 100-ml. beaker containing 25 ml. of water. When only approximately 1 to 2 ml. of hydrochloric acid remain in the bulb, close the stopcock to shut off the flow of hydrochloric acid, shut off the heat, lower the distillate until free of the condenser, and wash down the stem of the condenser with water. Discard both distillates.

Place a 200-ml. tall-form beaker containing 40 ml. of water under the condenser so that the tip of the condenser is about 0.25 inch from the bottom of the beaker. Place 45 ml. of a mixture of hydrochloric acid (15 ml.) and hydrobromic acid (30 ml.) in the acid bulb; when the temperature has dropped to 130° C., start the heat and begin to introduce the acid from the bulb when the temperature begins to rise. Introduce the acid into the flask at a rate of 30 to 40 drops per minute and maintain the temperature between 137° to 147° C. When only approximately 1 ml. of the acid remains in the bulb, close the stopcock to shut off the flow of acid, shut off the heat, and lower the distillate until free of the condenser. Shut off the flow of carbon dioxide and wash down the stem of the condenser with water.

Pipet 5 ml. of sulfuric acid (3 to 7) into the distillate, stir, place on a hot plate, and bring to a boil. Boil gently for 5 minutes and then cool to room temperature. Add 10 ml. of hydrogen peroxide (30%), stir, cover with a ribbed watch glass, and place on a hot plate. (Some brands of peroxide give a very high blank and should not be used. The authors have found Merck's Superoxol C.P. satisfactory.) Boil the solution gently until it becomes almost colorless or until no more red fumes of bromine are given off. Remove from the hot plate, shift the cover slightly, and add 10 ml. of hydrogen peroxide (30%) in small portions, stirring and waiting for the reaction to subside before each addition. Replace on the hot plate and boil gently until the solution is colorless. Remove from the hot plate and add at one time, an additional 5 ml. of hydrogen peroxide (30%). Replace on the hot plate and boil down to a volume of 5 to 10 ml. Remove and wash down the cover and sides of the beaker with water. Evaporate uncovered and without boiling to fumes of sulfur trioxide, cover with a flat watch glass, and allow to fume for 3 minutes. If the solution becomes slightly tan or brownish from the presence of some organic matter, add a small pinch of ammonium persulfate to destroy this organic matter and allow the solution to fume an additional minute. Remove, allow to cool, wash down the sides of the beaker with water and evaporate uncovered to fumes of sulfur trioxide. Then cover with a flat watch glass and allow to fume again for 3 minutes. Remove and allow to cool.

Add 10 ml. of water to the first beaker, swirl to mix, immediately add 5 drops of thioglycolic acid, and swirl to mix. Proceed in a like manner with any remaining solutions. Transfer each solution to a 50-ml. volumetric flask, quantitatively, with the aid of water. Swirl to mix and cool. The volume in each flask should be approximately 45 ml. Proceed in accordance with the method described above for the preparation of a calibration curve for tin.

Convert the photometric readings for the sample to milligrams of tin by means of the calibration curve.

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Spectrochemical Determination of Germanium in Silicates

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IN AN investigation of germanium-silicon ratios among coexisting silicates, it was found necessary to develop a quantitative spectrochemical method, capable of the determination of germanium contents of the order of 1 p.p.m. in mineral samples of less than half a gram—i.e., 0.5 γ of germanium.

Previous methods using the cathode excitation of solid samples in the direct current arc (*4*, *9*) proved insufficiently sensitive even with an intermittent arc, while such methods as feeding into the arc large amounts of sample mounted on paper strips (*8*), or the distillation of the sample from a furnace into the arc (*7*), required larger amounts of sample than were available.

General methods of chemical enrichment, in which several elements are coprecipitated and examined spectrographically (*6*), have been of limited sensitivity when applied to germanium. Specific methods of enrichment usually involved the distillation of germanium as chloride, and its precipitation as sulfide, prior to its spectrographic determination (*1*, *3*). Geilmann and Brunger (*3*) could detect 0.25 γ of germanium in this way in a semi-quantitative examination.

The present method differs from earlier enrichment methods in the choice of carrier for the coprecipitation of germanium sulfide, and in the choice of internal standard. The sensitivity (0.05 γ) is much greater than in other enrichment methods being of the same order as that found in the cathode excitation of solid samples [1 p.p.m. in a 50-mg. sample, or 0.05 γ (*4*)].

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SPECTROGRAPHIC EXAMINATION

Source, Emitator Unit (Bolidens Gruv A.B., Sweden).
Electrodes, 0.25-inch purified carbon rod (not graphite).

Upper cathode pointed. Lower anode with cavity 1/8 inch in diameter, 1/8 inch deep.

Excitation conditions, 30-second exposure at 7 amperes direct current (200-volt source).

Optical conditions. Intermediate image produced on a diaphragm which passed central portion of arc only, and aperture focused on prism. Seven-step sector mounted immediately before slit. Slit width 0.03 mm. (nominal).

Spectrograph, Hilger large quartz-glass model (Type E).

Plates, Ilford Chromatic and Long Range Spectrum.

Plate density measurement, Hilger nonrecording microphotometer.

DETAILED PROCEDURE

Take enough powdered mineral to contain 0.1 to 2.0 γ of germanium to fumes with hydrofluoric and sulfuric acids, and then to dryness twice with sulfuric acid, exercising care to remove all traces of fluorine. Dissolve the residue in the minimum amount of water and wash into an all-glass distillation apparatus of about 15-ml. capacity. Solution of the residue is assisted by prior warming with a few drops of sulfuric acid. Add 1 ml. of concentrated hydrochloric acid and distill carefully in a stream of air, collecting the distillate under water made ammoniacal, in a small conical centrifuge tube. (In practice, all the germanium was distilled when the distillate had neutralized 8 drops of concentrated ammonia.)

Add 2 ml. of tin solution ($\equiv$ 500 γ of tin) to the contents of the centrifuge tube together with 3 to 5 drops of sulfuric acid, and pass hydrogen sulfide through the solution. Leave corked overnight. Centrifuge, and decant off the supernatant liquid. Add 3 drops of ammonia and 3 drops of 6% hydrogen peroxide to dissolve the precipitate and transfer the resultant solution dropwise to the warmed electrode.

Using the sample electrode as anode and a pointed upper cathode, arc for 30 seconds at 7 amperes (200-volt source.)

The separations, at a constant density of 0.6, of the blackening curves (log I/I_0 against log relative exposure) (*5*) for the lines Ge 3039.06 A. and Sn 3032.77 A., are referred to concentration curves, previously prepared from standard solutions, covering the range 0.1 to 2.0 γ of germanium, precipitated with 500 γ of tin and treated as described.

SOLUTIONS

Germanium, 1 ml. $\equiv$ 200 γ. Dissolve 72.0 mg. of germanium dioxide in a few milliliters of water made alkaline with ammonia. Acidify and dilute to 250 ml. with 2% sulfuric acid. This solution may be further diluted with 2% sulfuric acid to give solutions in which 1 ml. $\equiv$ 20, 2, and 0.2 γ of germanium.

Tin, 1 ml. $\equiv$ 250 γ. Dissolve 387 mg. of ammonium chlorostannate [$(NH_4)_2SnCl_6$] in dilute hydrochloric acid and make up to 500 ml. (to contain about 2% hydrochloric acid).

DISCUSSION

In earlier investigations (*3*) the chloride had been distilled from a hydrochloric acid solution of optimum acidity of 3 to 4*N*, in a stream of chlorine to prevent distillation of arsenic. In the absence of arsenic, air and not chlorine was passed through the distillation apparatus. With this condition, complete distillation of 0.1 γ quantities of germanium did not occur until hydrochloric acid appeared in quantity in the distillate. This may have been due to the hydrolysis of germanium chloride on the walls of the apparatus, and was overcome by continuing distillation until constant boiling acid was coming over. The distillate was collected under water or weak ammonia to prevent volatilization of the germanium from the distillate. To obtain complete recovery of the germanium in as small a volume of distillate as possible, it was necessary to keep the amount of original solution to a minimum. Using the all-glass distillation apparatus of 12- to 15-ml. capacity the final distillate never exceeded 10 ml.

There was no loss of germanium on distillation, within the limits of spectrographic estimation. Four replicate solutions, each containing 0.4 γ of germanium precipitated without prior distillation, returned an average content of 0.40 γ. Four similar solutions, after distillation, returned an average of 0.41 γ. In the preparation of standard working curves the germanium solutions were not distilled each time but were coprecipitated *with* tin and treated subsequently as described.

The sulfide precipitate was very finely divided when first formed but flocculated on standing, and was then readily separated from the liquid by centrifugation and decantation.

Both germanium and tin oxides have similar volatility, ionization potential, etc., and appeared suitable for comparison. In addition their similarity in chemical behavior facilitated the chemical enrichment. The lines Ge 3039.06 A. and Sn 3034.12 A. seemed especially suitable for comparison by virtue of their closely similar excitation potentials. Unfortunately, under the exposure conditions necessary for maximum sensitivity of germanium estimation, and at the concentrations of tin necessary for coprecipitation, the line Sn 3034.12 A. was too intense, and the line Sn 3032.77 A. was used instead.

With the short exposures general background was small, while the unsymmetrical background of the Sn 3032.77 A. line due to the 3034.12 A. line was also small at the steps measured. Therefore no correction for background was made at the concentrations examined. At high concentrations (above 2 γ of germanium) the absolute intensity of the tin spectra seemed enhanced and this, together with the added background from the Sn 3034.12 A. line, may have caused the slight flattening of the working curve at high values. Over the working range of 0.1 to 2.0 γ the curve was linear.

A comparison of alternating current arc, anode, and cathode excitation (all at 7 amperes and 220 volts) showed anode excitation to give far more reproducible results and equally good sensitivity. The use of lower voltages and current gave no appreciable increase in reproducibility or sensitivity.

With anode excitation (7 amperes, 220 volts), a moving plate showed complete removal of germanium and nearly complete removal of tin in the first 5 seconds of exposure, while the last traces of tin were removed in 20 to 30 seconds. Subsequent exposure times were set at 30 seconds.

Wandering of the arc was eliminated largely by the use of a pointed upper cathode. Since the first 5 seconds of excitation were so critical, initiation of the arc by momentary contact was undesirable. In lieu of an automatic triggering device, the arc gap was set, and the arc initiated by touching with a third electrode.

REPRODUCIBILITY AND SENSITIVITY

The lower limit for quantitative estimation was less than 0.1 γ of germanium, while the Ge 3039.06 A. line was visible at concentrations of much less than 0.05 γ.

Reproducibility was of the order of $\pm$10%. Replicate analyses of a rock (pitchstone, Glen Shurig, Arran, Scotland) showed 1.62, 1.40, 1.27, and 1.60 p.p.m. of germanium (1.47 $\pm$ 0.15 p.p.m.), while the glassy base of the pitchstone which should be very similar contained 1.57, 1.63, 1.59, and 1.40 p.p.m. (1.55 $\pm$ 0.09 p.p.m.). A further pitchstone (Judd's No. 1 dike, Arran) contained 1.47, 1.50, 1.72, 1.39, 1.53, 1.37, and 1.56 p.p.m. of germanium (1.50 $\pm$ 0.11 p.p.m.).

Two flue dusts kindly provided by H. J. Cluley (Research Laboratories, The General Electric Co., Ltd., Wembley, England) and analyzed by him using his absorptiometric method (*2*), were examined by this spectrochemical method.

		Germanium, %	
		A	B
Absorptiometric analysis	(H.J.C.)	0.70	0.021
Spectrochemical analysis	(P.G.H.)	0.77	0.025

The results can be considered reasonably satisfactory in view of the thousandfold dilution necessary to bring the samples within the working range of the spectrochemical method.

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Study of Osmium and Ruthenium Distillations

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THE only recorded methods (*4*, *9*) for the quantitative separation of osmium and ruthenium involve selective oxidation by nitric acid to form octavalent osmium oxide. The methods possess one or both of the following disadvantages: The nitric acid must be removed from the ruthenium fraction before ruthenium (VIII) oxide can be volatilized quantitatively and the evolution of nitric oxide in distillations when reducing agents are present may cause low osmium results (*8*). It was desirable to devise entirely different methods of separation and since osmium and ruthenium are usually present as minor constituents, the new methods should be applicable to micro amounts of the metals.

It was known that when ruthenium(VIII) oxide is passed into a solution of hydrogen peroxide, the resulting solution can be boiled without loss of ruthenium. A similar solution of osmium was found to yield osmium(VIII) oxide upon heating and no osmium could be detected in the residual liquid after boiling for a considerable time. This process forms the basis of the separation procedures described. The authors were able to analyze solutions containing both metals by existing gravimetric and by modified colorimetric methods.

APPARATUS

The distillation apparatus used was a modification of that used by Allan and Beamish (*2*) and is shown in Figure 1. The two receiving tubes were of 30- and 20-mm. diameter, respectively.

Qualitative filtrate tests were carried out using the distillation apparatus shown in Figure 2.

Weighings were made using a Sartorius projection reading and an air-damped microbalance and transmittancies were measured with a Lumetron 402EF colorimeter using 20-mm. rectangular cells.

PREPARATION OF STANDARD SALTS AND SOLUTIONS

Ruthenium. Ruthenium sponge supplied by the Baker Platinum Co. was examined spectrographically and was found to contain a trace of iron. The sponge was brought into solution by dry chlorination at a temperature of 650° to 700° C. over a period of 16 hours. The metal was contained in a porcelain boat and was covered with fine sodium chloride crystals to a depth of about 3 mm. After allowing the boat and contents to cool in an atmosphere of chlorine they were transferred, along with a tube sublimate, to a solution of 20 ml. of concentrated sulfuric acid in 25 ml. of water, rinsing with 6*N* hydrochloric acid. The solution was filtered and evaporated until dense fumes were evolved. The filtration separated insoluble chloride which was rechlorinated after reducing to the metal in hydrogen. Ammonium chlororuthenate was then synthesized by the method of Rogers, Beamish, and Russell (*7*) and analyzed by direct ignition in a current of hydrogen. The percentages of ruthenium found in two crops of crystals were 30.24 and 30.43, respectively.

A solution was prepared by dissolving 0.4781 gram of the first crop in 0.5*N* hydrochloric acid, filtering off a small insoluble residue, and diluting with more of the acid to 500 ml. A gravimetric analysis of this solution by the thionalide method (*7*) gave a value of 0.2881 mg. of ruthenium per ml.

Osmium. Ammonium chloroosmate salt was prepared according to the procedure of Gilchrist (*5*) from osmium tetroxide supplied by Johnson, Matthey, and Mallory Co. The salt was analyzed by direct heating in hydrogen, followed by ignition in air. No residue remained after this treatment. The percentages of osmium in two crops of the crystals were 43.15 and 43.17, respectively.

A solution calculated to contain 0.3998 mg. of osmium per ml. was prepared by dissolving 0.9721 gram of the first crop in 0.5*N* hydrochloric acid, filtering, and diluting to 1000 ml. with the same acid. Gravimetric analysis of this solution by the thionalide method (*6*) gave a value of 0.4012 mg. of osmium per ml.

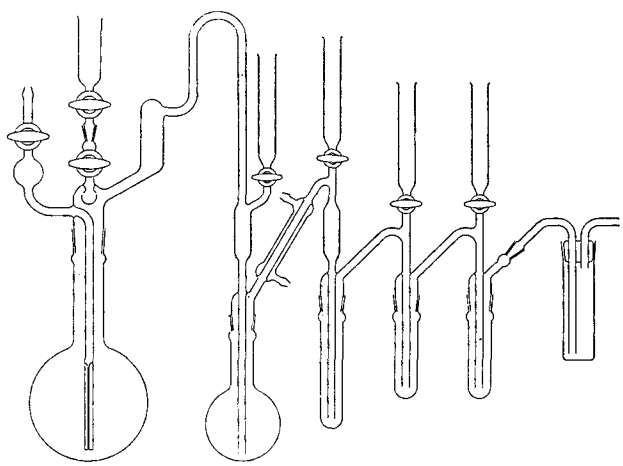

Figure 1. Distilling Apparatus

Filtrate Test. Filtrates from both ruthenium and osmium precipitations and other solutions were examined for the presence of the metals by means of the following procedure.

The filtrate or solution was placed in vessel *A* of the small distillation apparatus and 20 ml. of 70 to 72% perchloric acid were added. Fifteen milliliters of a 10% solution of thiourea in 6*N* hydrochloric acid were placed in receiver *C* and an ice bath was placed around trap *B*. The content of *A* was boiled until dense fumes were evolved, the water collecting in *B*. Throughout the distillation a stream of air was drawn through the system. After a few minutes' further heating the vessel *B* was brought to boiling for a few seconds. A blue or red color appearing in the thiourea solution indicated the presence of ruthenium or osmium, respectively. As little as 8 γ of osmium and fewer still of ruthenium could be detected in this way.

The authors advise strongly against the use of this test when it is applied to alcoholic solutions; dangerously explosive ethyl perchlorate may be formed. A serious explosion occurred when a solution having a high alcohol content was fumed with the acid. Treatment of any organic material with perchloric acid involves a hazard.

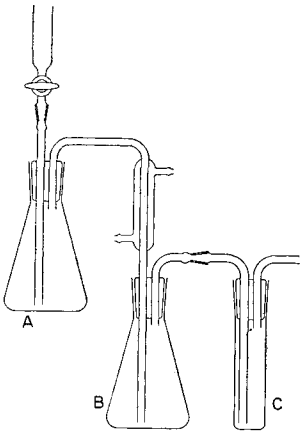

Figure 2. Distilling Apparatus

DISTILLATIONS

Thiers, Graydon, and Beamish (*10*) and Allan and Beamish (*1*) recommend parting lead buttons obtained from the fire-assay with perchloric acid from which osmium and some ruthenium distil. The present authors decided, therefore, to carry out separations of osmium and ruthenium after a preliminary distillation from perchloric acid. It was necessary first to determine the completeness of distillation of osmium from solutions of chloroosmate using perchloric acid as the oxidant.

Table I. Distillations of Osmium

(Osmium taken = 3.99 mg.)

No.	Osmium Recovered, Mg.	Error, Mg.
1	3.98	−0.01
2	3.94	−0.05
3	3.99	0.00
4	4.00	+0.01
5	3.97	−0.02
6	4.01	+0.02
7[a]	3.96	−0.03

[a] Experiment 7 was carried out with 3 mg. of ruthenium added to original sample solution.

Aliquots of the standard solution of ammonium chloroosmate were placed in the distillation flask, 100 ml. of water in the trap, 30 ml. of twice distilled 48% hydrobromic acid in the first receiver, and 10 ml. of this acid in each of the remaining receivers. The receiving solutions were chilled in ice baths. Sixty milliliters of 70 to 72% perchloric acid were added to the distillation flask and the solution was boiled while a current of air was drawn slowly (3 to 6 bubbles per second) through the train. The boiling was continued for 30 minutes after the acid was brought to fuming. Fifteen milliliters of perchloric acid were added to the trap and the resulting solution was boiled for 25 minutes. A bubbler tube containing thiourea solution was placed at the end of the train to detect incomplete retention in the receivers. The contents of the receivers were rinsed with 10% hydrobromic acid into a beaker and evaporated to about a 5-ml. volume. The osmium was determined by precipitation with thionalide. The results of three distillations are given in Table I, Nos. 1 to 3.

Qualitative tests on the trap and pot liquids revealed the absence of osmium.

The effectiveness of hydrogen peroxide as a receiving solution for osmium tetroxide and the completeness of distillation therefrom was investigated.

Aliquots of the standard osmium solution were treated to form osmium tetroxide and the vapors passed through the train in the manner described, except that the hydrobromic acid was replaced by 3% hydrogen peroxide, cooled in ice baths. It was observed that osmium was evolved upon warming the receiving solutions so that when these were transferred to the cleaned and chilled distillation flask, the operation was carried out as quickly as possible. A 5% solution of sulfuric acid was used to rinse the delivery tubes and receivers. It was found that if the sulfuric acid was not in turn thoroughly removed with a water rinse from the tubes and receivers, the osmium-thionalide complex did not coagulate properly. Forty milliliters of 30% hydrogen peroxide and 5 ml. of concentrated sulfuric acid were added to the distillation flask and the solution was boiled gently for 30 minutes. The trap liquid was then boiled for 25 minutes. The trap contained the same liquid throughout the whole procedure. The osmium was collected finally in hydrobromic acid and determined. The results of four samples carried through this procedure are given in Table I, Nos. 4 to 7.

It was expected that when ruthenium accompanied the osmium, the entire quantity would be found remaining in the peroxide solution. This was found to be the case. For small samples (less than 15 mg. of combined metals) no extra hydrogen peroxide was needed in the distillation flask before removal of the osmium. When larger samples were treated, the hydrogen peroxide was often completely decomposed by catalytic action of the noble metals before the osmium could be removed, in which case the ruthenium was no longer kept in the reduced state and distilled in part with the osmium. In these cases extra hydrogen peroxide was added in an attempt to reduce the ruthenium. In each case, the residues left upon volatilization of the osmium after precipitation were subjected to visual or spectrographic examination for the presence of ruthenium.

Attempts to precipitate ruthenium from the pot liquid were unsuccessful, so it was decided to redistil the ruthenium. This was accomplished by the addition of a further 10 ml. of concentrated sulfuric acid and the cautious adding of excess 10% sodium bromate solution, boiling, and collecting the vapors following the method of Thiers, Graydon, and Beamish (*10*). The ruthenium was precipitated with thionalide. Ruthenium sometimes condensed in the reagent inlet in the still head so a 5-ml. rinse of perchloric acid was added to the flask after the acid had been brought to fuming. The results of eight separations following, except where otherwise stated, these procedures are given in Table II.

Since it was necessary to determine very small quantities of the two metals, colorimetric methods of analysis were applied to the distillates. It was advantageous to use the reaction of thiourea with both metals so modifications of the methods of Ayres and Young (*3*) and Allan and Beamish (*2*) were employed.

Solutions of osmium and ruthenium were prepared by diluting aliquots of the standard solutions of osmium and ruthenium with 0.3*N* sulfuric acid to a known volume.

A standard curve was prepared by distilling aliquots of the dilute osmium solution from 20 ml. of perchloric acid, the vapors being passed by means of a current of air through a water trap containing 20 ml. of 1% potassium permanganate solution and three receivers containing, respectively, 15, 5, and 5 ml. of a 2%

Table II. Separations of Osmium and Ruthenium by Gravimetric Determination

No.	Metal	Metal Taken, Mg.	Metal Recovered, Mg.	Error, Mg.
1	Ru	2.88	2.83	−0.05
	Os	3.99	3.95	−0.04
2	Ru	2.88	2.90	+0.02
	Os	3.99	4.08	+0.09
3	Ru	2.88	2.87	−0.01
	Os	3.99	3.96[a]	−0.03
4	Ru	2.88	2.90	+0.02
	Os	3.99	4.00	+0.01
5	Ru	1.44	1.48	+0.04
	Os	9.99	10.01	+0.02
6	Ru	7.21	7.25	+0.04
	Os	2.00	2.01	+0.01
7	Ru	9.14	9.08	−0.06
	Os	8.46	8.41[b]	−0.05
8[c]	Ru	16.60	16.54	−0.06
	Os	21.72	21.80[d]	+0.08

[a] Osmium detected in filtrate.
[b] Osmium passed through last receiver.
[c] 150 ml. of 4.5% hydrogen peroxide was contained in first receiver and three additional receivers each containing 10 ml. of 3% hydrogen peroxide were employed.
[d] Excess reagent precipitated from solution.

thiourea solution in 1 to 1 ethyl alcohol–hydrochloric acid. The perchloric acid was fumed for 5 minutes and the permanganate trap brought to boiling. The two vessels were heated for 10 minutes further after which time the current of air was discontinued and water baths initially at 85° C. were placed about the receivers for 15 minutes. The receiving solutions were transferred to a 50-ml. volumetric flask; 1 to 1 ethyl alcohol–hydrochloric acid was used for rinsing and making up to volume. The resulting solution was filtered through a large Whatman's No. 42 filter paper into the transmittancy cell. A solution of 1 to 1 ethyl alcohol–hydrochloric acid was used as a blank solution.

Samples distilled into 3% hydrogen peroxide in the manner described previously, then distilled into thiourea from the peroxide solution to which 5 ml. of concentrated sulfuric acid were added, gave results in agreement with the standard curve.

A standard curve was prepared by distilling aliquots of the ruthenium solution from perchloric acid.

Twenty milliliters of perchloric acid were added to the solution in the distillation flask and brought to the fuming state. A further 5-ml. portion of acid was then added. The vapors were drawn through a permanganate trap and were absorbed in two receivers containing 15 and 5 ml., respectively, of 1 to 1 ethyl alcohol–hydrochloric acid at room temperature. The pot and trap were heated for the same periods as in the case of osmium. Eight milliliters of 5% thiourea in 1 to 1 ethyl alcohol–hydrochloric acid were added to the first receiver and 2 ml. to the second. The blue color developed almost immediately but not completely until the receivers had been heated in water baths as with osmium samples. The remainder of the treatment was identical to that used in determining osmium except for the filter employed in the transmittancy measurements.

Ruthenium in samples distilled into hydrogen peroxide was distilled into alcohol–hydrochloric acid upon addition of 5 ml. of concentrated sulfuric acid and excess sodium bromate. Most of the bromine formed upon adding bromate to the hydrogen peroxide solution was discharged from the receivers by bringing them to boiling for a few seconds. The remaining bromine was reduced by the thiourea. Attempts to oxidize the ruthenium quantitatively with permanganate were unsuccessful.

Solutions containing aliquots of both the osmium and ruthenium solutions were treated as described and the results of the colorimetric determinations are given in Table III. The original sample solution in Nos. 5 to 7 contained 5 mg. of each of platinum, palladium, rhodium, and iridium as well as osmium and ruthenium.

Table III. Separations of Osmium and Ruthenium by Colorimetric Determination

No.	Metal	Metal Taken, γ	Metal Recovered, γ	Error, γ
1	Ru	101	99	− 2
	Os	200	202	+ 2
2	Ru	502	507	+ 5
	Os	200	202	+ 2
3	Ru	101	106	+ 5
	Os	798	788	−10
4	Ru	502	503	+ 1
	Os	599	599	0
5	Ru	201	201	0
	Os	200	197	− 3
6	Ru	201	201	0
	Os	200	200	0
7	Ru	201	202	+ 1
	Os	200	206	+ 6

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Purification and Properties of Disodium Salt of Ethylenediaminetetraacetic Acid as a Primary Standard

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COMPLEXOMETRIC titrations have increased in popularity during the past few years. Especially, ethylenediaminetetraacetic acid, $[(HOOC.CH_2)_2N.CH_2.]_2$, or H_4Y, and and its sodium salts have been used for titrating directly various di- and trivalent cations, such as the alkaline earths (*1–3, 5, 6, 11, 13–15, 18, 19*), zinc (*3, 12*), nickel (*10*), cadmium (*3*), bismuth (*17*), lead (*8*), and iron (*5, 16*). Most of these titrations were performed on the 1 to 2% error level, but some authors reported errors as low as 0.2% (*6, 8*). Only Schwarzenbach (*3, 18, 19*) and Flaschka (*7*) have used the dihydrated disodium salt of the acid ($Na_2H_2Y.2H_2O$) as a primary standard at the 1% error level, but have given no instructions for its preparation prior to use. All of the other investigators standardized the disodium salt of ethylene diaminetetraacetic acid solution by titrating against a standard solution of the sought-for substance.

It is the purpose of this study to show that the dihydrated disodium salt may be conveniently used as a primary standard for the titration of several common metals at the 0.1% error level. The stability of its solutions and its high equivalent weight are particular advantages.

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PURIFICATION OF DIHYDRATED DISODIUM SALT

Of five manufacturers of the dihydrated disodium salt, none would guarantee the purity or assay value of their product within 99.9 to 100.1%. When three different lots of analytical reagent dihydrated disodium salt (Bersworth Chemical Co.) were analyzed by titration against reliable standard solutions of copper nitrate and by weight loss upon heating, the assay values ranged from 98.0 to 100.0%. The impure samples contained more water-insoluble material than the pure one, and discolored on heating at temperatures considerably below 150° C. It is therefore necessary to purify the available commercial products before using them as primary standards.

A single recrystallization from alcoholic solution served for purification of the poorest of the three lots of reagent grade product manufactured by Bersworth Chemical Co. A nearly saturated aqueous solution of the impure reagent was prepared at room temperature (about 10 grams of the dihydrated salt per

100 ml. of water). Alcohol was added slowly until a permanent precipitate appeared which was filtered off and discarded. The filtrate was diluted with an equal volume of alcohol, and the resulting precipitate was filtered, washed with acetone and then with ether, and then air-dried at room temperature overnight. The yield was around 75%. The product contained excess water, the assay value being about 99.5% $Na_2H_2Y.2H_2O$. The product was stable to heat and could be dried to the anhydrous form at temperatures up to 150° C. without appreciable decomposition. All the following work was performed using several lots of the reagent grade product (Bersworth Chemical Co.) purified in this way.

SOLUBILITY AND VAPOR PRESSURE OF DIHYDRATED DISODIUM SALT

To aid in selecting conditions for purification and drying of the dihydrated salt, rough solubility and vapor pressure data were obtained. In Table I are given solubilities and densities of saturated solutions at various temperatures. At each temperature, the solubility was determined by withdrawing a measured volume of the saturated solution, weighing, diluting quantitatively, and determining the dihydrated salt content by titration of an aliquot with standard 0.01000*F* calcium chloride solution. The vapor pressure–temperature data were obtained for several systems of varying compositions. A static method was used (*20*), and the pressure of the vapor phase was measured at several different temperatures for each system. The results of these measurements are shown in Figure 1. Mercury was used in the manometer for systems I and V, while butyl phthalate was used for the other systems.

A plot of the solubility-temperature data of Table I indicates no breaks or discontinuities. Also, within experimental error, systems ranging in composition from 75 mole % Na_2H_2Y + 25 mole % $Na_2H_2Y.2H_2O$ to 10 mole % Na_2H_2Y + 90 mole % $Na_2H_2Y.2H_2O$ all fall on the same vapor pressure–temperature plot. It therefore seems *probable that there are no stable* hydrates other than the dihydrate within the range of conditions studied.

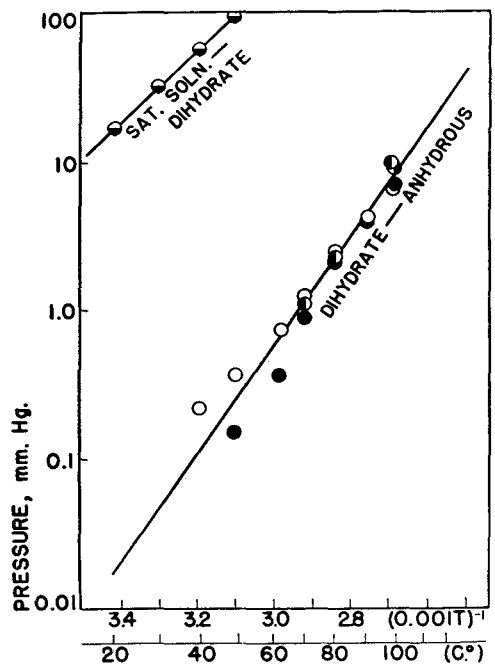

Figure 1. Vapor Pressures of Na_2H_2Y–H_2O Systems at Various Temperatures

System	Code Mark	Mole Percentage Composition Na_2H_2Y	$Na_2H_2Y \cdot 2H_2O$	H_2O
I	◒	..	5	95
II	◐	10	90	..
III	○	25	75	..
IV	●	67	33	..
V	◑	75	25	..

DRYING OF SALTS

Elevated temperature is required to dry the purified, wet dihydrate to a composition corresponding to the formula $Na_2H_2Y.2H_2O$, for the rate of loss of excess water from the recrystallized preparation is too low to be practical at temperatures of 60° C. and below. At 50% relative humidity (25° C.), it is felt that 80° C. is an optimum temperature for safe air-drying of the purified, wet dihydrate to its stoichiometrical composition. The data in Table II show that constant weight is attained within 4 days, and that no further losses occur up to at least 2 weeks. The assay values of two different preparations dried in this way were 100.03 and 100.05% $Na_2H_2Y.2H_2O$. At about 50% relative humidity (25° C.), air drying at 100° C. causes slow conversion to the anhydrous form.

Table I. Solubility of $Na_2H_2Y.2H_2O$ in Water at Various Temperatures

Temp., ° C.	$Na_2H_2Y.2H_2O$, Grams/100 Grams of Soln.	Density of Satd. Soln., G./Ml.
98.0	27.0	1.09
90.0	24.3	1.09
80.0	22.2	1.08
70.0	20.0	1.08
60.0	17.0	1.07
50.0	15.5	1.07
40.0	14.2	1.06
30.0	12.8	1.06
21.0	11.1	1.05
0.5	10.6	1.05

Table II. Change in Weight of Moist, Air-Dried $Na_2H_2Y.2H_2O$ at 80° C.

Wt., Gram	Time, Days
0.8725	0
0.8677	1
0.8667	2
0.8656	4
0.8659	7
0.8657	15

It is also possible to dry the disodium salt quantitatively to the anhydrous form. An inspection of Figure 1 shows that on a humid summer day temperatures above 120° C. are necessary to air-dry the salt to the anhydrous form. At 150° C., conversion to the anhydrous form is rapid and quantitative, but at temperatures over 150° C., charring may occur. The most satisfactory procedure is to heat the disodium salt in a vacuum oven overnight at 120° C. The assay values of two different preparations dried in this way were 100.00 and 99.99% Na_2H_2Y.

From Figure 1, it may be seen that the dihydrate is stable over a wide range of humidities, while the anhydrous form is hygroscopic under ordinary atmospheric conditions. The dihydrate is therefore the preferred form for use as a primary standard, as no particular precautions need be observed in its use. It may be weighed in open air and may be stored in a closed container or over sulfuric acid or calcium chloride desiccants for several weeks with no significant change in weight. However, a slow loss in weight is observed if the dihydrate is stored over phosphorus pentoxide. If the anhydrous form is used as a primary standard, it must be weighed in a closed container and stored over phosphorus pentoxide.

STABILITY OF SOLUTIONS

Betz (*2*) could detect no significant change in titer of 0.01*M* solutions after 8 months. This is confirmed by the authors' findings that 0.01*M* Na_2H_2Y changed less than 0.05% in titer after storage in borosilicate glass or polyethylene bottles for 5 months.

However, a decrease in titer of 1% in four months on storage in soft glass bottles has been reported by Goetz, Loomis, and Diehl (*9*).

TITRATIONS WITH PRIMARY STANDARDS

Solutions of 0.01*F* Na_2H_2Y were prepared from the dihydrate and anhydrous disodium salt as primary standards, and were titrated against standard solutions of copper nitrate, calcium chloride, and zinc chloride, using the high frequency technique to avoid indicator errors and corrections. These titrations are described in another paper (*4*). The results of 20 titrations gave an assay value of 100.00% Na_2H_2Y for the primary standard anhydrous form, and five titrations gave an assay value of 100.05% $Na_2H_2Y.2H_2O$ for the primary standard dihydrate. The relative standard deviation of a single titration was around 0.1%.

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Stoichiometry of Titration of Metal Ions with Disodium Salt of Ethylenediaminetetraacetic Acid

Using High Frequency Technique

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IT IS the purpose of this study to show that direct titrations of some typical metal ions [copper(II), zinc, calcium, and magnesium] with the disodium salt of ethylenediaminetetraacetic acid (Na_2H_2Y) are stoichiometrical over rather wide ranges of conditions, within relative errors of 0.1%. The titration of many kinds of metal ions with the disodium salt of ethylenediaminetetraacetic acid is described in the literature (*1*) usually at error levels of 0.5 to 2%, though in some cases greater accuracy is claimed. Very recently, it has been shown that the disodium salt of ethylenediaminetetraacetic acid standardized against copper as a primary standard reacts stoichiometrically with nickel and iron, at the 0.1% error level (*5*).

In most of these works, the titrant is standardized by titration against known solutions of the sought-for metal, or of another primary standard metal. If properly performed, this method is acceptable for circumventing errors due to reagent impurities, indicator blanks, side reaction, and nonstoichiometrical reaction between the reagent and sought-for substance. However, this method does not easily reveal the magnitudes and sources of the errors, nor does it allow the conclusion that the reaction on which the titration is based is stoichiometrical.

In proving the stoichiometry of any titration, an instrumental method of following the course of the reaction is preferable to the use of chemical indicators. Elimination of the indicator error allows easier resolution of the other errors mentioned above. In the particular case of the direct titration of the alkaline earths in ammoniacal solution, the differential high frequency titration method (*2*) is very advantageous, since the end point break is quite indistinct for the ordinary type of conductometric titration curve obtained by plotting conductance against volume of standard solution.

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TITRATION OF COPPER

A 0.00943*M* solution of the disodium salt of ethylenediaminetetraacetic acid was prepared from the dihydrate as a primary standard (*1*). A standard solution of copper nitrate was prepared from copper foil (assay value, 99.98% copper). The foil was cleaned first with ether, then with dilute nitric acid, then rinsed off with distilled water and air-dried before weighing. The weighed foil was dissolved in 5 ml. of redistilled water and 2.5 ml. of concentrated nitric acid and diluted to 1 liter in a volumetric flask, giving a solution which was 0.01000*M* in copper nitrate and about 0.02*M* in nitric acid.

Titrations of aliquots of the standard copper nitrate with the standard disodium salt were performed in end-point volumes of 80 to 100 ml., since the titration cell required 50 to 100 ml. of solution. Also, the concentration range for adequate sensitivity of the 30-megacycle instrument lies between 0.0001 and 0.01*M* sodium chloride, or solutions of other electrolytes with the same conductances. It was for this reason that the investigation was confined to titrations with 0.01*M*, rather than 0.1*M* solutions. The titration technique was quite similar to that described in an earlier publication (*2*). In the region of the equivalence point, standard disodium salt was added at a uniform rate (about 0.5 ml. per minute), and the rate of change of frequency was followed on a recording milliammeter, giving a recorded differential titration curve.

Results of titrations of different-sized aliquots of standard copper nitrate at different acidities are shown in Table I. Differential curves for some of the titrations of Table I are shown in Figure 1. In Figure 1, abscissas represent volume of standard disodium salt added, and ordinates represent a current which is proportional to the rate of change of conductance produced by

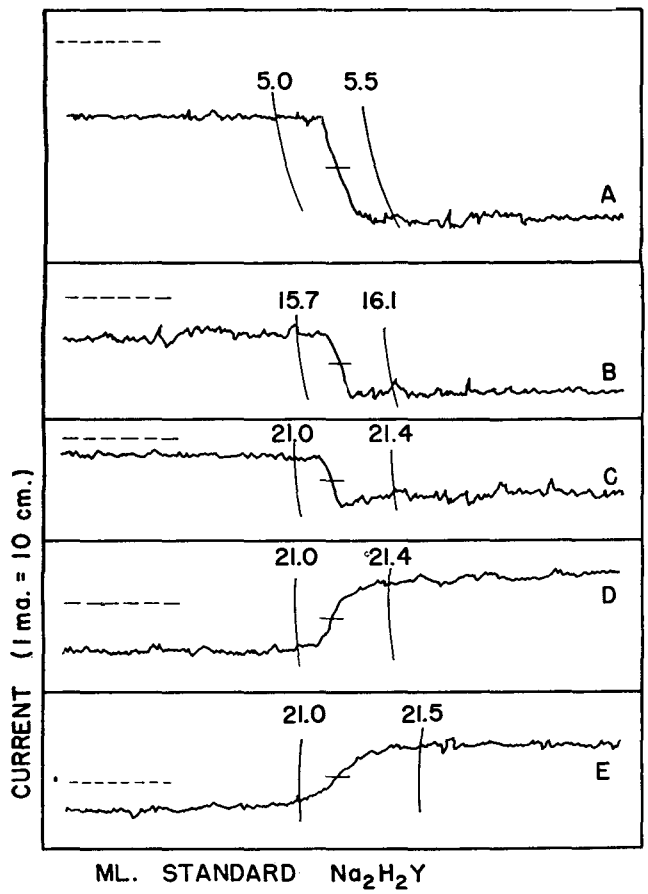

Figure 1. Some Differential Curves for Titration of Aliquots of 0.01000*M* Copper Nitrate with the 0.00943*M* Disodium Salt of Ethylenediaminetetraacetic Acid

For legend, see Table I

adding the disodium salt solution at a uniform rate. A pair of reference volumes is given for each curve, and the dotted ordinate representing a zero rate of frequency change is also shown.

The following conclusions may be drawn from the work associated with Table I and Figure 1.

1. From the 15 titrations in Table I, the median error corresponds to 0.00 ml. of 0.01*M* Na_2H_2Y, and the standard deviation of a single titration corresponds to 0.016 ml. of 0.01*M* Na_2H_2Y. The titration of copper(II) is therefore stoichiometrical within the precision of the work.

2. The titration of copper(II) may be performed with good accuracy down to pH 2.5. At pH below 2.5, the end point becomes diffuse, owing to the decreased stability of the CuY^{--} complex. Also, the magnitude of the high frequency end point change is decreased—i.e., the sensitivity is decreased owing to the high conductance of the acid solution.

3. The titration of copper(II) may be performed with high accuracy in ammoniacal solution. The use of concentrated ammonia is particularly advantageous for the high frequency method, since ammonia does not contribute appreciably to the conductance of the solution. The ammonia may be as concentrated as 2*M* without interference, so long as enough is present to prevent precipitation of cupric hydroxide. End points cannot be successfully established by the differential technique when copper(II) is in the form of a precipitate, apparently because the precipitate does not dissolve rapidly in the region of the end point. The ammonia used as a reagent in this work was redistilled and stored in a polyethylene bottle. When ordinary reagent grade concentrated ammonia was used, there was a blank corresponding to about 0.1 ml. of 0.01*M* Na_2H_2Y per 10 ml. of concentrated ammonia.

Table I. Titration of Aliquots of 0.01000*M* Copper Nitrate Solution[a] with 0.00943*M* Na_2H_2Y

$Cu(NO_3)_2$, Ml.	Other Reagents Added[b]	End Point pH	Na_2H_2Y Required, Ml. Theoretical	Na_2H_2Y Required, Ml. Observed	Error, Ml.	Curve in Fig. 1
1.00	1 ml. redist. NH_3	10	1.06	1.06 1.06	0.00 0.00	
4.98	1 ml. redist. NH_3	10	5.28	5.29 5.29	0.01 0.01	*A*
9.98	1 ml. redist. NH_3	10	10.58	10.57 10.59	−0.01 0.01	
14.99	1 ml. redist. NH_3	10	15.89	15.89 15.87	0.00 −0.02	*B*
19.97	1 ml. redist. NH_3	10	21.17	21.14 21.18 21.13	−0.03 0.01 −0.04	*C*
39.94	1 ml. redist. NH_3	10	42.34	42.34	0.00	
19.97	10 ml. redist. NH_3	11	21.17	21.20	0.03	
19.97	20 ml. 0.02*M* NaOH	3.5	21.17	21.17	0.00	*D*
19.97		2.5	21.17	21.16	−0.01	*E*

[a] Also contains about 0.02*M* HNO_3.
[b] Water added to make end-point volume 80 to 100 ml. in all cases.

Table II. Titration of Aliquots of 0.0100*M* Zinc Chloride Solution[a] with 0.00943*M* Na_2H_2Y

$ZnCl_2$, Ml.	Other Reagents Added[b]	End Point pH	Na_2H_2Y Required, Ml. Theoretical	Na_2H_2Y Required, Ml. Observed	Error, Ml.
1.00	1 ml. redist. NH_3	10	1.06	1.07 1.06	0.01 0.00
4.98	1 ml. redist. NH_3	10	5.28	5.31 5.32	0.03 0.04
9.98	1 ml. redist. NH_3	10	10.58	10.60 10.60	0.02 0.02
14.99	1 ml. redist. NH_3	10	15.89	15.89 15.89	0.00 0.00
19.97	1 ml. redist. NH_3	10	21.17	21.18 21.20	0.01 0.03
24.99	1 ml. redist. NH_3	10	26.50	26.47 26.48	−0.03 −0.02
19.97	20 ml. 0.020*M* NaOAc	3.5	21.17	21.15	−0.02
19.97		2.5	21.17	Obscure	

[a] Also contains about 0.004*M* HCl.
[b] Water added to make end-point volume 80 to 100 ml. in all cases.

TITRATION OF ZINC

A standard zinc chloride solution was prepared from zinc oxide as a primary standard (*4*). Reagent grade zinc oxide was ignited for 2 hours at red heat over a Meker burner. After cooling in a desiccator over calcium chloride, a 0.8138-gram portion was weighed out, dissolved in 5 ml. of water plus 2.0 ml. of concentrated hydrochloric acid, and made up to 1 liter in a volumetric flask, giving a solution which was 0.01000*M* in zinc chloride and about 0.004*M* in hydrochloric acid.

Aliquots of the standard zinc chloride were titrated with the same standard disodium salt used for the previously described titrations of copper nitrate, and using the differential high frequency method for establishing the end point. Results of titrations on different sized aliquots of the standard zinc chloride solution at different acidities are shown in Table II. The differential titration curves from which these end points were taken were very similar to those for copper (Figure 1), and are not reproduced in this paper.

The following conclusions may be drawn from the work associated with Table II.

1. From the 13 titrations in Table II, the median error corresponds to 0.01 ml. of 0.01*M* Na_2H_2Y, and the standard deviation of a single titration corresponds to 0.020 ml. of 0.01*N* Na_2H_2Y. The titration of zinc (Zn^{++}) is therefore stoichiometrical, within the precision of this work.

2. The titration of zinc(II) may be performed with good accuracy down to pH 3.5. At pH below 3.5, the end point be-

comes diffuse, owing to the decreased stability of the ZnY^{--} complex.

3. The titration of zinc(II) may be performed with high accuracy in ammoniacal solution, with the same advantages as described for the titration of copper(II). However, a large excess of ammonia should be avoided: the end point becomes less sharp for ammonia concentrations exceeding 0.5*M*, probably owing to formation of $Zn(NH_3)_4^{++}$ in competition with formation of ZnY^{--} in the region of the end point. A satisfactory procedure is to add enough concentrated ammonia to dissolve any zinc hydroxide which first forms, and then to add about 1 ml. in excess. Redistilled ammonia should be used, or a correction should be applied if ordinary reagent grade concentrated ammonia is used.

TITRATION OF CALCIUM

A standard calcium chloride solution was prepared from a special grade of calcium carbonate as a primary standard. Reagent grade calcium carbonate, and reagent grade calcium carbonate labeled "low in alkalies" could not be reliably used as primary standards for calcium. Analysis of various lots acidimetrically, gravimetrically, and by titration with Na_2H_2Y indicated discrepancies of 0.1 to 0.5% in the calcium carbonate assay values. However, Mallinckrodt standard luminescent (S.L.) grade calcium carbonate is manufactured to meet very high purity standards. When a sample of S.L. grade calcium carbonate was dried for 2 hours at 130° C., an acidimetric assay gave 99.95% calcium carbonate. [The calcium carbonate was dissolved in excess standard hydrochloric acid and the excess hydrochloric acid was back-titrated with standard barium hydroxide.] Also, duplicate analyses of the same lot by measurement of the weight loss on ignition to calcium oxide gave 99.98 and 99.94% calcium carbonate. Since making these tests, another lot of S.L. grade calcium carbonate was used to prepare mixtures of calcium carbonate and calcium sulfate, which have been used as unknowns by students to measure weight loss on ignition. Results over two semesters (140 students) indicate an assay value over 99.95% calcium carbonate. These results on only two lots of S.L. grade calcium carbonate can only indicate the adequacy of this material as a general primary standard for calcium, but it seems reasonable to conclude that the particular lots used are suitable primary standards for testing the stoichiometry of the reaction between calcium and the disodium salt of ethylenediamine tetraacetic acid.

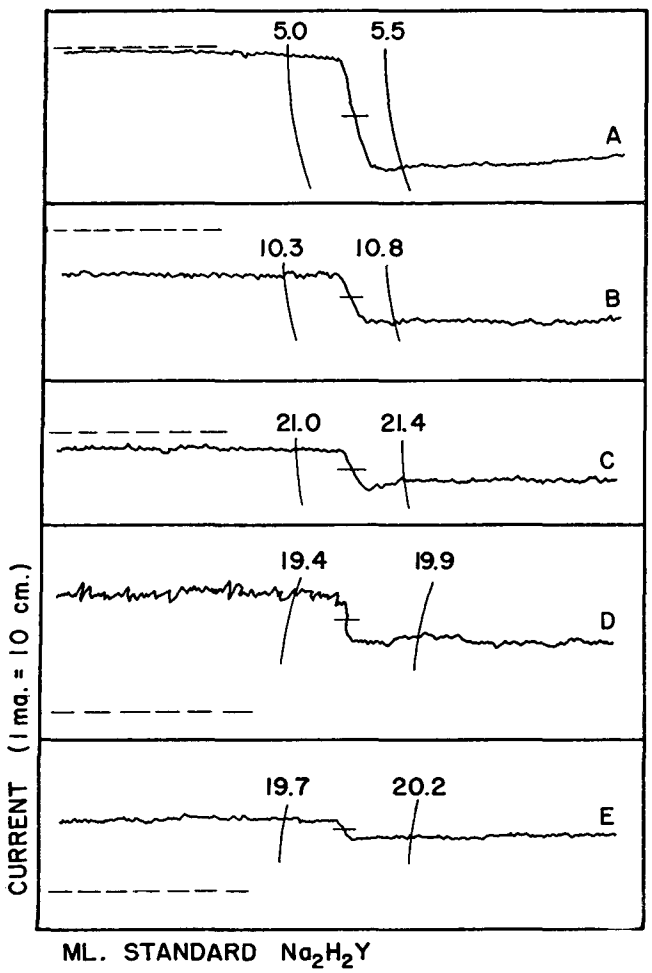

Figure 2. Differential Curves for Titration of 0.01000*M* Calcium Chloride with Standard Disodium Salt of Ethylenediaminetetraacetic Acid

For legend, see Table III

Table III. Titration of Aliquots of 0.01000*M* Calcium Chloride Solution[a] with Standard Na_2H_2Y Solution

$CaCl_2$, Ml.	Other Reagents Added[b]	End Point pH	Na_2H_2Y Required, Ml. Theoretical	Na_2H_2Y Required, Ml. Observed	Error, Ml.	Curve in Fig. 2
1.00	1.0 ml. redist. NH_3	10	1.06[c]	1.07	0.01	
4.98			5.28[c]	5.29	0.01	*A*
				5.31	0.03	
9.98	1.0 ml. redist. NH_3	10	10.58[c]	10.59	0.01	
				10.60	0.02	*B*
14.99	1.0 ml. redist. NH_3	10	15.89[c]	15.89	0.00	
				15.89	0.00	
19.97	1.0 ml. redist. NH_3	10	21.17[c]	21.19	0.02	*C*
				21.18	0.01	
				21.19	0.02	
24.99	1.0 ml. redist. NH_3	10	26.50[c]	26.50	0.00	
				26.53	0.03	
19.97	0.25 ml. redist. NH_3	..	21.17[c]	21.19	0.02	
19.97	10 ml. ethylenediamine	..	21.17[c]	21.16	−0.01	
				21.17	0.00	
19.97	6.0 ml. 0.10*M* NaOH	10	19.67[d]	19.64	−0.03	*D*
19.97	9.0 ml. 0.10*M* NaOH	11	19.97[e]	19.95	−0.02	
				19.94	−0.03	*E*
19.97	10.0 ml. 0.10*M* NaOH	11	19.97[e]	19.96	−0.01	
				20.01	0.04	

[a] Also contains about 0.004*M* HCl.
[b] Water added to bring end-point volume to 80 to 100 ml.
[c] 0.00943*M* Na_2H_2Y.
[d] 0.01015*M* Na_2H_2Y.
[e] 0.01000*M* Na_2H_2Y.

A standard calcium chloride solution was prepared by dissolving an accurately weighed portion of the dried S.L. grade of calcium carbonate in 5 ml. of water plus 2.0 ml. of concentrated hydrochloric acid and diluting to 1 liter in a volumetric flask, giving a solution containing 0.01000*M* calcium chloride and an excess of about 0.004*M* hydrochloric acid. Various sized aliquots of this calcium chloride solution were titrated under various conditions against standard disodium salt solutions. Most of the titrations were made with the same 0.00943*M* Na_2H_2Y used for the previously described copper and zinc titrations, but different standard disodium salt solutions were used for a few titrations. Results are shown in Table III. Differential titration curves for some of the titrations of Table III are shown in Figure 2.

The following conclusions may be drawn from the work associated with Table III and Figure 2.

1. From the 20 titrations in Table III, the median error corresponds to 0.01 ml. of 0.01*M* Na_2H_2Y, and the standard deviation of a single titration corresponds to 0.020 ml. of 0.01*M* Na_2H_2Y. The median error of 0.01 ml. seems fairly significant, but even if significant, it amounts to a relative error of only 0.05% for titration volumes around 20 ml. Hence, it may be said that the reaction between calcium and Na_2H_2Y is stoichiometrical, within a relative error of 0.1%.

2. The titration of calcium with Na_2H_2Y may be performed with good accuracy at pH 8 or higher, and the basicity of the solution may be adjusted with redistilled concentrated ammonia, ethylenediamine, or sodium hydroxide. If sodium hydroxide is used, a large excess must be avoided, or the magnitude of the end point change—i.e., sensitivity—is reduced, even though the sharpness of the end point change is unaffected. See curve *E*, Figure 2. It is not necessary to use carbonate-free sodium hydroxide since moderate amounts of carbonate do not interfere. Addition of 1 ml. of 0.010*M* sodium carbonate to an aliquot of

Table IV. Titration of Aliquots of 0.01048*M* Magnesium Sulfate Solution with Standard Na_2H_2Y Solution[a]

$MgSO_4$, Ml.	Na_2H_2Y Required, Ml. Theoretical	Observed	Error, Ml.
1.00	1.11[b]	1.13	0.02
4.98	5.53[b]	5.58	0.05
		5.56	0.03
9.98	11.09[b]	11.10	0.01
		11.11	0.02
14.99	16.65[b]	16.66	0.01
		16.68	0.03
19.97	22.18[b]	22.17	−0.01
		22.20	0.02
19.97	20.62[c]	20.65	0.03

[a] Water added to make end-point volume 80 to 100 ml. in each case; 1.0 ml. of redistilled NH_3 added 1 to 2 ml. before end point in each case.
[b] 0.00943*M* Na_2H_2Y.
[c] 0.01015*M* Na_2H_2Y.

standard calcium chloride produced no significant change in the volume of standard Na_2H_2Y required for titration. At pH less than 8, the end point becomes diffuse, owing to instability of the CaY^{--} complex.

TITRATION OF MAGNESIUM

Fresenius and Jander (*3*) recommend magnesium sulfate heptahydrate as a primary standard for magnesium, but give no specific directions for treatment prior to use. They also mention that magnesium sulfate as a weighing form for magnesium may be prepared from other salts by addition of sulfuric acid and igniting at 650° to 750° C. Accordingly, primary standard magnesium sulfate was prepared as follows:

Reagent grade magnesium sulfate heptahydrate was dried to a plasterlike mass by heating 1 hour at 110° C., and was then ground to a fine powder. About 1.5 grams of this partially dried material were placed in a platinum crucible and ignited at 650° C. for 0.5 hour. (Tests showed that constant weight was attained within 0.25 to 0.5 hour.) The anhydrous magnesium sulfate was cooled in a desiccator over phosphorus pentoxide. The anhydrous magnesium sulfate was too hygroscopic to permit selection of a certain weight. Instead, the covered crucible plus magnesium sulfate was weighed, then most of the contents were quickly emptied into a beaker, and the covered crucible was reweighed. The weight of magnesium sulfate was found by difference. The magnesium sulfate in the beaker was dissolved in water and made up to 1 liter in a volumetric flask, giving a solution containing 0.01048*M* magnesium sulfate.

Aliquots of this standard magnesium sulfate solution were titrated with results as shown in Table IV. The following conclusions were drawn from the work associated with Table IV.

1. From the 10 titrations in Table IV, the median error corresponds to 0.02 ml. of 0.01*M* Na_2H_2Y, and the standard deviation of a single titration corresponds to 0.025 ml. of 0.01*M* Na_2H_2Y. The median error of 0.02 ml. seems definitely significant, but amounts to a relative error of *only 0.1%* for titration volumes of 20 ml. It may be concluded that the titration of magnesium with Na_2H_2Y is stoichiometrical within a relative error around 0.1%. No attempt was made to resolve and reduce this error, since it was considered passable.

2. The differential curves for the titration of magnesium sulfate are very similar to those for calcium chloride, but end points are less sharp, the inflected portions being spread over 0.3 to 0.4 ml. in most cases. Magnesium chloride solutions give much sharper end points, the inflected portions being spread over only 0.1 to 0.2 ml. for most titrations. The mechanism by which sulfate interferes and spreads out the end point was not investigated.

3. The end point pH should be 10 or higher. Below pH 10, end points become diffuse, because of the instability of the MgY^{--} complex. Care must be used in making the solutions basic. If enough base is added to the original aliquot to neutralize the acid liberated and to give a pH of 10 at the equivalence point, the original solution becomes rather strongly basic. In such cases, a fairly sharp end point is observed several tenths of a millimeter too soon, followed by a diffuse end point in the region of the calculated equivalence point. This phenomenon is more perceptible the longer the time required to reach the end point, and it may be due to binding of some of the magnesium as magnesium hydroxide in the strongly basic solution. No difficulty of this sort was experienced when Na_2H_2Y was added to within 1 to 2 ml. of the end point before adding base; addition of 1 to 10 ml. of redistilled concentrated ammonia gave a single, sharp end point. This disadvantage may be unique to the differential high frequency method and may not be important in other methods of establishing the end point where longer times may be allowed for equilibrium after addition of each portion of standard Na_2H_2Y.

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Semimicrodetermination of Hydroxyl Group in Long Chain Alcohols

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THE common methods for determination of hydroxyl groups involve the use of acylating agents or the determination of active hydrogen (*3*). Neither of these methods distinguishes between long and short chain alcohols. The need arose in these laboratories for a rapid method for the determination of hydroxyl groups in fatty alcohols which would utilize small samples and in which low molecular weight alcohols would not interfere. The method developed is based on sulfation of the alcohol with chlorosulfonic acid, neutralization of the sulfation mixture, and titration of the sodium alkyl sulfate with cetyl trimethylammonium bromide. Since short chain alcohols (C_1 to C_4) give sodium alkyl sulfates which are not titrated by cetyl trimethylammonium bromide under the conditions used, they would not be expected to interfere in the hydroxyl group determination.

EXPERIMENTAL

Since Epton's method (*1*) for determining anionic detergents was directly applicable to the second step of this determination, experimentation on only the first step was necessary. Using 1-octanol, 1-decanol, 1-dodecanol, 1-tetradecanol, 1-hexadecanol, and *N*-(2-hydroxyethyl)lauramide, two variables—concentra-

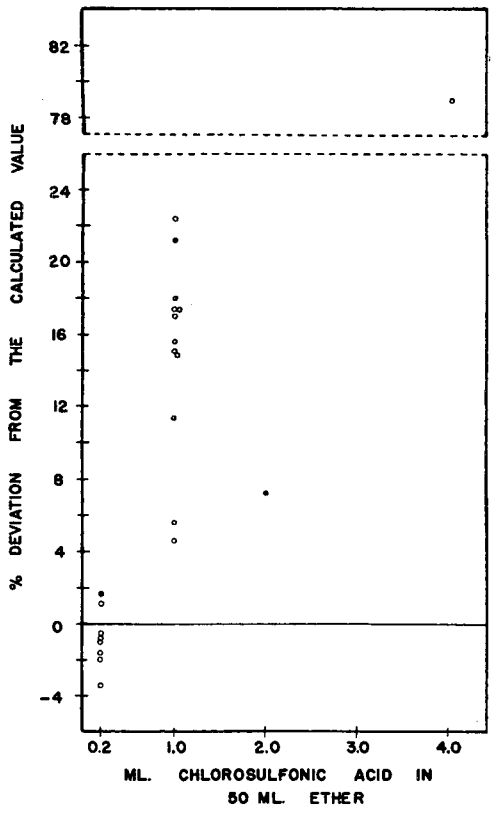

Figure 1. Effect of Chlorosulfonic Acid Concentration

tion of chlorosulfonic acid and sample size—were studied. As shown in Figure 1, a concentration of 0.2 ml. of chlorosulfonic acid in 50 ml. of ether (50-mg. sample size) gives satisfactory results; higher concentrations give high results. Here, the "calculated value" is 1701 divided by the molecular weight. Figure 2 shows that acceptable sample size ranges from 50 to 200 mg. Actually, from the standpoint of convenience—e.g., water solubility of the sodium alkyl sulfate formed—it is desirable that the upper limit be placed at 150 mg.

Reagents. Ether, C.P., anhydrous.

Chlorosulfonic acid, Monsanto Chemical Co.

Methylene blue solution. Methylene blue (0.1 gram, Eastman Kodak P573) is dissolved in 100 ml. of water. A 30-ml. aliquot is transferred to a 1000-ml. volumetric flask, 500 ml. of water, 6.8 ml. of concentrated sulfuric acid and 50 grams of sodium dihydrogen phosphate are added, and the solution is diluted to 1000 ml.

Chloroform.

Cetyl trimethylammonium bromide, Eastman Kodak T5650.

Method. Samples, 0.050 to 0.150 ± 0.0001 gram, are weighed into a 250-ml., wide-mouthed Erlenmeyer flask, 50 ml. of absolute ether are added, and the mixture is stirred until solution is complete. Chlorosulfonic acid, 0.2 ml., is introduced; the tip of the pipet is kept beneath the surface of the ether to prevent spattering and is then washed with absolute ether. Normal sodium hydroxide, 15 ml., is added rapidly with stirring, and the ether is evaporated on the steam bath. With the use of Hydrion paper, dilute sulfuric acid, and 1*N* sodium hydroxide, the pH is adjusted to 8. At no time should the solution be acidic because of the rapid, acid-catalyzed hydrolysis of alkyl sulfates. It is transferred quantitatively to a 250-ml. volumetric flask and made up to volume with water. (In the case of water-insoluble sulfates, ethyl alcohol may be added to facilitate solution, not exceeding 10% ethyl alcohol by volume.)

A 10-ml. aliquot of this solution is pipetted into a 100-ml. glass-stoppered cylinder. Methylene blue solution, 25.0 ± 0.5 ml., and chloroform, 10.0 ± 0.5 ml., are added, and the mixture is titrated with an aqueous solution of 1.500 ± 0.001 grams of cetyl trimethylammonium bromide per liter. In the early stages of the titration the mixture should be agitated by rocking after each addition of reagent, and toward the end, by vigorous shaking. A maximum of 5 ml. of ethyl alcohol may be used to break emulsions. The end point is reached when the blue color is the same intensity in both the chloroform and aqueous layers. (Usually the end point can be detected more accurately by observing the sample in a box whose inner walls are painted a rose color.)

The cetyl trimethylammonium bromide solution (CTAB) used in this work was standardized against a sodium alkylbenzenesulfonate, whose purity was established by elemental analysis.

Table I. Application of the Method to Alcohols and Miscellaneous Compounds

Sample[a]	OH, % Calculated[b]	Ac_2O-pyridine method[c]	Semimicro-method
Monohydric alcohols			
Primary			
1-Butanol	23.0	...	0
1-Butanol	23.0	...	0
1-Hexanol	16.65	...	11.25, 15.13, 13.31[d]
1-Heptanol	14.65	...	11.86, 8.10, 13.25[d]
1-Octanol	13.10	12.92	12.52, 12.44[d]
1-Octanol	13.10	12.25	12.44
1-Decanol	10.77	10.40	10.44, 10.50[d]
1-Decanol	10.77	10.44	11.13
1-Hendecanol	9.86	...	9.80, 9.70
1-Dodecanol	9.14	...	9.00, 9.05, 8.96
1-Tetradecanol	7.95	7.86	8.01, 8.07
1-Hexadecanol	7.04	6.92	6.94
1-Octadecanol	6.31	6.25	6.31
1-Docosanol	5.22	...	5.09
6-Methyl-1-tetradecanol	7.58	...	7.46
6-Methyl-1-hexadecanol	6.64	...	6.70
2-Methyl-1-octadecanol	6.01	...	6.01
4-Methyl-1-octadecanol	6.01	...	5.74
4-Methyl-1-octadecanol	6.01	...	5.95, 6.01
6-Methyl-1-octadecanol	6.01	...	6.25
Secondary			
2-Butanol	23.0	...	11.28
4-Tetradecanol	7.95	8.31, 8.62	7.98
Methylcyclohexanol	14.92	14.23	10.89[d], 11.22
Tertiary			
2-Methyl-2-hendecanol	9.16	...	2.21, 3.09
2-Methyl-2-hendecanol	9.16	...	3.44, 3.44
Glycols, glycerol, and glycerides			
Ethylene glycol	54.9	...	0
Glycerol	55.3	...	0
Monostearin	9.52	9.22	0
Distearin	2.73	2.76	0
1,2-Hexadecanediol	13.18	...	9.49, 11.60
Mercaptans			
Lauryl mercaptan	8.43[e]	7.52	7.28, 7.35
tert-Dodecyl mercaptan	8.43[e]	...	5.43
Olefins			
1-Tetradecane	0	...	1.06, 0.49
Diisobutylene	0	...	0.58
Triisobutylene	0	...	0.76
Tetraisobutylene	0	...	0.55
4-Phenyldodecene	0	...	0.91
Miscellaneous			
2,4,5-Trichlorophenol	8.62	...	0
Cholesterol	4.40	4.48	3.88
Mixture of fatty acid amides of ethanolamine	6.46	...	6.43, 6.52, 6.43 6.28, 6.49
Mixture of 50% 1-hendecanol and 50% glycerol	4.93[f]	...	5.05, 5.08, 4.82
Mixture of 90% 1-dodecanol and 10% ethyl alcohol	8.22[f]	...	8.13
Mixture of 75% 1-dodecanol and 25% ethyl alcohol	6.86[f]	...	6.98
Mixture of 50% 1-dodecanol and 50% ethyl alcohol	4.55[f]	...	5.07
Mixture of 75% 1-dodecanol and 25% trilaurin	6.86	...	6.86
Mixture of 25% 1-dodecanol and 75% trilaurin	2.28	...	2.26

[a] All compounds tested were either purchased, reagent grade chemicals, or distilled preparations made in these laboratories by standard methods. Analyses on different preparations of same compound are entered separately.
[b] % OH calculated = No. OH groups × 1701/molecular weight.
[c] Method used here is identical in all major respects to that of Hafner, Swinney, and West (*2*).
[d] Amount of chlorosulfonic acid used in these determinations was 0.3 ml., rather than 0.2 ml.
[e] % thiol group, expressed in terms of % hydroxyl.
[f] These OH contents were calculated assuming that glycerol or ethyl alcohol contain no OH.

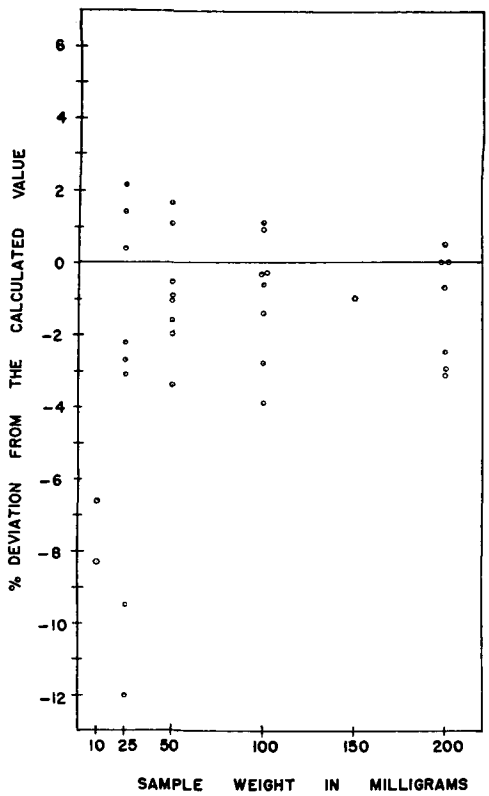

Figure 2. Effect of Sample Size

Calculation.

$$\frac{\text{Ml. of CTAB} \times N \text{ CTAB} \times 1701}{\text{Mg. of sample}} = \% \text{ OH}$$

PRECISION

Ten determinations on a sample of Eastman Kodak 1-dodecanol gave 8.86, 8.92, 8.95, 8.71, 8.77, 8.77, 8.86, 8.89, 8.89, and 8.92% OH (calculated 9.14); estimated standard deviation is 0.079. These values imply a bias toward low results if the sample is pure. By the acetic anhydride–pyridine method this sample contains 9.16 and 9.10% OH. Since another sample of 1-dodecanol gave 9.00, 9.05, and 8.96% OH by the semimicro method, there is no known explanation for the low values obtained above. The results in Table I do not indicate a bias toward low results.

APPLICATION OF THE METHOD

The results of the application of the method to a variety of materials which react with chlorosulfonic acid are tabulated in Table I. Normal, primary alcohols from 1-decanol to 1-docosanol and slightly branched primary alcohols within this range are analyzed accurately. Accuracy (95% with 1-octanol) and precision decrease as the homologous series is descended; 1-butanol is inert. Only three secondary alcohols were analyzed, but the results are consistent with the range established by the primary alcohols. The tertiary alcohol, 2-methyl-2-hendecanol, gave low results, which, very likely, is a general property of tertiary alcohols. As would be expected, the amide group in $RC(:O)NHC_2H_4OH$ does not interfere in the accurate determination of the hydroxyl group.

Ethylene glycol, glycerol, and mono- and distearin are inert. In the light of the inertness of 1-butanol, that of ethylene glycol and glycerine is not surprising. On the other hand, mono- and distearin are sufficiently long chained to be analyzed by this method. The explanation lies in the fact that the ester links hydrolyze during the first step in the determination. 1,2-Hexadecanediol, which bears a structural resemblance to a monoglyceride but lacks its ester link, analyzes for from 70 to 80% of its hydroxyl content.

Mercaptans, olefins, and cholesterol also react, but incompletely, so that they would be expected to interfere in the determination of fatty alcohols. It is entirely possible that an accurate analysis of these interfering compounds could be developed by a slight alteration of the existing method. For example, it is known that the polyisobutylenes are sulfonated in 90% yield by chlorosulfonic acid in ether when a 3-hour reaction time is used (*4*).

Glycerol does not interfere in the analysis of 1-hendecanol, and neither ethyl alcohol (up to 25%) nor trilaurin interferes with the analysis of 1-dodecanol.

Where comparisons were made, the accuracy by this method for the most part was equivalent to or better than that obtained by the acetic anhydride–pyridine method.

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Determination of Organic Halogen with Sodium Biphenyl Reagent

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THE determination of organic halogen is one of the common analyses encountered in analytical work and a voluminous literature exists covering many useful methods. All of the methods for the determination of halogens in organic compounds involve first, decomposition of the sample to reduce the halogen to ionizable form, and second, determination of the halide ion by conventional means. For sample decomposition the Parr peroxide bomb, Winter combustion (*8*), oxygen bomb (*1*), sodium fusion (*3, 4*) and sodium in liquid ammonia (*7*) have all been used in this laboratory for sample decomposition. However, in spite of these and other excellent methods, problems are occasionally encountered for which none of the existing methods is ideally suitable or directly applicable. For a rapid routine control test all of the methods cited are too time consuming. Likewise for samples of low halogen content, in the 0.01 to 1.0% range, the accuracy of the more common methods leaves something to be desired because of the limitation on sample size.

The use of sodium naphthalene and sodium biphenyl for the determination of organic halogen has been suggested by Benton and Hamill (*2*) and Pecherer *et al.* (*5*), respectively. The method described is an extension of the use of reagents of this type in a very simple and rapid analytical procedure. A convenient method for the preparation of the alkali metal biphenyl reagent is described. The limited stability of this type of reagent, which may have been an objection to its use in many laboratories, has been overcome by the manner of storage recommended. The reagent used for decomposition of the organic halide consists of a solution of sodium or lithium biphenyl in ethylene glycol dimethyl ether. Following extraction with water, the halide ion may be determined by conventional volumetric or gravimetric means.

The Volhard chloride titration was used for most of the work described.

EXPERIMENTAL

Apparatus. Standard laboratory apparatus required include 125- or 250-ml. iodine titration flasks, 250-ml. separatory funnels, and burets. A modified separatory funnel as shown in Figure 1 was found convenient for this work. These funnels were made on special order by Corning Glass Co.

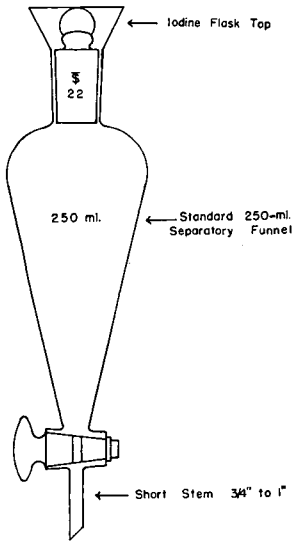

Figure 1. Modified Extraction Funnel

Inside diameter of funnel tip, 3/16 inch

Reagents. Biphenyl, minimum melting point 68° C.; halogen-free.

Ethylene glycol dimethyl ether, halogen-free and must contain <0.3% of water.

Toluene, reagent grade.

Sodium metal, C.P.

Nitric acid, C.P., approximately 3*N*.

Silver nitrate approximately 0.1*N*, standardized.

Ammonium thiocyanate, approximately 0.1*N*, standardized.

Indicator, saturated solution of C.P. ferric alum, 1*N* in nitric acid.

Nitrobenzene, reagent grade.

Reagent Preparation. In a dry 2-liter, 3-necked flask equipped with a sealed stirrer of adjustable speed, an inlet for nitrogen gas, and a reflux condenser, place 300 ml. of dry toluene and 58 grams of metallic sodium. With the stirrer off, and with a slow stream of nitrogen passing through the flask, warm until the toluene starts to reflux and the sodium is entirely melted. Start the stirrer and agitate vigorously until sodium is finely dispersed, then cool to 10° C. or below. Remove the reflux condenser and add 1250 ml. of anhydrous ethylene glycol dimethyl ether (Arapahoe Chemical Co.). With the stirrer operating at moderate speed and with a slow stream of nitrogen passing through the flask, add 390 grams of biphenyl. The reaction should commence within a few minutes, as evidenced by a blue or green color which gradually darkens to black. The temperature should be maintained below 30° C. by means of an oil bath or other cooling medium which would not involve hazard should the reaction flask containing metallic sodium break. The reaction should be complete in 1 hour. The reagent must be protected from air and moisture.

Stability of Reagent. The reagent prepared in the manner described, if protected from moisture and air, will have a useful life of 1 to 2 months when stored at 25° C. It has been found convenient in this laboratory to store the main lot of reagent in a number of 250-ml. bottles with foil-lined caps in a refrigerator at 5° C. Stored in this manner the reagent is usable after more than 1 year.

Analytical Procedure. Place 10 to 15 ml. of dry halogen-free toluene (benzene, ether, or other dry, inert, water-immiscible solvent also may be used) in a clean dry separatory funnel. Add the weighed sample to the funnel stopper, and shake to dissolve. Add 20 ml. of biphenyl reagent, stopper, and shake for 30 seconds (invert and carefully vent the funnel after first few seconds). The funnel contents may become warm. A dark green color should remain. If it clears or turns brown, add more reagent. After 5 minutes, extract with 20 ml. of distilled water, agitating cautiously until the excess reagent is destroyed as evidenced by disappearance of the dark green color. Draw off the lower aqueous layer and then extract twice with 50 ml. of dilute (3*N*) nitric acid. To complete the determination, combine the extracted fractions, add 5 ml. of ferric alum indicator, 1 drop of standard thiocyanate, then silver nitrate in excess (about 5 ml.) as indicated by disappearance of the red color. Add 2 ml. of nitrobenzene and shake vigorously to agglomerate the silver halide. Remove stopper, wash the solution from it back into the flask. Backtitrate with thiocyanate to a permanent reddish-brown color. Record buret readings, including the first drop of thiocyanate.

Determine a blank for each lot of reagent by extracting 20 ml. of the sodium biphenyl with water and dilute nitric acid in the manner described, completing the titration in the usual manner.

Notes. The sample size should be selected to contain 0.02 to 0.15 gram of chlorine or its equivalent.

In handling very volatile samples the sample should be sealed in a thin glass ampoule.

It is essential for quantitative halogen recovery, regardless of the nature of the sample, that complete solution be effected. A wide variety of solvents are available such as benzene, various ethers, dioxane, or petroleum solvents such as heptane.

With samples which are difficultly soluble in cold solvents, it may be advisable to dissolve the sample in a separate flask by gentle refluxing with the best available solvent. In some instances it has been satisfactory to reflux the sample with biphenyl reagent and the solvent for a few minutes. The rate of decomposition of the biphenyl reagent is accelerated at elevated temperatures and under such conditions additional reagent may be necessary.

It was found in the course of running a large number of determinations that the usual 250-ml. separatory funnel was not entirely satisfactory, for two reasons: It was difficult to rinse off the glass stopper after successive extractions without losing some wash solution and the funnel stems did not drain. Both of these difficulties made quantitative extraction uncertain. A separatory funnel of the design shown in Figure 1 having an iodine flask–type top and a short stem which is less prone to remain filled with a column of water, was found more satisfactory.

Analysis of Various Compounds. A number of pure chlorine- and bromine-containing organic compounds were analyzed by the described procedure to check the accuracy and range of applicability of this method. The compounds shown in Table I were selected to include both aliphatic and aromatic halogens of varying structure and stability. In Table II are shown the results obtained on a variety of research samples which in general contained the halogen compound as a minor constituent. Results by a recognized alternative method are also shown.

Effect of Reaction Time. Pecherer, Gambrill, and Wilcox (*5*) have studied reaction times from 10 minutes to 24 hours for the reaction between sodium biphenyl and ethylene bromide and ethylene chloride in gasolines. Their work indicated the halogen recovery to be quantitative at the shortest time studied. Benton and Hamill (*2*) state "the formation of sodium halide is

Table I. Analysis of Chloro and Bromo Compounds

Compound	Halogen, Wt. % Calcd.	Found	Difference, %	Sample Source
1,4-Dichlorobutane	55.82	55.8	0.0	Wyandotte Chemicals Corp. research lab. sample n^{20}_D 1.457
		56.0	+0.2	
1,2-Dichloroethane	71.74	71.6	−0.1	Eastman Kodak Co. White Label as received
		71.8	+0.1	
1-Chloro-3-ethyl-3-methylpentane	23.82	23.8	0.0	Universal Oil Products research sample as received
		24.4	+0.6	
3-(Chloromethyl) heptane	23.82	24.5	+0.7	Universal Oil Products research sample as received
		24.5	+0.7	
Ethyl chloroacetate	28.94	29.2	+0.3	Eastman Kodak Co. White Label as received
		29.3	+0.4	
Hexabromobenzene	86.94	86.4	−0.5	Sample obtained from Dow Research Laboratories
		86.2	−0.6	
4-Chloroaniline	27.80	27.3	−0.5	Eastman Kodak Co. recrystallized
		27.6	−0.2	
1-Bromo-4-fluorobenzene	45.67[a]	45.7	0.0	Eastman Kodak Co. White Label as received
		45.9	+0.2	
4-Chloro-α,α,α-trifluoro-3-nitrotoluene	15.7[b]	15.0	−0.7	Hooker Electrochemical Co.
		14.7	−1.0	
Hexachlorobenzene	74.75	74.7	0.0	Hooker technical grade
		74.7	0.0	
Hexachlorocyclohexane	73.2	72.2	−1.0	Commercial Solvents, technical grade
1-Bromonaphthalene	38.61	38.5	−0.1	Eastman Kodak Co. as received
		38.7	+0.1	

[a] Bromine only determined.
[b] Chlorine only determined.

Table II. Comparison of Sodium Biphenyl Reagent with Other Methods for Analysis of Complex Mixtures

Sample Description	Halogen, %: Sodium biphenyl method	Halogen, %: Check method
Alkyl chloride in a benzene alkylate	1.09 1.10	1.13, oxygen bomb
Alkyl chloride in kerosine	2.31 2.30	2.20, oxygen bomb
Alkylbenzyl chloride in an alcohol	11.5	11.3, Parr peroxide bomb
Alkylbenzyl chloride in an ester	1.68	1.63, Parr peroxide bomb 1.56
Sodium chloroethane sulfonate	20.4	21.3, Parr peroxide bomb
Alkylbenzyl quaternary ammonium salt	11.49 11.35	11.4, Parr peroxide bomb
Alkylbenzyl chloride	10.7 10.8	10.3, Parr peroxide bomb 10.4, gravimetric chloride
Dichloroamine B	31.5 30.9	Specification 31% minimum, Wyandotte Chemicals Corp.
1,2-Dichloroethane in approximately 70-20 ethyl alcohol–water solution	6.8 6.8	See next sample for verification of result
Synthetic sample similar to above	3.24 meq. Cl found	3.24 meq. Cl present

probably instantaneous." On the basis of the author's experimental work it would appear that the reaction is very rapid. Even a 10-second reaction time was sufficient where the sample was readily soluble and no insoluble reaction products were formed. For quantitative recovery of the halogen the sample should be entirely in solution before the reagent is added. In instances where an insoluble reaction product may be formed, as is the case with 4-chloroaniline, a longer reaction period might prove advisable. For most materials the over-all procedure is very rapid, requiring only the time necessary to carry out the various mechanical manipulations.

DISCUSSION

Reagent Preparation. The method of reagent preparation described offers some advantages over previously described procedures (*5*, *6*). By reducing the metallic sodium to a very finely divided form in toluene the reaction with biphenyl in ethylene glycol dimethyl ether is greatly facilitated. The presence of unreacted sodium in the final reagent is highly undesirable because of the potential danger involved during the water-extraction step of the analytical procedure. The presence of a small amount of toluene in the reagent facilitates separation of the water layer when the analytical procedure is carried out. The use of a sodium dispersion of particle size 20 to 50 microns (obtained from National Distillers Chemicals Corp.) in the preparation of the reagent was investigated. Sodium in this form was found extremely convenient and the reaction with biphenyl was rapid, requiring only 15 minutes in comparison to 60 to 90 minutes for the procedure as outlined. Difficulty was encountered in the use of this reagent because of the formation of an emulsion in carrying out the water extraction step. This was attributed to the presence of traces of oleic acid and pyridine used as a stabilizer in the sample of sodium dispersion. Where substantial quantities of biphenyl reagent are used, however, freshly prepared sodium dispersions which require no stabilizers might be employed to advantage.

The literature (*2*, *5*, *6*) mentions several possible solvents for the reagent and the list includes ethylene glycol dimethyl and diethyl ethers, methyl isopropyl ether, dioxane, and tetraethylene glycol dimethyl ether. This study confirmed the results of Pecherer *et al.* (*5*) that ethylene glycol dimethyl ether is the most satisfactory solvent of those mentioned. The stability of either the biphenyl or naphthalene reagent in the corresponding diethyl ether is very poor. The solubility of sodium biphenyl in dioxane is too low for practical purposes.

Lithium Biphenyl. In connection with the studies on reagent stability, lithium biphenyl was prepared in a manner similar to that described for the sodium compound. This reagent gave quantitative recovery of halogen from monochlorobenzene and hexabromobenzene. Results of stability and storage tests indicate the lithium reagent to be more stable than the sodium reagent. In view of the very good stability of the sodium reagent when stored in a refrigerator at 5° C., there is little to recommend the use of the lithium biphenyl reagent.

Analytical Results. The results shown indicate quantitative recovery of chlorine and bromine within the limit of the method for a wide variety of organic compounds including mono and polyhalogen substituted aliphatics, aromatics, and aromatic halides containing other negative substituents which may render the halide particularly refractory. Benton and Hamill (*2*) have indicated that the method appears to have broad applications but indicate several compounds which did not give satisfactory results with sodium naphthalene. Compounds for which the method did not appear applicable included 4-chloroaniline, some nitro-substituted aliphatic and aromatic compounds, and hexabromobenzene. In this investigation quantitative recovery of halogen was obtained with all of these compounds using the biphenyl reagent. No chloro or bromo compounds have been found to date for which the reagent is ineffective. Application to fluorine compounds was not investigated. The method is particularly adapted to samples containing small amounts of halogen as there is no limit on sample size, although it is equally satisfactory with small samples having a higher halogen content. The method is less suitable for samples containing large amounts of substances with reactive hydrogen such as water, alcohol, etc. The procedure is particularly suitable for routine work because it is simple, rapid, and readily adaptable to multiple determinations. A single determination can be made in 20 minutes once a stock of reagent has been prepared. For routine work eight samples per hour can be run. The method has been used in the author's research and control laboratories for the past 5 years.

Accuracy and Precision. In making this study the organic compounds analyzed were in general used as received without special purification; accordingly, an exact assessment of the accuracy of the method has not been made. From the results shown, however, the accuracy is probably 2 parts per 100 or better. A precision study of the method in which 12 replicate analyses were made on *p*-dichlorobenzene gave a maximum deviation of 1.5 parts per 100. The Volhard titration method was used throughout this study for the final determination of ionic halogen. With some samples which tend to give colored extracts potentiometric titration can be employed to advantage.

ACKNOWLEDGMENT

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Determination of Periodic Acid in Highly Colored Solutions

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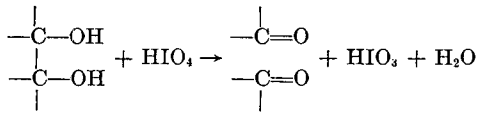
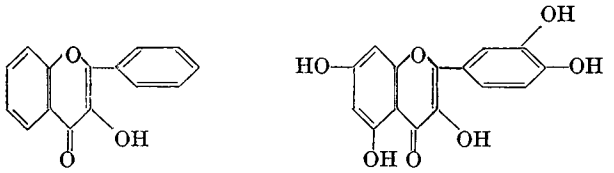
PERIODIC acid has long been known to react quantitatively with 1,2-glycols and their oxidized derivatives according to the following equation:



This reaction has been discussed by Smith (*16*), and the work up to 1942 has been reviewed by Jackson (*4*).



I II

When flavonol(I) and related compounds such as quercetin-(II) are treated with periodic acid, highly colored solutions are produced. It is impossible to determine directly the amount of periodate consumed by these compounds, for the color of the solutions masks the starch iodine end point on which the analytical method depends. For this reason, a method of making these determinations was sought. This paper reports an investigation of the possibility of separating the excess periodate from the colored organic degradation products by means of an ion exchange resin. For a successful separation, conditions under which the resin retains the periodate ions but not the less acidic organic reaction products and a method of quantitatively recovering the periodate from the resin must be found.

EXPERIMENTAL

Resin. The resin used in this work was Amberlite IRA-400, obtained from Resinous Products and Chemical Co. The chloride form was soaked overnight in water and slurried into a large column. The resin was converted to the acetate form by passing sodium acetate solution (2*M*) over the resin until the effluent gave no test for chloride ion. This was followed by a distilled water wash to remove the excess sodium acetate. The resin was removed from the column and stored for use in the experiments. The air-dried resin showed a loss of weight of 14% on drying overnight at 70° C.

Column. Two sizes of columns were used. The smaller ones were constructed from borosilicate glass tubing 8 mm. in outside diameter and about 20 cm. long. To the upper end of the tube was sealed a 6-cm. length of tubing 16 mm. in outside diameter. The narrow portion of the column had a small constriction near the bottom. The resin was held in place by a glass bead seated loosely on the constriction. The larger column was 25 mm. in inside diameter and 20 cm. long, and the resin was supported on a coarse porous glass plate sealed into the tube. Both columns had a stopcock at the bottom to control the flow of liquid. The columns were provided with funnels at the top into which the solutions could be poured. These funnels also served as a part of a continuous flow setup in which a 1-liter separatory funnel served as a reservoir (*10*).

Procedure. The appropriate amount of the resin in the acetate form was soaked in water and slurried into the column. This amounted to 1.6 grams of air-dried resin for the small columns and 13.4 grams for the large columns. In each case, a resin bed approximately 10 cm. in length resulted. The bed was then washed with several column volumes of water. When the column was to be used for the analysis of a reaction mixture in an organic solvent, it was then washed with the solvent to prevent the precipitation of any reaction products. Washing with the organic solvent was accompanied by a considerable shrinkage of the resin bed. The reaction mixture was then poured on the column and allowed to flow through slowly. A nominal flow rate of 1 ml. per minute was used for the small column runs and 3 ml. per minute for the large column runs. The reaction flask and the funnel were washed well first with the solvent and then with water, and the washings were added to the column. The column was then washed again with water. All of the column effluents for these adsorption and washing stages were tested qualitatively for periodate except in those cases in which the color of the solution precluded such a test. In all runs reported here, these tests were negative, indicating that this procedure resulted in the quantitative removal of periodate from the reaction mixture. The periodate was then eluted from the column with 5% potassium hydroxide solution at a flow rate of 2 ml. per minute for the small columns and 5 ml. per minute for the large columns. The column effluents were analyzed as described below. The total volume of effluent collected was about 150 and 500 ml. for the small and large column runs, respectively.

Analytical Method. Periodate analyses were performed according to the standard method which has been described by Jackson (*4*) or Smith (*16*). Sulfuric acid (2*N*) was added to the strongly alkaline column effluent until the solution was barely pink to phenolphthalein. Addition of solid sodium bicarbonate (0.1 to 0.5 gram) discharged the color. An accurately measured excess of standard arsenite solution and 2 ml. of 20% potassium iodide solution were added and the solution was allowed to stand for 10 minutes. The excess arsenite was then titrated with standard iodine solution, starch being added near the end point.

Table I. Recovery of Periodate from IRA-400

Form of resin. Acetate
Eluent. 5% KOH
Flow Rate. 2 ml./min. for runs A, B, and C (small column). 5 ml./min. for runs D, E, and F (large column)

Run	A	B	C	D	E	F
Periodate added, mmoles	1.053	0.913	1.098	23.56	19.05	19.05
Effluent						
Cut 1, volume, ml.	51	50	100	155	403	490
IO_4^- found, mmoles	0.997	0.862	1.091	19.03	18.73	18.83
Cut 2, volume, ml.	50	50	100	315	106	...
IO_4^- found, mmoles	0.036	0.043	0.002	4.23	0.10	...
Cut 3, volume, ml.	50	50	...	...	...	...
IO_4^- found, mmoles	0.005	0.004	...	...	...	...
Total periodate found, mmoles	1.038	0.909	1.093	23.26	18.83	18.83
Recovery, %	98.6	99.6	99.5	98.7	98.9	98.9

RESULTS

Quantitative Recovery of Periodate. A number of experiments were performed in which a known amount of periodate ion was adsorbed from aqueous solution on the resin column and then removed with various eluents. The initial experiments utilized the chloride form of the resin and were unsuccessful because of the loss of 5 to 8% of the periodate. This loss can be accounted for quantitatively by assuming that the periodate is reduced to iodate by some substance in the system. It is believed that the chloride ion is responsible for this reduction of periodate, for in one experiment when a high concentration of chloride ion was present, a gas was formed in the resin bed. This gas had the odor of chlorine and gave a positive test with moist starch-iodide paper. This suggested that quantitative recovery of the periodate might be achieved if the resin were converted to a form which is not oxidized by periodate. The acetate form was decided upon, and its use led to recoveries of 99.0 ±0.6% of the added periodate. This is indicated by the data recorded in Table I.

Capacity of Resin. The break-through capacity of the resin was determined by passing standard periodate solution (0.729*M*) through the column until the periodate appeared in the effluent.

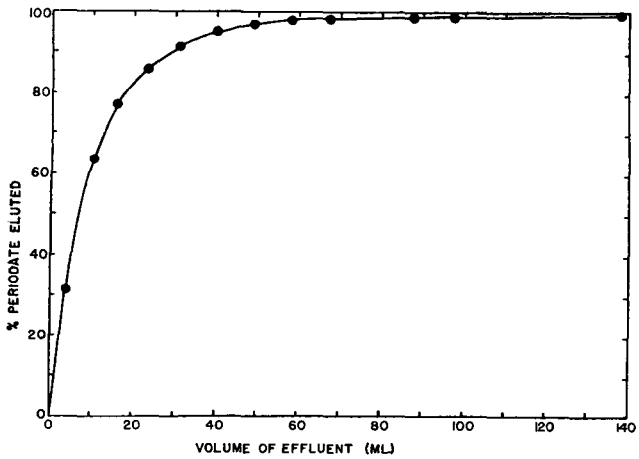


Figure 1. Elution of Periodate from IRA-400

Eluent, 5% KOH
Flow rate, 2 ml. per minute

The small columns containing the usual amount of 1.6 grams of air-dried resin were used for these experiments. It was found that, at a flow rate of 2 ml. per minute, 2.32 millimoles of periodate were adsorbed before break-through, while at a flow rate of 1 ml. per minute, 2.98 millimoles were adsorbed. The flow rate used in the adsorption of the periodate from reaction mixtures was 1 ml. per minute. It can be seen that the amount of periodate used in any of the runs did not approach the capacity of the resin.

Elution of Periodate. It was desirable to know the rate at which the periodate is removed from the resin by 5% potassium hydroxide solution. This was determined by adsorbing 0.726 millimole of periodate on a small column of resin under the usual conditions and eluting with 5% potassium hydroxide. Numerous small fractions of the column effluent were taken and analyzed. An elution curve is shown in Figure 1. The periodate is removed very rapidly, over 90% coming off in the first 30 ml. and 98% in 58 ml. Total recovery in this experiment was 99.3%.

Runs on Compounds of Known Behavior toward Periodate. In order to ensure that the column procedure did not interfere with the stoichiometrical relationships between the periodate and a reactive organic substance, six compounds whose reactions with periodate have been previously investigated were selected for study. The products from the oxidation of all of these substances are colorless, so that analyses could be performed both with and without use of the resin. The results of these experiments are reported in Table II. In all cases, the results obtained with the resin checked closely with the simultaneous experiments carried out without putting the reaction mixture through the column. All reactions were carried out in aqueous solution except that of benzoin where the solvent was a 9 to 1 by volume mixture of ethyl alcohol and ethyl acetate. This solvent has been recommended by Willard and Boyle (*18*) for periodate oxidations.

RUNS ON FLAVONOL AND QUERCETIN

The consumption of periodate by flavonol and quercetin was measured using the ion exchange method. The results of these experiments are reported in Table III.

DISCUSSION

Flavonol. Flavonol, melting point 169° C., was prepared according to the directions given by Reichel and Steudel (*15*). The compound was dissolved in 25 ml. (80 ml. for run C) of the ethyl alcohol–ethyl acetate solvent described above. The periodic acid was added and the mixture was allowed to react at room temperature for the length of time indicated. When the reaction mixture was passed through the column, the organic reaction products appeared in the washings. A light yellow crystalline solid, melting point 171° to 174° C., was obtained on evaporation of the solvent. The characterization of this material will be described elsewhere (*17*). While the action of periodic acid on flavonol produced a colored solution, the solution, if diluted sufficiently, could be titrated directly without use of the ion exchange method. The results of such a titration is reported as run D in Table III.

Quercetin. Quercetin, prepared from rutin by the method of Krewson and Couch (*6*) and having a melting point of 313° to 315° C., was also oxidized at room temperature in 25 ml. of the ethyl alcohol–ethyl acetate solvent. A deep red color rapidly developed in the solution. Within 5 minutes this had changed to a dark yellow. The results clearly indicate a rapid consump-

Table II. Consumption of Periodate

Compound	Sample Used Mg.	Sample Used Mmoles	Periodate Added, Mmoles	Periodate Consumed With resin	Periodate Consumed Without resin	Ratio, Moles HIO_4 / Moles Compound With resin	Ratio, Moles HIO_4 / Moles Compound Without resin	Ratio, Moles HIO_4 / Moles Compound Theoret. value, reference
Ethylene glycol[a]	38.4	0.619	0.729	...	0.613	...	0.99	1 (*8, 9*)
	27.3	0.440	0.729	...	0.439	...	1.00	
	36.8	0.593	0.729	0.597	...	1.01	...	
	33.2	0.535	0.729	0.545	...	1.02	...	
Diethanolamine[b]	66.5	0.632	1.437	...	1.283	...	2.03	2 (*11*)
	48.4	0.461	1.078	...	0.909	...	1.98	
	47.9	0.456	1.078	0.874	...	1.92	...	
	46.4	0.442	1.078	0.864	...	1.95	...	
Sorbitol[c]	15.6	0.0857	0.729	...	0.427	...	4.99	5 (*12, 13*)
	16.1	0.0884	0.729	...	0.437	...	4.94	
	14.2	0.0779	0.729	0.407	...	5.22	...	
	16.2	0.0889	0.729	0.460	...	5.18	...	
Glucose[d]	21.2	0.107	0.729	...	0.536	...	5.01	5 (*2, 7*)
	21.8	0.110	0.729	...	0.551	...	5.01	
	21.4	0.108	0.729	...	0.542	...	5.02	
	26.4	0.113	0.729	0.657	...	4.94	...	
	20.5	0.103	0.729	0.516	...	5.01	...	
Methyl-D-glucopyranoside[e]	40.1	0.206	0.729	...	0.426	...	2.06	2 (*3, 5*)
	47.9	0.247	0.729	...	0.501	...	2.03	
	43.6	0.224	0.729	0.468	...	2.08	...	
	42.8	0.220	0.729	0.456	...	2.07	...	
Benzoin[f]	171.2	0.808	1.078	0.800	...	0.99	...	1 (*1*)
	128.4	0.606	1.078	0.610	...	1.01	...	
	1435[g]	6.77	7.60	6.74	...	1.00	...	
	3358[g]	15.84	25.9	...	15.4	...	0.98	

[a] Redistilled, center cut, b.p. 197°. Total volume of solution, 10 ml., reaction time, 12 hr. at room temp.
[b] Matheson. Total volume of solution, 10 ml., reaction time, 2.5 hr. on steam bath.
[c] Matheson, m.p. 163–5°. Total volume of solution, 10 ml., reaction time, 12 hr. at room temp.
[d] Baker C.P. Column runs and first control, total volume of solution, 10 ml., reaction time, 14 hr. at room temp. Second and third controls carried out in 20 ml. of a periodate solution which was 0.05*M* in sodium bicarbonate as recommended by Reeves (*14*), reaction time, 1.25 hr. at room temp.
[e] Prepared from glucose, m.p. 166°. Total volume of solution, 10 ml., reaction time, 14 hr. at room temp.
[f] Eastman Kodak practical, recrystallized from ethyl alcohol, m.p. 134°. Small column runs: sample dissolved in 25 ml. ethyl alcohol–ethyl acetate mixture, 10 ml. of aqueous periodic acid added, reaction time, 24 hr. at room temp. Large column runs: 80 ml. ethyl alcohol–ethyl acetate mixture, 10 ml. aqueous periodic acid, reaction time, 17 hr. at room temp. Control: 50 ml. ethyl alcohol–ethyl acetate mixture, 25 ml. aqueous periodic acid, reaction time, 36 hr. at room temp.
[g] Large column runs.

Table III. Periodate Oxidation of Flavonol and Quercetin

Compound	Run	Sample Used Mg.	Sample Used Mmoles	Periodate Mmoles added	Periodate Mmoles consumed	Reaction Time, Hr.	Ratio, Moles HIO_4 / Moles Compound
Flavonol	A	121.0	0.508	0.723	0.531	69	1.04
	B	139.3	0.586	0.723	0.558	45	0.95
	C	678.5[a]	2.85	7.60	2.73	17	0.96
	D	112.2	0.473	0.723	0.474	69	1.00
Quercetin	A	43.0	0.142	0.718	0.306	0.25	2.15
	B	41.6	0.138	0.718	0.301	0.50	2.20

[a] Large column run.

tion of 2 moles of periodate. In an experiment which ran for 94 hours, over 3.5 moles of periodate were consumed. A more detailed study of this slower oxidation and an examination of the highly colored reaction products are now in progress.

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Determination of Boron in Boron-Carbon Film Resistors

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PYROLYTIC carbon film resistors are prepared by "cracking" of hydrocarbon gases in a closed chamber and deposition of carbon on suitable ceramic bodies. The nature and properties of the films obtained depend on the reaction conditions as well as the ceramic surface. Recently, it has been found that addition of boron compounds to the reaction mixture produces films with new and interesting properties (*3*). It was, therefore, of great interest to determine the amount of boron in these films, and correlate this with film properties.

The titration of boric acid with alkali in the presence of mannitol has long been used to determine boron (*4*). Wilcox (*6*) titrated 250 to 5500 γ of boron with a precision of 5 to 10% while with known quantities in this range he obtained recoveries of 100 ± 3%. Foote (*2*) obtained recoveries of 100 ± 1% when titrating known amounts of boron in the range 500 to 10,000 γ.

The experience of these workers as well as others (*5*) was useful in developing a procedure suitable for the determination of boron in the coatings of boron-carbon ceramic resistors.

APPARATUS

Beckman Model G pH meter.
Kimble microburet, platinum alloy tip, 5-ml. capacity, 0.01-ml. subdivisions.
Magnetic stirrer.
Kimble Resistant glass beakers and flasks.

REAGENTS

Sulfuric and nitric acids, concentrated, C.P.
Saturated sodium hydroxide, prepared in "boron-free" flask.
Sodium hydroxide, 0.015*N*, carbonate-free.
Mannitol, C.P.
Methyl red indicator solution, 0.1%.
Standard boric acid solution. Dissolve 0.5715 gram of C.P. boric acid in water and dilute to 1 liter; 1 ml. ≈ 100 γ of boron.

PROCEDURE

Weigh a number of clean, dry ceramic resistors containing a total of 200 to 500 γ of boron in the film. Place in a 150-ml. Kimble Resistant glass flask with standard-taper joint. Add 3 ml. of concentrated sulfuric acid, or enough to wet and cover the ceramic bodies, and 5 to 10 drops of concentrated nitric acid. Assemble the flask with a reflux water-cooled condenser and heat the flask gently with a small flame or a Glas-Col heater. Five minutes will usually suffice to dissolve the film completely; more nitric acid may be added dropwise through the top of the condenser, if necessary. Allow to cool, dilute carefully with water, and transfer quantitatively to a 100-ml. beaker. If the volume is more than 50 to 60 ml., evaporate to this volume, by placing in an oven at 125° C.

Table I. Titration of Known Amounts of Boron

B, γ	NaOH, Ml.	γ/Ml.
100	0.61	164
199	1.17	170
299	1.68	178
399	2.25	178
199	1.11	179
199	1.18	168
		Av. = 173; σ = 5.8

Table II. Determination of Boron in Coating of Ceramic Resistors

(All weights in micrograms)

Sample	Weight of Coating	Total B Titrated	B in Coating, %
A18	3080	286	9.3
	3140	638	9.1[a]
	3160	267	8.5
	3020	306	10.1
		Av. 9.3;	σ = 0.6
B50	2470	209	8.5
	2410	675	8.9[a]
	1970	196	9.9
	3410	302	8.9
		Av. 9.1;	σ = 0.5
C100	1250	145	11.6
	1400	150	10.7
			Av. 11.2
D400	790	48	6.1
	640	40	6.2
			Av. 6.2

[a] Corrected for NBS borax added to sample.

Wash the ceramic bodies thoroughly with water, dry at 105° C., cool, and weigh. The weight of the coating is equal to the loss in weight of the ceramics corrected for the loss in weight of a similar number of uncoated ceramic bodies carried through the same procedure.

The boron in the solution is determined as follows. Add 3 drops of methyl red indicator and, while stirring, neutralize with the saturated sodium hydroxide added dropwise from a buret. Add only 1 drop in excess. Make the solution just barely acid with 1 to 10 sulfuric acid and add 2 drops in excess. Cover the beaker, bring to a boil, and boil gently for 5 minutes. Cool in ice water until the solution has reached room temperature.

Set up the beaker for titration with pH electrodes. Adjust the pH with the 0.015N sodium hydroxide to a value between 7.0 and 7.3. Add 3.0 grams of mannitol and titrate with 0.015N sodium hydroxide back to the same pH. The sodium hydroxide is standardized against the stock boric acid solution in exactly the same way. The sample titration is corrected for a blank which has been carried through the entire procedure.

RESULTS

Table I, II, and III give data obtained when boron was determined in known solutions, coatings of ceramic resistors, and in National Bureau of Standards borax, respectively.

DISCUSSION

The above results indicate that boron can be determined in the coatings of boron-carbon resistors with a precision and accuracy within about 5% where the amount of boron titrated varies from 50 to 500 γ.

No account was taken of possible interferences except that due to carbonates. According to Feigl (*1*) telluric and germanic acids are activated by polyhydroxy compounds, but their presence is unlikely. Most cations likely to interfere are similarly not present in the coatings, though they may be introduced from the ceramic. Interferences arising from the latter are minimized by always running uncoated ceramic bodies through the procedure and correcting the sample titration for any blank titration.

Table III. Determination of Boron in NBS Borax Carried through Analytical Procedure

B, Titrated	Recovery, %
321	103.8
593	96.4
517	96.4
617	102.4
372	99.0
859	98.5

Av. = 99.4; σ = 2.8

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Benzilic Acid as a Reagent in Gravimetric Determination of Zirconium

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DURING the investigation of the zirconium-precipitating action of a number of glycolic acid derivatives by Oesper and Klingenberg (*5*) benzilic acid was found to give a very voluminous precipitate. Venkataramaniah and Rao (*6*) investigated this reaction further and found that quantitative precipitation occurs in solutions up to 0.225N in hydrochloric acid solution. The following work, carried out independently, parallels the results obtained by Venkataramaniah and Rao, but also studies the reaction under a wider range of conditions with the resultant extension of the quantitative precipitation beyond the 0.225N hydrochloric acid range. (Contrary to the statement of Venkataramaniah and Rao, benzilic acid was not "totally rejected" as a zirconium reagent by Oesper and Klingenberg. The study of benzilic acid was delayed in favor of the more promising halomandelate reagents.)

REAGENTS

Benzilic acid. Commercial benzilic acid is purified by recrystallization from hot water containing a little hydrochloric acid. By keeping the temperature below 95° C. the main contaminant, benzil, remains as a solid and can be removed from the dissolved benzilic acid by filtration.

Zirconium sulfate solution. Commercial zirconium sulfate tetrahydrate is dissolved in distilled water containing 333 ml. of 12N hydrochloric acid per liter of solution.

Zirconyl chloride octahydrate. Zirconium sulfate tetrahydrate is dissolved in water and zirconium hydroxide is precipitated by the addition of ammonium hydroxide. The gelatinous mass is washed by reverse filtration until aliquots of the wash solution give negative tests for sulfate ion. The washed zirconium hydroxide is dissolved by the addition of hydrochloric acid, heating if necessary. White, tetragonal crystals of zirconyl chloride octahydrate are obtained by evaporation of the solution.

Zirconyl chloride solution. Zirconyl chloride octahydrate is dissolved in distilled water containing 250 ml. of 12N hydrochloric acid per liter of solution.

EXPERIMENTAL

Quantitative Action of Benzilic Acid. After considerable experimentation the following procedure was developed for the determination of zirconium.

To a solution containing 0.0010 to 0.0600 gram of dissolved zirconium in a 250-ml. beaker are added 15 ml. of 12N hydro-

Table I. Analysis of Zirconium Solutions by Various Methods

Method	Reference to Procedure	$Zr(SO_4)_2$ Solution, Gram ZrO_2/Ml.[a]	$ZrOCl_2$ Solution A, Gram ZrO_2/Ml.[a]	$ZrOCl_2$ Solution B, Gram ZrO_2/Ml.[a]
Benzilate	..	0.0104	0.0089	0.0278
p-Bromomandelate	(*5*)	...	0.0089	0.0278
p-Chloromandelate	(*5*)	...	...	0.0279
Cupferrate	(*3*)	0.0104	...	0.0279
Hydroxide	(*3*)	0.0104	0.0090	0.0280
Mandelate	(*5*)	0.0104	0.0089	0.0278
Phosphate	(*3*)	0.0104	0.0089	...

[a] Based on average of nine analyses.

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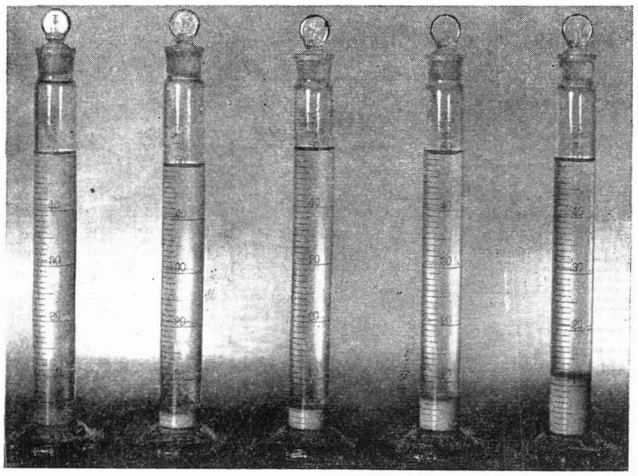

Figure 1. Volume of Precipitate Produced with Zirconium by Various Reagents

Zirconium as ZrO_2, 0.0278 gram per ml.
Time of standing, 24 hours
Left to right. Diammonium hydrogen phosphate, mandelic acid, *p*-chloromandelic acid, *p*-bromomandelic acid, benzilic acid

chloric acid and water to give a total volume of 50 ml. This is heated to boiling and 100 ml. of a hot 2% solution of benzilic acid is added. (Solid benzilic acid may also be added to the solution diluted to 150 ml. with distilled water.) A milky precipitate appears immediately. This is digested at 95° C. for approximately 10 minutes, whereupon the precipitate coagulates into flocks, then becomes more granular and collects into a coherent mass towards the center of the beaker. The precipitate is filtered while hot on a No. 40 Whatman filter paper and washed five or six times with hot water. (Gooch or Selas crucibles may also be used.) The paper and contents are dried, charred, and ignited in a muffle furnace at 1000° C. using porcelain or platinum crucibles. The ignited material is then cooled and weighed.

Table I compares the results obtained with solutions of zirconium sulfate and zirconyl chloride using benzilic acid and other reagents.

Weighting Effect of Benzilic Acid. A comparison of the amount of precipitate obtained from equivalent amounts of zirconium when treated with various reagents is shown in Figure 1. The methods of precipitation were the same as those used to obtain the data in Table I.

Effect of Acidity and Foreign Ions. In studying the effect of acidity on the precipitation the results agreed approximately with those reported by Venkataramaniah and Rao (*6*)—i.e., using 1% benzilic acid, the precipitation became incomplete as the acidity was raised beyond 0.23*N*. However, it was observed that this effect could be counteracted by increasing the concentration of the benzilic acid. This is strikingly illustrated by the photographs in Figures 2 and 3, and the analytical results summarized in Figure 4. This data was used in selecting the conditions of precipitation as outlined above. The value of using a higher acidity lies in the fact that precipitation of foreign ions is noticeably lessened. This is illustrated by the data in Table II. Part A represents the results obtained by the method previously described using 2% benzilic acid solutions, but with no added hydrochloric acid. Part B represents results obtained using 2% benzilic acid solutions with 15 ml. of hydrochloric acid per 150 ml. of solution. In this case tin and iron were found to interfere no longer.

Application to Steel Samples. Five steel samples containing silica, sulfur, phosphorus, manganese, carbon, iron, chromium, nickel, molybdenum, niobium, tungsten, cobalt, and zirconium were analyzed by the procedure developed by Klingenberg and Papucci (*4*) except that benzilic acid was used as the reagent. The results are given in Table III.

Table II. Determination of Zirconium in Presence of Foreign Ions

Ion added	Amount, gram	ZrO_2 present, gram	ZrO_2 found, gram	Number of determinations
	A. Precipitation in Low Acid Concentration			
Al	0.25	0.0089	0.0088	12
Ca	0.50	0.0089	0.0086	12
Ba	0.50	0.0089	0.0088	12
Ti	0.43	0.0089	0.0178	18
Th	0.65	0.0089	0.0084	15
Fe	0.50	0.0089	0.0146	27
	B. Precipitation in 10% Hydrochloric Acid			
Al	0.25	0.0278	0.0278	12
Ca	0.50	0.0278	0.0277	12
Fe	0.50	0.0278	0.0278	12
Cu	0.50	0.0278	0.0278	9
Ni	0.50	0.0278	0.0278	9
Mn	0.50	0.0278	0.0278	9
Bi	0.50	0.0278	0.0278	9
Ce	0.18	0.0278	0.0278	9
Sn	0.25	0.0278	0.0277	12
Zn	0.50	0.0278	0.0277	12
U	0.20	0.0278	0.0277	12
Th	0.65	0.0278	Erratic	18
Ti	0.43	0.0278	Erratic	27
V	0.20	0.0278	Erratic	27

Table III. Determination of Zirconium in Steel Samples

Method	Sample No.	Wt. ZrO_2, Gram	Zr, %	No. of Detns.
Mandelate	2034	0.0018	0.07	6
p-Bromomandelate		0.0018	0.07	6
p-Chloromandelate		0.0018	0.07	6
Benzilate		0.0018	0.07	6
Mandelate	2154	0.0030	0.07	6
p-Bromomandelate		0.0030	0.07	6
Benzilate		0.0030	0.07	6
Mandelate	2058	0.0017	0.06	6
p-Bromomandelate		0.0017	0.06	6
Benzilate		0.0016	0.06	6
Mandelate	2225	0.0042	0.11	6
p-Bromomandelate		0.0042	0.11	6
Benzilate		0.0044	0.11	6
Mandelate	2156	0.0041	0.10	6
p-Chloromandelate		0.0041	0.10	6
Benzilate		0.0041	0.10	6

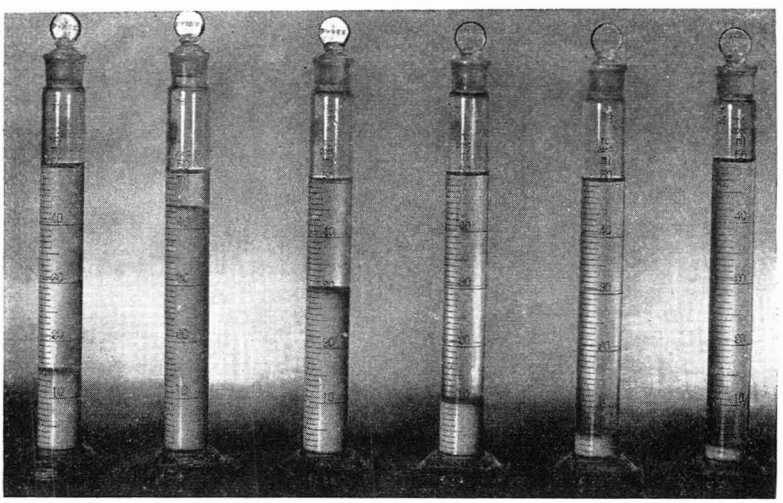

Figure 2. Inhibition of Precipitation of Zirconium with 1% Benzilic Acid by Increasing Acidity

Zirconium as ZrO_2, 0.0278 gram per ml.
Time of standing, 15 minutes
Left to right. No added HCl, 5% HCl, 10% HCl, 15% HCl, 20% HCl, 25% HCl

Possibility of Direct Weighing. Because the amount of zirconium in the zirconium benzilate precipitate is rather small, it would be advantageous if the zirconium could be determined by weighing the zirconium benzilate as such. To test this, the procedure described above was followed, except that Selas crucibles replaced the filter paper, and filtration and washing were carried out with the aid of suction. After washing free of excess benzilic acid the precipitates were dried, weighed, ignited to zirconium oxide, and weighed again. As the data in Table IV show, no reproducible results could be obtained with the zirconium benzilate precipitates although the same precipitates when ignited to zirconium oxide were reliable.

Composition of Zirconium Benzilate. In connection with the preceding work on the direct weighing of zirconium benzilate an investigation of the composition of the precipitate was undertaken. Zirconium benzilate was prepared as described above, collected on Selas crucibles using suction, and washed as follows: (*a*) with hot water, (*b*) with 20% ethyl alcohol, and (*c*) with 2*N* hydrochloric acid solution. The precipitates were then analyzed for carbon, hydrogen, zirconium, and oxygen (by difference). The results are given in Table V. Although no definite conclusions can be reached from the data, the empirical formulas approximate the coordination types postulated by Blumenthal (*1*) and Feigl (*2*). The basic salt type of compound formulated by Venkataramaniah and Rao (*6*) is ruled out for zirconium benzilate prepared under the conditions described in this work.

Table IV. Determination of Zirconium as Zirconium Benzilate

Zirconium Oxide Taken, Gram	Zirconium Benzilate, Gram	Zirconium Oxide Calcd. from Zirconium Benzilate,[a] Gram	Zirconium Oxide Obtained by Ignition, Gram
0.0279	0.2178	0.0249	0.0278
0.0279	0.2172	0.0260	0.0276
0.0279	0.2209	0.0272	0.0278
0.0279	0.2566	0.0315	0.0280
0.0279	0.2131	0.0262	0.0278
0.0279	0.2238	0.0274	0.0279
0.0279	0.1934	0.0237	0.0278
0.0279	0.2081	0.0255	0.0276
0.0279	0.2091	0.0257	0.0280
0.0279	0.2118	0.0260	0.0278
0.0279	0.2151	0.0264	0.0277
0.0279	0.2034	0.0250	0.0279
0.0279	0.2154	0.0264	0.0276
0.0279	0.2180	0.0266	0.0277
0.0279	0.2183	0.0268	0.0275
0.0279	0.2211	0.0272	0.0279
0.0279	0.2564	0.0215	0.0280
0.0279	0.2235	0.0274	0.0277
0.0279	0.2242	0.0275	0.0278

[a] Zirconium oxide content calculated on assumption that original precipitate is zirconium tetrabenzilate (G.F.—0.1229).

Table V. Elemental Analysis of *Zirconium Benzilate*

	Carbon, %	Hydrogen, %	Zirconium, %	Oxygen, %	Empirical Formula
Sample *a* (washed with hot water)	65.5	4.1	12.0	18.4	$C_{41}H_{31}O_9Zr$
Sample *b* (washed with 20% ethyl alcohol)	65.6	4.3	9.5	20.6	$C_{52}H_{44}O_{12}Zr$
Sample *c* (washed with 2*N* hydrochloric acid)	64.5	3.4	9.5	22.6	$C_{51}H_{32}O_{11}Zr$

Empirical formula suggested by Feigl. $C_{56}H_{40}O_{12}Zr$ or $C_{56}H_{44}O_{12}Zr$.
Empirical formula suggested by Blumenthal. $C_{42}H_{33}O_{10}Zr$.
Empirical formula of Venkataramaniah and Rao. $C_{14}H_{12}O_4Zr.4H_2O$.

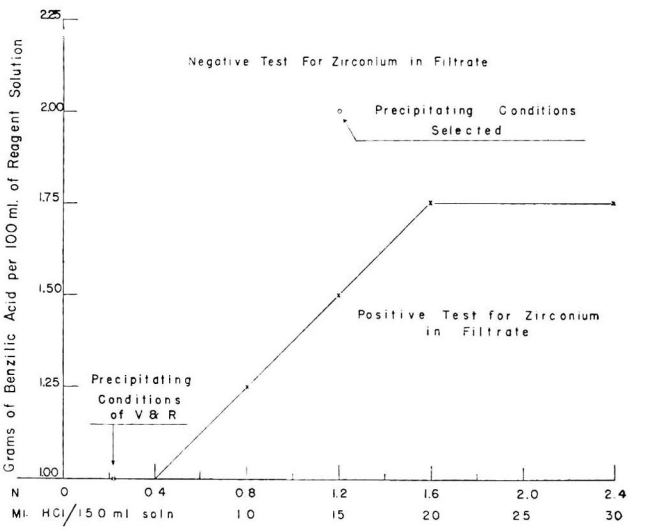

Figure 4. Effect of Acidity on Precipitation of Zirconium with Benzilic Acid

X. Points of reproducible quantitative results where 0.0278 gram per ml. of ZrO_2 taken equaled 0.0278 gram per ml. of ZrO_2 obtained, based on average of six analyses.

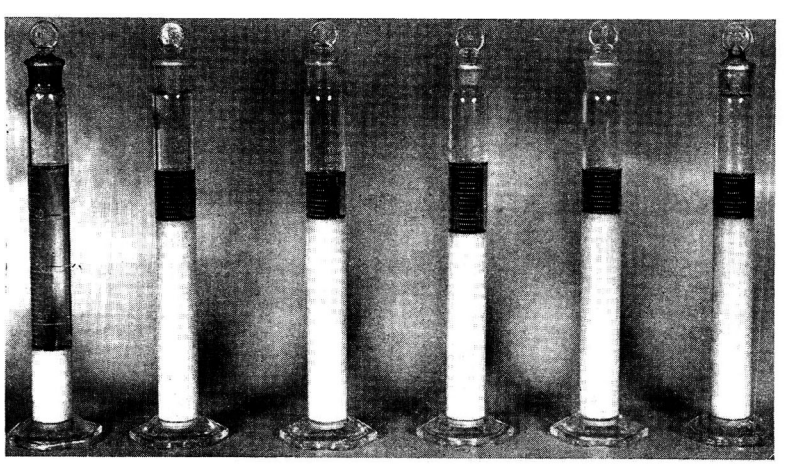

Figure 3. Precipitation of Zirconium by Benzilic Acid in Solutions of Increasing Acidity and Benzilic Acid Content

Zirconium as ZrO_2, 0.0278 gram per ml.
Time of standing, 15 minutes
Left to right. No added HCl, 5% HCl, 10% HCl, 15% HCl, 20% HCl, 25% HCl

SUMMARY

Benzilic acid can be used as a reagent for the gravimetric determination of zirconium and will precipitate zirconium quantitatively with increasing acidity if the quantity of benzilic acid used is also increased. The zirconium benzilate precipitate filters, washes, and ignites readily; and the voluminous nature of the precipitate is advantageous in the detection and determination of small quantities of the element although direct weighing is not possible. Benzilic acid also acts selectively in the presence of many of the foreign ions normally appearing with zirconium and can be utilized in the determination of zirconium in steel alloys.

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A Convenient Technique for Micro Zerewitinoff Determinations

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IN THE course of the synthesis of a number of 1-methylcycloalkanols it was observed that certain of the cycloalkanones reacted peculiarly. Instead of undergoing the usual rapid addition of the methyl Grignard reagent, these ketones resisted the addition and liberated large quantities of methane, presumably as a result of reaction with hydrogen in the alpha position (*2*). It appeared desirable to investigate this phenomenon by applying the quantitative methods of the Zerewitinoff determination (*11*, *13*). Because certain of the cyclic ketones are difficult to obtain, it was decided to operate on a micro scale in order to conserve the stock of these materials. Accordingly the authors attempted to apply the procedure and apparatus described by Siggia (*10*).

Unfortunately, they were unable to obtain consistent results for the quantity of Grignard reagent which was adding to the carbonyl group and that which was reacting to give the enolate. A careful examination of the procedure revealed that the difficulty was due to the solubility of methane in the solvents utilized. This difficulty has been previously noted (*6*, *7*, *12*). The various procedures which have been utilized for analyses of this kind have been reviewed in a recent publication (*9*).

In an apparatus of small volume, such as that described by Siggia (*10*), the partial pressure and, therefore, the solubility of methane will vary greatly from determination to determination, unless the quantity of methane liberated is controlled within relatively narrow limits. This is difficult to accomplish in determinations which involve variable percentages of addition to a functional group and reaction with active hydrogen.

One possible solution is to increase the volume of the apparatus so that the partial pressure of the methane liberated becomes very small and its solubility becomes negligible. This procedure is apparently the basis of certain of the older methods which have been utilized (*4*, *5*, *8*). However, it introduces the possibility of large errors unless the temperature is carefully controlled within very narrow limits.

It was finally decided to modify the apparatus of Siggia to permit evacuation and subsequent introduction of a methane atmosphere. The solubility of methane in the solvent could be readily determined. By operating under a constant methane atmosphere, the solubility was independent of the quantity of methane liberated in the course of the analysis. This modification permitted reliable utilization of the procedure for the study in question as well as for other typical analyses based on reactions of the Grignard reagent.

APPARATUS

In the course of the investigation it proved advantageous to introduce certain additional modifications and simplifications into the apparatus. As finally evolved, the apparatus is simple (Figure 1); yet it permits satisfactory analyses on the micro scale with considerable economy of time and effort. Thus the utilization of evacuation permits the drying of the equipment to be completed in a few minutes *in situ* and eliminates the need for extensive drying in an oven. Moreover, the evacuation permits introduction of the methane atmosphere within a matter of seconds in place of the tedious flushing procedure previously used to provide a nitrogen atmosphere free of oxygen.

In order to keep the total volume of the apparatus as small as possible, the reaction vessels (Figure 2, *A*) were constructed from standard-taper 19/38 male joints. In this way, possible contamination of the solution from stopcock grease was avoided. Moreover, the economy of the design permitted the use of a number of reaction flasks, so that several determinations could be carried out consecutively without delays resulting from cleaning and preparing a single reaction vessel. The vessel was constructed with a flat bottom to permit ready weighing and easy stirring by means of a glass-enclosed iron rod.

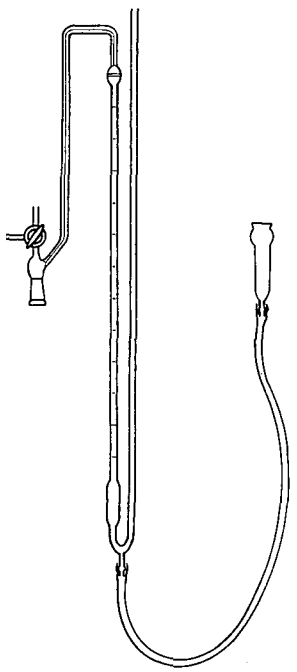

Figure 1. Modified Apparatus for Zerewitinoff and Related Determinations

The volume of the reaction vessel was approximately 7.5 ml. Since the volume was so small, minor variations in the temperature could be tolerated without significant error in the results. Moreover, the design of the apparatus permitted the reaction bulb to be immersed in a beaker with water so that the reaction vessel could be quickly heated to complete the reaction and then as quickly brought back to 25° C. for measurement of the gas liberated.

The reaction vessel fitted into an outer joint, *B*, carrying a three-way stopcock, *C*. The horizontal arm of this stopcock was used for evacuation by a pump and for filling the apparatus with the methane atmosphere. The vertical arm, fitted with a rubber serum cap, was used to introduce the reactants in solution. These solutions were introduced with the aid of 1- and 2-ml. hypodermic syringes graduated to 0.01 ml. These syringes were equipped with 20-gage needles, 4 inches in length, which reached through the bore of the open stopcock to the flat bottom of the reaction flask. In this way the solutions could be added without danger that droplets might splash onto the walls of the vessel and thereby escape the reaction mixture.

The reaction chamber was connected through a capillary tube to the gas buret, *D*, with a total volume of 5.00 ml., graduated to 0.01 ml. A sintered gas dispersion tube, *E*, retained the mercury in the buret while the apparatus was being evacuated.

PROCEDURE

All reagents utilized were the purest commercial products available and were redistilled or recrystallized before use. The methane used was drawn from a cylinder and passed through a purification train consisting of concentrated sulfuric acid, *n*-amyl ether, and calcium hydride. The solution of methyl magnesium iodide in *n*-amyl ether was prepared as described by Siggia (*10*). The reagent was stored in an ampoule fitted with a rubber serum cap which could be covered with a ground-glass cover for storage over extended periods. The Grignard reagent was standardized in the apparatus by decomposing a measured volume of the reagent with a solution of phenol (excess) in the same solvent and by measuring the methane liberated. In calculating the normality, a correction was applied for the solubility of methane in the solvent.

The solubility of methane in the solvent was determined in the following manner. The apparatus was evacuated and then checked for leaks. Methane was then introduced until the pressure was atmospheric. The reaction vessel was immersed in a beaker of water at 25° C. and the buret reading was noted. A measured amount (0.50 ml.) of *n*-amyl ether was introduced into

the reaction vessel by means of the hypodermic syringe and the vessel was stirred by means of the rotating magnet. Equilibrium was generally attained within less than 5 minutes. The increase in the buret reading was less than the 0.50-ml. increase to be expected from the volume of the solvent introduced. The difference gave the volume of methane which dissolved in 0.50 ml. of the solvent. Additional samples of solvent can be introduced and the solubility measurement checked without disturbing the apparatus.

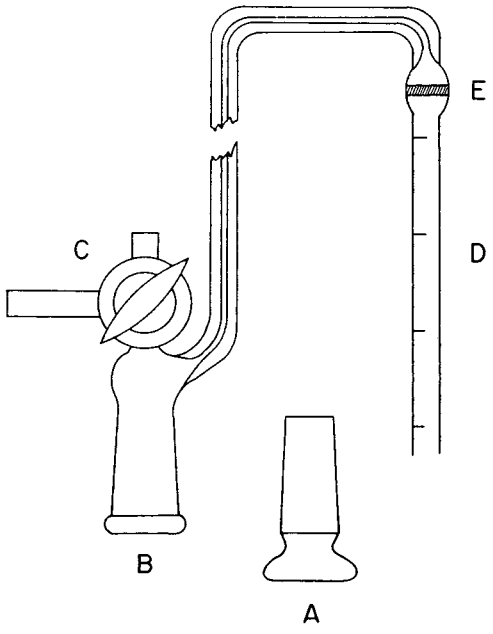

Figure 2. Details of Reaction Chamber

In the actual determinations, substances with low vapor pressures could be weighed directly in the reaction vessel, and solvent could be added after the usual evacuation and introduction of the methane atmosphere. Alternatively the substance could be weighed in a small volumetric flask, and *n*-amyl ether added to prepare a solution of known concentration. The flask was enclosed with a rubber serum cap. After the reaction vessel had been evacuated and the methane atmosphere had been introduced, an aliquot of the solution was removed with the hypodermic syringe from the small volumetric flask and introduced through the rubber serum cap and the three-way stopcock into the reaction flask. The solution was stirred and maintained at 25° C. by means of a water bath. As soon as equilibrium had been reached, as shown by a constant buret reading, the mercury in the buret was adjusted to the zero mark by allowing excess methane to escape through the three-way stopcock.

Table I. Determination of Active Hydrogen

Substance	Sample Used, Mg.	Methane Formed, Ml. Found	Methane Formed, Ml. Calcd.	Active Hydrogen, Moles Found	Active Hydrogen, Moles Calcd.
Acids					
Benzoic acid	5.58	1.14	1.143	0.997	1.00
Pivalic acid	4.56	1.12	1.113	1.006	1.00
Alcohols					
1-Hexanol	9.60	2.39	2.395	0.998	1.00
Cyclohexanol	9.23	2.39	2.360	1.014	1.00
Benzyl alcohol	9.59	2.21	2.253	0.981	1.00
Benzhydrol	15.78	2.23	2.133	1.021	1.00
Triphenylcarbinol	21.19	2.06	2.038	1.011	1.00
1,4-Butanediol	3.94	2.18	2.18	1.964	2.00
Phenols					
Phenol	8.64	2.34	2.302	1.016	1.00
2,6-Di-*tert*-butyl-*p*-cresol	15.79	1.82	1.787	1.021	1.00
Resorcinol	4.05	1.85	1.860	1.988	2.00
Hydroquinone	4.66	2.16	2.156	2.004	2.00
Amines					
Aniline	7.58	2.05	2.041	1.004	1.00
Diphenylamine	15.57	2.32	2.345	0.999	1.00

Using the same technique, 1.00 ml. of the Grignard reagent was then introduced. For substances which react slowly, the reaction was speeded up by immersing the reaction flask in a beaker of hot water for several minutes. After cooling to 25°, the buret was again read and the mercury brought back to the zero mark. The excess of reagent was then decomposed by adding 1.00 ml. of a 2*M* solution of phenol in *n*-amyl ether. After several minutes the quantity of methane liberated was again determined.

In applying the method it was desirable to correct for traces of active hydrogen in the solvent. This was done by making blank determinations on the methane liberated by adding the reagent to the solvent. The same experiment could be used to standardize the reagent. All values reported in this paper were corrected for the observed blanks.

RESULTS AND DISCUSSION

The apparatus and procedure were tested with a variety of compounds. Typical results for the reaction of the reagent with organic compounds containing one and two reactive hydrogen atoms per molecule are summarized in Table I.

It is apparent that excellent agreement was obtained between the number of the observed active hydrogen atoms and those predicted by theory. Even compounds which are highly hindered, such as triphenylcarbinol and 2,6-di-*tert*-butyl-*p*-cresol, reacted smoothly. Aniline reacted to liberate only 1 mole of methane per mole of the base, whereas difunctional molecules, such as 1,4-butanediol, resorcinol, and hydroquinone, reacted to give the predicted 2 moles of gas.

Table II. Determination of Groups Adding the Grignard Reagent

Substance	Sample Used, Mg.	Active Hydrogen, Moles/Mole Compd.	Reagent Added, Moles/Mole Compd.
Ketones			
Di-*n*-propyl ketone	10.00	0.060	0.948
Diisopropyl ketone	9.76	0.045	0.946
Pinacolone	8.18	0.046	0.914
Acetophenone	10.71	0.043	0.951
Propiophenone	13.17	0.027	0.963
Acetomesitylene	10.90	1.005	0.008
Desoxybenzoin	17.79	0.034	0.947
Benzophenone	15.97	0.013	0.984
Fluorenone	18.07	0.020	0.981
Aldehydes			
Butyraldehyde	5.23	0.097	0.940
n-Heptaldehyde	9.37	0.069	0.937
p-Hydroxybenzaldehyde	5.41	1.014	0.948
Esters			
Ethyl acetate	3.84	0.098	1.994
Ethyl benzoate	6.96	0.016	2.060

The results obtained with compounds which contain functional groups capable of adding the Grignard reagent are summarized in Table II.

Simple esters, such as ethyl acetate and ethyl benzoate, appear to react simply, adding 2 moles of the reagent. Ketones without enolizable hydrogen, such as benzophenone and fluorenone, add quantitatively 1 mole of the reagent. A substance such as *p*-hydroxybenzaldehyde, which contains both reactive hydrogen and a group capable of adding the Grignard reagent, showed both 1 mole of active hydrogen and 1 mole of Grignard reagent utilized in addition.

Ketones containing enolizable hydrogen, as well as related aldehydes, appear to show 2 to 6% of active hydrogen, with the exception of the hindered ketone, acetomesitylene, which reacts only to form the enolate. The active hydrogen analyses for these ketones do not represent enol present as such in the reaction mixtures. All experimental studies show that there is present in simple ketones only very minute equilibrium concentrations of the enol forms. Even in the case of acetomesitylene, which reacts with the methyl Grignard reagent to liberate an equi-

molar quantity of methane (Table II), the lithium aluminum hydride technique of Hochstein shows a maximum of 1 to 3% of enol present (*3*). Presumably the methane arises through a direct reaction of the Grignard reagent with the active hydrogen atoms in the alpha position to the carbonyl group.

A possible source of error in applying the method is the presence of traces of moisture (or other impurities containing active hydrogen) in the samples and solvents. In certain cases the slowness or incompleteness of the reaction constitutes another source of error. Care must also be taken that all parts of the apparatus and accessories, especially the hypodermic syringes and needles, are thoroughly clean and dry. It is desirable that these be kept in a desiccator over a suitable drying agent when not in use.

These precautions are necessary in all methods utilizing the Zerewitinoff analysis. In the authors' opinion, the present apparatus offers considerable advantages in simplicity over older, more complex assemblies (*4, 5, 8, 10*). The time required per analysis is small. In spite of the simplicity in equipment and the saving in time, the accuracy and reproducibility of the measurements are satisfactory and compare very favorably with those realized by other methods (*9*).

It is apparent that the method can be applied to other reactions in which a gas is either evolved or absorbed. It had been hoped to utilize the procedure for analyses based on the reactions of lithium aluminum hydride and sodium borohydride. Unfortunately, time did not permit this study. The apparatus has been applied in the authors' laboratories for a study of the reaction of hydrogen chloride with certain highly hindered tertiary alcohols (*1*). It proved entirely satisfactory in this application.

ACKNOWLEDGMENT

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Precipitation of Barium Chromate from Homogeneous Solution

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A COMMONLY used method for the separation of barium from strontium is that of Skrabal and Neustadtl (*2*) which employs a double precipitation of barium chromate. Modifications of this procedure have been proposed by Beyer and Rieman (*1*) who added a buffer to an acid solution containing barium and dichromate to raise the pH to 4.6. The present paper describes a modification of these procedures in which the pH of the acid solution is slowly raised by the use of urea (*3*) thus effecting precipitation of barium chromate in the form of large, readily filtered and easily washed crystals which exhibit minimized coprecipitation.

PROCEDURE

Add 10 grams of urea and 6 grams of ammonium acetate to a solution containing 0.1 gram of barium in a 250-ml. beaker. Dilute to 150 ml. and adjust the pH of the solution to approximately 1.7 to 1.8 with hydrochloric acid or ammonia. Then add 20 ml. of a 10% solution of potassium dichromate. Place the beaker on a hot plate set to give a solution temperature of about 95° to 98° C. In about an hour dense crystals will begin to form throughout the solution. After 2.5 hours remove the beaker, cool, and determine the pH; a high temperature glass electrode may also be used with the hot solution. The final pH should be approximately 5.7. If the pH is below this value, reheat until pH 5.7 is reached—around pH 5.5 the pH will change about 0.1 pH unit for each 4 minutes of heating. When the pH is approximately 5.7, filter the solution while hot, reheating if necessary, as there is some tendency toward erratic results if the solution is cooled and then filtered. Wash the precipitate thoroughly with a 0.5% potassium dichromate solution adjusted to pH 5.7. Finally, wash with three small portions of cool distilled water. Dry the precipitate of barium chromate at 120° C. for 2 hours before weighing.

Table I. Determination of Barium

(Barium taken, 0.0972 gram)

pH	Barium Found, Gram (Av.)	No. of Detns.	Standard Deviation[a], Mg.
5.1	0.0969	3	0.3
5.4	0.0965	3	0.5
5.5	0.0967	3	0.5
5.7	0.0971	3	0.1
5.8	0.0969	4	0.1
6.0	0.0970	3	0.2
6.4	0.0971	3	0.0

[a] S.d. $= \sqrt{\frac{d_1^2 + d_2^2 + \ldots . d_n^2}{n - 1}}$.

PRELIMINARY INVESTIGATIONS

Materials Used. Barium chloride, C.P., was recrystallized once from distilled water. Strontium chloride, C.P., was freed from barium by adding enough ammonium dichromate to precipitate all of the barium along with some strontium. The strontium in the filtrate was then precipitated with ammonium carbonate, filtered, washed thoroughly with distilled water, then dissolved with hydrochloric acid. The precipitation of strontium carbonate was repeated four times to effect the complete removal of chromium.

Effect of pH. The original solution must be below pH 2 before potassium dichromate is added, or some precipitate will form. As the urea hydrolyzes in the hot solution, there is a gradual increase in pH with the initial precipitate forming at about pH 3.5. The final pH must be close to 5.7. If it is several tenths of a unit below this figure, some barium will remain in solution; if it is several tenths of a pH unit above, some additional strontium may precipitate. The pH values in this investigation were obtained after cooling the solution to room temperature. Except where noted, the precipitates were always filtered from hot solution.

There is evidence in the literature that barium chromate is quantitatively precipitated at pH 4.6 (*1*). However, barium chromate is not quantitatively precipitated at this pH under the conditions employed in the present separation. At pH 4.6 a sizable portion of barium remains in solution. Quantitative precipitation does not occur until the pH range 5.5 to 6.0 is reached.

Table II. Comparison of Volumetric and Gravimetric Results[a]

(Barium taken. 0.0972 gram = 0.1792 gram of $BaCrO_4$)

pH	$BaCrO_4$ Found, Gram		Ratio, Grav./Vol.
	Gravimetric	Volumetric	
5.1	0.1760	0.1757	1.002
5.4	0.1771	0.1773	0.999
5.4	0.1781	0.1776	1.003
5.5	0.1777	0.1781	0.998
5.7	0.1778	0.1784	0.996
6.4	0.1790	0.1785	1.003
		Av.	1.000

[a] Described procedure was followed, except that solutions were cooled and allowed to stand several hours before filtering.

Attempts to obtain better buffering action with reagents other than acetate were limited by the strong oxidizing properties of the chromate ion as well as by the complexing and precipitating properties of the possible buffers.

Quantities of Reagents Selected. The various amounts of reagents were chosen because they produced the largest crystals, gave a reasonable time for hydrolysis, and gave the most reproducible results.

DISCUSSION OF RESULTS

Determination of Barium. The results obtained with the recommended procedure are given in Table I. Low results were obtained where the final pH was too low. The higher the pH the more quantitative the precipitation of barium, but unfortunately the tendency for strontium to coprecipitate also increases. A pH of about 5.7 is most suitable. At this recommended pH, about 0.1 to 0.2 mg. of barium appears to remain in solution.

An attempt was made to determine the composition of the precipitate, since slight fluctuations in the weight of the precipitate were obtained. Barium chromate precipitates obtained in different experiments from the same quantity of barium chloride stock solution were dissolved and the resulting solutions were heated to boiling with ammonium persulfate and titrated potentiometrically with standard ferrous ammonium sulfate.

The results given in Table II indicate that the barium found gravimetrically is equal to the chromium found volumetrically.

Determination of Barium in Presence of Strontium. The data obtained using the recommended procedure are shown in Table III. Approximately 100 mg. of barium can be separated in a single precipitation from about 40 mg. of strontium; 100 mg. of strontium require a double precipitation.

Table III. Determination of Barium in the Presence of Strontium

pH	Barium Found, Gram	Difference, Mg.
Barium Taken, 0.0972 Gram.	Strontium Taken, 0.039 Gram	
5.0	0.0971	−0.1
5.3	0.0971	−0.1
5.4	0.0972	0.0
5.5	0.0969	−0.3
5.5	0.0973	0.1
5.5	0.0976	0.4
5.6	0.0975	0.3
5.8	0.0974	0.2
6.0	0.0973	0.1
Barium Taken, 0.0972 Gram.	Strontium Taken, 0.097 Gram	
4.9	0.0969	−0.3
4.9	0.0981	0.9
5.0	0.0977	0.5
5.3	0.0985	1.3
5.7	0.0984	1.2
5.8	0.0976[a]	0.4
5.8	0.0980[b]	0.8
6.0	0.0975[c]	0.3
6.1	0.0984	1.2
Upon Reprecipitation		
5.6[a]	0.0971	−0.1
5.5[b]	0.0968	−0.4
5.8[c]	0.0970	−0.2

[a, b, c] Samples reprecipitated.

Determination of Barium in Presence of Calcium. A good separation of barium and calcium is indicated by the results given in Table IV. The pH does not have to be controlled as closely as is the case when strontium is present. A complete separation can be obtained with a single precipitation.

Table IV. Determination of Barium in Presence of Calcium

(Barium taken, 0.0972 gram. Calcium taken, 0.1 gram)

pH	Barium Found, Gram	Difference, Mg.
5.6	0.0972	0.0
6.6	0.0972	0.0
7.0	0.0974	0.2

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Chromatographic Separation of Acid Obtained from Oxidation of Alpha-Pinene

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IN CONNECTION with the oxidation of α-pinene, a constituent of turpentine, to pinonic and pinic acids (*1*, *4*), a satisfactory method of qualitative and quantitative analysis was needed. The crude oxidation products obtained contain a number of mono- and dicarboxylic acids. Most of the acids involved are cyclic compounds, including cyclobutane and cyclopentane derivatives as well as acids containing γ-lactone structures. Some of these acids are produced as by-products and some are formed from impurities present in commercial α-pinene.

Marvel and Rands (*3*), Ramsey and Patterson (*5*, *6*), Higuchi, Hill, and Corcoran (*2*), and others have reported simultaneous qualitative and quantitative analysis of certain straight-chain acids by partition chromatography. The insolubility of the acids under consideration in aliphatic hydrocarbons prevented use of the procedure presented by Ramsey and Patterson (*6*) for acids of comparable molecular weight.

Data from chromatograms employing the method presented by Marvel and Rands (*3*) are reported as well as the results of a

modification of their procedure and one other procedure employing benzene and benzene–1-butanol as the developing solvents. Some of the monocarboxylic acids (especially pinonic) were not developed enough for separation or positive identification on columns employing chloroform as the mobile phase. A substantial improvement in the separation and identification of these acids was obtained on columns employing benzene as the mobile phase.

APPARATUS

A borosilicate glass chromatographic column 60 cm. long and 18 mm. in inside diameter was used. A glass wool plug was used to support the immobile phase and a disk of filter paper was placed on top.

REAGENTS

Water-saturated chloroform, technical grade.
Water-saturated benzene, ACS or C.P. grade.
1-Butanol redistilled over potassium carbonate.
Silicic acid, Mallinckrodt chromatographic grade.
Distilled water.
Phenol red indicator.
Aqueous sodium hydroxide solution, 0.01 or 0.02*N*.

PROCEDURE

Method I. Marvel-Rands (*3*). Samples of 10 to 30 mg. of the pure acids were developed on columns following the standard procedure presented by Marvel and Rands—namely, increasing the polarity of the eluting solvent in increments of 5% 1-butanol.

Method II. Modified Marvel-Rands. Columns and samples were prepared according to the procedure of Marvel-Rands. The polarity of the developing solvent was increased in increments of 1% 1-butanol.

To ensure water saturation the 1-butanol–chloroform solutions were shaken with 1 ml. of water per 100 ml. of solution and were separated.

Method III. Benzene. This method employs water on silicic acid as the immobile phase and benzene, benzene–1-butanol as the mobile phase.

PREPARATION OF COLUMN AND SOLUTIONS. The silicic acid–water mixture was slurried with about 100 ml. of benzene and poured into the column. The mixture was stirred to prevent the trapping of air bubbles in the silicic acid. The column was settled with 5 pounds of air pressure and then packed firmly by hand with a close-fitting plunger. The flow rate of these benzene columns was much faster than the flow rate of chloroform columns. From 7 to 10 ml. were eluted per minute when the columns were run under 1 pound of air pressure. No change in peak effluent volumes was found when the columns were run without any pressure.

From 0.1 to 0.5 meq. of the sample to be chromatographed was made to a volume of 5 ml. A 2-ml. aliquot was carefully placed on top of the column and forced into the column with a little pressure. The sides of the column were then rinsed with another 2-ml. aliquot of benzene. The 4 ml. of eluant collected were discarded and the collection of 10-ml. fractions was begun. Developing solutions used were benzene and mixtures of benzene and 1-butanol of the following compositions: 100 ml. of benzene; 100 ml. of 1% 1-butanol–99% benzene v./v.; 100 ml. of 2% 1-butanol–98% benzene v./v.; 100 ml. of 3% 1-butanol–97% benzene v./v.; 100 ml. of 4% 1-butanol–96% benzene v./v.; 100 ml. of 5% 1-butanol–95% benzene v./v.; and 100 ml. of 10% 1-butanol–90% benzene v./v.

To ensure water saturation the 1-butanol–benzene solutions were shaken with 1 ml. of water per 100 ml. of solution and were separated. The developing solutions were added to the column in 50-ml. portions, each portion being added when 10 ml. of the preceding solution was still above the column.

A 2-ml. aliquot of the remaining sample solution was titrated, with 0.01*N* or 0.02*N* aqueous sodium hydroxide using 2 ml. of 0.003% phenol red indicator, to determine the total amount of acid added to the column. The per cent of the total acid present in each fraction $= \frac{\text{titration minus blank} \times 100}{\text{aliquot titration}}$. The percentages of the individual acids present in the sample are calculated from the amount of acid in each fraction forming the peak. In cases where the separation of the acids is not complete, the value of the minimum point between the curves is divided equally between the two acids.

STANDARDIZATION OF SILICIC ACID. The peak effluent volumes obtained with these columns are sensitive to changes in the water content of the silicic acid. Different batches of silicic acid used in this work were found to vary greatly in the amount of water required to form a satisfactory slurry, so that each batch had to be standardized in order to duplicate the peak effluent volumes. The problem was approached from the standpoint of a constant amount of water, and the amount of silicic acid was varied until the peak effluent volume of a particular acid was reproduced. The criterion for a "standard" column was: 14 ml. of water ground with that amount of silicic acid which, when slurried with benzene and packed into a column, would give a peak effluent volume of 200 for propionic acid. Propionic acid was chosen as a standard for two reasons: It is readily available in pure form and its peak effluent volume of 200 is such that it is sufficiently sensitive to minor variations in the composition of the column.

The variation in the initial composition of different batches of silicic acid is illustrated by the four different batches of silicic acid used in this work. Peak effluent volumes were reproduced when 20, 18, 15, and 20 grams, respectively, of the four different lots of silicic acid were ground with 14 ml. of water. Silicic acid sitting open in the laboratory will gain or lose water rapidly as the room temperature and humidity change. Care should be taken to reseal bottles of silicic acid once they are opened. Once a batch has been standardized, portions can be weighed out into bottles, stoppered tightly, and stored in a desiccator; or these portions can be ground with 14 ml. of water, placed in evaporating dishes, and stored in a desiccator over water until they are used.

In the search for a suitable acid to use for standardization of the columns, the following peak effluent volumes were observed: benzoic acid, 40; *m*-hydroxybenzoic acid (this acid had to be dissolved in 10% 1-butanol–benzene), 290; butyric acid, 90; propionic acid, 200; and acetic acid, 440.

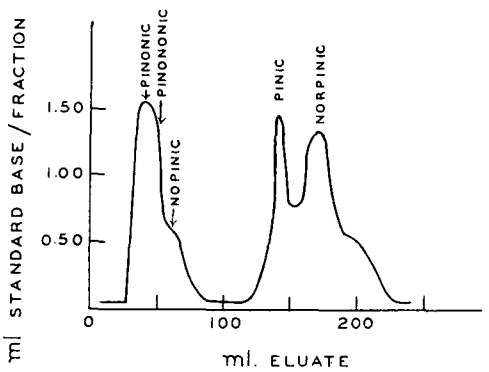

Figure 1. Chromatogram of Acid Mixture by Marvel-Rands Method

Table I. Peak Effluent Volumes of Acids Obtained by Marvel-Rands, Modified Marvel-Rands, and Benzene Methods

Acid	Molecular Formula	Peak Effluent Volume		
		Method I[a]	Method II[a]	Method III[b]
d-Camphoric	$C_{10}H_{16}O_4$	30[c]	30[c]	30[d]
Pinonic	$C_{10}H_{16}O_3$	40	40	80
Pinononic	$C_9H_{14}O_3$	50	50	180
Nopinic	$C_{10}H_{17}O_3$	60	60	150
Pinolic	$C_{10}H_{18}O_3$	70	70	200
Homoterpenylic	$C_9H_{14}O_4$	70	70	280
Terpenylic	$C_8H_{12}O_4$	110, 140	110	340
Terebic	$C_7H_{10}O_4$	140[c]	160[c]	350[d]
Pinic	$C_9H_{14}O_4$	140	250	300
Norpinic	$C_8H_{12}O_4$	170[c]	350	380
Hydroxypinic	$C_9H_{14}O_5$	330[c]		750[d]

[a] Values obtained with one batch of silicic acid.
[b] Values obtained with four different batches of silicic acid.
[c] Dissolved in 10% 1-butanol–chloroform.
[d] Dissolved in 10% 1-butanol–benzene.

Table II. Analysis of a Sample of Crude Pinic Acid

Acid	Peak Effluent Volume	Found, %
Unidentified	30	1.6
Pinonic	80	11.9
Unidentified	240	9.8
Pinic	300	70.9
Unidentified	445	1.0
% recovery from column	95.2	

EXPERIMENTAL RESULTS AND APPLICATION

The peak effluent volumes of pure acids that would be expected as products of the oxidation of commercial α-pinene using the three methods described above are tabulated in Table I. Unless it is so noted in the footnotes, the samples were dissolved in water-saturated chloroform or benzene, depending on the type of column. The recovery of pure acids was 99 to 100% for all columns. Recovery on samples of pilot plant batches of crude pinic acid was from 95 to 100%.

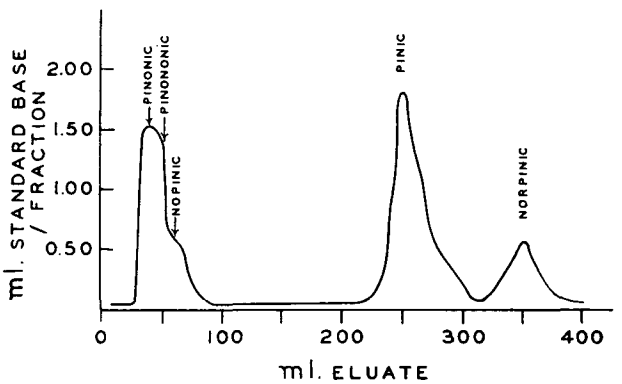

Figure 2. Chromatogram of Acid Mixture by Modified Marvel-Rands Method

Figures 1, 2, and 3 show the separation of a synthetic mixture of pure acids using each of the three methods. The Marvel-Rands and modified Marvel-Rands procedures do not separate this mixture of the monocarboxylic acids (pinonic, pinononic, and nopinic). However, in the absence of pinononic acid, pinonic and nopinic acids are almost completely separated. The only real advantage of the modified Marvel-Rands technique is the complete separation of the dicarboxylic acids present (pinic and norpinic). The good separation of both the monocarboxylic and the dicarboxylic acids using benzene as the mobile phase is illustrated in Figure 3.

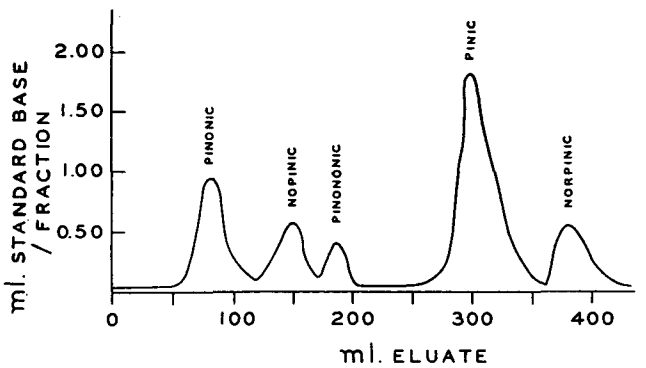

Figure 3. Chromatogram of Acid Mixture by Benzene Method

Homoterpenylic, terpenylic, and terebic acids would be likely to occur together in some samples produced under acidic oxidation conditions. The terebic acid is so insoluble in benzene or chloroform that it can be filtered out of the sample solutions and developed separately. Homoterpenylic and terpenylic acids are separated to the same degree with either the modified Marvel-Rands procedure or the benzene method. Terpenylic acid is developed as two peaks with the Marvel-Rands method.

This benzene method has been successfully applied to the analysis of crude samples obtained by the oxidation of α-pinene. A sample of crude pinic acid (prepared in a pilot plant by oxidation of commercial α-pinene with potassium permanganate to pinonic acid followed by the oxidation of pinonic acid with a deficiency of calcium hypochlorite to pinic acid) gave the results tabulated in Table II.

ACKNOWLEDGMENT

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Improved Colorimetric Determination of Urinary 17-Ketosteroids

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A RECENT paper by Masuda and Thuline (*5*) describing a method for estimating 17-ketosteroids in urine prompts a report on a similar modification which has proved to be of value in this laboratory for some time. Several investigators (*3*, *5*, *7*, *8*) have attempted to improve the colorimetric determination of 17-ketosteroids by employing organic solvents to extract the pink chromogens formed in the Zimmermann reaction. Aqueous potassium hydroxide was used to develop the color of the steroid with dinitrobenzene and chloroform, ether or amyl acetate to extract it from 60% (*3*) or 68% (*5*, *7*, *8*) alcohol. The procedure described here differs in that: the absolute alcohol technique of Callow *et al.* (*4*) was adopted for the color formation, the alcohol concentration of the pink solution was made to 37% before extraction, and a novel apparatus was introduced to extract the steroid chromogens. These modifications practically eliminated the interfering substances that absorbed strongly at 400 mμ and permitted an average recovery of 96% of the crystalline steroid which was added to urine extracts. The apparatus described

Table I. Per Cent Transmittance of Pink Chromogens at 515 mμ

DEAA, γ	Time[a], Minutes 5	10	15	20	30
20	80.0	79.8	80.1	80.7	80.8
40	61.8	61.8	62.0	62.5	62.5
60	50.9	50.6	50.7	51.0	51.3

[a] Timing began after addition of 1 ml. of absolute alcohol to ether.

permits the method to be carried out routinely with a minimum of manipulation.

APPARATUS

The 12-ml. test tube for the Zimmermann reaction and the 65-ml. separatory funnel (available from Delmar Scientific Laboratories, Chicago 51, Ill.) employed for the extraction of the pink reaction product are presented schematically in Figure 1.

The absorption spectra were measured in a Beckman Model B spectrophotometer with test tube adapter.

PROCEDURE

The directions of Robbie and Gibson (*6*) or Buehler *et al.* (*2*) were followed for the hydrolysis and extraction of the urine. The color was developed by the method of Callow *et al.* (*4*) in the test tubes shown in Figure 1. A reagent blank was run with each set of determinations. About 3 minutes before the end

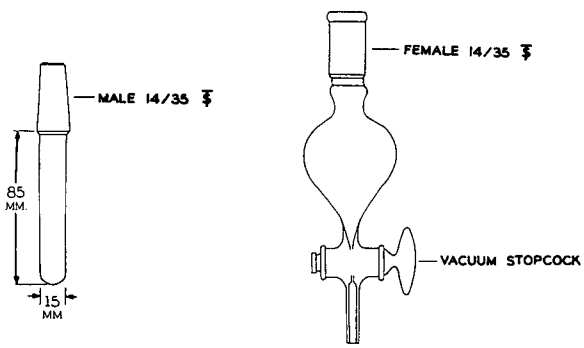

Figure 1. Test Tube and Separatory Funnel for Extraction of Zimmermann Reaction Product

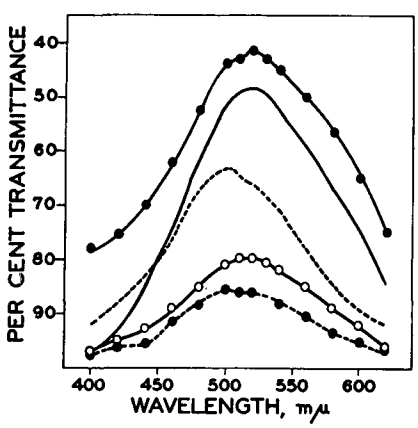

Figure 2. Absorption Spectra of Ether-Extracted Pink Chromogens Stabilized with Alcohol

——— Crystalline DEAA (80 γ)
O—O—O Crystalline estrone (102 γ)
--------- Pregnanolone from urine
·---·---· Etiocholan-3-α-ol-17-one from urine
·—·—· For comparison the pink color of DEAA (80 γ) developed by method of Callow *et al.* (*4*)

of the 1 hour allowed for the color formation, 8.0 ml. of distilled anhydrous ether were added from a buret to each of the separatory funnels (see Figure 1), one for each test tube. Then, the subsequent steps were performed in diffuse light. Exactly 1 hour after the addition of the 2.5*N* alcoholic potassium hydroxide, 1 ml. of water was added to each test tube and the contents were mixed. The test tube was inserted into the mouth of the separatory funnel while it was held in an almost horizontal position. The contents were vigorously shaken in order to extract the pink chromogens. The inverted test tube was withdrawn, and after the two phases separated (2 to 3 minutes) the aqueous layer was removed. Then, 1 ml. of absolute alcohol was added to the ether solution in the separatory funnel. The pink solutions were poured into round cuvettes and read against the reagent blank (prepared in the same manner) at 515 mμ. Crystalline dehydroepiandrosterone acetate (DEAA) was used to establish the standard curve. The Girard separations were carried out according to the procedure of Beher and Gaebler (*1*).

RESULTS AND DISCUSSION

Table I demonstrates that the pink color of the ether solution was stable for approximately 15 to 20 minutes.

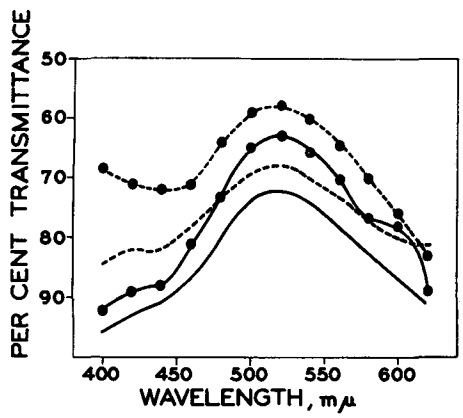

Figure 3. Comparison of Absorption Spectra of Pink Chromogens Given by Urinary 17-Ketosteroids by Callow Technique (*C*) and by Present Method (*P*)

·---·---· *C* before Girard separation (53 γ)
--------- After Girard separation (35 γ)
·—·—· *P* before Girard separation (47 γ)
——— After Girard separation (35 γ)

The transmittance spectra resulting from the application of the new method to several steroids are presented in Figure 2. (When the ether extraction method was applied to crystalline androsterone, etiocholane-3-α-ol-17-one, epiandrosterone, and dehydroepiandrosterone the spectra showed maxima at 515 to 520, 515, 520, and 515 mμ, respectively. These measurements were made with a Beckman DU spectrophotometer.) All showed more than 90% transmittance at 400 mμ. This is in contrast to the other procedures (*3, 7, 8*) in which the pink chromogens after extraction absorbed as much as 60% at this wave length. Thus, even with crystalline steroids the present procedure appears to be superior in the elimination of the chromogenic material which exhibits strong absorption at 400 mμ. Estrone interfered to a small extent since the absorbance of 102 γ at 515 mμ was that given by 20 γ of dehydroepiandrosterone acetate.

The ether extractable chromogens from 80 γ or less of dehydroepiandrosterone acetate were found to obey Beer's law. Higher concentrations were not investigated.

The absorption spectra of the chromogenic material obtained from a neutral urine extract by the application of both the Callow technique and the new procedure are presented in Figure 3. When the former was employed, the Girard separation eliminated many of the substances which caused high absorption at 400 mμ. However, with the present method there was very little change observed in the shape of the spectra after the Girard

separation. This demonstrates that for crude urine extracts it probably gives a measure of those steroids remaining after the Girard separation, thereby making the latter unnecessary when the total 17-ketosteroid content of the urine is desired. Most of the spectra from urine extracts exhibited a minimum of 90% transmittance (Figure 3) and closely approximated in shape those in Figure 2.

A determination of the 17-ketosteroids of several neutral urine extracts was made. The data are summarized in Table II together with the higher values found by the absolute alcohol technique (urines E and F are exceptions). The quantities of 17-ketosteroids obtained by the extraction method before and after the Girard separations (urine samples A and B) agreed well with those found by the Callow procedure following the Girard separations. This again indicates that the extraction method measures the ketonic steroids which are separated by the Girard reagent.

Table II. Application of Extraction Method to Neutral Urine Extracts

	Urine Sample	Hydrolysis and Extraction Procedure, Reference	Mg. 17-KS, Colorimetric Methods	
			Present	Callow *et al.* (*4*)
A	Pooled male 1	(*6*)	4.67	6.70
A	After Girard separation		4.48	4.43
B	Pooled male 1	(*2*)[a]	4.67	6.19
B	After Girard separation		4.54	4.80
C	Pooled male 2	(*6*)	5.78	6.24
D	Pooled male 2	(*2*)[b]	6.20	6.33
			Per 24 Hours	
E	Male arthritic	(*6*)	12.5	11.5
F	Female virilism during cortisone therapy	(*6*)	12.3	12.1
G	Female virilism	(*6*)	15.7	17.4

[a] 48-hour ether extraction.
[b] 72-hour ether extraction.
Urines E, F, and G were made available through the courtesy of D. M. Bergenstal, Department of Medicine, University of Chicago.

The average recovery of dehydroepiandrosterone acetate which was added to different amounts of urine extract was 96% (Table III). The recovery from the larger extract tended to be lower than that from the smaller aliquot. This was also noted by Masuda and Thuline (*5*), although no quantitative data were presented.

Table III. Recovery of Crystalline Dehydroepiandrosterone Acetate Added to Neutral Urine Extracts

Urine Sample	Urine Extract, γ 17-KS	DEAA Added, γ	DEAA Recovered, γ	Recovery, %
C	22.5	20	21.0	105
	45.0	20	18.8	94
E	26.7	20	18.8	94
	53.4	20	17.6	88
F	22.3	20	19.3	97
	44.5	20	16.1	81
G	23.7	20	20.3	102
	23.7	40	40.8	102
	47.4	20	20.9	105
				Av. 96

ACKNOWLEDGMENT

The authors are indebted to the Schering Corp. for crystalline dehydroepiandrosterone acetate and to F. A. Travers of the Ciba Pharmaceutical Products, Inc. for the crystalline epiandrosterone. Thanks are due to M. Edward Davis, Department of Obstetrics and Gynecology, University of Chicago, for the crystalline estrone, urinary pregnanolone, and etiocholan-3-α-ol-17-one. David Fukushima kindly supplied crystalline androsterone and etiocholan-3-α-ol-17-one. Discussions with George V. LeRoy have been very helpful.

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Improved Fractional Melting Apparatus

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IN VIEW of the utility of fractional melting as a means of purification (*1*), an improved fractional melting apparatus with compressible conduction vanes has been developed which is sturdier than the others described previously (*1*). This apparatus is referred to as fractional melting apparatus 5. The reader is referred to the earlier publication for background and experimental detail. A test of performance of the apparatus with and without using the vanes to press out the melted substance is described.

APPARATUS

A scale drawing of the apparatus is shown in Figure 1. The apparatus consists of four sections: the melting chamber, 18, and vane system, 27, the shield supplied with a heater, 17, the shield or temperature equalizer, 16 (which is not supplied with a heater), and the external cryostat envelope, 15.

The melting chamber is provided with a compressible spiral vane system 27, which is the basis of the high efficiency of the apparatus. This type of vane system proved to be mechanically superior to and simpler in design than the one used in the fractional melting apparatus 3 (*1*). The vanes are made by cutting disks from No. 36 gage sheet steel, perforating them at random, and drilling a central and a radial hole for the vane guide tube, 28, and the transfer tube, 30, respectively. The disks are cut along one radius (opposite the radial hole) and twisted approximately 15°. The twisted disks are then hard-soldered end to end to form a continuous spiral. The pitch of the spiral is about 0.25 inch when the spiral is expanded the full length of the melting chamber. The lower end of the spiral vane is soft-soldered to the bottom of the melting chamber, and the top is hard-soldered to the main activator vane, 20.

The main activator vane, 20, consists of a copper disk 1/16 inch thick. This vane is hard-soldered to the plunger tube, 19, which has a perforated cap, 12. The plunger tube, 19, is partially slotted along one side and the slot is made to ride on a key mounted in the cryostat pumping tube, 14. This device pre-

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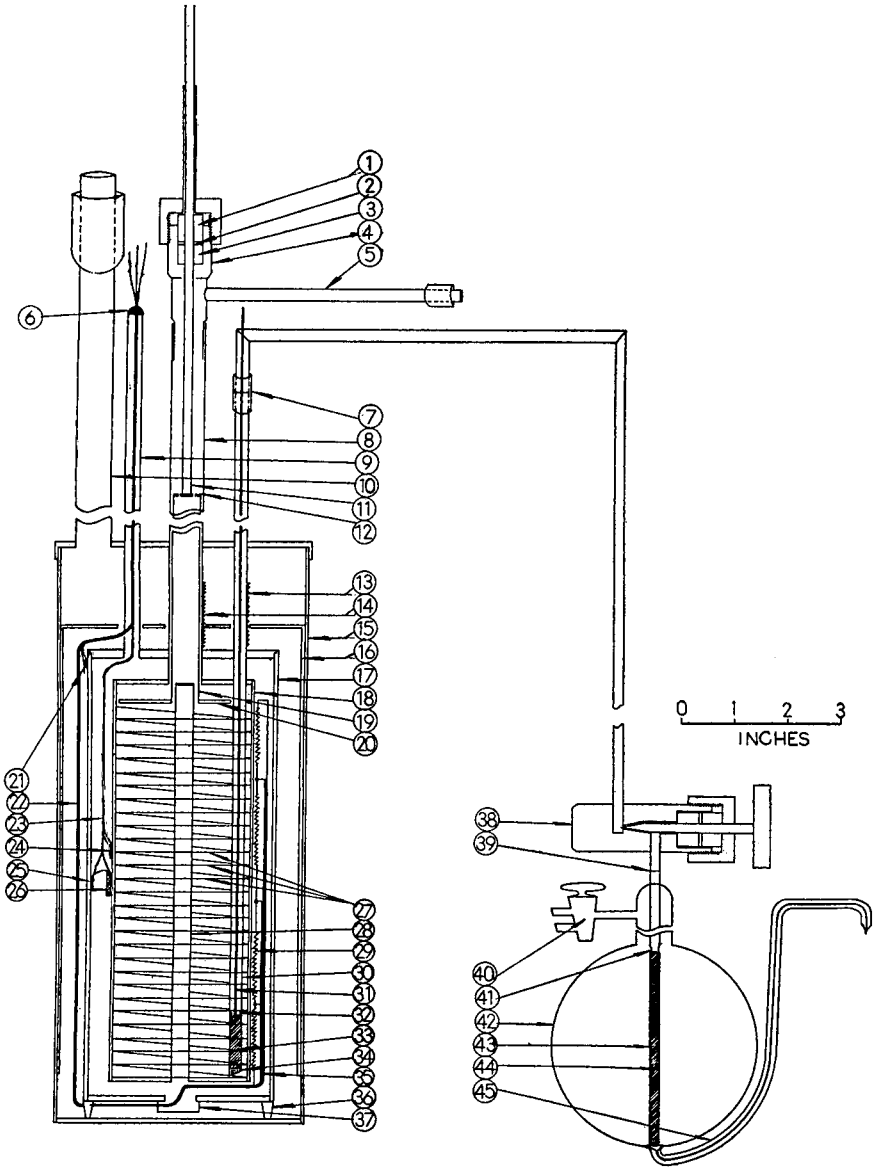

Figure 1. Improved Fractional Melting Apparatus

1. Brass gland
2. Stainless steel washer
3. Teflon packing
4. Stuffing box for stainless steel activator rod, 11.
5. Filling line to melting chamber for evacuation and pressure
6. Electrical supply wires pass through de Khotinsky seal
7. Connection for transfer tube
8. Filling line to melting chamber, continued
9. Electrical supply wires exit tube
10. Cryostat pumping tube for evacuation of cryostat envelope
11. Stainless steel vane activator rod
12. Perforated plate connected to vane activator rod, 11 and guide tube, 19. Perforations allow melting chamber to be evacuated or filled with nitrogen gas under pressure.
13. Transfer tube heater (12 ohms)
14. Filling line heater (22 ohms)
15. Cryostat envelope (Monel metal)
16. Copper temperature equalizer
17. Copper shield provided with heater
18. Melting chamber
19. Guide tube for vane activation
20. Master vane to which is connected upper end of spiraled vane. Master vane is also connected to the guide tube, 19.
21. Electrical supply wires to shield heater (not shown)
22. Electrical supply wires from calorimeter heaters
23. Electrical supply wires to difference couple and thermocouple
24. Thermocouple soldered to melting chamber and wrapped around it 10 times for thermal contact. Bakelite lacquer is used for making wires fast
25. Difference couple junction on shield (soldered)
26. Difference couple junction on melting chamber (insulated electrically)
27. Spiraled vane system
28. Guide tube
29. Four calorimeter heaters. The resistance of each heater is approximately 34 ohms. All are connected in series with tap wires taken out between them. There are five heater leads in all
30. Transfer tube
31. No. 16 bare copper wire for conduction heater
32. Constriction
33. Glass wool
34. Drilled solder plug
35. Electrical supply wires from calorimeter heater
36. Corks for supporting shield
37. Radiation shield
38. Needle valve
39. Kovar glass seal
40. Three-way stopcock to evacuate receiving flask, 42, or to fill it with nitrogen gas under pressure
41. Constriction
42. Receiving flask for impure liquid fraction
43. Glass tube with glass wool filter, 44
44. Glass wool filter
45. Drain for receiving flask

vents the spiral vane system from turning. The perforated cap, 12, is hard-soldered to the stainless steel activator rod, 11. The activator rod, 11, passes out of the apparatus through the stuffing box, 4. The stuffing box, 4, is packed with a Teflon washer, 3, compressed by a screw cap acting through a brass gland, 1, and a stainless steel washer, 2. The Teflon stuffing box proved to be vacuum-tight, even when the vanes were being activated. The needle valve, 38, on the transfer tube, 30, is also provided with Teflon packing.

The heater element, 29, is wound in four sections on the outside of the melting chamber. The absolute thermocouple used for measuring the temperature of the melting chamber is soldered to the side wall of the melting chamber. The electrical supply wires to this thermocouple are wrapped (10 turns) around the wall of the melting chamber and fastened there with Bakelite lacquer. This last measure prevents false readings of the thermocouple by reducing heat leak. The transfer tube, 30, and filling line, 5, for the melting chamber are wound with heaters, 13 and 14, respectively. These heaters are not necessary for the operation of the apparatus; they serve merely as a convenience when time is short and for inexperienced operators who have not yet learned to control the liquid air level in the refrigerant bath Dewar flask. They are to be used when the plunger tube, 19, sticks owing to solidification of sample in that region. Also, if the liquid air level is not controlled properly, the transfer tube, 30, may become plugged in the region wrapped with the auxiliary heater, 13.

Figure 1 shows the arrangement of the receiving flask, 42, for receiving the impure liquid fractions. The other details of construction and operation are similar to those of the fractional melting apparatus 3 (*1*). It is the purpose of this paper not only to present the improved design but to show how essential are the compressible vanes.

RESULTS

Two identical samples were prepared by mixing 475 ml. of Phillips' iso-octane (2,2,4-trimethylpentane) (lot 126) with 25 ml. of Phillips' *n*-heptane (lot 159). The samples were used to test the effect of compression of the vane system on the efficiency of purification. Table I summarizes the progress of purification when the vanes are compressed after each operation to squeeze out the liquid from the crystals. Column 1 lists the amount of liquid withdrawn after observing the corresponding equilibrium temperature listed in column 2. Column 3 lists the fraction of material existing as liquid compared to the total amount of material remaining in the melting chamber during measurement of the equilibrium temperature, and column 4 lists the purity,

Table I. Progress of Purification of Iso-octane with Compressing of Vanes

Liquid Withdrawn, Ml.	Equilibrium Temp., °K.	Fraction of Liquid	Purity Calcd. from Temp., %	Purity Calcd. from Washing, %	Yield, %	Theoretical Yield, %
0	161.05	0.10	94.4	...	100.0	..
28	163.36	0.10	99.1	96.0	94.4	..
28	163.76	0.10	99.4	97.6	88.8	..
36	164.15	0.115	99.40	99.6	81.6	..
23	165.48	0.101	99.91	99.8	77.0	96
36	165.71	0.095	100.00	99.98	69.6	87
30	165.71	0.050	100.00	99.998	64.0	80
0	165.71	0.141	100.00	99.998	64.0	80
0	165.71	0.347	100.00	99.998	64.0	80

calculated by means of the melting point equation, of the material remaining in the melting chamber (this includes the solid and liquid portions).

Column 5 lists the purities calculated by the batch theory of washing, assuming all of the impurity to be dissolved in the melt. The amount of liquid remaining after withdrawing the melted liquid (as completely as possible) was estimated from the difference between the amount of liquid melted, as determined from the added energy, and that withdrawn into the receiving flask. Column 6 lists the actual yields (in percentage of the original charge) and column 7 lists the percentage of the theoretical yield obtained. The theoretical yield was estimated from a eutectic diagram calculated assuming the applicability of Raoult's law and the absence of solid solution.

A lower purity is calculated by batch theory of washing because the actual operation is effectively continuous, the descending washings occupying a relatively small volume. For this reason the purity calculated by means of the melting point equation is considerably more accurate than that calculated by the theory of washing. That equilibrium is reached with respect to composition is indicated by the fact that the equilibrium temperature did not change with time. Moreover, after the equilibrium temperature indicated that all impurity had been removed, melting half the remaining material produced no rise in the equilibrium temperature (see the last three entries in Table I).

The second purification was effected by keeping the vanes stationary in the expanded position. The results are listed in Table II. No attempt was made to apply the theory of washing, since the melt no longer made contact with all of the crystals. Column 1 lists the amount of liquid withdrawn from the melting chamber. Column 2 lists the corresponding equilibrium temperatures before the liquid was withdrawn, and column 3 lists the purities calculated by means of the melting point equation. Column 4 lists the actual yields and column 5 lists the percentage of the theoretical yield obtained based on Raoult's law and eutectic composition.

When the vanes were not compressed, larger quantities had to be melted before each withdrawal as the amount which could be removed without squeezing was greatly reduced.

Comparison of the two tables shows that the purification efficiency is increased by a factor of about 3 at the 99.98% level of purity when the compressible vane system is used. The time for equilibration was about 2 hours when the vanes were immobilized, as compared to 15 to 20 minutes when the vanes were activated. The last fraction in the purification without compressing the vanes had not come to equilibrium even after 3 hours.

Table II. Purification of Iso-octane without Compressing of Vanes

Liquid Withdrawn, Ml.	Equilibrium Temp., ° K.	Purity Calcd. from Temp., %	Yield, %	Theoretical Yield Obtained, %
0	163.64	...	100	...
101	164.34	98.5	80	100
110	165.26	99.6	58	73
70	165.55	99.86	44	55
66	165.62	99.92	31	39
33	165.70	99.99	25	31
45	...	...	13.6	17

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Estimation of Fluorine in Biological Material

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IN CONNECTION with the estimation of fluorine in blood, Smith and Gardner (*2*) drew attention to the loss of fluorine as a volatile iron fluoride when the blood is ashed preparatory to the Willard-Winter distillation (*3*). For this reason, they adopted a preliminary sulfuric acid distillation (before ashing) to free fluorine from the iron. To obtain reliable results in the case of other biological materials, it was also found that a preliminary distillation is necessary owing to the almost universal occurrence of iron in plant and animal tissues.

Silica in plant materials also interferes with fluorine recovery (*1*). This interference was reduced by preliminary distillation of the unashed sample or by fusion of the lime-ashed sample with sodium hydroxide before distillation of the fluorine from perchloric acid. An earlier observation (*4*) made in these laboratories, to the effect that magnesium oxide is a good adsorbent for the fluoride ions, considerably facilitated the fluoride analytical procedure which was thereby rendered more rapid.

PROCEDURE

One-half gram of material is submitted to Willard-Winter distillation, employing sulfuric acid. The distillate, which is kept just alkaline to phenolphthalein, is brought to boiling, 0.2 gram of light magnesium oxide is added, and the boiling is continued for 5 minutes more. The magnesium oxide with the adsorbed fluoride is separated by centrifugation or filtration and submitted to the Willard-Winter perchloric acid distillation in the presence of barium and silver perchlorates to withhold the interfering sulfate and chloride ions. The fluoride in the distillate is determined by titration by the Smith and Gardner technique (*2*).

RESULTS

The fluorine content of a sample of tea as determined by the present method was 180 p.p.m., whereas the values obtained by the conventional ashing method ranged from 30 to 120 p.p.m., depending on the temperature of ashing, period of ashing, the fixative, and the quantity of the fixative employed.

The method is now being extended to other biological materials.

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Spectrochemical Study of Gravimetric Procedure For Barium, Strontium, and Calcium

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GRAVIMETRIC methods for the separation and determination of barium, strontium, and calcium have been adequately reviewed by many authors (*5*, *8*) and no further attempt at review is made here. Previous work has indicated that the agreement of the results obtained by the various procedures is often largely through a compensation of errors and that changes in the concentration of any one of the constituents of a mixture of alkaline earths may affect the separation of the others. This investigation was originated because of the great variation between the chemical and spectrochemical analysis when both synthetic and chemically analyzed standards are used as spectrochemical standards.

Material balance studies made with the aid of spectrochemical analyses offer a method for determining the merits of a gravimetric procedure. It is possible to determine the amount of coprecipitation and the losses due to solubility. The effectiveness of different precipitating agents and variations in procedure may be studied and evaluated. The material balance values represent a correction of the gravimetric results for inherent errors.

EXPERIMENTAL

The spectrochemical data were obtained by employing a large Litthrow-prism type instrument with glass optics. A modified total energy method, given by Hunter and Headlee (*4*), was used throughout. This procedure requires very few standards and lends itself well to this type of analysis. Kodak Process Panchromatic plates in the wave-length range 4000 to 6500 A. were used in all determinations. The arc was energized by a direct current source at 12 amperes using a 2-minute excitation time with a 10-micron slit and a 6-step sector in the light path.

Spectrochemical standards were made by adding weighed quantities of metal carbonates to the desired matrix. The standards were mixed in a mechanical agate mortar for 0.5 hour, and then on a mixing wheel for 15 minutes. At least four determinations of each standard were made to determine its homogeneity. Standards were prepared to match the matrices of the precipitates and solids in concentrations which gave approximately the same transmission values. The wave lengths chosen for the analyses were for barium, 6141.7 A., 4554.0 A.; for strontium, 4607.3 A. (<0.3%), 4962.3 A.; for calcium, 4302.5 A.; and for sodium, 5895.9 A. An accuracy of 10% was obtained.

Analytical reagent grade barium nitrate and strontium nitrate were used to make purified barium and strontium salts by recrystallization. These were used for the preparation of known mixtures and matrices for spectrochemical standards. A "special grade" calcium carbonate was used for calcium. All other reagents used for both the chemical and spectrochemical determinations, except the impure barium carbonate, were analytical reagent grade chemicals. All reagents were analyzed spectrochemically for impurities as shown in Table I.

Table I. Reagent Purity Determinations as Per Cent of Reagent Anion

Reagent	Ba	Sr	Ca	Na
$CaCO_3$ (special)	<0.001	0.10	...	0.18
$BaCO_3$ (purified)	...	<0.001	0.31	...
$BaCO_3$ (impure)	...	4.00	0.20	...
$SrCO_3$ (anal.)	0.63	...	0.58	...
$Ba(NO_3)_2$ (anal.)	...	0.15	...	0.28
$Sr(NO_3)_2$ (anal.)	0.06	...	...	...
$SrSO_4$ (purified)	<0.001	...	<0.001	0.25
$BaCrO_4$ (purified)	...	<0.001	<0.001	0.20
Blank (solids)[a]	<0.001	<0.001	<0.001	0.38

[a] Blank determination of all reagents used in chemical analysis in average amounts used.

The chemical analyses were carried out according to the directions given by Hildebrand and Lundell (*1*). The directions include the concentrated nitric acid method (*6*) for the separation of calcium from barium and strontium and the chromate method (*7*) for the separation of barium from strontium. Mixtures of the carbonates (0.2- to 0.3-gram sample) were treated with dilute nitric acid and evaporated to dryness on a steam bath. The dried nitrates were then extracted with concentrated nitric acid according to the modification by Knowles (*1*). The filtrate containing the soluble calcium nitrate was evaporated to dryness. The calcium was precipitated with ammonium oxalate and weighed as calcium oxide. Barium was separated from strontium by precipitation of barium chromate with ammonium dichromate from an ammonium acetate–buffered solution (*2*). Strontium was precipitated from the ammoniacal filtrate as strontium carbonate with ammonium carbonate, thus removing interfering chromate ions. The precipitate was then redissolved with dilute hydrochloric acid and precipitated as strontium sulfate from a dilute sulfuric acid–alcohol mixture (*3*).

Table II. Separation and Determination of Barium

(Values are per cent carbonate)

Sample[a]	1	2	3	4	5	6
Ba from $BaCrO_4$ ppt.	95.86	95.82	45.42	9.87[b]	9.62	4.75
Coprecipitants (detn. spec.)						
Sr	0.25	0.17	0.49	0.21	0.06	0.06
Ca	0.01	<0.01	<0.01	0.03	<0.01	<0.01
Na and other cations	0.60	0.56	0.26	0.21	0.06	0.04
Ba corrected for coprecipitants	95.00	95.09	44.67	9.42	9.50	4.65
Solubility losses of Ba (detn. spec.)						
Ba in $SrSO_4$	0.62	0.55	0.28	0.12	0.09	0.06
Ba in CaO	...	...	...	0.15	0.09	0.10
Ba in filtrate solids	0.04	<0.01	<0.01	0.06	<0.01	<0.01
Ba material balance value	95.66	95.64	44.95	9.75	9.68	4.81
Ba taken	95.80[c]	95.80[c]	45.30	9.71	9.71	5.00

[a] See Table V for composition and number of determinations.
[b] Indicates single precipitation.
[c] Impure $BaCO_3$, Table I; 95.80 ± 0.4%.

The procedure was modified in several analyses by precipitating strontium directly from the barium filtrate by the addition of dilute sulfuric acid and alcohol. The filtrate from the barium precipitation was first reduced to a small volume after the addition of sufficient nitric acid to keep the ions in solution until the acetic acid boiled off. To this small volume were added a tenfold volume of 6*N* sulfuric acid and then an equal volume of alcohol. The precipitate was washed and treated as in the usual procedure. All filtrates were combined and evaporated to dryness and ignited to 700° C. to give a matrix of chromic oxide, from the excess ammonium dichromate.

All precipitates and filtrate solids were analyzed spectrochemically in order to determine the impurities present. These were determined against standards containing the impurities as the carbonates. Each impurity was then calculated as per cent carbonate of the original sample and is given as such in Tables II, III, and IV, where each value represents the mean of several determinations. Sample compositions and the number of determinations are listed in Table V.

Table III. Separation and Determination of Calcium

(Values are per cent carbonate)

Sample[a]	4	5	6
Ca from CaC_2O_4 precipitate[b]	79.88	80.97[c]	91.30[c]
Coprecipitants (detn. spec.)			
Ba	0.15	0.09	0.10
Sr	0.51	0.53	0.50
Na and other cations	0.37	0.94	0.86
Ca corrected for coprecipitants	78.85	79.41	89.84
Ca not dissolved in concd. HNO_3			
Ca in $BaCrO_4$	0.03	<0.01	<0.01
Ca in $SrSO_4$	0.07	0.18	0.09
Ca in filtrate solids	0.93	0.40	0.35
Ca material balance value	79.88	79.99	90.28
Ca taken	79.94	79.94	90.00

[a] See Table V for composition and number of determinations.
[b] Ca absent in filtrate solids.
[c] Indicates single precipitation.

The gravimetric results are corrected for coprecipitation errors by subtracting the coprecipitants present. To this value (listed as "corrected for coprecipitants" in the table) is added the amount of the element found in the other products. This represents the total of the element present in all the products and is designated the material balance value.

DISCUSSION AND RESULTS

The chemical separation and determination of barium by the chromate method (Table II) gives good results within the limits of accuracy for routine analyses. These results agree well with the material balance values. The accuracy attained is due, however, to a compensation of errors, since the impurities present in the barium chromate precipitates are nearly equal to the losses due to the solubility of the barium compounds. Double precipitations of the barium chromate produce a coprecipitation error much less than that of single precipitations. Additional losses due to solubility on the second precipitation can be neglected if the volume of the solution is kept at a minimum. Strontium coprecipitation increases with the increasing strontium concentration.

Table IV. Determination of Strontium

(Values are per cent carbonates)

Sample[a]	1	2	3	4	5	6
Procedure	Reg.	Mod.	Reg.	Reg.	Mod.	Mod.
Sr from $SrSO_4$ precipitate	0.56	3.74	51.95	6.10	9.79	4.52
Coprecipitants (detn. spec.)						
Ba	0.51	0.55	0.28	0.12	0.09	0.06
Ca	<0.01	0.06	0.04	0.07	0.18	0.09
Cr	<0.01	0.02	<0.01	<0.01	0.02	0.01
Na and other cations	<0.01	<0.01	0.58	0.08	0.07	0.04
Sr corrected for coprecipitants	0.05	3.11	51.05	5.83	9.43	4.32
Prior coprecipitation (detn. spec.)						
Sr in $BaCrO_4$	0.25	0.17	0.49	0.21	0.06	0.02
Solubility losses of Sr (detn. spec.)						
Sr in CaO	...	...	...	0.51	0.53	0.50
Sr in filtrate solids	2.35	0.70	2.00	2.04	0.16	0.12
Sr material balance value	2.65	3.98	53.54	8.59	10.18	4.96
Sr taken	4.00[b]	4.00[b]	54.70	10.35	10.35	5.00

[a] See Table V for composition and number of determinations.
[b] Determined spectrochemically ±0.4%.

Table V. Comparison of *Gravimetric* Results with Material Balance Values

Sample	1	2	3	4	5	6
No. of determinations	6	4	3	3	1	3
$BaCO_3$						
Gravimetric	95.86	95.84	45.42	9.87[a]	9.62	4.75
Material balance	95.66	95.64	44.95	9.75	9.68	4.81
Taken	95.80	95.80	45.30	9.71	9.71	5.00
$SrCO_3$						
Gravimetric	0.56[b]	3.74	51.95[b]	6.10[b]	9.79	4.52
Material balance	2.65	3.98	53.54	8.59	10.18	4.96
Taken	4.00[c]	4.00[c]	54.70	10.35	10.35	5.00
$CaCO_3$						
Gravimetric	[d]	[d]		79.88	80.97[a]	91.30[a]
Material balance	0.12	0.06	<0.01	79.88	79.99	90.28
Taken	0.20[c]	0.20[c]		79.94	79.94	90.00
Total						
Gravimetric	96.42	99.58	97.37	95.85	100.38	100.57
Material balance	98.43	99.68	98.49	98.22	99.85	100.05

[a] Single precipitation.
[b] Regular procedure for strontium determination.
[c] Determined spectrochemically.
[d] Not determined.

The concentrated nitric acid separation of calcium from barium and strontium is not complete, as shown in Table III. The error to the calcium analyses, however, seems to be largely compensated, since the amount of barium and strontium dissolved in the nitric acid ("coprecipitants" with calcium oxalate) is nearly equal to the calcium remaining with the insoluble barium and strontium nitrates during the extraction. Double precipitations of calcium oxalate must be made to remove the high sodium content which causes the gravimetric results based on a single precipitation to be about 1% high. The amounts of barium and strontium occluded in the calcium oxalate precipitate remained essentially the same in the second precipitation. The calcium which remains with the insoluble barium and strontium nitrates during the extraction is found in the barium chromate, strontium sulfate, and filtrate solids. Most of the calcium is found in the latter, owing to the solubility of calcium chromate and calcium sulfate.

The strontium content of the barium chromate and the calcium oxalate represents a loss of 6 to 11% of the total strontium present (see Table IV).

Gravimetric analyses for strontium by the method outlined gave erratic results, with errors much greater than expected, owing to the strontium lost in the separations. The errors appeared to be largely due to the incomplete precipitation of strontium carbonate in the ammoniacal chromate-acetate solution, since spectrochemical analyses of the filtrate solids after removal of the strontium carbonate showed up to 3% out of the original strontium present, or a loss of about 8 mg. of strontium carbonate. This procedure has been justified on the basis that it provided for removal of interfering chromate ions before the precipitation of strontium sulfate. A modified procedure was tried, in which strontium sulfate was precipitated directly from the chromate-acetate solution. These procedures are designated as "regular" and "modified" in the tables. Precipitates were obtained which gave results in good agreement with the amount of strontium present. Spectrochemical analysis of the precipitates showed chromium present in amounts less than 0.5%, even though the precipitates were definitely colored by the chromic ion (formed by the reduction of chromate by the alcohol). The filtrate solids from this procedure showed a much lower concentration of

strontium. In samples containing large amounts of barium, the strontium sulfate contains a considerable concentration of barium.

A comparison of gravimetric and material balance values (Table V) shows that the latter are for the most part in better agreement with the theoretical and differ from it by no more than 0.4%, except in the strontium determination by the regular procedure. The error here is probably due to the inaccuracy of the spectrochemical determination of strontium when present in high concentration in the filtrate solids. Analyses of known mixtures in the matrix of chromic oxide gave low and erratic values for high concentrations of the alkaline earths. The material balance values themselves are slightly low. This is due in part to the uncertainty of the anion content of the precipitates which, for purposes of calculation, were assumed to contain one anion only. It will be seen that the material balance procedure gives satisfactory results even for the high gravimetric values obtained by single precipitations.

These studies show that gravimetric results may be corrected spectrochemically to give close to theoretical percentages. This holds particularly for elements present in low concentrations which as a rule coprecipitate wholly or in part with the major elements. The method has not been widely applied to work of this type but appears to have possibilities for further extension not only to studies of chemical procedures but to the complete analyses of minerals. Wider use of analyses of this type would lead to standardization of methods among laboratories and to the preparation of more reliable standards for spectrochemical work.

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Volumetric Determination of Gallium

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A REVIEW of the literature has disclosed only one volumetric method for the determination of gallium. Kirschman and Ramsey (*3*) were able to determine gallium by potentiometric titration with potassium ferrocyanide. Recently, Belcher, Nutten, and Stephen (*1*) have determined gallium by titration with potassium ferrocyanide using 3,3′-dimethylnaphthidine or 3,3′-dimethylnaphthidine sulfonic acid as indicator. The latter investigators titrated small amounts of gallium (0.74 to 2.94 mg.) with an average error of ±0.25%. The authors have developed a volumetric method for the determination of this less familiar element using 8-quinolinol.

Gallium is precipitated quantitatively over a considerable pH range with 8-quinolinol (8-hydroxyquinoline). Geilmann and Wrigge (*2*) have adapted the gallium derivative of 8-quinolinol to a gravimetric determination of the metal. Sandell (*8*) has developed a fluorometric method for the determination of gallium using 8-quinolinol. This quantitative method is especially applicable to microgram quantities of the metal and has been used by Sandell in determination of gallium in silicate rocks. Lacroix (*5*) has extended the fluorometric method to the determination of microgram (1.4 to 4.28) quantities of gallium in bauxite.

Moeller and Cohen (*6*) have made use of 8-quinolinol in a spectrophotometric determination of gallium. The tripositive gallium is quantitatively extracted from an acetate-buffered (pH 3.0 to 6.2) salt solution with a chloroform solution of 8-quinolinol. The resulting solution is analyzed with a spectrophotometer.

Various metals such as zinc, iron, cobalt, nickel, copper, aluminum, and gallium are quantitatively precipitated with 8-quinolinol. These precipitates can be used in the volumetric determination of the metals, since the 8-quinolinol can be readily brominated (*4*). However, to date such a volumetric method has not been reported for gallium.

Gallium is precipitated with 8-quinolinol according to the equation:

$$Ga^{+++} + 3C_9H_7ON \rightarrow Ga(C_9H_6ON)_3 + 3H^+$$

The bromination of 8-quinolinol using potassium bromate–potassium bromide solution takes place as follows:

$$Br\bar{O}_3 + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

$$C_9H_7ON + 2Br_2 \rightarrow C_9H_5Br_2ON + 2H^+ + 2Br^-$$

REAGENTS AND APPARATUS

Gallium. The metal (2.8148 grams, 99.9% pure), obtained from the Aluminum Co. of America, East St. Louis, Mo., was dissolved in approximately 150 ml. of 6*N* nitric acid and diluted to 1 liter (pH 0.6).

Potassium Bromate–Potassium Bromide. Approximately 2.79 grams of anhydrous potassium bromate, 24 grams of potassium bromide, and 2 grams of potassium hydroxide (all J. T. Baker's C.P.) were dissolved in water and diluted to 1 liter. This solution should be stored in a borosilicate glass container. The solution (approximately 0.1*N* with respect to potassium bromate) was standardized as follows: Fifteen milliliters of concentrated hydrochloric acid was diluted to 150 ml., 4 grams of solid potassium iodide was added and allowed to dissolve, and to this solution a measured volume of potassium bromate–potassium bromide solution was added. By this procedure there is no loss of bromine from vaporization. The liberated iodine was titrated with sodium thiosulfate using starch as the indicator. The sodium thiosulfate was standardized against 0.1000*N* potassium dichromate.

8-Quinolinol, J. T. Baker's C.P. A 2.5% solution was prepared by dissolving 5 grams of the reagent in 200 ml. of 1.2*N* acetic acid (pH 3.74).

Methyl Red, 0.1% solution in 95% ethyl alcohol.

Sodium Hydroxide, 2*N* aqueous solution.

Phenolphthalein, 1% solution in 95% ethyl alcohol.

Starch, 2% aqueous solution.

Apparatus. All pH measurements were made using a Beckman pH meter, Model G.

PROCEDURE

Pipet a sample of a solution containing tripositive gallium into a 250-ml. beaker and dilute to approximately 100 ml. After 1 drop of phenolphthalein indicator solution is introduced, add dilute sodium hydroxide until the solution turns red. While stirring this solution, at room temperature, add a slight excess

Table I. Analysis of Gallium Nitrate Solutions

Gallium, Gram		Error, %
Taken	Found	
0.01407	0.01410	+0.21
0.01407	0.01410	+0.21
0.01970	0.01970	±0.00
0.01970	0.01972	+0.10
0.01970	0.01966	−0.20
0.02815	0.02820	+0.18
0.02815	0.02820	+0.18

of the 8-quinolinol solution. The pH at which complete precipitation occurs was found to be 3.6. Cover the solution with a watch glass and heat on the steam bath for 1 hour. The initial precipitate is dense and flocculent; however, on heating this substance is transformed into fine crystals.

Separate the precipitate by filtration using a sintered-glass crucible of fine porosity. Wash the precipitate thoroughly with distilled water. Dissolve the precipitate in 60 ml. of hot 1.5*N* hydrochloric acid and catch the resulting solution in the original beaker. Transfer this solution to a 500-ml. iodine flask, dilute to approximately 175 ml., add 4 to 6 drops of methyl red solution, and titrate slowly with standard potassium bromate–potassium bromide solution. The indicator is oxidized and thus becomes colorless with excess potassium bromate–potassium bromide solution.

Add about a 5-ml. excess of this solution, swirl and stopper the flask, then add immediately, in small portions, 4 grams of potassium iodide in about 15 to 20 ml. of water. Add these samples to the well of the flask and admit by loosening the stopper. Finally rinse the well and the stopper with distilled water and titrate the liberated iodine with standard sodium thiosulfate solution using starch as indicator.

Blank determinations by titration have proved to be negligible.

DISCUSSION

It is evident that gallium must be separated from those metals which are also precipitated with 8-quinolinol at a pH of approximately 3.6. Prodinger (*7*) lists the different methods that may be used in separating gallium from other metals.

From the above equations it can be shown that the equivalent weight of gallium is $^1/_{12}$ the atomic weight. Then the total amount of gallium in a sample is given by the following:

$$\text{Ml. of } KBrO_3 \times N \text{ of } KBrO_3 \times 1/12{,}000 \times 69.72 = \text{grams of gallium}$$

Some representative results are shown in Table I.

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Titrations in Nonaqueous Solutions

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IN THE course of work being carried out on tobacco smoke, it became desirable to determine the total amounts of titratable acids and bases, both strong and weak. The ASTM method (*1*) using organic solvents and the calomel–glass electrodes system was found to be inapplicable to the materials encountered in this work.

GLASS ELECTRODES WITH GLACIAL ACETIC ACID LIQUID JUNCTION

In the last few years, the method of Conant and Hall (*2, 5*) for titrating weak bases in glacial acetic acid with perchloric acid in glacial acetic has been greatly improved. Recently, Pifer, Wollish, and Schmall (*6*) described a titration cell using the Beckman No. 1170 fiber-type calomel electrode and glass electrode. In the authors' experience using the Beckman No. 270 fiber-type calomel electrode, the quantities of the order of 2 mg. of weak bases, such as aniline and pyridine, could not be titrated successfully with the solvents and titrants described. The potentials were not steady and the end points were not reproducible. The difficulty seemed to be caused by the liquid junction potential which changed as the potassium chloride solution flowed from around the calomel electrode into the solution being titrated. This difficulty was obviated by the use of a glacial acetic acid bridge, separated from the solution being titrated by a fine sintered-glass disk, into which the calomel electrode could dip. The potential of this liquid junction does not change in a manner that interferes with the potential changes due to the neutralization of the base being titrated. The titration cell is easily cleaned (with solvents such as acetone) and a new junction can be made with fresh glacial acetic acid for each titration. This type of liquid junction is a simplification of that used by Hall and Conant (*5*) in which a supersaturated solution of lithium chloride in acetic acid in a U-tube separated the solution being titrated from the beaker or saturated potassium chloride solution into which the siphon of a calomel half-cell dipped, in a chloranil–calomel electrode combination. Fritz (*3*) describes the use of a silver–silver chloride electrode in place of the calomel half-cell to eliminate the liquid junction difficulties. The advantages of the titration cell de-

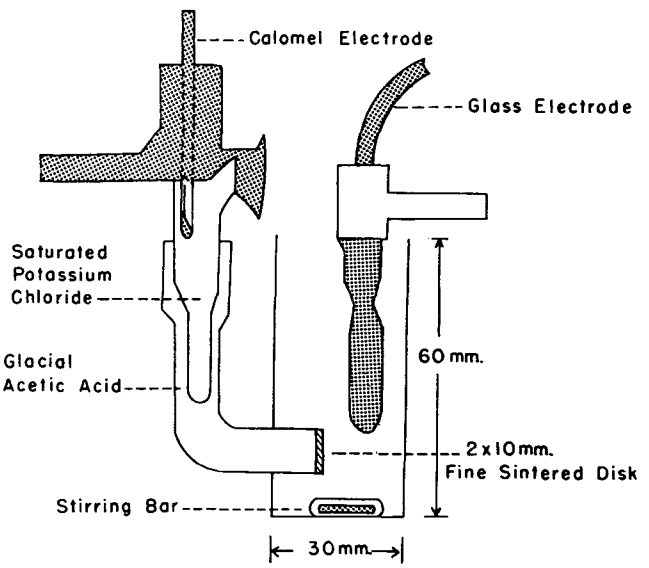

Figure 1. Titration Cell with Glacial Acetic Acid Liquid Junction

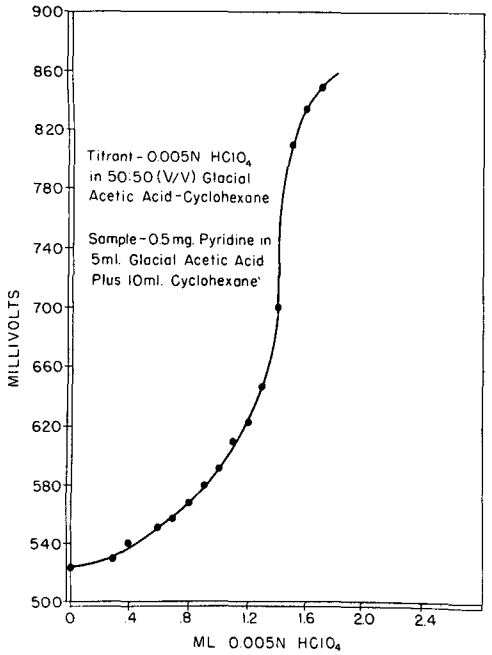

Figure 2. Titration of Pyridine

scribed in this paper are that commercial rugged type electrodes can be used, excessive leakage of potassium chloride solution from the calomel electrode does not interfere, and that leakage of acetic acid into the solution being titrated has little or no effect since acetic acid is the solvent.

Apparatus. The cell and the electrode arrangement are shown in Figure 1. A Beckman No. 290 glass electrode and a Beckman No. 270 calomel electrode were used in conjunction with the Beckman Model G pH meter for determining the potentials. Stirring was accomplished with a Precision Scientific Co. Mag-Mix. An iron bar enclosed in a 15 × 3 mm. borosilicate glass tube served as a stirring bar. The pH meter, the Mag-Mix case, and the glass electrode holder were grounded.

Procedure. The samples were dissolved in 15 ml. of glacial acetic acid and placed in the titration vessel. Titrations were carried out with 0.005*N* perchloric acid in glacial acetic acid. Better end points were obtained by using 5 ml. of cyclohexane and 10 ml. of glacial acetic acid as the solvent, although the potential readings were less steady in the initial stages of the titration. A 5-ml. microburet (Scientific Glass Co. Catalog No. M2935) was used with potential readings taken every 0.1 ml. The easily determined end point potential obtained in the titration of 0.5 mg. of pyridine in cyclohexane glacial acetic acid is shown in Figure 2.

ANTIMONY ELECTRODE

Fritz and Lisicki (*4*) reported the successful titration of weak acids such as phenols using an antimony-glass electrode cell with butylamine as solvent. The authors' results with this method have been equally good. However, they have found that the antimony electrode behaved erratically and sometimes did not function at all unless the electrode surface was renewed prior to each titration. Evidently, an inactive film is formed on the antimony, so that the electrode does not respond to changes in basicity. The antimony electrode (Figure 3) was prepared in the following manner:

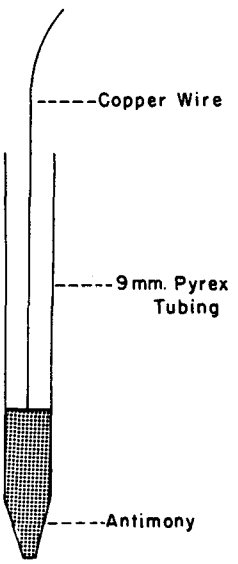

Figure 3. Antimony Electrode for Titration of Weak Acids

A 9-mm. borosilicate glass tube was sealed at one end and successive portions of antimony metal powder (General Chemical Co.) were melted in it so that a solid rod of antimony about 30 mm. in length was formed in the glass tube. The end of the glass tube was then ground off on a wet belt sander to leave a 12-mm. length of antimony exposed. Electrical connection was then made by soldering a copper wire to the electrode (see Figure 3). It was found that only by removing the oxide coating from the electrode surface with sand paper before a titration would the electrode function properly or at all. When this was done reproducible potentials and end points were obtained.

Another factor that must be regarded is that the end point potential in the titration of phenols is slowly reached. For this reason, it is necessary to wait until the potential is really constant before making a reading. It is also necessary to use freshly distilled butylamine in the titrations if a high blank titration is to be avoided. Figure 4 illustrates the titration of thymol with sodium methylate in 10% methanol–benzene (volume/volume) as titrant and butylamine as solvent.

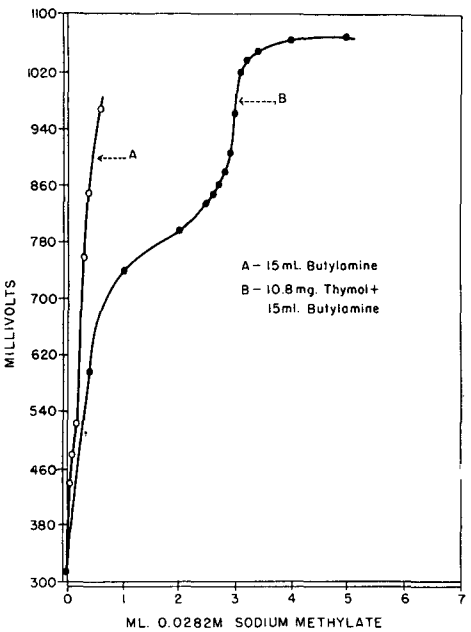

Figure 4. Titration of Thymol

By using these titration cells and exercising the precautions described, the quantities in tobacco smoke of acids and bases with dissociation constants of the order of 10^{-5} as differentiated from the quantities of acids and bases with dissociation constants the order of 10^{-9} have been determined.

ACKNOWLEDGMENT

The titration cell was constructed by J. D. Graham, Jr., Duke University.

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Determination of Chlorine in Water

Suggested Use of 3,3′-Dimethylnaphthidine

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MANY reagents have been proposed for the determination of chlorine in water, but only two, benzidine and its 3,3′-dimethyl-derivative (*o*-tolidine), have achieved widespread use. The yellow colors produced when these substances are treated with oxidizing agents (in this case, chlorine water) are not very stable and fade rapidly.

In their studies of substituted benzidines and related compounds as reagents in analytical chemistry the authors have recommended 3,3′-dimethylnaphthidine (3,3′-dimethyl-4,4′-diamino-1,1′-dinaphthyl) as a reagent for the detection of zinc (*1*) and vanadium (*2*) and as a redox indicator in the titration of zinc (*3*), cadmium, calcium, indium (*4*), and gallium (*5*), with potassium ferrocyanide. In the presence of oxidizing agents this compound gives an exceptionally stable, purple-red meriquinonoid product. The reaction is very sensitive, exceeding that of any other benzidine-type compound for the many oxidizing agents examined.

The sensitivities of 3,3′-dimethylnaphthidine and certain other substituted benzidines towards chlorine have now been determined. These values are recorded in Table I with those of benzidine and 3,3′-dimethylbenzidine included for comparison.

These figures give some indication of the relative sensitivities of the various amines under the experimental conditions employed. It is seen that the reagents at present in use are neither the most sensitive nor the most suitable. From the standpoint of color stability, the *N*- and *N,N′*-alkylated benzidines are superior to the simple diamines—a fact which has been observed from their behavior towards many other oxidizing agents (*6*). None, however, is as sensitive as 3,3′-dimethylnaphthidine. The favorable characteristics of high sensitivity, stability of color, and ease of color measurement make the reagent ideally suited to the colorimetric determination of chlorine.

Table I. Comparative Sensitivities

Amine	Comparative Sensitivity	Color
1. Benzidine	1.0	Pale yellow; fades rapidly
2. 3,3′-Dimethylbenzidine	1.0	Pale yellow; fades rapidly
3. 3-Methylbenzidine	0.5	Pale yellow; fades rapidly
4. 3,3′-Diethylbenzidine	0.5	Pale yellow; fades rapidly
5. *N*-Methylbenzidine	0.5	Pale yellow; fades slowly
6. *N,N′*-Dimethylbenzidine	0.25	Pale yellow; fades very slowly
7. *N,N′*-Tetramethylbenzidine	0.20	Pale yellow; fades very slowly
8. *N,N′*-Diethylbenzidine	0.25	Pale yellow; fades slowly
9. *N,N′*-Tetramethylbenzidine	0.5	Pale yellow; fades slowly
10. Naphthidine	1.0	Transient pink
11. 3,3′-Dimethylnaphthidine	0.1	Pink-red; very stable

Table II. Limiting Sensitivities under Conditions for Determination of Chlorine

Amine	1	2	3	4	5	6	7	8	9	10	11
Sensitivity, p.p.m. chlorine	0.1	0.07	0.1	0.5	0.1	0.2	0.1	0.08	0.07	0.5	0.04

The usual procedure in water analysis necessitates a Nessler tube comparison. Under these conditions the sensitivities are improved, as shown in Table II.

The colors obtained with 3,3′-dimethylnaphthidine and a range of standard chlorine solutions measured using the EEL photoelectric colorimeter (Evans Electroselenium, Ltd., Harlow, Essex, England) show that Beer's law is obeyed and that the colors formed are sufficiently reproducible to enable accurate results to be obtained on as little as 0.05 p.p.m. of chlorine. A typical curve is shown in Figure 1. The EEL colorimeter is a simple single-cell, direct-reading instrument; using a more sensitive absorptiometer it should be possible to detect less than 0.01 p.p.m. of chlorine.

REAGENTS AND SOLUTIONS

Chlorine waters of appropriate strength are obtained by the dilution of a strong solution of chlorine in water the strength of which is accurately known by thiosulfatimetric titration.

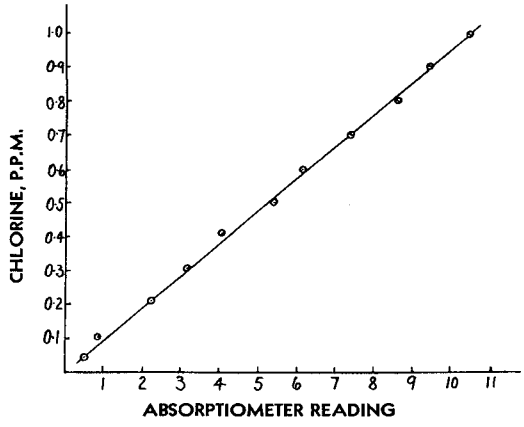

Figure 1. Typical Curve Obtained in Determination of Chlorine Using 3,3-Dimethylnaphthidine

With the exception of 3,3′-dimethylnaphthidine (0.1% in glacial acetic acid), all the amine reagents are used as 0.1% solutions in 1*N* hydrochloric acid. This compound was synthesized by the authors according to the method of Fries and Lohmann (*7*). It is now available commercially from British Drug Houses, Ltd., Laboratory Chemicals Group, Poole, Dorset, England.

PROCEDURES

Determination of Sensitivities. To 10 ml. of chlorine solution contained in a test tube, add 1 ml. of the amine reagent and observe the color. Dilute the chlorine solution until the color is just detectable when viewed against a white background.

Detection of Chlorine under Conditions of Actual Analysis. Place 100 ml. of the chlorine solution in a Nessler tube, add 1 ml. of reagent, and mix thoroughly. Allow to stand for 1 minute and observe the color. Repeat with more dilute chlorine solutions until the color is just apparent.

Determination of Chlorine (0.05 to 1.0 P.P.M.) in Water Using 3,3′-Dimethylnaphthidine. To 100 ml. of sample contained in a graduated flask, add 1 ml. of 0.1% solution of 3,3′-dimethylnaphthidine in glacial acetic acid and mix the solution thoroughly. Allow to stand for 5 minutes and record the intensity of the color, photoelectrically, using a green filter—e.g., Ilford 404 Green. Compare with values obtained from standard calibration curves.

DISCUSSION AND RESULTS

Of the several amines examined, all are more sensitive than either benzidine or 3,3′-dimethylbenzidine. In particular, 3,3′-dimethylnaphthidine is the most sensitive, and it is recom-

mended as a reagent for the detection and determination of chlorine. Accurate results are obtained with as little as 0.05 p.p.m. of chlorine and the color formed is more stable than that given by any of the other amines. The color begins to fade only after 15 to 20 minutes, and then only at a very slow rate. Reproducible results are obtained, even in the lowest range of 0.05 to 0.5 p.p.m. examined. Comparisons can be made using standard calibration curves.

Acetate buffers retard the development of the color and mineral acid interferes even in 0.01*N* concentration. Other oxidants present in the solution will also interfere, but the procedures used in water analysis take full account of these interferences. In general, treated waters do not contain significant amounts of oxidants, other than chlorine.

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Sulfuric Acid–Induced Fluorescence of Corticosteroids

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OF THE relatively large number of corticosteroids tested by Reichstein and Shoppee (*5*) and by Wintersteiner and Pfiffner (*9*), only three substances, corticosterone, 17-hydroxycorticosterone, and 4-pregnene-11β,17α,20β,21-tetrol-3-one, were found to exhibit sulfuric acid–induced fluorescence. 17-Hydroxy-11-dehydrocorticosterone, an 11-keto compound, was included in the group of fluorescent steroids by Wintersteiner and Pfiffner (*9*). However, if purified by chromatography, 17-hydroxy-11-dehydrocorticosterone does not fluoresce when treated with sulfuric acid (*1*).

Sulfuric acid–induced fluorescence has been confined to the qualitative analysis of cortical steroids. The experimental results presented demonstrate that the phenomenon may be adapted to the quantitative analysis of corticosterone and 17-hydroxycorticosterone by reacting ethanolic solutions of these steroids with sulfuric acid.

EXPERIMENTAL

Relation Between Wave Length of Excitatory Beam and Intensity of Fluorescence. Three light sources were used to determine the wave lengths of light which excite ethanolic sulfuric acid solutions of 17-hydroxycorticosterone to a maximal degree of fluorescence: an AH-3 Hanovia mercury arc lamp, a Beckman hydrogen discharge tube, and a Beckman tungsten filament lamp.

MERCURY ARC LAMP. Various combinations of primary filters were introduced into the path of light emitted by the mercury arc of a Farrand Model A fluorometer. The secondary light filter was fixed (a combination of Wratten gelatin No. 16 and No. 74 secondary light filters). A 10 × 75 mm. Corning No. 9820 test tube containing a mixture of 0.1 ml. of absolute ethyl alcohol and 1.0 ml. of concentrated sulfuric acid was placed in the carriage compartment and the sensitivity dial adjusted to a reading of 5 on the galvanometer scale. To an optically matched tube containing 0.25 γ of 17-hydroxycorticosterone dissolved in 0.1 ml. of absolute ethyl alcohol was added 1 ml. of concentrated sulfuric acid; the mixture was stirred and the tube placed in the path of the excitatory light beam. Maximal galvanometer deflection above the blank reading of 5 was obtained with a combination of Corning No. 5113 and No. 4489 filters which limited transmission to the region of the 436 mμ mercury line.

HYDROGEN AND TUNGSTEN LAMPS. A standard 4-ml. quartz absorption cell containing 50 γ of 17-hydroxycorticosterone in 3 ml. of 1 to 10 ethanolic sulfuric acid solution was placed in the carriage compartment of a Beckman DU spectrophotometer. A plate containing an upright metal tube 6 inches long and 1 inch in diameter was substituted for the regular carriage top plate. The intensity of fluorescence emitted by the steroid solution was estimated by eye for the various settings of the wave selector dial of the spectrophotometer.

With a slit width of 0.015 mm., those wave lengths of light from the hydrogen discharge tube which excited maximal degrees of fluorescence in the steroid solutions appeared to be in the spectral region 470 to 480 mμ. Wave lengths of light greater than 535 mμ or less than 440 mμ failed to excite visible fluorescence. Studies with the tungsten filament lamp were in essential agreement with those which employed the hydrogen lamp.

The ethanolic sulfuric acid solution of 17-hydroxycorticosterone had a distinct absorption peak at 475 mμ. This observation indicates that light energy is absorbed from the same region of the spectrum which excites maximal fluorescence of the steroid.

The discrepancy between the results obtained with the mercury arc lamp and those obtained with the tungsten and hydrogen lamps deserves comment. The tungsten and hydrogen lamps emit a continuous spectrum, whereas the mercury lamp emits a discontinuous spectrum which is characterized by the fact that a relatively large fraction of the total energy is in the 436 mμ area. Wave lengths less than 440 mμ did not excite visible fluorescence in the Beckman with the tungsten and hydrogen lamps. The fact that the mercury lamp induced fluorescence at this wave length is probably due to the fact that the emission at 436 mμ is

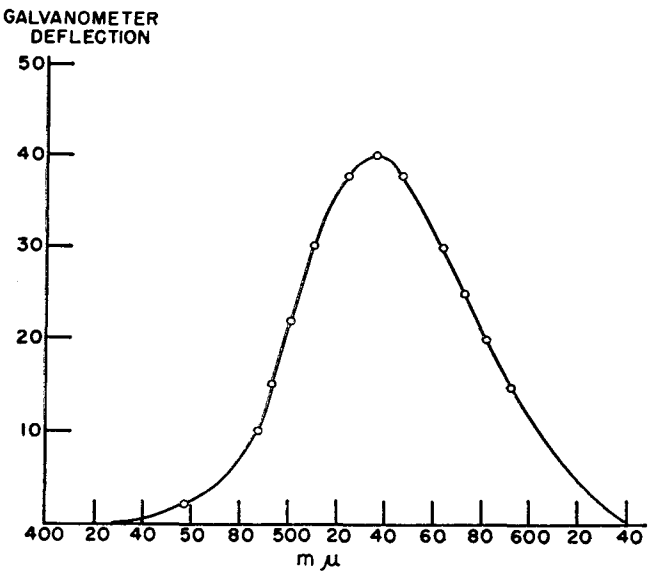

Figure 1. Emission Spectrum of Fuorescence Produced by 17-Hydroxycorticosterone in Ethanolic Sulfuric Acid Solution

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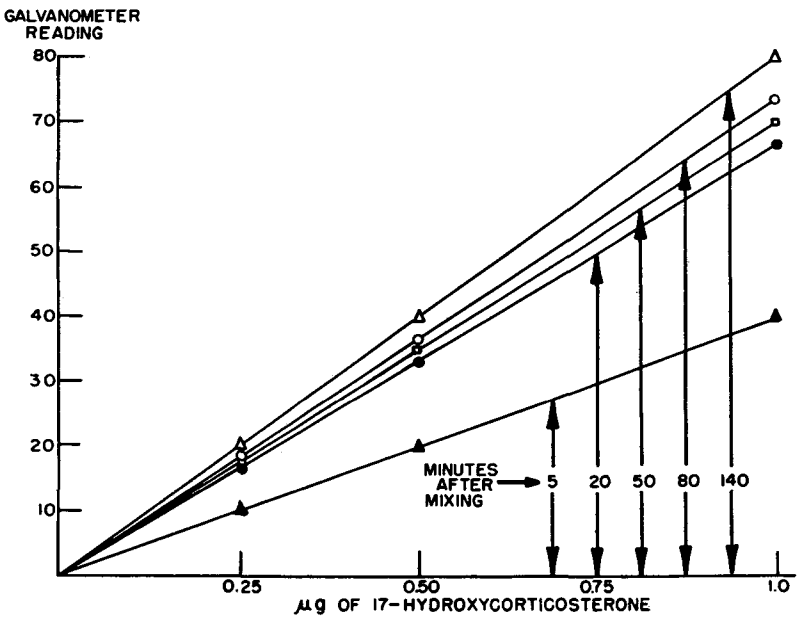

Figure 2. Effect of Time on Development of Fluorescence

of much higher intensity than that of the tungsten or hydrogen lamp. In addition, the fluorometer has a system of condensing lenses for concentrating the emission of the mercury lamp; the Beckman adaptation had no such system. Although optimal excitation of fluorescence is produced by wave lengths of light in the spectral region of 475 mμ, wave lengths of light some distance from this value will also induce fluorescence provided the intensity of the emitted light is relatively great. From a practical point of view the fluorometer with mercury lamp is the instrument of choice at this time.

Spectral Characteristics of Fluorescence. BECKMAN SPECTROPHOTOMETER. The intensity of fluorescence produced by 17-hydroxycorticosterone was determined for the various wave length settings of a Beckman DU spectrophotometer. The standard light housing was replaced with a specially constructed housing which contained a compartment to hold a tube of fluorescent steroid, an AH-3 Hanovia mercury arc lamp, and a combination of Corning No. 5113 and No. 4489 primary light filters. The filtered beam of excitatory light entered the tube compartment at 90° to the emitted fluorescent beam which in turn was directed into the spectrophotometer for resolution and analysis of intensity.

The spectral characteristics of the fluorescence were determined in a manner similar to that described for the wave-length calibration of the Beckman spectrophotometer (*3*). The selector switch was placed in the "1.0" position, the sensitivity dial turned to the middle of its range and the transmittance scale set at 3% transmission. With 200 γ of 17-hydroxycorticosterone in 10 ml. of 1 to 10 ethanolic sulfuric acid solution the maximum deflection of the indicator needle was observed to occur in a range between 530 to 550 mμ. The relative intensities of the various wave lengths of light emitted by the fluorescent steroid are shown in Figure 1.

FILTERS. Various secondary light filters were placed between the fluorescent steroid and the photoelectric cell of the Farrand fluorometer. The galvanometer was set to zero by adjustment of the dark current dials with a blank tube in place. Of the numerous filters tested, a combination of Wratten gelatin filters, No. 16 and No. 74, produced the greatest galvanometer deflection. This combination of filters is characterized by a relatively sharp transmittance band between 530 and 545 mμ. When filters were used whose transmittance bands were either higher or lower in the spectrum, the galvanometer response was markedly decreased. These results are in harmony with those obtained with the Beckman spectrophotometer.

Method for Routine Quantitative Analysis of Steroids. For the quantitative analysis of fluorescent steroids, a 10 × 75 mm. Corning No. 9820 test tube containing 0.1 ml. of redistilled absolute ethyl alcohol and 1 ml. of reagent grade concentrated sulfuric acid was placed in the excitatory beam of the fluorometer. The dark current dials were turned to the extreme right and the sensitivity dials adjusted for a galvanometer reading of 5. The light shutter of the fluorometer was then opened and the dark current dials were adjusted for a galvanometer reading of zero. The steroid solutions were prepared in optically matched tubes. One milliliter of concentrated sulfuric acid was added rapidly to 0.1 ml. of absolute ethyl alcohol containing 0.005 to 30 γ of 17-hydroxycorticosterone and the mixture stirred thoroughly with a footed glass rod. After standing 20 minutes the tubes were placed in the fluorometer and the galvanometer readings recorded. The sensitivity dials of the fluorometer were adjusted so that the greatest concentrations of steroid read between 80 and 100 on the galvanometer scale.

RESULTS

The data in Figure 2 show that the intensity of the fluorescence increases with time after mixing. Since 20 minutes after mixing the rate of increase in intensity of fluorescence is relatively slow, this time has been selected for routine analyses.

The sensitivity of the fluorescent technique is illustrated in Figure 3. Good reproducibility is obtained with amounts of steroid equal to or greater than 0.05 γ but a distinct spread in the

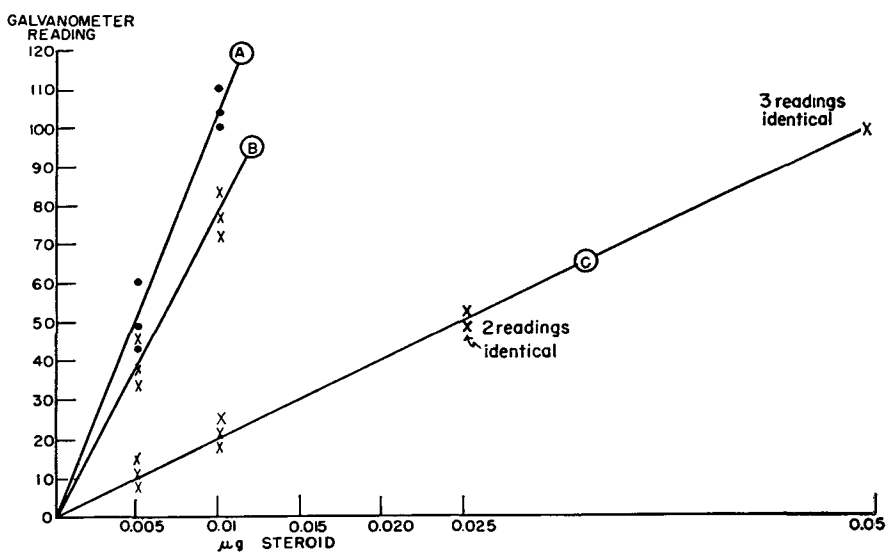

Figure 3. Reproducibility and Sensitivity of Fluorescent Technique for Analysis of 17-Hydroxycorticosterone

0.005, 0.01, 0.025, and 0.05 γ of steroid in 0.1 ml. of ethyl alcohol were treated with 1.0 ml. of sulfuric acid and compared at three different sensitivity settings (A, B, C) of fluorometer

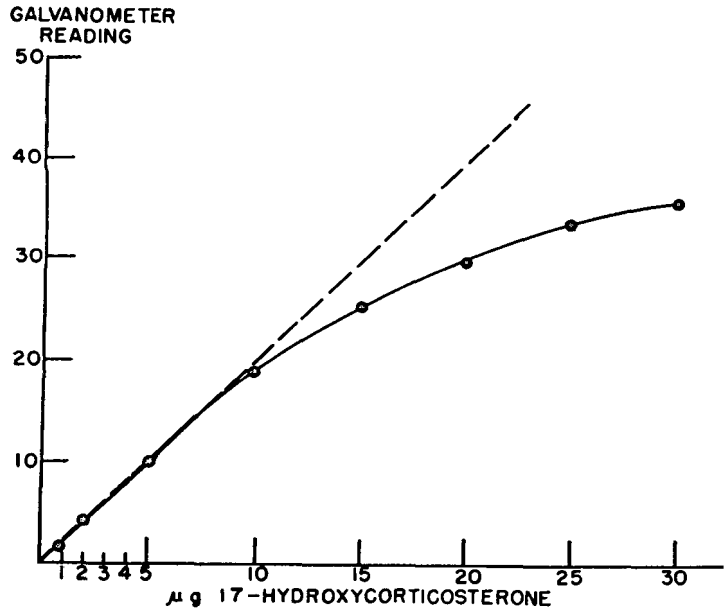

Figure 4. Self-Absorption Effect of Fluorescence Produced by Quantities Greater than 6.5 γ of 17-Hydroxycorticosterone

readings of triplicate samples is observed at 0.005 and 0.01 γ. Reproducibility is poor for quantities of steroid less than 0.005 γ.

The self-absorption effect of the fluorescence produced by amounts of steroid greater than 5 γ is shown in Figure 4. The increments of galvanometer readings for equivalent and equal increments of steroid steadily decrease from 5 to 30 γ.

Of the substances available, five steroids of the pregnane series (I, Ia, VI, VIa, and XII in Table I) produce a characteristically intense fluorescence in ethanolic sulfuric acid solution. These are the three steroids and their corresponding 11-hydroxy epimers observed by Reichstein and Shoppee (*5*) and by Wintersteiner to produce fluorescence. Several of the cortical steroids exhibited degrees of fluorescence between 5 and 15% of that produced by 17-hydroxycorticosterone. Steroid IV exhibited a fluorescent value of 12.5. This fluorescence is probably a property of the steroid itself rather than a contaminant, since several samples of the compound, including one which was rechromatographed and recrystallized, gave similar values.

The analysis of three samples of steroid V showed fluorescent values of 12.5, 12.0, and 7.0 per microgram, which indicates the presence of a variable amount of contaminant in these samples. The true fluorescent values of V is probably not greater than 7.0, the value listed in Table I. The two tetrahydro compounds, III and VII, which exhibited fluorescence equal to 14.3 and 14.6% of 17-hydroxycorticosterone were synthesized from fluorescent compounds I and VI and the possibility that trace amounts of these mother substances are present and responsible for the fluorescence has not been ruled out. No attempt was made to purify III and VII and several other compounds listed in Table I because of the minute quantities available.

Compound II, a saturated 11β-hydroxy compound, exhibits very little fluorescence in comparison to the corresponding unsaturated compound I. Two synthetic 12ξ hydroxypregnane compounds (XVIII, XIX) which do not belong to the cortical steroid group exhibited appreciable fluorescence. Other steroids known to fluoresce are in the estrogen series. The comparative values of estrone and estradiol, determined by the ethanolic-sulfuric acid procedure, are included in Table I. Androgens appear to exhibit very little fluorescence.

A comparison of the intensity of the fluorescence produced by corticosterone with that produced by 17-hydroxycorticosterone is shown in Figure 5. The spectral characteristics of the fluorescent light emitted from corticosterone in a mixture of ethyl alcohol and sulfuric acid appear to be identical with those of 17-hydroxycorticosterone. However, the maximal degree of fluorescence of corticosterone is induced by light of wave length in the 455 to 460 mμ region, which is somewhat shorter than that exciting the maximum degree of fluorescence of 17-hydroxycorticosterone. A comparable difference is also noted in the absorption characteristics of the two compounds in a mixture of ethanol and sulfuric acid. Corticosterone has an absorption peak at 455 to 460 mμ in contrast to 17-hydroxycorticosterone which exhibits maximum absorption at 475 mμ.

DISCUSSION

Certain generalizations about the structure activity relationship of steroid fluorescence may be made from the data presented in Table I. Presence of hydroxyl at position 11 of the steroid nucleus appears to be necessary for the production of a high degree of fluorescence (compare I and Ia with IV and with V and compare VI and VIa with VIII and IX). The α,β unsaturated ketone group in ring A also exerts a strong influence on fluorescence. Saturation of this group in the 11-hydroxy series results in a marked reduction in the degree of fluorescence produced (compare I and Ia with II and with III and compare VI and VIa with VII). However, in the 12-hydroxy series, the saturated compound appears to exhibit the greater degree of fluorescence (compare XVIII with XIX). Hydroxyl at position 17 exerts a minor influence on fluorescence (compare I and Ia with VI and VIa).

Since a number of substances other than I, Ia, VI, VIa, and XII fluoresce in the presence of sulfuric acid, the application of the phenomenon to quantitative analysis of biological fluids and tissues must necessarily depend upon techniques designed to

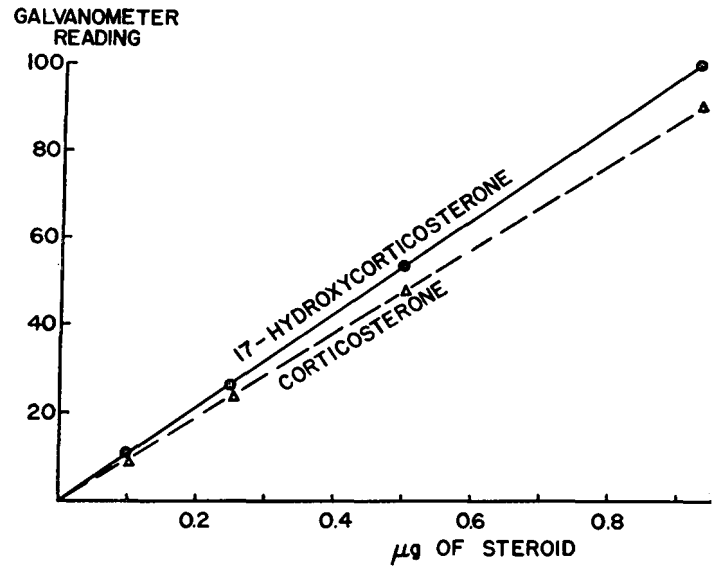

Figure 5. Comparison of Fluorescence of Corticosterone and 17-Hydroxycorticosterone

0.1, 0.25, 0.5, and 1.0 γ of each steroid in 0.1 ml. of ethyl alcohol were treated with 1.0 ml. of concentrated sulfuric acid and compared in fluorometer

Table I. Relative Fluorescence of Steroids

Steroid No.	Steroid	Fluorescence per Microgram, Galvanometer Reading
I	17-Hydroxycorticosterone (F_K)[a]	100.0[b]
Ia	4-Pregnene-11α,17α,21-triol-3, 20-dione (Epi F_K)	100.0
II	Pregnane-11β, 17α, 21-triol-3, 20-dione diacetate (dihydro F_K)	5.0
III	Allopregnane-3α, 11β, 17α, 21-tetrol-3-one, 3, 21 diacetate (tetrahydro F_K)	14.3
IV	17-Hydroxy-11-desoxycorticosterone	12.5
V	17-Hydroxy-11-dehydrocorticosterone (cortisone)	7.0
VI	Corticosterone (B_K)	87.0
VIa	4-Pregnene-11α, 21-diol-3, 20-dione (Epi B_K)	88.0
VII	Allopregnane-3α, 11β, 21-triol-20-one, 21 acetate (tetrahydro B_K)	14.6
VIII	11-Dehydrocorticosterone	0.8
IX	11-Desoxycorticosterone	4.5
X	Allopregnane-21-ol-3, 20-dione, acetate	0.5
XI	Allopregnane-3α, 21-diol-20-one, diacetate	7.5
XII	4-Pregnene-11β, 17α, 20β, 21-tetrol-3-one (tetrol E_R)[c]	80.0[d]
XIII	4-Pregnene-17α, 20β, 21-triol-3-one, 20, 21 diacetate (pregnenetriol)	3.2
XIV	11-Hydroxyprogesterone	4.1
XV	4-Pregnene-3, 20-dione (progesterone)	0.8
XVI	4-Pregnene-17α-ol, 3, 20-dione (17-hydroxyprogesterone)	0.6
XVII	Allopregnane-3α, 17α, 21-triol-20-one (pregnanediol)	4.5
XVIII	4-Pregnene-12 ξ, 21-diol-3, 20-dione, 21 acetate	15.0
XIX	Pregnane-12 ξ, 21-diol-3, 20-dione, 21 acetate	32.0
XX	4-Pregnene-21-ol-3, 20-trione, acetate	2.0
XXI	Testosterone	0.5
XXII	4-Androstenedione-3, 17	1.6
XXIII	Estrone	31.0
XXIV	Estradiol	106.0

[a] Subscript K refers to Kendall's designation.
[b] Galvanometer set at 100 with 1.0 γ of 17-hydroxycorticosterone.
[c] Subscript R refers to Reichstein's designation.
[d] Estimated value due to tendency of substance to form hydrated crystals.

extract, purify, and resolve the cortical steroids. The cortical steroids may be readily separated from fats, cholesterol, and estrogens by partitioning techniques. They may be separated from each other by paper chromatography (*2, 10*) or by a silicic acid microcolumn (*7*).

The steroids listed in Table I include only a small fraction of known cortical steroids. Cortical steroids, other than those listed in Table I, may be found to fluoresce with sulfuric acid.

The fluorescent technique in conjunction with a silica gel microcolumn (*7*) has been applied to the quantitative analysis of 17-hydroxycorticosterone and corticosterone in biological fluids and tissues. Sweat (*6*) has employed the technique to determine the rate of enzymatic synthesis of 17-hydroxycorticosterone from 17-hydroxy-11-desoxycorticosterone in adrenal mitochondrial preparations. The technique has been utilized by Sweat and Farrell (*8*) to determine the concentration of 17-hydroxycorticosterone and corticosterone *in the* adrenal venous blood of the dog and rat. The fluorescent method is accurate and reproducible. It is more sensitive than the phenylhydrazine technique of Porter and Silber (*4*). The fluorescent procedure is relatively simple and appears to be less susceptible to background interference than is the phenylhydrazine reaction.

Quantities of steroid between 0.05 and 5.0 γ produce a rectilinear relation between amount and galvanometer reading. This is a suitable range for analytical work. A range between 0.25 and 1.25 γ has been found to be most advantageous for analysis of biological materials. For quantities of steroid greater than 5.0 γ it must be remembered that self-absorption is great enough to produce significant deviation from the rectilinear relation between quantity of steroid and galvanometer reading. A typical standard curve for the quantitative analysis of 17-hydroxycorticosterone is shown in Figure 5.

ACKNOWLEDGMENT

The author wishes to acknowledge the valuable technical assistance of Ella Sandberg and the helpful advice and friendly criticisms of George Sayers and Gordon Farrell throughout the course of this investigation. The crystalline steroids used in these studies were kindly supplied by Leonard R. Axelrod, Karl Folkers, Thomas F. Gallagher, William J. Haines, Dwight Ingle, Tadeus Reichstein, and George Rosenkranz.

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Reactions of Certain Unsaturated Steroids with Acid Iron Reagent

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THE present-day prominence of sterols containing different kinds of double bond configurations has increased the importance of both the qualitative and quantitative analysis of these compounds. The chemistry of the Δ^5 unsaturated sterols have been thoroughly investigated (*2, 3*) and up to this time there have been a few main reactions commonly used to develop colors from which the quantity of the sterols may be determined (*1, 5, 6, 10*). Many other reactions have appeared which give qualitative evidence, usually involving the formation of a colored ring at the interface of two liquids of different densities (*4, 7–9, 11*).

The purpose of the present investigation is to show the color reaction of iron with steroids in a glacial acetic acid–sulfuric acid medium (*12*). The main emphasis is placed on those sterols which have Δ^5 unsaturation with the idea of determining specificity for these particular compounds. A large number of different steroids were used in the study.

REAGENTS

Ferric Chloride Solution. Weigh out 1 gram of ferric chloride hexahydrate and dissolve it in 10 ml. of glacial acetic acid.

Color Reagent. Pipet 1.0 ml. of the ferric chloride solution into a 100-ml. volumetric flask and dilute to the mark with concentrated sulfuric acid with mixing.

Glacial Acetic Acid.

Steroid Solutions. Weigh out 25 mg. of the steroid to be tested. Transfer to a 100-ml. volumetric flask and dissolve and dilute to the mark with glacial acetic acid.

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Table I. Colors of Steroids Tested with Iron Reagent

Compound Tested	Color Formed
Cholesterol	Purple
Cholestanol	Yellow
Dehydroisoandrosterone	Red
Isoandrosterone	Yellow
Methyl-Δ^5-3β-hydroxyetiocholenate	Green
Δ^5-Pregnenolone	Reddish-purple
$\Delta^{5,16}$-Pregnenolone acetate	Brownish-orange
Testosterone	Pale yellow
Δ^5-Androstene-17β-acetoxy-3-ethylene-cyclic hemithioketal	Blue-violet
Cholesterol acetate	Purple
Cholesterol oleate	Purple
Cortisone	Pale yellow
Kryptogenin acetate	Pink
7-Dehydrodiosgenin acetate	Purple
Stigmasterol	Purple
Sitosterol	Blue-violet
$\Delta^{4,7}$-22-Isospirostadiene-3-one	Yellow
Cholesteryl iso methyl ether	Red-violet
Estradiol	Pale yellow
Ergosterol acetate	Brownish
Pregnane-3β-ol-20-one	Yellow
17-Methyl-androstan-3β-17β-diol	Yellow
17-Methyl-Δ^5-androsten-3β-17β-diol	Purple

PROCEDURE

Pipet 1.0 ml. of steroid solution into a test tube. Add 2.0 ml. of glacial acetic acid. Pipet in 2.0 ml. of the color reagent by carefully allowing it to flow down the side of the test tube, thus producing two layers. Record the colors of the several rings formed for aid in qualitative analysis and then strike the bottom of the tube sharply while holding it at the top between the thumb and forefinger to effect mixing. The color of the solution formed may be used as a qualitative test or the measurement of the absorbance at the proper wave length may be used as a quantitative test for the Δ^5 sterols such as cholesterol, pregnenolone, stigmasterol, sitosterol, and others. The colors are stable and show no change over a period of several hours.

DISCUSSION AND RESULTS

The compounds tested were several saturated and unsaturated steroids where the latter included Δ^4, $\Delta^{4,7}$, Δ^5, $\Delta^{5,7}$, and $\Delta^{5,16}$ unsaturated steroids. The colors all appear almost immediately after mixing, and Table I shows the colors obtained with the available compounds which were reacted with the iron reagent. The Δ^4 and the $\Delta^{4,7}$ steroids give a brownish-yellow or purple ring, while only a thin yellow ring appears at the interface of the two liquids with the saturated compounds. The Δ^5, the $\Delta^{5,7}$, and the $\Delta^{5,16}$ steroids give a multicolored ring (usually 3 to 4 colors) which may include any combination of purple, green, yellow, red, pink, orange, violet, and brown.

Most Δ^5 compounds such as cholesterol (*12*) and Δ^5 pregnenolone produced linear curves up to 100 p.p.m. obeying Beer's law over the entire range. The authors used a Coleman Jr. spectrophotometer for measurements. This preliminary work was carried out with a large variety of pure compounds but the work in progress is directed toward more specific determinations.

ACKNOWLEDGMENT

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Kjeldahl Method as Applied to Determination of Nitrogen in Nitrates

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THE fact that nitrates in excess of the salicylic acid capacity in the modified Kjeldahl method give nitrogen results that are only slightly low has resulted in acceptance of unscientific practices. In this study are recorded some developments indicating the need for corrections in current Kjeldahl methods prior to 1950, and in the Gunning method current today, as applied to materials of high-nitrate content. Incidental to this work are some previously unreported findings enabling us to deal more informatively with Kjeldahl procedure. Some applications of these developments are suggested.

The modified Kjeldahl method is designed to deliver the correct percentage of nitrogen in nitrates. Most other nitrogen-bearing compounds succumb to the reduction and/or digestion features of the method.

The seventh (1950) edition of the Association of Official Agricultural Chemists' methods for the determination of nitrogen in fertilizers by the modified Kjeldahl procedure (*2*) increased the salicylic acid from 1 gram per 30 ml. of sulfuric acid to 2 grams. The Gunning variation of the method was retained without change at 1 gram per 30 ml. of sulfuric acid.

Prior to this edition, both variations of the method (*1*) directed, for converting the nitrates to nitrosalicylic acid: "Place 0.7 to 3.5 grams, according to the nitrogen content of material to be analyzed, in a Kjeldahl digestion flask. Add 30 ml. of sulfuric acid containing 1 gram of salicylic acid, shake thoroughly until mixed, allow to stand at least 30 minutes with frequent shaking. . . ." If these variations of the method are applied literally to the analysis of sodium nitrate, both will give nitrogen results about 0.20% low.

DEFICIENCIES OF KJELDAHL METHOD

Since 1 gram of salicylic acid is converted to nitrosalicylic acid by 0.6160 gram of sodium nitrate, a 0.0840-gram residue of unconverted sodium nitrate will be left from a 0.7-gram sample to follow through in the method, unless some dinitrosalicylic acid is formed. If the residue does not go into dinitrosalicylic acid, the

implication of the method is that the nitrogen result should be 1.98% low, instead of 0.20% low. In the interest only of correct results, some analysts weigh out not more than 0.5 gram of sodium nitrate. In so doing there has been a drift from an official method giving slightly erroneous results on high-content nitrates, to an unofficial method on the empirical level giving correct results. The situation, as described, is responsible for this study of the Kjeldahl methods.

The modified Kjeldahl procedure involves three main steps in the conversion of nitrates to ammonia, as follows:

1. Solution of the nitrates in salicylic-sulfuric acid, for converting the nitrates to nitrosalicylic acid.
2. Treatment of the nitro compound with sodium thiosulfate or zinc dust to reduce the nitro group to an amino group.
3. Prolonged digestion of the amino compound with the sulfuric acid to convert the amino group to ammonium sulfate.

REDUCTION STUDIES

All three of these steps are essential to a quantitative conversion of the nitrates to ammonia, but if the second step of the method is omitted, the conversion will be about 99% complete. As evidence of this, two 0.35-gram portions of sodium nitrate were treated according to the modified Kjeldahl procedure, with nitrogen results 16.44 and 16.48%, the average of which is very close to the theoretical 16.48%. Concurrently with these, two other determinations, with the second step omitted, gave 16.20 and 16.28% nitrogen. Undoubtedly the heat breakdown of the nitrosalicylic acid results in reducing substances that are able to convert the nitro group almost quantitatively to an amino group.

If the 0.35-gram portion of sodium nitrate be treated according to the modified Kjeldahl procedure, but with the salicylic acid omitted, the recovery of the nitrogen as ammonia by the sodium thiosulfate will be about 75% effective. In the heat breakdown of nitrosalicylic acid the reducing substances formed are much more effective in recovering nitrogen from the nitro group than sodium thiosulfate is in recovering nitrogen from sodium nitrate.

EVIDENCE OF EXCESS NITRATES

Early in this investigation, when the amounts of sodium nitrate taken were varied (in order to note the effect on the nitrogen results), a red color developed at times when the salicylic-sulfuric acid was heated to hasten the solution of the nitrates. Thus, with 0.7-gram portions of sodium nitrate the red color developed, and when the Kjeldahl cycle was completed the nitrogen results were about 0.20% low. On the other hand, with 0.35-gram portions no color developed, and the results were correct. A little sodium nitrate introduced into a sulfuric acid solution of Eastman 5-nitrosalicylic acid which had been partially reduced to aminosalicylic acid by sodium thiosulfate further confirmed the finding that nitrates produce a red coloration in a sulfuric acid solution of amino-salicylic acid.

That this coloration takes place in concentrated sulfuric acid makes it very useful in following the course of the reactions of the Kjeldahl method.

NO DINITROSALICYLIC ACID FORMED

When more than 0.6160 gram and less than twice that amount of sodium nitrate reacts with 1 gram of salicylic acid in sulfuric acid, a red color develops on heating to 100° C., showing that the sodium nitrate in excess of the 0.6160 gram required to produce mononitrosalicylic acid does not go into dinitrosalicylic acid, but goes into the second step of the method as nitrate. For 50 years chemists have been overlooking a potential warning in the Kjeldahl method when the nitrate was in excess of the salicylic acid capacity.

ASSESSING EACH STEP

When duplicate 1.3258-gram portions of Eastman 5-nitrosalicylic acid were treated according to the modified Kjeldahl procedure, the weights of nitrogen recovered were 0.1008 and 0.1015 gram, the average of which was very close to the theoretical 0.1015 gram. Since this material represents the product of the first step of the Kjeldahl method, this determination started at the second step of the method, where sodium thiosulfate is added. There was, of course, no salicylic acid in the sulfuric acid used in this digestion.

In order to reproduce the conditions obtaining when 0.7 gram of sodium nitrate is treated with 1 gram of salicylic acid (which produces 1.3258 grams of nitrosalicylic acid and a 0.0840-gram residue of sodium nitrate) the determination above was repeated, but to the 1.3258 grams of nitrosalicylic acid was added 0.0840 gram of sodium nitrate (which contributed an additional 0.0139 gram of nitrogen toward the whole). The nitrogen recovered totaled 0.1137 gram instead of the 0.1154 gram started with, showing that the combined effect of the breakdown products of the nitrosalicylic acid and the sodium thiosulfate enables the method to recover as ammonia about 90% of small residues of nitrate still in the Kjeldahl cycle at the second step of the method.

It follows that when 0.7 gram of sodium nitrate is treated with 1 gram of salicylic acid according to the modified Kjeldahl procedure, the nitrogen recovered will consist of that in the 0.6160 gram reacted to nitrosalicylic acid, plus 90% of that in the 0.0840-gram residue following through from the first step of the method. The two sources will contribute, respectively, 0.1015 and 0.0125 gram of nitrogen for a total of 0.1140 gram, as against the 0.1154 gram present in 0.7 gram of sodium nitrate. This recovery is the equivalent of finding 16.28% nitrogen in a sodium nitrate containing 16.48%.

CHOICE OF METHODS AND APPLICATION OF DEVELOPMENTS

A spate of methods for nitrogen in nitrates, both in the texts and in the literature, attests previous efforts to find better conditions. In the writer's hands, Arnd's alloy, in a simple distillation of the nitrate from a solution containing magnesium chloride, was found to give results about 0.25% low. Devarda's alloy, from a very dilute solution of caustic, gives theoretical results (*3*) but the distillation is far from simple.

If a nitrogen method is required which is almost universally applicable, this may be had in the modified Kjeldahl method (*2*). The Gunning variation (*2*) of the method may be made equally applicable by increasing the salicylic acid from 1 to 2 grams per 30 ml. of sulfuric acid, or by reducing the factor weight from 0.7 to 0.35 gram.

If a method is required which is applicable to nitrates only (and most other inorganic nitrogen compounds), it is evident that the Kjeldahl method may be considerably simplified and the work expedited without prejudice to the results. The method may be modified as follows:

Weigh 0.7 gram of a nitrate or other inorganic nitrogen compound into a Kjeldahl flask, add 30 ml. of sulfuric acid containing 2 grams of salicylic acid, and with the flask held in an upright position, rotate the contents in the tip of a Bunsen burner or other heat source for about 15 seconds or until very hot to the touch and all nitrates are in solution. To the still hot contents of the flask add 3 to 4 grams of anhydrous sodium thiosulfate and rotate the contents vigorously and up the sides of the flask to include all of the nitrogen compound. Place the flask at once over a full flame or other heat source for 10 minutes or more, add 15 grams of anhydrous sodium sulfate or potassium sulfate, and digest vigorously for 1 to 2 hours. Cool, dilute to half the flask capacity, and add about 0.05 gram of 20-mesh zinc and caustic soda or potash to strong alkalinity. For a sodium nitrate distill into 17 ml. of 0.5*N* acid, for a potassium nitrate into 15 ml. of acid, and for an ammonium nitrate into 35 ml. of acid, all diluted with 50 ml. of water. Back-titrate with 0.1*N* caustic, using methyl red or cochineal indicator.

DISCUSSION OF DEVELOPMENTS

No loss of nitrogen need be feared from heating the contents of the flask in the first step of the method when no organic matter is present. The nitrates react as soon as they are in solution, and nitrosalicylic acid is very stable to heat. The solution may be heated to the boiling point before adding the sodium thiosulfate and the loss of nitrogen will be only about 0.10%. The method suffers from the same interfering substances as the classical Kjeldahl method. Chlorides present with the nitrate will cause a slight loss of nitrogen as $NOCl_2$. Starch and tobacco and most other organic compounds present with the nitrate develop reducing substances on heating in sulfuric acid before the nitrate is in solution, and these reducing substances apparently take oxygen from the NO_2 group in its transition stage from the nitrate to the salicylic acid, with some loss of nitrogen. If these organic compounds are added after the nitrate is in solution, the nitrogen found on completing the Kjeldahl cycle will be the sum of that in the nitrate plus that in the organic compound.

The results reported here represent work on a reagent grade of sodium nitrate which passed a 14-mesh sieve but was retained on a 30-mesh, and was dried at 110° C. This greatly facilitated manipulation and minimized errors due to absorption of moisture, adherence to brushes, etc., and made a very acceptable standard in Kjeldahl work. Treating 0.7 gram of this material by the proposed method gave results ranging from 16.40 to 16.48% nitrogen, and left little to be desired as to precision and accuracy.

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Differential Photometric Detection in Coulometric Titration

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EXPERIMENTS in the coulometric titration of acid and base with photometric detection of the end point were complicated by the formation of bubbles during titration (*2*). These bubbles were formed by the generating electrode and produced a density in the solution which the photometric detection section of the automatic titration apparatus was unable to distinguish from a change in density due to a change in the color of the indicator employed. It was found possible to titrate automatically those systems in which the end point was characterized by a change in the indicator which produced an increase in the absorbance of the solution with several false terminations of the titration to allow the bubbles to leave the solution. However, if an indicator were used which caused a decrease in absorbance at the end point, the absorbance due to the formation of bubbles compensated for the decrease in density due to the color change of the indicator, and a variable overtitration inevitably occurred.

To overcome the adverse effect of the absorbance arising from the formation of bubbles, a differential or ratio-detecting photometric unit was designed and constructed. The principle on which this unit operates is as follows: Light from a tungsten lamp passes through the solution being titrated and is separated by a beam splitter into two beams of equal intensities at right angles to each other. Each beam passes through a tube, which may contain a colored solution to serve as an optical filter, and terminates on the photocathode of a photoelectric tube.

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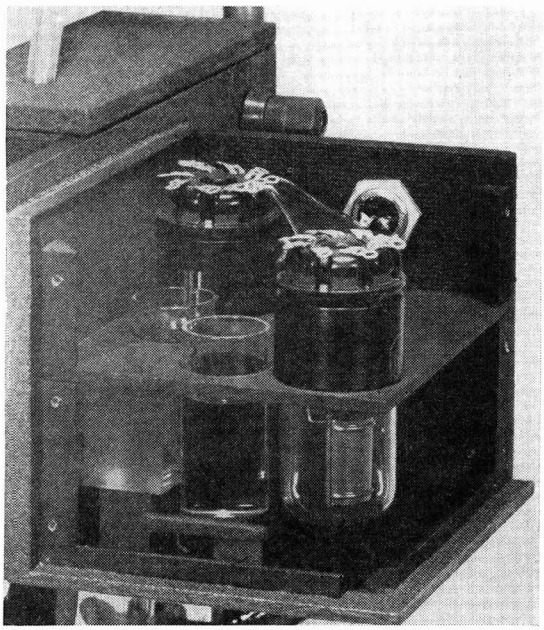

Figure 1. Differential Phototube Assembly

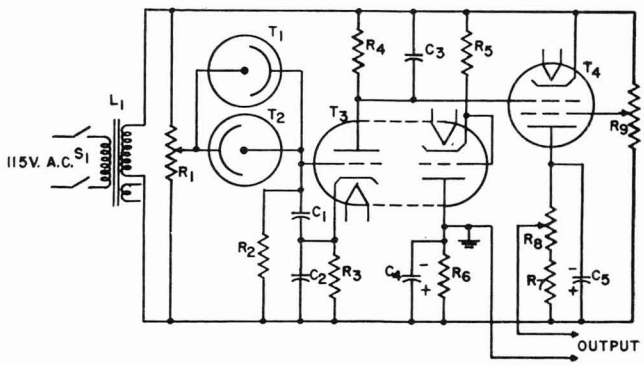

Figure 2. Circuit Diagram for Differential Photometric Detection Unit

C_1. 0.01 μf., mica
C_2. 0.25 μf., 400 volts
C_3. 0.1 μf., 400 volts
C_4. 4 μf., 200 volts
C_5. 4 μf., 200 volts
L_1. 115 volts, 30 ma., 6.3 volts, 1 ampere
R_1. 20,000 ohms, 2 watts
R_2. 22 megohms, 0.5 watt
R_3, R_4. 0.25 megohm, 2 watts
R_5. 56,000 ohms, 0.5 watt
R_6. 68,000 ohms, 0.5 watt
R_7. 10,000 ohms, 1 watt
R_8. 5000 ohms, 10 watts
R_9. 20,000 ohms, 4 watts
S_1. Double-pole, double-throw switch
T_1, T_2. No. 929
T_3. No. 12AX7
T_4. No. 6AS5

Considering the case of a two-color indicator, such as thymol blue, there are two colored forms which the indicator may adopt, and the ratio of their concentrations in a solution is a function of the hydrogen ion concentration of that solution. If an indicator which is predominantly in its acidic form is placed in front of one phototube and the same indicator predominantly in its basic form is placed in front of the other phototube and that same indicator is used in the titration, then the light coming through the solution when it is acidic will pass through the filter containing the acidic form of the indicator with little absorption, but will be attenuated by passing through the filter containing the indicator in its basic form. Such an arrangement produces a ratio of light intensities which will not be affected by an over-all diminution of the light transmitted through the solution being titrated, such as is caused by the formation of bubbles. When the indicator changes from its acidic to its basic form in the course of the titration, the ratio of light intensities definitely changes, for now the phototube behind the filter composed of the acidic form of the indicator receives less of the light being transmitted by the solution than does the other phototube.

A photograph of the interior of the phototube housing is shown in Figure 1. Light comes into this unit from the left after passing through the solution being titrated. The beam splitter is at the extreme left of the figure, and the tubes containing a solution of the indicator in its acidic and basic forms are placed between the prism and their respective phototubes.

The electrical circuit diagram of the unit which converts the output of the phototubes into a direct current potential proportional to the ratio of the light incident on the phototubes is shown in Figure 2. This circuit is a modification of a circuit published by RCA in 1948 for the measurement of light-intensity ratios (*1*).

The absorption characteristics of two-color indicators differ appreciably, and optimum operation of the differential photometric detection device was obtained by experimentally varying the concentration of the extreme colored forms of the indicator in the filter tubes. The concentration was adjusted so that minimum response in electrical output was achieved when the intensity of light incident on the titration vessel was attenuated to simulate the formation of bubbles, preferably by use of a diaphragm in the light beam, and so that maximum response was obtained when the indicator in the titration vessel was varied from its acidic to its basic colored form.

The operation of the device was studied using the indicators thymolsulfone-phthalein (thymol blue), *m*-cresol purple, bromothymol blue, and bromocresol purple. It was found possible to detect photometrically the equivalence point in a coulometric titration of either an acid or a base using the above two-color indicators, even when the absorbance decreased at the end point.

ACKNOWLEDGMENT

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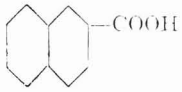
CRYSTALLOGRAPHIC DATA

80. 2-Naphthoic Acid (Beta-Naphthoic Acid)

Contributed by JOHN KRC, JR., and RALPH HINCH, JR., Armour Research Foundation of Illinois Institute of Technology Chicago 16, Ill.



Structural Formula for 2-Naphthoic Acid

THREE modifications of 2-naphthoic acid have been observed in these studies.

Excellent crystals of modification I (melting point 185° C.) and of modification II (melting point 177.5° C.) can be obtained from sublimation (Figures 1 and 2). In general, the temperature of the condensing surface determines which of these two modifications is obtained by sublimation. A surface temperature of 75° C. gives crystals of II; a temperature above 110° C. favors crystals of I. Intermediate temperatures give varying proportions of these two modifications. Modification III (melting point 176° C.) was not obtained from sublimation but only from the melt (Figure 3).

Good crystals of 2-naphthoic acid I can be obtained by macrorecrystallization from alcohol, ether, chloroform, and benzene. Modifications II and III were not obtained from solution.

2-Naphthoic acid, as used in these studies, was purified by the following procedure:

The compound was dissolved in water by the addition of a minimum amount of 10% sodium hydroxide. Charcoal was added and the solution was filtered. The compound was fractionally precipitated with hydrochloric acid. The center cut was recrystallized once from ethyl alcohol–water and once from toluene-ligroin, with center cuts taken from each of these recrystallizations. The compound was then dried over calcium chloride for 48 hours at 4 mm. of mercury.

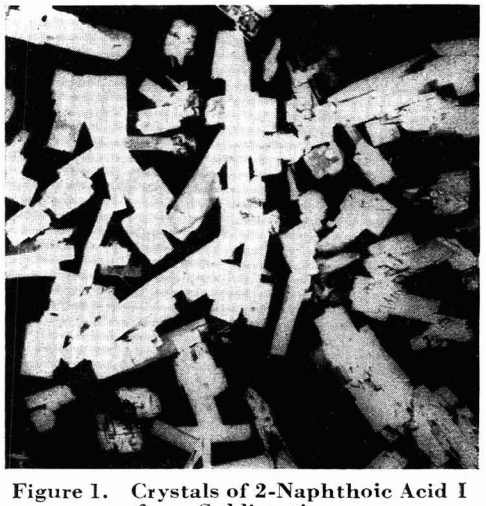


Figure 1. Crystals of 2-Naphthoic Acid I from Sublimation

Crossed nicols

Figures 4 and 5 are orthographic projections of modifications I and II as obtained from sublimation.

2-NAPHTHOIC ACID I

CRYSTAL MORPHOLOGY

Crystal System. Monoclinic.

Form and Habit. Plates and needles elongated parallel to b lying on orthopinacoid {100} showing clinopinacoid {010} and basal pinacoid {001}; crystals from solution sometimes show clinodome {011}, negative hemipyramid {111}, and positive hemipyramid {11$\bar{1}$}.

Axial Ratio. $a:b:c = 6.25:1:1.34$.

Beta Angle. 103°.

Cleavage. Excellent parallel to 001; good parallel to 010.

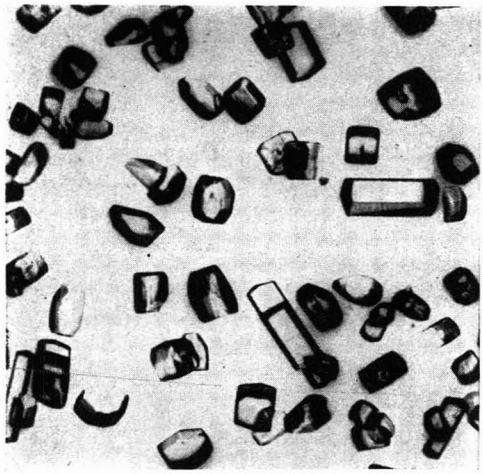


Figure 2. Crystals of 2-Naphthoic Acid II from Sublimation

X-RAY DIFFRACTION DATA

Cell Dimensions. $a = 31.14$ A.; $b = 4.985$ A.; $c = 5.64$ A.

Formula Weights per Cell. 4 (3.99 calculated from x-ray data).

Formula Weight. 172.17.

Density. 1.340 (flotation and density balance); 1.344 (x-ray).

Principal Lines for Modification I

d	I/I_1	d	I/I_1
15.49	10	2.95	1
8.15	1	2.87	1
7.61	4	2.74	1
5.49	10	2.69	2
5.28	1	2.59	1
5.00	6	2.52	1
4.82	1	2.43	4
4.70	4	2.39	1
4.45	4	2.35	1
4.21	4	2.29	3
4.15	4	2.24	3
4.02	1	2.19	1
3.85	8	2.15	1
3.63	1	2.12	3
3.54	8	2.10	2
3.45	1	2.02	2
3.38	8	1.896	1
3.29	1	1.871	2
3.22	9	1.840	1
3.03	4	1.803	1

OPTICAL PROPERTIES

Refractive Indices (5893 A.; 25° C.). $\alpha = 1.634 \pm 0.002$. $\beta = 1.664 \pm 0.002$. $\gamma = 1.90 \pm 0.005$.

Optic Axial Angles (5893 A.; 25° C.). $2E = 80°$. $2V = 45°$ (calculated from β and $2E$); $2V = 44°$ (calculated from α, β, and γ).

Dispersion. Inclined, very strong.

Optic Axial Plane. 010.

Sign of Double Refraction. Positive.

Acute Bisectrix. γ.

Extinction. $\alpha \wedge c = 24°$ in obtuse β.

Molecular Refraction (R) (5893 A.; 25° C.). $\sqrt[3]{\alpha\beta\gamma} = 1.730$. R (calcd.) = 47.8; R (obsd.) = 51.5.

2-NAPHTHOIC ACID II

CRYSTAL MORPHOLOGY

Crystal System. Orthorhombic.

Form and Habit. Plates and tablets lying on macropinacoid {100} showing basal pinacoid {001}, brachy pinacoid {010}, prism {110}, brachydome {011}, orthodome {101}, and bipyramid {111}.

Axial Ratio. $a:b:c = 0.579:1:0.352$.

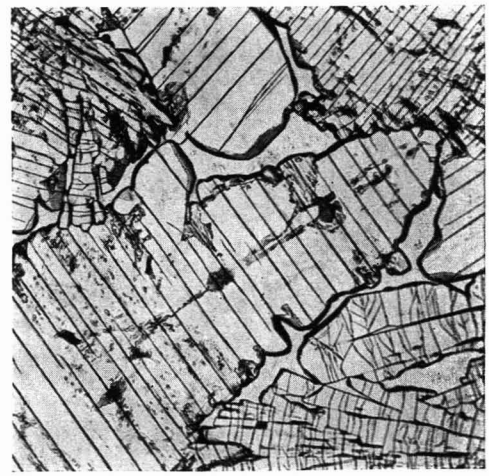


Figure 3. 2-Naphthoic Acid III Recrystallized from Melt

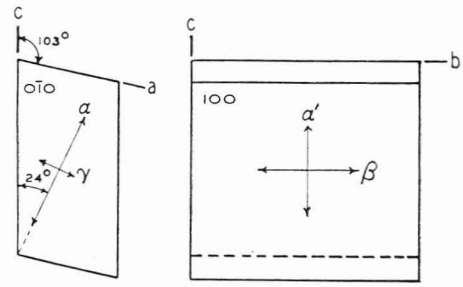


Figure 4. Orthographic Projection of Typical Crystal of 2-Naphthoic Acid I from Sublimation

Interfacial Angles (Polar). $100 \wedge 101 = 58.7°$; $100 \wedge 110 = 30.0°$; $100 \wedge 111 = 60.2°$; $010 \wedge 110 = 60.0°$; $010 \wedge 011 = 70.6°$; $001 \wedge 101 = 31.3°$; $101 \wedge \bar{1}01 = 62.6°$; $101 \wedge 10\bar{1} = 117.4°$; $110 \wedge \bar{1}10 = 119.9°$; $110 \wedge 1\bar{1}0 = 60.1°$; $111 \wedge \bar{1}11 = 59.7°$.

Hardness. Pressure parallel to a on plates lying on 100 results in plates of decreasing thickness and discontinuities within these crystals.

Cleavage. Excellent parallel to 001; poor parallel to 010.

X-RAY DIFFRACTION DATA

Cell Dimensions. $a = 11.77$ A.; $b = 20.34$ A.; $c = 7.16$ A.

Formula Weights per Cell. 8 (7.98 calculated from x-ray data).

Formula Weight. 172.17.

Density. 1.331 (flotation and density balance); 1.334 (x-ray).

Principal Lines for Modification II

d	I/I_1	d	I/I_1
7.92	3	2.94	1
7.46	3	2.82	4
6.34	1	2.48	1
6.04	3	2.21	1
5.76	5	2.13	1
5.55	2	1.990	4
4.20	9	1.781	Weak
4.09	9	1.625	1
3.71	4	1.405	Weak
3.50	4	1.259	1
3.41	7	1.149	1
3.34	4	1.125	1
3.21[a]	1		

[a] This line may possibly be due to small amount(s) of modification(s) I and/or III, possibly present as "impurities" in the sample for which these data were obtained.

Optical Properties

Refractive Indices (5893 A.; 25° C.). $\alpha = 1.450 \pm 0.001$. $\beta = 1.724 \pm 0.005$. $\gamma = 1.955 \pm 0.005$.

Optic Axial Angles (5893 A.; 25° C.). $2H = 84°$. $2V = 73°$ (calculated from β and $2H$); $2V = 72.5°$ (calculated from α, β, and γ).

Dispersion. $v > r$, strong.

Optic Axial Plane. 100.

Sign of Double Refraction. Negative.

Acute Bisectrix. $\alpha = c$.

Extinction. Parallel and symmetrical.

Molecular Refraction (R) (5893 A.; 25° C.). $\sqrt[3]{\alpha\beta\gamma} = 1.697$. R (calcd.) = 47.8; R (obsd.) = 49.8.

2-NAPHTHOIC ACID III

Principal Lines for Modification III

d	I/I_1	d	I/I_1
7.66	5	3.22[a]	1
6.50	2	2.93	1
5.95	7	2.81	1
		2.66	1
5.79	7		
5.59	5	2.52	1
5.07	2	2.45	1
4.78	2	2.28	1
4.41	1	2.13	3
4.16	1	2.03	1
3.85[b]	1	1.835	1
3.43	8	1.783	3
3.36	8		

[a] This line may possibly be due to small amount(s) of modification(s) I and/or II, possibly present in the sample for which these data were obtained.
[b] This line may possibly be due to a small amount of modification I, possibly present as an "impurity" in the sample for which these data were obtained.

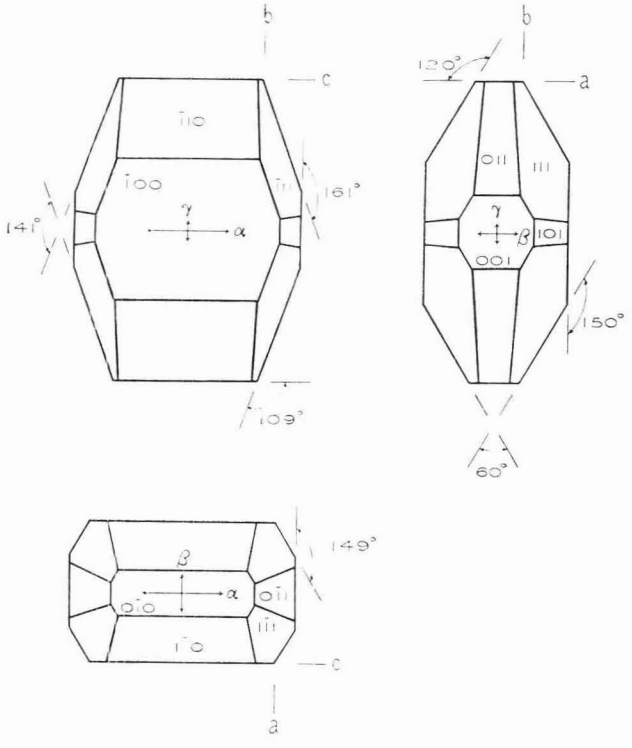


Figure 5. Orthographic Projection of Typical Crystal of 2-Naphthoic Acid II from Sublimation

Fusion Data. 2-Naphthoic acid I, the modification from solution, melts at 185° C. with sublimation. On cooling, either modification I or modification III crystallizes spontaneously from the melt. Modification I crystallizes as needles which show off-center optic axis figures; III crystallizes as irregular plates which on further cooling show shrinkage cracks with parallel extinction. Modifications I and II can be obtained by sublimation. Solution phase transformations II → I and III → I are observed at room temperature. Solid-solid transformations II → I and III → I are observed up to the melting points of II and III, respectively (Figure 6).

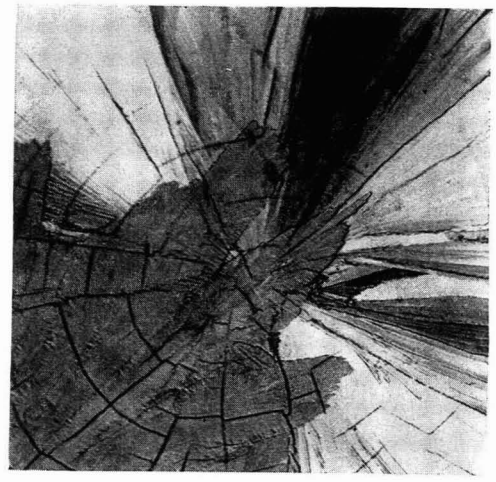


Figure 6. Crystals of Modifications II and III from Fusion during Transformation III → I

Pseudomorph is shown at lower left. Crossed nicols

ACKNOWLEDGMENT

The authors acknowledge the assistance of Donald E. Laskowski, who purified the 2-naphthoic acid, and of Joan French, who determined the powder diffraction data.

Contributions of crystallographic data for this section should be sent to Walter C. McCrone, Analytical Section, Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Ill.

Society for Analytical Chemistry

At the 80th annual general meeting of the Society for Analytical Chemistry, held in London March 3, the following officers and members of council were elected.

President. D. W. Kent-Jones, The Laboratories, Dudden Hill Lane, Willesden, London N.W. 10.

Past Presidents on Council. Lewis Eynon, G. W. Monier-Williams, J. R. Nicholls, G. Taylor.

Vice-Presidents. C. A. Adams, A. J. Amos, T. McLachlan.

Honorary Treasurer. J. H. Hamence.

Honorary Secretary. K. A. Williams, 161 Rosebery Ave., London E.C. 1.

Council. D. C. M. Adamson, A. L. Bacharach, R. C. Chirnside, M. Corner, D. C. Garratt, J. Haslam, C. L. Hinton, H. W. Hodgson, H. M. N. H. Irving, A. G. J. Lipscomb, R. E. Stuckey, C. Whalley.

At the ninth annual general meeting of the Physical Methods Group, held in London November 24, the retiring chairman, J. Haslam, gave an address.

Physical Methods in the Analysis of Plastic Materials. Some Observations of an Analytical Chemist. J. Haslam, Plastics Division, Black Fan Road, Welwryn Garden City, Herts.

Physical methods are largely used in the plastics industry; but although some of them are purely physical, many of the tests require preliminary chemical separations before a physical method can be applied. Of the purely physical methods, the determination of relative viscosity at a specified concentration in a suitable solvent is in regular routine use.

Potentiometric titration has supplied information on the speed of hydrolysis of nylon, polymethyl methacrylate, and polyvinyl chloride that was difficult to get by chemical means. Chromatography has yielded valuable results in the examination of nylon polymers, as has partition between immiscible solvents in the analysis of their hydrolysis products. Spectrographic methods are largely used in the examination of plastics and their constituents after chemical or

physical separation. The infrared is the most used region, in the analysis of nylon and polyvinyl chloride, and for simple and mixed plasticizers it often leads to results not otherwise obtainable.

The visible region is used in the identification of dyestuffs; and the ultraviolet in the determination of the efficiency of ultraviolet absorbers in Perspex sheet, in the detection of catechol in nylon, of acenaphthalene in its copolymers, and, in conjunction with a fluorescent screen, for the detection of butyl phthalate in Perspex. The carbon arc is useful in the detection of inorganic fillers.

The refractive index is of importance in the examination of monomers and plasticizers.

Amperometric titration has been used, with a rotating platinum indicator electrode and a reference half cell containing potassium iodide–mercuric iodide and potassium chloride solution, for the determination of lauryl mercaptan by means of standard silver nitrate solution.

The polarograph has been used in the determination of phthalate esters in the presence of castor oil, which invalidates the fluorescein and phenolphthalein tests, and also for the determination of zinc in fillers.

The method of partition between immiscible solvents has enabled fatty acids from the hydrolysis products to be separated and determined.

In plastics containing fillers the microscope is indispensable and in conjunction with Wallace's lycopodium method it has been used for the determination of coconut-shell flour, used in phenol formaldehyde molding powder to give a polished finish to the goods.

Many of the methods described have already been published in *The Analyst*.

An ordinary meeting of the Polarographic Discussion Panel of the Physical Methods Group was held December 9 in London, when two papers were presented and discussed.

Studies with the Rotating Platinum Cathode. D. J. FERRETT, Inorganic Chemistry Laboratories, Oxford.

A description was given of the application of the rotating platinum cathode to the estimation of metal ions and oxygen at low concentrations under automatic recording conditions.

The rotation of the electrode increases the sensitivity of this instrument at least 20-fold over that of the dropping mercury electrode. Careful control of rotation speed is essential, however, and a negative feed-back circuit is needed to ensure constancy in speed.

With a systematic cleaning procedure of the electrode, the use of a platinum anode and other procedures which have been found essential, it is possible to obtain reproducible results for Cu^{++}, Au^{+}, Ag^{+}, Hg_2^{++}, Cd^{++}, In^{+++}, Pb^{++}, and Tl^{+}. Concentrations of $10^{-6}M$ can be measured with ease and accuracy. The smoothness of the current-voltage plots enables the method to be applied to differential techniques.

Polarographic Determination of Indium in Zinc and Zinc-Base Alloys. G. F. REYNOLDS AND H. I. SHALGOSKY, Chemical Inspectorate, Ministry of Supply, Royal Arsenal, Woolwich, London S.E. 18.

Procedures were described for the determination of indium in zinc and in various types of zinc alloys. In all cases the sample is dissolved in hydrochloric acid and any copper present is filtered off. In the absence of lead, polarography for indium may be carried out directly on this solution after the addition of iodide. If aluminum is absent, the indium is separated by stirring the solution with an excess of carbonate-free zinc oxide on which the indium collects. This is then filtered off, dissolved in hydrochloric acid, and polarographed. In all other cases the aluminum and indium are precipitated from the solution as hydroxides, redissolved in acid, and reprecipitated. The precipitate is then dissolved in hydrochloric acid and polarographed for indium. All these methods provide complete elimination of the interference of cadmium. Radioactive indium has been used to prove the efficiency of the separations, which enable microgram amounts of indium to be determined.

The ninth annual general meeting of the Biological Methods Groups was held in London December 11, preceded by a joint meeting with the Pharmaceutical Society.

Occurrence and Importance of Pyrogens. T. D. WHITTET, University College, Gower St., London W.C. 1.

The occurrence of pyrogens in water supplies and in drugs was discussed, the need for freedom from pyrogens of large-volume intravenous solutions was emphasized, and the possibility of serious contamination of certain drugs was reviewed. These factors were illustrated by reference to the tests for pyrogens of the various pharmacopeias. Sources of possible pyrogenic contamination in the preparation of intravenous injections were pointed out, and the dangerous consequences of the injection of contaminated solutions were stressed. The methods of eliminating pyrogens were briefly outlined and the need for control was discussed. Some suggestions were made to simplify the preparation of apyrogenic solutions in hospitals.

Routine Pyrogen Testing. K. L. SMITH, Boot's Pure Drug Co., Ltd., Beeston, Notts.

The control of preparations from large scale manufacture by applying official tests for freedom from pyrogens was considered, and the manipulative procedures involved in such control were discussed.

Leucocyte Response in the Rabbit to the Pyrogen from *Proteus vulgaris*, Mononuclear and Temperature Responses. M. DAWSON AND J. P. TODD, Glasgow Royal Technical College, Glasgow, Scotland.

The paper described experimental work. Rabbit leucocyte response to a freeze-dried pyrogen from *P. vulgaris* has been investigated and differential counts have been carried out. The relative percentage of small lymphocytes fell, the maximum fall occurring about 3 hours after injection. The fall has been expressed as a percentage of the initial level. At the high dose level injected the small lymphocyte percentage fall had a coefficient of variation of 20% and the temperature rise a coefficient of 39%. At the two lower dose levels the responses were of equal variability. The small lymphocyte response remained quantitative over the three doses, but the temperature response failed to distinguish between the middle and high doses.

Rabbit Responses to Human Threshold Doses of a Bacterial Pyrogen. J. G. DARE, Department of Pharmacology, University of Leeds, Leeds.

The paper described experimental work. The minimal effective dose of a pyrogen prepared from *P. vulgaris* has been determined for a large group of healthy young adults. The rabbit's dose–temperature-response curves, to the same preparation, in several different experimental circumstances have also been determined. These curves are from rabbits previously untreated and from rabbits in which tolerance to pyrogens has been developed, and in each case both of the experimental techniques previously described [Dare, *J. Pharm. Pharmacol.*, **5**, 528 (1953)] were used.

The expectations of correctly detecting the presence of the pyrogen by the pharmacopeial test, in these circumstances, at various doses within the minimal effective dose range in man, have been calculated by the method previously described [Dare, *Ibid.*, **5**, 898 (1953)].

Standards of Pyrogenic Activity. W. L. M. PERRY, National Institute for Medical Research, Mill Hill, London N.W. 7.

The paper described experimental work. The purposes of providing reference standards of pyrogenic activity are: the control of preparations intended to produce hyperthermia in man; the control of pyrogenic contamination of other biological products intended for parental use in man; and the furtherance of research on the nature and action of pyrogens. The World Health Organisation is studying the possibility of providing an international reference preparation of pyrogen for these purposes. Attention was drawn to some of the difficulties of making and using such a preparation: variety of type and source of pyrogen, varying sensitivity of animals, dosage-response relationships, antigenicity, and mode of action.

The 43rd ordinary meeting of the Physical Methods Group was held February 9 in London, when coulometric analysis was discussed.

Principles of Coulometric Analysis. E. Bishop, Washington Singer Laboratories, University College of South Wales, Prince of Wales Road, Exeter.

Faraday's classical laws relate quantity of electricity to quantity of ion discharged at an electrode in an electrolytic process. Instead of weighing the amount of substance produced at an electrode, the weight can be calculated from the amount of electricity (ampere-seconds or coulombs) passed and the chemical equivalent of the substance, provided the process proceeds with 100% efficiency. On this basis are founded the coulometric methods of analysis in which the number of coulombs required for a reaction is measured. These methods may be direct, when the test material is plated out on or anodically stripped from an electrode, or oxidized or reduced in solution; or indirect, when an intermediate material, such as bromine or ferrous ion, is generated at the electrodes and used to produce a chemical reaction. The first type usually employs constant voltage and the second constant current electrolysis.

Instead, therefore, of adding a standard solution of acid, base, oxidizing, reducing, or precipitating agent from a buret, as in volumetric titrations, the reagent is generated electrolytically and the amount measured electrically in coulometric titrations. Since the quantity of electricity corresponding to 10^{-12} equivalent can be readily measured, the method has a high sensitivity. The principles on which the various methods of electrolysis, reaction, and detection of end point are based were reviewed, and the status of the method examined.

Automatic Coulometric Titrimeter. N. BETT, G. MORRIS, AND W. NOCK, I.C.I., Ltd., Ardeer, Scotland.

Coulometric titrimetry using external generation of the titrant was examined by manual methods and the experimental error was shown to be of the order of 0.1% for titrations of 25 ml. of 0.01*N* acid or alkali. To enable 0.1*N* solutions to be tested, a modified form of electrolysis cell and a specially stabilized current supply were devised.

As in coulometric analysis an electric current rather than a flow of solution has to be controlled, this method is particularly suitable for automatic operation. An automatic Titrimeter based on this current supply and an electrically operated stop watch was constructed; this was found to titrate 25 ml. of 0.1*N* acid or alkali in 4.5 minutes with a standard deviation less than 0.2%.

It was found that the electrolysis cell was insufficiently reliable for routine use, and an improved form employing glass sinters as diaphragms was constructed.

The availability at this point of an instrument capable of recording quantity of electricity by integration removed the need for accurate stabilization of the electrolysis current, and allowed for use of a two-speed approach to the end point.

Details of the final form of automatic Titrimeter were given.

Titrations involving the generation of iodine were also described and reference was made to some other coulometric processes which are feasible. Some recent developments of the coulometric apparatus were given; in particular, an automatic buret was described.

Apparatus and Techniques for Semimicro Coulometric Analysis. G. PACKMAN, Chemical Inspectorate, Ministry of Supply, Royal Arsenal, Woolwich, London S.E. 18.

Several types of coulometer, gas, silver, and iodine, were investigated for use in work on a milligram scale, and it was concluded that the last was the most satisfactory. The necessary experimental conditions were worked out. An electrolytic cell of 2.5-ml. capacity and an indicator electrode system were designed, suitable for both controlled potential and constant current operation.

A procedure was devised to meet a special case where it was necessary to reduce an element before coulometrically oxidizing it, and to carry out both operations with the same cell and electrodes. Difficulties arose which do not appear in more usual methods where the sample, already in the lower oxidation state, can be added to a suitable medium (which has been preadjusted to end-point conditions) and then oxidized. A combination of controlled potential reduction and constant-current oxidation was found satisfactory, and the performance was checked over the range 5 to 50 meq., ferrous ion being used in the first instance as a substitute.

The tenth annual general meeting of the Microchemistry Group, held in London January 29, was followed by an ordinary meeting of the Society for Analytical Chemistry, organized by the Microchemistry Group. A film entitled "Old Masters of Microchemistry" was shown and the following papers were presented and discussed.

Organic Ion Exchange. L. SAUNDERS, Gibside, Kingsmead Road, Loudwater, Bucks.

The development of ion exchange resins that are stable in solvents such as ethanol and acetone has greatly increased the value of these resins in organic chemistry. They can be used in preparative work such as the extraction of alkaloids from natural materials and the isolation of pure amino acids from protein hydrolyzates, or for analytical purposes. A growing volume of literature indicates that under the right conditions, ion exchange methods of analysis can be made quantitative.

The main advantage of these resins is that they can be set up in columns through which the solution with which they react is passed. The resin can subsequently be regenerated without removal from the column. The applications of ion exchange resin columns to organic analysis can be broadly divided into three groups:

1. A column consisting of a mixture of a strong cation with a strong anion exchanger is used to remove all small ions from a solution or a colloid sol. This method can be used to estimate amino acids in the presence of gelatin or protein.

2. A column of strong anion exchanger in the hydroxyl form can be used to remove anions from a solution, replacing them quantitatively with hydroxyl ions. A solution which is initially neutral will give an alkaline effluent which can be titrated with acid. A procedure of this type has been proposed as a method of estimating the alkaloid content of alkaloidal salts.

3. A column of weak anion exchanger can be used to remove organic bases from solutions. The base can be washed on the resin and subsequently be displaced from the resin for estimation. This technique has been used for the estimation of streptomycin in fermentation broth, of hexa- and decamethonium in blood serum, and of quinine and other alkaloids. To attain quantitative absorption of base, the solution that is put on to the weak cation exchanger column should be alkaline. This method cannot therefore be used for the estimation of alkaloids in their salts. However, a satisfactory assay of quinine in quinine salts can be achieved by allowing the salt solution in alcohol to flow first over a strong anion exchanger column; the alkaline effluent from this is then passed through two weak cation exchanger columns in series. Quinine is quantitatively absorbed by these columns and is subsequently displaced from them by passing a saturated solution of anhydrous ammonia in ethanol or methanol through the two columns connected in parallel. The quinine in the combined effluent can then be estimated by evaporation to dryness and weighing or by polarimetric measurements.

Ion exchange resins have also been used with neutral organic materials. For example, sugars can be separated from one another by the formation, with borate solutions, of complexes that are then taken up by anion exchangers in the borate form. Samuelson *et al.* have used a strong anion exchanger in the bisulfite form to remove aldehydes and ketones from solution; a separation of aldehydes from ketones can then be achieved by fractional elution.

Inorganic Ion Exchange. G. H. OSBORN, Cherry Tree Cottage, Merley Ways, Merley, Wimborne, Dorset.

An up-to-date review was given of the techniques now used in the application of ion exchange resins to inorganic analysis—simple cation and anion exchange, chromatography, complexing, differential elution, redox applications, insoluble substances, ionophoresis, ion exchange membranes, and ion exclusion. The paper deals with general principles, but a few specific applications of recent date were mentioned.

Ninth Annual Microchemical Symposium

THE Ninth Annual Microchemical Symposium, sponsored by the Metropolitan Microchemical Society, was held March 19 and 20 at Brooklyn College, Brooklyn, N. Y. Its theme was the standardization of microchemical apparatus and methods. The following papers were presented:

The Philosophy of Standardization. MELVIN W. GREEN, American Council on Pharmaceutical Education, Chicago, Ill.

Various types of standards, such as those of buyer and seller, informative standards, nomenclature standards, and general industrial standards, were discussed. The influence on standards of newer techniques of analysis, such as the increased uses of instrumental analysis and the application of statistics, was touched upon. The paper was oriented largely from the viewpoint of drug standards, especially official standards as found in the United States Pharmacopeia and National Formulary. The importance of collaborative assays and the democratic approach to establishing methods and tolerances was stressed. Because of the speaker's current interest in educational standards in pharmacy, the field of educational standards and accreditation was discussed briefly.

Design of Experiments in Analytical Chemistry. GRANT T. WERNIMONT, Eastman Kodak Co., Rochester, N. Y.

An experiment may be called "designed" when it is planned so that the results can be used to give unambiguous answers to certain specific questions that motivated the experiment. A designed experiment always includes a written statement of (1) a list of objectives, usually in the form of specific questions, (2) a description of how the experiment is to be performed, and (3) an explanation of the statistical analysis to be used.

It is important to recognize the concept of a measurement process when experiments are being designed in analytical chemistry. This process consists of a series of unit operations on a sample from some bulk of material. The process yields an analytical result which is an attribute of the sample useful for making an inference about the bulk.

Research in analytical chemistry is of two types. The first includes experiments on the fundamental aspects of the various unit operations in an analytical process. The second consists of experiments to arrange a consecutive series of unit operations so that they form an analytical process useful for some specific purpose.

The simplest experimental design is arranged as a sequence of small rational subgroups, so that the variation of results within and among the subgroups can be studied. Complete factorial experiments make it possible to examine efficiently the effects of two or more postulated causes of variation in the results. Each of the effects can be studied separately; and the combined effects can also be evaluated. More complex designs such as the Latin square, the incomplete block, and the Youden square can be used for experiments in analytical chemistry where it is not desirable or possible to set up extremely close control of experimental conditions.

It is most important to realize that the validity of any experiment comes from the experimental design and not from the statistical analysis of the results.

Preparation of Pure Chemicals for Standards. H. V. FARR AND A. E. RUEHLE, Mallinckrodt Chemical Works, St. Louis, Mo.

The past half century has seen American chemical production grow from a trickle to a flood. Chemical analysis has changed from a troublesome chore, hampered by doubtful methods and impure reagents, to the keystone of research leading to ever greater chemical technology. This has been the outgrowth of parallel developments in analytical methods, manufacturing procedures, reagent standardization, equipment design, and training a group of highly skilled and experienced chemists. Some typical examples of the mutual dependence of the factors leading to this growth were given, and modern approaches to manufacturing of reagent chemicals were discussed.

Testing Microbalances. L. B. MACURDY, National Bureau of Standards, Washington, D. C.

New test methods to separate the effects of environmental conditions from the mechanical precision of the balance now being developed at the National Bureau of Standards were described. A method has been devised which under ideal conditions will provide separate estimates of these effects and also provide a basis for predicting the performance of a balance in terms of the precision obtained by various methods of weighing. Under nonideal conditions there is only partial separation of environmental effects from the precision of the balance. Other topics are terminology for describing balance performance; effects of the observer; blunder; the optimum relation between sensitivity, readability, and precision; and what to do about trends in the data.

Standardization of Microchemical Methods in the Association of Official Agricultural Chemists. CLYDE L. OGG, Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture, Philadelphia 18, Pa.

Since the studies related to the standardization of microchemical methods have been conducted as a function of the Association of Official Agricultural Chemists, the objectives, membership, and operating procedures of this organization were discussed briefly. The procedure by which a method is established as "official" was outlined so that the action that has been and will be taken in the work on microchemical methods may be understood more clearly.

To establish an official or standard procedure it is necessary at some point in the process to select a particular method or procedure for final testing. The approach that has been followed in making this selection, the reasons for this approach, and the tools used to implement it were discussed. The method selected must be subjected to collaborative testing to ascertain if it will produce reliable results when used by different chemists in different laboratories. Problems associated with this step are how many collaborators are needed, how many and what samples should be analyzed, how many determinations should be made per sample, and what are reliable results.

The highlights of the studies on micromethods for carbon and hydrogen, nitrogen (Kjeldahl and Dumas), sulfur, chlorine, and bromine were reviewed and the plans for future work presented.

Standardization of Glassware. JAMES J. MORAN, Kimble Glass Co., Toledo, Ohio.

Standardization of glass apparatus benefits the user by making available uniform equipment of satisfactory construction from more than one source of supply. Standardization also permits manufacture of items in advance of actual need by the user, so that stocks can be kept on hand by suppliers for quick delivery.

Standardization should be the result of the combined efforts of makers, dealers, and users, so that the glassware meeting specifications will give satisfactory service at the lowest cost. This is the case today with most of the equipment shown in the catalogs of laboratory supply houses, following the recommendations of the Committee on Microchemical Apparatus of the Division of Analytical Chemistry of the AMERICAN CHEMICAL SOCIETY.

In the study of a piece of apparatus, preparatory to the writing of a standard specification, many factors must be taken into account. The chief ones are: What is the apparatus required to do; what form will offer the most convenience to the user; what kind of glass should be used; what other items must fit into or over the apparatus; can the instrument be built from standard factory parts; are interchangeable parts desirable; what tolerances can be permitted to decrease costs?

To illustrate the procedure, several examples were given, chosen from among the large number of glass instruments already considered by the Committee on Microchemical Apparatus.

Optical Society of America

THE spring meeting of the Optical Society of America was held at the Hotel Statler, New York, N. Y., March 25 to 27. The papers abstracted below were among those presented.

Recording Spectrometer for the Infrared. R. H. NOBLE, Leeds and Northrup Co.

An industrial version of the Ebert monochromator has been described [Fastie, W. G., *J. Opt. Soc. Amer.*, **42**, 641 (1952)], indicating its usefulness for emission spectroscopy over a wide spectral range. Reflective optics and very low scattered radiation make this same instrument ideal for infrared absorption work when used with appropriate gratings and dectectors. Lead sulfide photoconductors permit theoretical resolving power to be approached, using a 7500-line-per-inch plane replica in both first and second orders. Absorption records for several gases were shown and analytical applications were discussed.

Use of a Diffraction Grating in a Perkin-Elmer Double-Pass Infrared Monochromator. R. C. LORD AND T. K. MCCUBBIN, JR., Spectroscopy Laboratory, Massachusetts Institute of Technology.

A 300-line-per-mm. Bausch & Lomb original echellete grating has been installed in place of the Littrow mirror (with the prism removed) in a Perkin-Elmer Model 99 double-pass monochromator. Several minor changes to the monochromator and a careful focusing of the entire optical system were necessary. An Eastman Kodak lead sulfide cell which the Perkin-Elmer Co. supplied in the standard thermocouple mounting served as radiation detector. This detector was used at room temperature with 13-cycle chopping and a Perkin-Elmer Model 107 amplifier. A 150-watt tungsten projection lamp and a zirconium concentrated arc were used as sources. Lines as close together as 0.25 cm.$^{-1}$ in the absorption spectra of methane from 2.2 to 2.5 microns and of water vapor from 2.2 to 2.8 microns could be separated.

Photoelectric Raman Spectrograph. JOHN U. WHITE, NELSON L. ALPERT, AND ARTHUR G. DEBELL, White Development Corp., Stamford, Conn.

A photoelectric recording Raman spectrograph has been built for the measurement of small samples. Employing a d.c. helical arc, grating monochromator, and 1P21 photomultiplier tube, it can survey a complete Raman spectrum in 6 minutes and make an accurate record in an hour. Special features are an image slicer and multiple traversal sample tubes for liquids and gases. Construction and performance were discussed.

Infrared Absorption Spectra of Thirteen Organic Compounds from 25 to 50 Microns. EARLE K. PLYLER AND NICOLO ACQUISTA, National Bureau of Standards, Washington, D. C.

The infrared absorption spectrum of nine ethane and four benzene derivatives has been measured with a cesium iodide prism in the spectral region from 25 to 50 microns. These materials have several long wave-length bands which are produced by the bending vibrations of C—Cl and C—Br groups. All compounds measured show from three to six bands in this region. Several of the bands have been classified and supplement the spectrum of these materials, which have previously been measured to 25 microns.

Official German Standard Color Chart. MANFRED RICHTER, Materialprufüngsamt, Berlin-Dahlem.

The official German standard color chart (DIN-Farbenkarte) is based on a hue circle, and on saturation and lightness scales divided in psychologically equivalent steps [Richter, Manfred, "Das System der DIN-Farbenkarte," *Die Farbe*, **1**, 85 (1953); Weise, H., "Farbtoleranzen und DIN-Farbenkarte," *Die Farbe*, **1**, 111 (1953).]

Each color is identified by a hue number, T, degree of saturation, S, and degree of darkness, D. The DIN-Farbenkarte in the form of transparent gelatin filters was exhibited, and the application of the DIN system to practical color problems arising in industry was discussed.

Propagation of Errors in Spectrophotometric Colorimetry. DAVID L. MACADAM, Eastman Kodak Co., Rochester, N. Y.

Errors of spectral reflectance, assumed to be equally uncertain at every wave length, determine ellipsoids in tristimulus space. The chromaticity diagram can be interpreted as a plane in this space. It intersects the ellipsoids of uncertainty in ellipses, all of the same shape and orientation. The axes of these ellipses are proportional to their distances from the alychne, divided by the luminous reflectance. These ellipses do not, however, represent uncertainties of chromaticities. The latter, correctly determined [Nimeroff, I., *J. Opt. Soc. Amer.*, **43**, 531–3 (1953)] are represented by elliptical intersections of the chromaticity diagram with lines from the origin, tangent to the ellipsoids. In the constant luminance diagram [MacAdam, D. L., *J. Opt. Soc. Amer.*, **43**, 536–8 (1953)] the ellipses of uncertainty have their axes all pointing toward ($U = W = 0$). The minor axes are equal in length to the diameters of the circles. The major axes are those diameters multiplied by $(1 + r^2)^{1/2}$, where r is the distance of the ellipse from ($U = W = 0$, $V = 1$). For the case specified, the uncertainties of chromaticities cannot be represented by equal-sized circles in any plane. For that purpose, a chromaticity diagram would have to be constructed on a surface of constant negative curvature which resembles a champagne glass.

Accurate Determination of Tristimulus Values with the Aid of a Retardation Plate. EUGENE ALLEN, American Cyanamid Co.

One of the biggest difficulties in determining tristimulus values from curves run on a recording spectrophotometer is the wave-length calibration. When hand integration is used, the wave-length scale is ordinarily established with the help of a correction curve derived from the didymium peaks. This procedure is not only tedious but may lead to loss of precision because of the necessity for interpolation between adjacent grid lines. A retardation plate [Bue, G. L., and Stearns, E. I., *J. Opt. Soc. Amer.*, **35**, 465 (1945)] can be used for constructing a wave-length grid by setting the pen at a maximum or minimum of the transmittance curve of the plate and then allowing the pen to travel up and down the paper. Because of the sharpness of the peaks, this grid can be drawn very accurately, and makes available approximately 55 ordinates for integration of spectrophotometric curves. The curve, plotted on transparent paper, is aligned over the grid, and the reflectance or transmittance for each of the wave lengths can be read with considerable precision. Each value is then multiplied by an appropriate factor and the products are summed to give the tristimulus value. The procedure is thus similar to the weighted ordinate method of integration, except that readings are taken at the retardation plate wave lengths instead of at every 10 mμ. The weights to be applied are calculated for the retardation plate wave lengths from a table of running sums. Since errors of paper positioning and irregularity in the wave length cam will not affect the results by the proposed method, considerably greater accuracy should be obtained. The proposed procedure is also more convenient, since no wave-length correction or interpolation is required.

Angular-Dependence Light Scattering. A High Resolution Recording Instrument for the Angular Range 0.05° to 140°. W. H. AUGHEY AND F. J. BAUM, Chemical Department, E. I. du Pont de Nemours and Co.

A unique optical instrument for the measurement of light scattering in physically nonhomogeneous systems was described. The scattering data provide a basis for the size characterization of optical inhomogeneities in the radius range 0.1 to 100 microns. The useful angular range of the instrument extends from about 0.05° to 140°. Angular resolution of 0.02° is readily attainable for characterizing large inhomogeneities at small angles. Scanning rates are 0.1, 0.4, 1.0, 4.0, and 20° per minute. Light intensities varying by a factor of 10^8 are measured through the use of an optical attenuator which facilitates use of a 1P21 multiplier phototube at a low level of illumination. The phototube output is charted by a special high-impedance recorder having a full-scale sensitivity of 0.004 microampere. Angles are marked by an auxiliary pen on the recorder.

Photoelectric Tristimulus Colorimeter. GRADY T. HICKS AND W. S. PLYMALE, JR., U. S. Naval Research Laboratory.

In 1942 Hunter [Hunter, R. S., *J. Opt. Soc. Amer.*, **32**, 509 (1942)] surveyed the work which had previously been performed in tristimulus colorimetry. He also described a photoelectric tristimulus colorimeter which he had developed using a source-filter-photocell combination. This instrument was designed primarily to determine the trichromatic coefficients of nonfluorescent reflecting and transmitting materials. In 1951, Sziklai [Sziklai, G. C., *J. Opt. Soc. Amer.*, **41**, 321 (1951)] reported on an instrument using filter-photomultiplier combinations for measuring the color of self-luminous sources. Both these instruments were designed to measure the color of a relatively intense light source. The instrument described in this paper was designed to measure the color of self-luminous phosphors excited by radioactive materials. Since these phosphors have low luminance values—i.e., <100 μl.—and correction filters attenuate the light considerably, it is necessary to use photomultiplier rather than phototubes as detectors. One feature of the instrument is the external amplification of the output signal. Separate dark current controls are provided for each tube. Another feature of the instrument is the use of an integrating sphere to distribute equal flux on the photomultiplier tubes with no change in spectral energy distribution and with only small losses in light intensity from the source.

Variable Angle Glossmeter. RICHARD S. HUNTER, Hunter Associates Laboratory, Falls Church, Va.

Since gloss results from directionally selective reflectance, critical control of the angular conditions of light travel is necessary in all gloss measurements. A new glossmeter has been built in which both axial and field angles are variable at will. Axial angles of incidence and view are established by the positions of arms which extend from two hubs on a central pivot. These hubs may be moved in opposite directions and at identical angular rates so as to keep angles of incidence and view equal and opposite. The light source, lenses, stops, and receptor photocell are mounted on individual blocks which are attached, as on an optical bench, to the swinging arms. Source and receptor field stops and also the aperture stop are cut into brass plates which may be inserted into slots in these blocks. Measurements of gloss by most of the standardized methods and by many others not used before are possible with the new apparatus.

Inherent Limitations of Psychophysical Scales for Gloss, Transparency, and Diffuse Lightness. RICHARD S. HUNTER, Hunter Associates Laboratory, Falls Church, Va.

The light flux leaving an object in space may vary with directions of incidence and view as well as with wave length. Materials technologists frequently become impatient with the number and variety of psychophysical scales offered for the measurement of gloss and other features of objects attributable to this geometric selectivity. They feel there should be specific basic methods for these features analogous to those for color measurement which are the subject of international standardization. Both spectral and geometric selectivity are described by curves, but only in the case of color is it possible visually to match different spectral distributions with mixtures of only three primary lights and thereby specify colors in a tridimensional system. There are no visually equivalent mixtures of standard light stimuli for the appearances of objects having different goniophotometric curves. Therefore, there is no singular set of scales for the geometric aspects of appearance. Instead, there are many different geometric scales, each of which is useful because the numbers it gives correlate with visual ratings of some appearance property of a particular type or class of object. Thus only partial, not absolute, measurements of the geometric attributes of appearance are possible.

Vacuum Ultraviolet Spectrometer of Compact Design. S. G. FRANKLIN, General Electric Co.

A vacuum ultraviolet spectrometer, constructed for the Naval Research Laboratory, and based on the design of Parkinson and Williams [Parkinson, W. W., Jr., and Williams, F. E., *J. Opt. Soc. Amer.*, **39**, 705 (1949)] and Johnson [Johnson, P. D., *J. Opt. Soc. Amer.*, **42**, 278 (1952)], was described. Interesting features include a stable, low-voltage, air-cooled hydrogen source, entrance and exit slits whose width may be changed without disturbing the vacuum system, an end-sensitive photomultiplier detector, and a linear wave-length scale. Simplicity of design results in compactness and ease of operation. No diffusion pump is required for most measurements, and pump-down time is minimized by the small volume of the vacuum chamber. The 15,000-line-per-inch, 1-meter replica grating is rotated about a point on the Rowland circle, resulting in a simple mounting and a vacuum chamber whose dimensions are only 9 inches in diameter $\times$ 48 inches long. The vacuum chamber, complete with source and detector, is mounted on the top of a 72 $\times$ 36 inch laboratory table with auxiliary equipment for operation of the instrument mounted in the table frame. Possible applications of the instrument include absorption and photoconductivity measurements, phosphor excitation, and other solid state physical studies in the 1000 to 2000 A. region.

A Simple High-Precision Slit Mechanism. W. G. FASTIE AND H. M. CROSSWHITE, The Johns Hopkins University.

A metal ring which distorts under weight or pressure provides highly reproducible motion for slit jaws. The jaws can be connected to diametrically opposite points of the ring and pressure applied at

90° to the points of support to provide bilateral motion of the slit jaws. Preliminary results indicate that a 3-inch diameter ring will be reproducible to a few microns and can be distorted several hundred microns. The slit opening is directly proportional to the weight or pressure applied to the ring. Two designs were described, one operated by weights, the other by hydraulic pressure, with the slit setting indicated on a pressure gage. The mechanical formulas were presented and applications to high speed spectroscopy and servomechanical systems were discussed.

Adjustable Curved Slits for an Ebert Monochromator. H. M. CROSSWHITE AND W. G. FASTIE, The Johns Hopkins University.

The desirability of using curved slits in an Ebert spectrometer has been pointed out [Fastie, W. G., *J. Opt. Soc. Amer.*, **42**, 647 (1952)]. We have succeeded in making a pair for a 30-inch focal length instrument by modifying the ideas of the preceding paper such that the compressible ring itself forms the outer jaws of the slit pair. The inner jaws are on a single rigid piece which is a section of a circular plate machined to exactly match the i.d. of the ring. The matching 4-inch diameter circles are ground to a sharp edge and form the slits, both 1 inch long. The ring compression is obtained by weights operating on a balance arm. Details of construction and performance were given.

Radiation Time Lags in Short Oscillating Spark Discharges. HEINZ FISCHER, Air Force Cambridge Research Center.

Systematic investigations in the oscillating spark discharge prove that the radiation maximum in the unresolved spectrum occurs approximately at the time when the spark current has its maximum. Radiation time lags, as they are observed frequently, result from improper technique of current measurements due to the influence of di/dt. Sharp radiation pulses $<5 \times 10^{-8}$ sec. half-width are produced with small capacitor energy but a considerable broadening of the pulse and shift of the absolute radiation maximum into later oscillations are obtained by increased gas pressure and large capacitor energy. This effect is connected with energy storage in the channel such as imprisonment of radiation.

Hydrogen-Deuterium Analysis with a Fabry-Perot Interferometer. ROBERT O'B. CARPENTER, RALPH MCDONOUGH, AND NORMAN HAPGOOD, JR., Baird Associates, Inc.

The properties of the Fabry-Perot interferometer which make it a most suitable instrument for high-resolution spectrochemical analysis of small isotope shifts were discussed, with particular application to the hydrogen-deuterium problem. The etalon spacing of about 0.024 inch places the deuterium alpha fringe midway between successive orders of the hydrogen fringe. The interferometer is enclosed in a vacuum tank, in order that the pressure variation will scan or tune the fringes through the wave lengths. The transmitted intensity *vs.* wave length is then recorded with a photomultiplier and a strip chart recorder. By careful attention to the reflectivity, flatness, and parallelism of the etalon, the apertures, the source width, and electronic noise, it is possible to reach a sensitivity sufficient just to detect the deuterium in ordinary water, 0.016% concentration. Possible modifications pushing the limit still lower in concentration were discussed.

Colorimetric Calibration of Colorant Systems. HUGH R. DAVIDSON AND HENRY HEMMENDINGER, Davidson and Hemmendinger, Easton, Pa.

If a set of colorants is to be used in making large numbers of specified colors, a calibration of the relationship between colorant composition and colorimetric specifications provides a very efficient means of procedure. In the case discussed, samples exemplifying the Munsell renotation were painted from such a calibration. A set of six chromatic paints plus black and white was first chosen on the basis of color gamut, fastness, and other physical properties. Since mixtures of two chromatic paints plus black and white provide three degrees of freedom, such mixtures are sufficient to obtain any color within the gamut of the chosen paints. The required calibration, therefore, must relate the ratios of chromatic paints, black, and white to colorimetric specifications within the gamut. This calibration was made by painting samples of a constant ratio type colorant mixture system, determining the CIE and Munsell specifications, then establishing graphs of the relation between colorant ratios and colorant coordinates. The mixture formulas for the desired Munsell renotation samples were then read from these graphs. Although the project described involved the use of paints, the same principles may be used for other types of colorants.

Application of the Two-Beam Interference Microscope to the Study of Surfaces. W. L. GRUBE AND S. R. ROUZE, Research Laboratories Division, General Motors Corp.

Interference microscopes that have recently become available have overcome many of the operational difficulties previously experienced. As a result the two-beam interference microscope is finding increasing use in the laboratory in the study of surface topography. Present instruments are capable of examining surface detail in the range of 2 to 100 microinches peak-to-valley. A number of applications to the study of surfaces important in industry were presented. These include: (1) the measurement of thickness of electrodeposited coatings, (2) the study of the leveling properties of electrodeposits, (3) the measurement of the erosion or shrinkage of paint films upon weathering, (4) the investigation of hardness measurement indentations, (5) the examination of industrial sheet steel finishes, and (6) the control of the geometry of accurate surface roughness standards. Replica techniques which make it possible to use the instrument to study curved and inaccessible surfaces were also discussed.

Continuous Measurement of Atmospheric Ozone by an Automatic Photoelectric Method. RALPH STAIR, THOMAS C. BAGG, AND RUSSELL G. JOHNSTON, National Bureau of Standards.

This paper describes an automatic photoelectric instrument and method for the continuous measurement of the ozone in the earth's atmosphere at low altitudes. The method is physical rather than chemical in character and is based upon the optical absorption characteristics of ozone in the Hartley and Huggins ultraviolet bands. The instrument makes use of a low-pressure mercury arc which is situated at a distance of 1450 feet from the recording station that employs a 1P28 photomultiplier as a detector. The light beam is modulated, at 510 cycles per second, so that the output of the photomultiplier is fed into a tuned a.c. amplifier and amplified to the recorder level. By means of a Geneva mechanism which changes glass filters, the radiant energy from the lamp is separated into bands primarily at wave lengths 253.7, 365.5, and 405.0 mμ. From the ratios of the deflections for the different spectral regions it is possible to determine ozone concentration in the range from a few tenths of 1 part to many parts per 100,000,000.

Color-Difference Standards. HENRY HEMMENDINGER AND HUGH R. DAVIDSON, Davidson and Hemmendinger, Easton, Pa.

There exist numerous extensive collections of color standards, containing samples at intervals large in comparison with the smallest perceptible differences. It is desirable that these collections be supplemented by standards of small color differences, for use in visual or instrumental observations involving the evaluation of differences. A logical procedure for specifying the colors to be used in representing uniform color differences consists of sampling points on the surfaces of the ellipsoids of constant color difference first described by MacAdam [MacAdam, D. L., *J. Opt. Soc. Amer.*, **32**, 247–74 (1942)], and subsequently verified with respect to surface colors by Ingle and Rudick [Ingle, G. W., and Rudick, L., *J. Opt. Soc. Amer.*, **43**, 501–4 (1953)] and by Davidson and Friede [Davidson, H. R., and Friede, E., *J. Opt. Soc. Amer.*, **43**, 581–9 (1953)]. Using a modification of the colorant calibration described by Davidson and Hemmendinger, we have painted sets of samples having constant color differences, distributed around twenty reference points covering a wide gamut of color space. Each set consists of the standard and six samples differing from it by four MacAdam units. One pair of samples differs from the standard only in Munsell hue, one pair only in Munsell chroma, and one pair only in lightness. The complete collection of 140 colors will be made generally available, together with their spectrophotometric curves and colorimetric specifications. Other sizes of color differences, as well as sets centered on different standards, can be readily prepared.

Use of Charts for Rapid Calculation of Color Differences. H. R. DAVIDSON, Davidson and Hemmendinger, Easton, Pa., and J. J. HANLON, Mohawk Carpet Mills, Inc., Amsterdam, N. Y.

Considerable evidence has been gathered by various workers during the last few years indicating that the MacAdam visual sensitivity ellipses [MacAdam, D. L., *J. Opt. Soc. Amer.*, **32**, 247–74 (1942)] may be used effectively for evaluation of surface color differences [Ingle, G. W., and Rudick, L., *J. Opt. Soc. Amer.*, **43**, 501–4 (1953); Davidson, H. R., and Friede, E., *J. Opt. Soc. Amer.*, **43**, 581–9 (1953)]. Previously described methods of using the ellipses, however, leave much to be desired in the way of simplicity and speed. We have prepared a series of charts based on the MacAdam ellipses and the data of Davidson and Friede which we find very useful. Following a suggestion by MacAdam [MacAdam, D. L., *J. Opt. Soc. Amer.*, **33**, 18–26 (1943)] we plot Δx and Δy directly on the appropriate non-Cartesian uniform chromaticity chart. The chromaticity difference is then read as a linear distance from the origin, and is plotted against ΔY on a second chart. The linear distance of the point from the origin in the second chart is a direct measure of the color difference. Thus two simple plotting operations and two distance measurements suffice to calculate the color difference. Color tolerances for production control are represented in both diagrams by circles rather than ellipses. Copies of the charts may be obtained from Technical Department, Mohawk Carpet Mills, Inc., Amsterdam, N. Y.

Microdetermination of Nitrogen in Volatile Compounds. William J. Schenck[1], Eli Lilly & Co., Indianapolis, Ind.

THE determination of nitrogen in volatile compounds is a difficult and sometimes impossible task. The standard Dumas procedure will repeatedly give low results for volatile compounds because the compound will usually be swept through the combustion tube in the initial sweeping-out process.

One method that was used to overcome this difficulty was simply to seal the volatile liquid in a capillary and explode the capillary in the combustion tube with heat. This will give good results if care is taken.

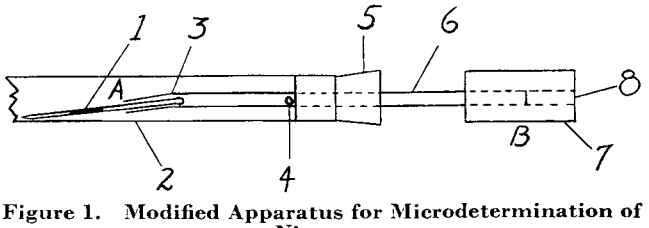


Figure 1. Modified Apparatus for Microdetermination of Nitrogen

A. **Capillary inserted here**
B. **Pressure applied here to break capillary**

1. **Sample capillary**
2. **Combustion tube**
3. **Copper tubing is beat 3° to 5° at this point**
4. **Copper tubing is perforated at this point to allow complete sweeping out of combustion tube**
4. **Rubber stopper**
6. **15- to 20-cm. length of copper tubing, 2.5-mm. diameter, 1-mm. bore**
7. **Rubber tubing**
8. **Carbon dioxide inlet**

The more volatile compounds, however, will explode so violently that they may still go through the combustion tube without being burned. Splintered glass is also left mixed in with the removable copper oxide filling, rendering it useless for future determinations. A modification in the manipulation of the sample has been developed to overcome this difficulty.

PROCEDURE

One end of a capillary is sealed and the opposite end drawn out to a fine hair; the capillary is cleaned with a piece of chamois, cooled, and weighed. After weighing, the capillary is warmed along the sealed end, then the open end is dipped into the liquid. On cooling, the liquid will be drawn up into the capillary. After sufficient sample has been drawn into the capillary, it is removed from the liquid, wiped clean, and cooled by being placed on a piece of dry ice, and then the open end is sealed by touching it in the flame of a microburner. After the sample has reached room temperature, it can be weighed.

After weighing, the capillary is scored very lightly with a glass cutter and inserted into the copper tube at point *A* in Figure 1. Great care must be taken at this point in inserting the capillary and copper tube into the combustion tube. After the initial sweeping-out process is completed, the capillary is broken by pressing up at point *B*. The combustion tube is then warmed, starting as close as possible to the stopper. The analysis is completed as it would be for any ordinary sample.

The length of the capillaries used for the samples was approximately 4.5 cm. The bore of the capillaries was about 0.5 mm. As the samples occupied approximately 1 cm. of the capillaries' length, this left a volume of air (trapped in the capillary when the sample capillary is sealed) of about 0.0075 cc. Considering that 79% of the air in the capillaries was nitrogen and inert gases, this should give 0.006 cc. of gas in a blank determination.

Using distilled water as the sample in three blank determinations, no measurable blanks were found. By first burning samples of acetanilide, then breaking a capillary with distilled water as the sample in the combustion tube, an increase in volume was found. For three determinations, blanks of 0.004, 0.002, and 0.004 cc. were found. These blank volumes were disregarded because of the margin of error in the determinations. Using very small samples, blank determinations would have to be taken into account.

The results from this method were favorable (Table I). The greatest drawback to this method is that the sample must be handled with great care, so that the capillary will not be broken before the analysis is begun.

[1] Present address, University of Southern California, Los Angeles, Calif.

Table I. Comparison of Results Using Four Different Methods

Compound	B.P., °C.	Nitrogen Found: Open capillary, %	Capillary sealed one end, %	Capillary sealed, exploded in combustion tube, %	Present method, %	Nitrometer Reading Corrected, Present Method, Cc.	Theory, %
Allylamine	52.5– 53.5	6.55	18.86	24.32	24.26	0.705	24.54
		12.88	21.49	24.38	24.46	0.824	
		11.45	26.55	24.52	24.38	0.792	
sec-Butylamine	45.2	2.53	7.62	19.16	18.99	0.538	19.15
		7.60	8.27	18.93	18.89	0.402	
		6.56	7.09	18.87	19.04	0.697	
n-Butylamine	77 – 79	10.39	11.99	13.44	13.57	0.332	13.58
		10.99	13.38	13.19	13.42	0.538	
		12.01	13.27	13.50	13.49	0.366	
Pyridine	115 –116	9.39	19.20	16.74	17.48	0.365	17.71
		12.48	15.31	13.49	17.80	0.536	
		15.39	14.22	17.53	17.74	0.532	
Isopropylamine	33 – 34	8.58	17.40	23.35	23.29	0.859	23.70
		trace	21.41	23.43	23.52	0.613	
		17.51	14.90	23.42	23.56	0.883	

Use of Toggle Valves and Teflon in Hydrocarbon Analysis. R. A. Brown and D. J. Skahan, The Atlantic Refining Co., Philadelphia, Pa.

IT HAS been the practice in this laboratory to determine C_1 to C_5 components of liquid hydrocarbons by mass spectrometer analysis of distilled fractions. Four low temperature columns operated by one analyst are used for this work.

In practice, two fractions are collected, a C_1–C_4 gas and a C_5 liquid. Accurate analysis of these cuts depends upon taking representative samples for the mass spectrometer. Gases. in particular, must be thoroughly mixed prior to sampling. This is normally done by three strokes of a Toepler pump, compressing and expanding it with mercury. Errors due to poor mixing are further reduced by using capillary tubing for manifolds and collecting the distillate gas in a single gas bottle. Mixing by the Teopler ensures that the small volume of gas originally in manifold lines will be mixed with that from the bottle.

Nonrepresentative samples can also occur as a result of cross contamination, principally through sorption of hydrocarbons in stopcock grease. Compounds absorbed from a given sample subsequently desorb, to appear as impurities in following samples. To minimize such contamination glass manifolds equipped with spherical joints have been periodically disassembled and cleaned, but this procedure has never been satisfactory, owing to shutdown time and the fact that stopcock grease was still present.

In order to eliminate cross contamination of samples completely, work was initiated on a manifold having no glass stopcocks. Apparatus of this kind has now been in satisfactory use for almost 2 years in manifolds as well as other sample-handling systems.

APPARATUS

Valves and Teflon Packing Glands. A small needle toggle valve supplied by the Hoke Valve Corp. (Catalog No. 462) was selected to replace stopcocks. Initially, these valves were equipped with Hycar rubber seats, which were replaced with Teflon. A cork borer was used to cut a disk from a Teflon sheet 0.16-inch thick, and this disk was then pressed into the stem by use of a vise. A small rubber O-ring seal was used in the valve assembly, but numerous tests showed that this introduced no hydrocarbon cross contamination. In use, the valve was found to be consistently vacuum-tight, with the exception of an occasional leaky valve seat.

To substitute valves for stopcocks it was necessary to find a convenient method for making glass-to-metal connections. Several things were tried, including wax seals, iridium-soldered joints, and glass attached to Kovar, which in turn was soldered to the valve. Each of these techniques is workable, but the Teflon packing gland diagrammed in Figure 1 was more convenient. Connections are made as shown, in which 2-mm. capillary tubing is snugly fitted inside the reamed-out valve nipple. The connection is made vacuum-tight by gentle tightening of the packing nut with a wrench.

Manifold and Packing Gland Applications. The valve unit shown in Figure 2 consists of the valve and glass connectors having joints which are ground flat to enable easy assembly of the system. The joints are sealed with phthalic anhydride cement after valves have been tightened in position on a Transite board. To allow freedom for positioning the valve, the brass rod holding the valve should be smaller in diameter than the hole in the Transite through which it fits.

Teflon packing glands are also used to attach sample tubes to the manifold, as shown for a liquid pentane container in Figure 3. It is important to cap volatile material such as this during storage prior to mass spectrometer analysis and for this purpose a Teflon seated cap, diagrammed also in Figure 3, is used. Pentane was stored at room temperature for 2 months without measurable loss using the seal shown. In addition, the apparatus was found suitable for sample shipment via air express. Packing glands used as described here are tightened by means of 6-inch wrenches.

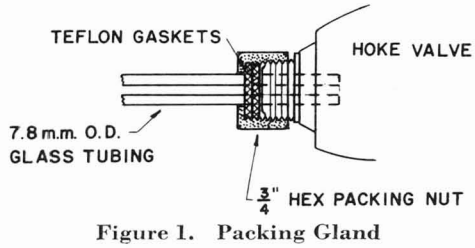


Figure 1. Packing Gland

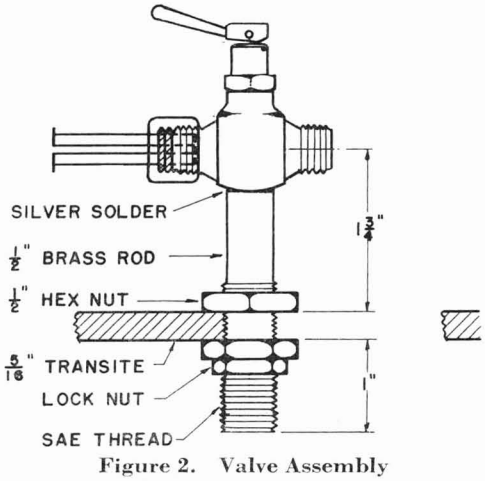


Figure 2. Valve Assembly

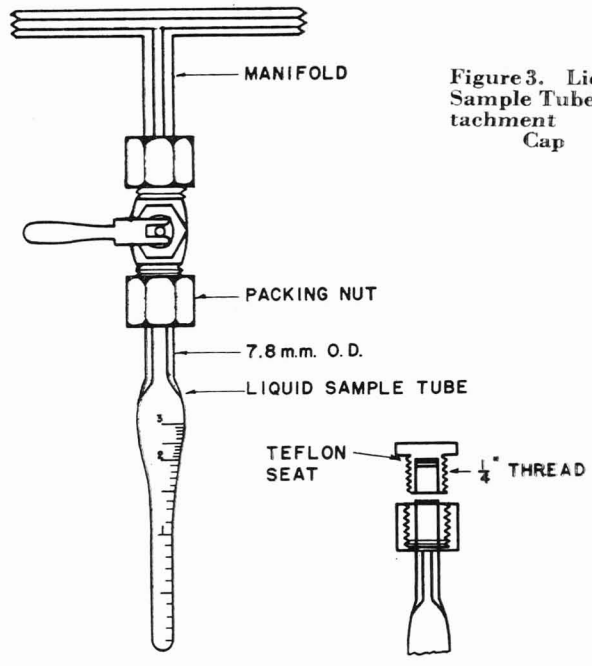


Figure 3. Liquid Sample Tube Attachment and Cap

OPERATION

Experience has shown that the apparatus is of rugged construction. The equipment built after the experimental model has been in use almost a year without breakage. Occasionally, leakage through valve seats occurs, but this can usually be remedied by warming the valve in its closed position and rotating the valve stem to reseal the Teflon seat. Dirt or even mercury on the valve seat can also cause leaks, so that visual inspection of the seat may sometimes locate leakage trouble.

There appears to be no need to clean the apparatus, although no dirt or oil should be allowed to remain in the apparatus, as either material absorbs hydrocarbon gases. Mass spectrometer sample inlet systems having no glass stopcocks have been in operation for many years without being cleaned and the same sort of service is anticipated for these manifolds. A valve manifold which had been in continuous use for 6 months showed no measurable absorption of 2-butene. By contrast, a stopcock manifold which had been in use for only a month absorbed 8 ml. of the gas in 5 minutes.

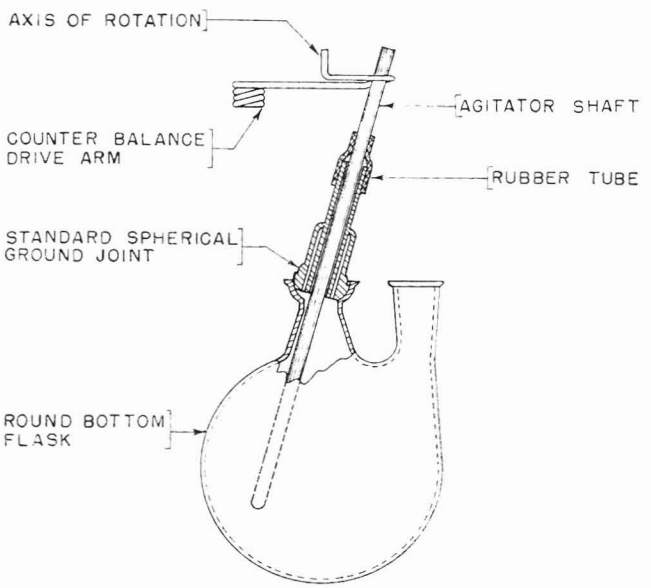
PRESENTED before the American Petroleum Institute, New York, N. Y., May 1953.

Apparatus for Stirring a Reaction Mixture through a Vapor-Tight Seal. J. Russell Skidmore, Dow Chemical International, Ltd., Midland, Mich.

VERY often the chemist wishes to carry out a reaction aided by agitation or stirring in a totally enclosed or vapor-tight system. This usually requires a mechanical seal of some kind. In some instances, a magnetic stirrer is adequate, and no seal is required.

Liquid seals—e.g., mercury-filled seals—are not entirely satisfactory, especially for vacuum or pressure systems. Cylindrical seals with graphite or Teflon sleeve bearings have been used with

some success, and a satisfactory seal can be made from a ground-glass syringe. A far less satisfactory seal is prepared with a spherical glass joint, one part of which is stationary and the other part rotates about the axis of rotation of the stirrer to which it is attached.



An improvement in such a seal can be obtained by the use of a center of rotation—the center of the spherical joint instead of, or in addition to, an axis of rotation. The diagram illustrates schematically the stirring mechanism which utilizes a spherical glass joint to effect a vapor-tight seal. The stirring rod in action describes a cone in the reactor about the center of rotation. The shaft should be left free to rotate about its axis to ensure symmetrical wearing of the seal.

The zone of influence in the reactor is large, depending upon the length of the driving arm or its height above the seal. Because of the large zone of influence, the rate of rotation usually required is slow; 50 to 300 r.p.m. is satisfactory for most conditions. The stirring rod does not require paddles, blades, or other appendages, though these may be added as desired. When the viscosity of the reactants is low, better mixing will be obtained by indenting the side walls of the flask.

These units have been test operated for long periods of time under a vacuum of 0.05 mm. of mercury and under pressure (with a spring load on the seal) of 18 inches of water. No spring load is required for satisfactory operation at atmospheric pressure. The seal should be lubricated with suitable lubricant, depending upon the nature of the reaction under observation. The sketch shows a rubber sleeve to permit adjustment or replacement of the stirring rod, but if desired, the rod may be welded to the seal for an all-glass system.

The counterbalanced drive arm shown may easily be prepared from a piece of heavy iron wire such as $\frac{1}{8}$-inch uncoated welding rod. It could be made as well of a disk of metal, or plastic, or any of various substances which might be available. Its dimensions are not critical; it should be adaptable to a chuck or coupling attachment for a driving mechanism and should provide an opening or hole through which the agitator shaft extends to maintain it in a fixed position relative to the center of rotation.

At least two types of motors are available to drive such stirrers; a stirrer motor with a cone drive mechanism, and a variable speed motor with a gear-reduced shaft. Other systems may be set up as needed, depending upon the amount of work to be done by the stirrer.

The stirrer has become so useful that it is being installed for many reactions not *requiring vapor*-tight or closed systems.

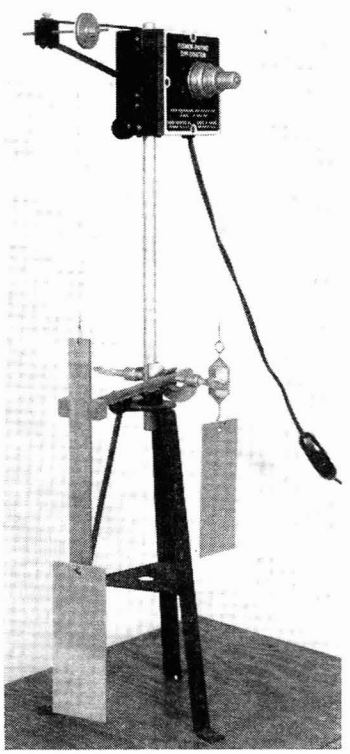
Improved Dip Coater. A. G. Roberts and R. S. Pizer, Organic Plastics Section, National Bureau of Standards, Washington 25, D. C.

It is frequently desirable during the course of extensive laboratory test programs to conserve a limited supply of the materials under investigation. Even if unlimited quantities are available, it is usually desirable to carry out a given series of tests with a minimum of material in order to reduce the effect of container-to-container variations. The conservation problem may become acute in cases where the dip-coating technique is employed with coating solutions which are activated just prior to use and which have a short pot life that necessitates their being discarded after each few hours of use. The day-to-day need for freshly mixed materials may consume an enormous amount of material, from the laboratory point of view. In these circumstances, the use of the minimum quantity of material per coating batch is an obvious necessity.

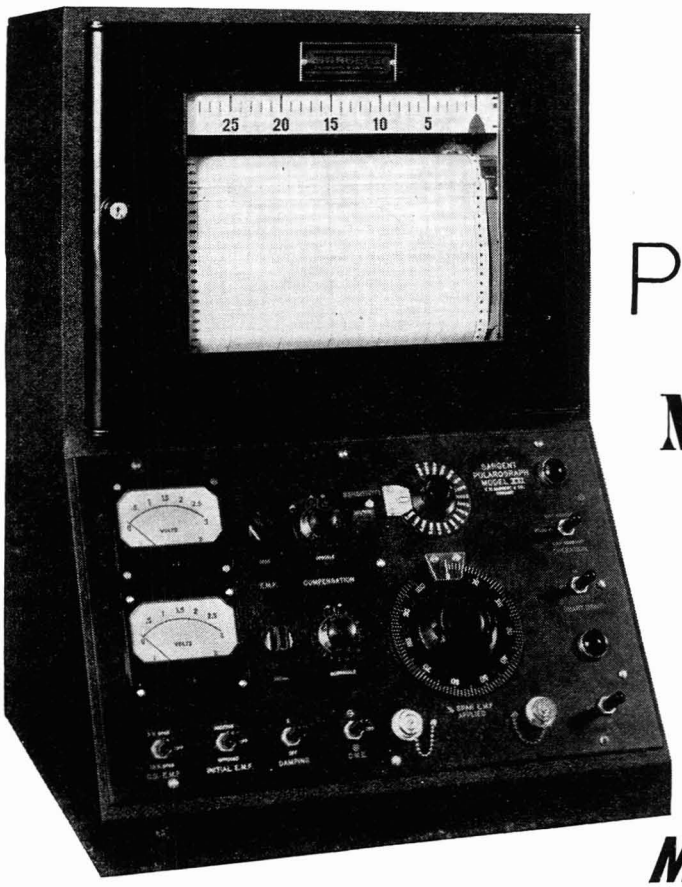
Containers of the smallest dimensions that will satisfactorily accommodate the specimens to be coated are easily constructed; however, the persistent tendency of flat specimens to rotate or swing against the sides of a narrow container during the dip-coating operation constitutes a vexing problem. This problem has been met simply and effectively in this laboratory by construction of a special specimen holder for use with the conventional type of laboratory dip coater.

Undesirable motion of the test panel being dipped can be prevented, for example, by replacing the specimen-holding plumb bob of the familiar Fisher-Payne dip coater [Payne, H.F., Ind. Eng. Chem., Anal. Ed., **15**, 48 (1943)] with a rigid brass strip sliding vertically through the grooves of a fixed brass mounting attached by a rod and conventional clamp to a ring stand.

The rod is soldered into the back of the slide holder. A pin is soldered near the bottom of the brass strip at an angle of about 45° from the vertical, which causes the specimen to slide against the flat face of the brass strip and remain firmly in place throughout the dip-coating operation. The diameter of the mounting hole in the test specimen must be sufficiently larger than that of the mounting pin to permit the panel to slide freely down the pin and come to rest in a vertical position. The minimum diameter, D, of the mounting hole is given by the relation $D = 1.4\ P + T$, where P is pin diameter and T the test panel thickness.



The improved specimen holder is shown. The dip-coater attachment is easily constructed and will considerably increase the utility of the conventional dip coater where conservation of coating materials is important.



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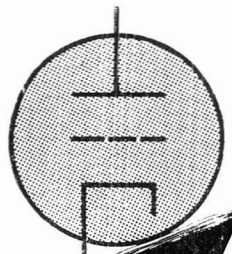

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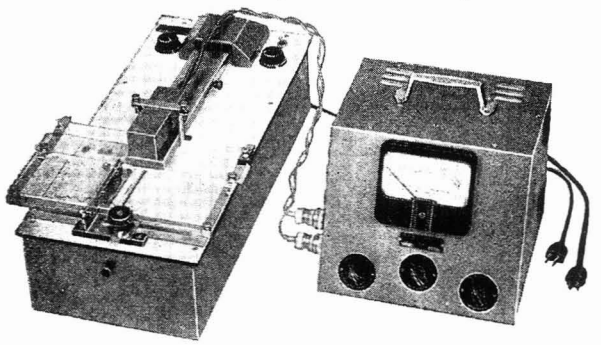

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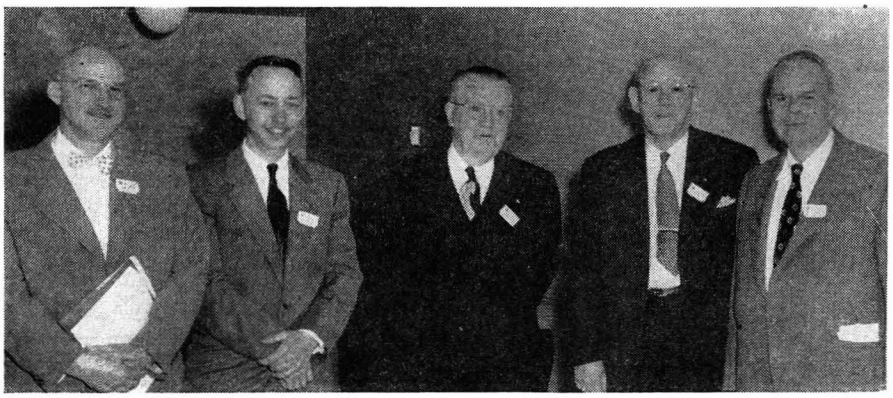

G. Frederick Smith (center) and the men who paid tribute to him at symposium in his honor held at Kansas City by the Division of Analytical Chemistry. Left to right. Charles A. Goetz and Harvey Diehl, Iowa State College; G. L. Clark, University of Illinois; and Hobart H. Willard, University of Michigan

Analysts Honor Fisher Award Winner, G. F. Smith, at Kansas City

KANSAS CITY.—"An effective teacher, a skillful and ingenious investigator, and a businessman whose services have lengthened the lives of analytical chemists everywhere" was the characterization of G. Frederick Smith, University of Illinois, at a program given in his honor by the Division of Analytical Chemistry at the AMERICAN CHEMICAL SOCIETY meeting held here in March.

The several speakers on the program have all been closely associated with Smith. H. H. Willard, University of Michigan, for example, was Smith's instructor. Willard, like Smith, has been the recipient of the Fisher Award. Harvey Diehl and C. A. Goetz, Iowa State College, were former students of Smith. G. L. Clark, University of Illinois, has been a coworker.

Smith was born at Lucasville, Ohio, in 1891 and was reared in Columbus, Ohio. He studied at Ohio State University and the University of Michigan, receiving his Ph.D. in 1922. Except for a 6-month Army hitch and 18 months with General Electric (Nela Park, Ohio), Smith has been with the University of Illinois.

Clark said that Smith, as an instructor of undergraduate and graduate students, has proved to be "an unbelievable store of information" and an original and good-natured instructor who has used ingenious lectures and experiments in his teaching.

Willard and Goetz said that Smith got started in the business of making and selling analytical reagents when he found that perchloric acid, a valuable analytical reagent, was not available in a pure form at a reasonable cost. His interest in perchloric acid and its derivatives as oxidizing and dehydrating agents stemmed from his Ph.D. work. Sales of the acid today total about 1,000,000 pounds a year compared to a 300-pound figure for 1920.

His company, the G. Frederick Smith Chemical Co., has followed a practice of trying to supply useful reagents not generally available elsewhere. This has led to the production of ceric compounds and periodic acid and its derivatives. As a sales promotion device, Smith has prepared and distributed about 30,000 copies of 14 monographs on analytical reagents and their applications. Coworkers and former students have cooperated in this endeavor. Much of the material contained in these booklets has been the result of original research by Smith and other workers.

Smith has also developed another company, Aeration Process Co., of which he is the president. The product of this concern is Instantwhip.

In addition to the half-day session in honor of Smith, there were three other half-day sessions devoted to general papers. There were no symposia or panel discussions at the divisional meeting. Typical papers, described below, covered a wide range of analytical procedures, reagents, and equipment.

Dipyridines, diquinolines, terpyridines, and 1,10-phenanthrolines constitute one of the most versatile groups of organic chelating agents ever applied to a wide variety of analytical problems, G. Frederick Smith said in his Fisher Award address given before the Analytical Division at Kansas City. These agents are sensitive and selective to the extent that they can be used to differentiate between 1.0 and 1.1 mg. of iron in a bathtub full of water. Functional groups in these heterocyclic nitrogen compounds are:

ferroine

cuproine

terroine

These compounds react with various metals to form five-member (chelate) rings.

Resistance to decomposition under drastic destructive conditions characterizes these heterocyclic nitrogen compounds. They are used as oxidation indicators, in microdetection and quantitative determinations and removal of trace elements, as masking (sequestering) agents, and in anion separations.

Based on physical, chemical, and stereochemical concepts, Smith said that it is possible to predict quantitatively, changes in such properties as color and oxidation-reduction potential, which result when substitutions of various functional groups are made in reagents containing the ferroine, cuproine, and terroine groups.

The successful application in a wide variety of analytical determinations of chelating agents such as ethylenediaminetetraacetic acid (EDTA) has been carried out by a group of research chemists at Iowa State College.

One new application, of interest in the atomic energy field, was reported by James S. Fritz. His titrimetric method, applied to zirconium identification, can be done in about 5 minutes compared to the several hours required in the more conventional method of digesting, filtering, washing, cooling, and weighing the sample.

By using disodium dihydrogen ethylenediamine tetraacetate in an acid solution, stable, soluble complexes are formed. Sharp end points are obtained using visual indicators. This method has the advantage that most metals, including tin, titanium, uranium, and aluminum, do not interfere. Iron, if reduced to the ferrous state, does not interfere. Interfering ions include thorium, molybdenum, bismuth, antimony, and tungsten.

Stability constants of complexes formed by 1,2-cyclohexenediaminetetraacetic acid (CDTA) and various metal salts are better in most cases than those formed with ethylenediaminetetraacetic acid, Thomas C. Loomis reported.

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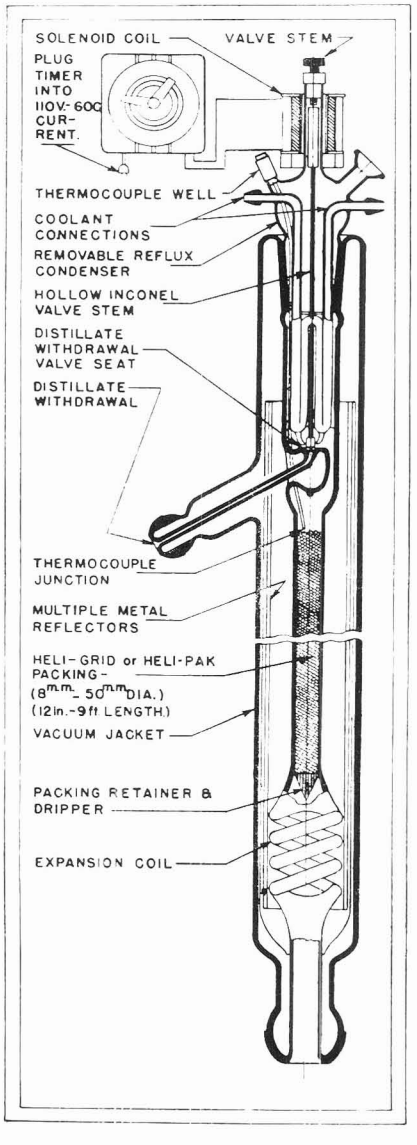

Diagram of "Hyper-Cal" Type Fractionating Column

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The "Mini-Cal" is a small version of the "Hyper-Cal" similar in general design, but with external flexible bellows in jacket, designed for least holdup, available in 8 mm. packing diameter, 12", 18" or 24" packed length, usually with "Heli-Grid," for distillation of small and medium size samples.

Concentric Glass Tube similar to the "Mini-Cal," as above described, but all-glass, with 24" double concentric glass tube fractionating section; tests up to 60 plates at low thruputs, suitable for distillation of highly corrosive liquids.

Spinning-Band Column. This is a specialized column, same vacuum jacket and general reflux head construction as other columns, but the column section consists of 5 mm. (or 15 mm.) wide band, *spinning* in a 24" precision bore empty tube. Suitable variable speed motor, magnetic drive, and mountings are supplied with this column. This column has the lowest pressure drop and liquid holdup of any packing of similar capacity; can be used successfully at pressures as low as 1 mm. Hg. abs. or even lower.

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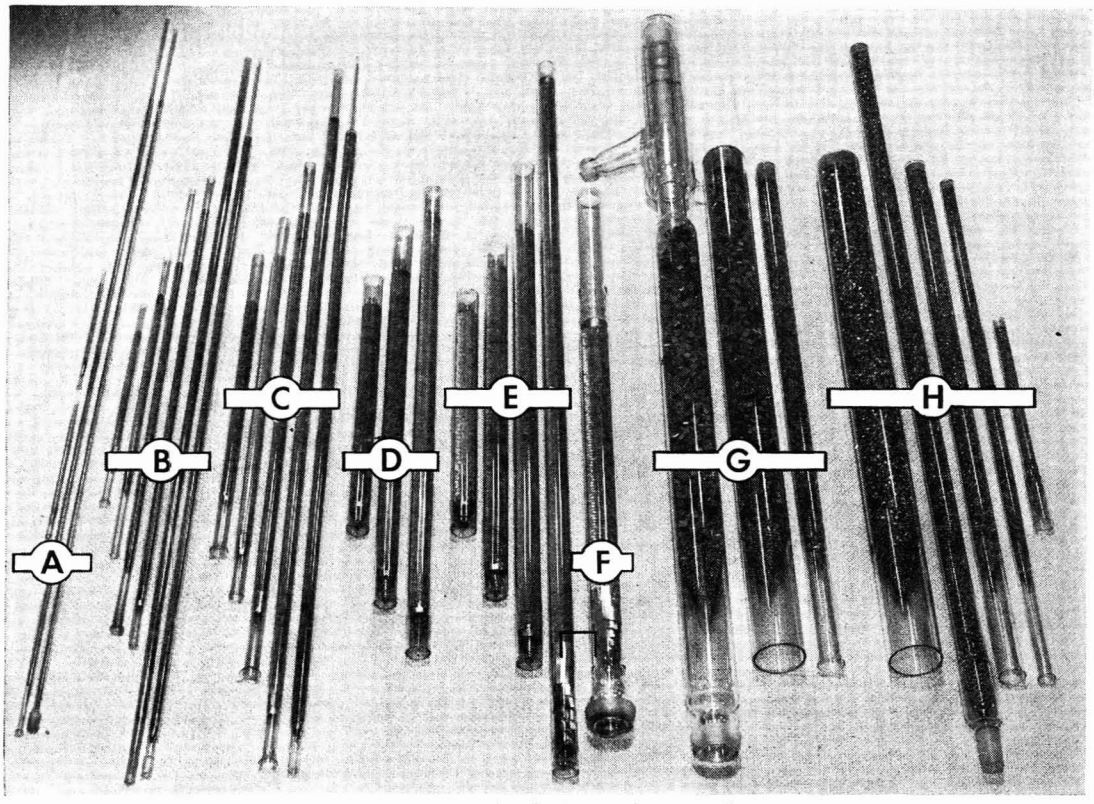

	HELI-GRID
A	4.7 mm.
B	8 mm.
C	13 mm.
D	22 mm.
E	25 mm.
F	1¼ inch
	OCTA-PAK
G	.300 inch
	.200 inch
	HELI-PAK
H	.092 x .175 x .175
	.050 x .100 x .100
	.035 x .070 x .070

All three packings use the principle of effective distribution and vapor-contacting of reflux liquid with *precisely* spaced wire or screen shapes as illustrated.

The "Heli-Grid" is designed as an integral precisely fabricated unit in *precision bore glass tubing* and is the best available high-efficiency type packing.

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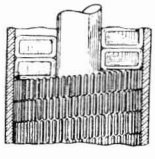

*__"HELI-GRID,"__ Integral Wire Coil Assembly

SIZES: (a) 8 mm., 13 mm., 15 mm., 25 mm., and 30 mm. diam.; (b) 12", 24" or 36" long units in precision bore Pyrex glass tubing.

H.E.T.P., as low as 0.2", (see I.E.C. Anal. Ed. *13*, p. 639, 1941).

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PRESSURE DROP per plate, very low.

APPLICATION: In all low-temperature and small size columns; for maximum plate No. in one column; or for best utilization of platinum or other material as packing for special research.

Actual Sizes

*__"HELI-PAK"__ Wire Coil Type

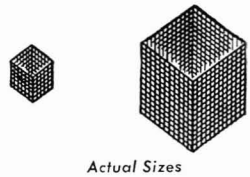
THREE SIZES: (a) 0.035" x 0.070" x 0.070"; (b) 0.050" x 0.100" x 0.100"; (c) 0.092" x 0.175" x 0.175".

H.E.T.P. as low as 0.2", lowest and smallest reported for any random packings; permits use of short columns of adequate plates.

HIGH EFFICIENCY FACTOR for superior analytical and all-around performance.

LOW PRESSURE DROP, less than 0.7 mm. H_2O per plate, important in vacuum fractionation.

APPLICATION: *Size A* for micro columns, 6.5 mm. to about 8 mm. dia.; *Size B*—balanced for most distillation requirements—8 to 25 mm. dia.; *Size C*—15 mm. up to 100 mm. or larger dia., vacuum and low pressure drop work.



Actual Sizes

*__"OCTA-PAK"__ Wire Screen Type

TWO SIZES: 0.200" and 0.300".

H.E.T.P. proportionate to packing size, but compares favorably with all other random packings of similar dimensions.

AMPLY STRONG to withstand loading in tall large diameter columns and frequent handling.

BALANCED HIGH CAPACITY, Low H.E.T.P., and Low Pressure Drop.

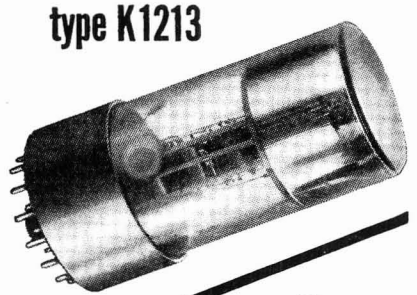
APPLICATION: For larger columns, 2" up to 12" diam., where cost per plate per unit distilling capacity is important; with large free space and low pressure drop characteristics making it specially suitable for vacuum fractionation.

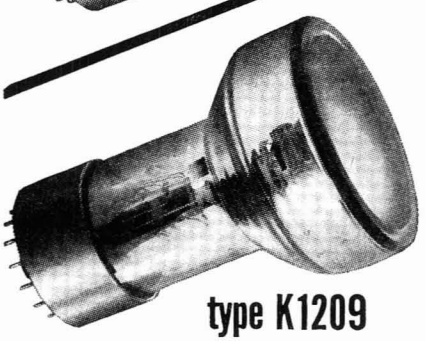
Write for descriptive circulars and prices on the packings.

Patents and Patents Pending

12-Dynode MULTIPLIER PHOTOTUBES by DU MONT

type K1213





type K1209

Twelve-dynode multiplier phototubes—a line exemplified by the 3-inch Type K1213 and the 5-inch Type K1209 shown here — are now offered by Du Mont for those applications where extremely high gain is required — or where optimum signal-to-noise ratio, at conventional gain is a major consideration.

Among the features contributing to the excellent operating characteristics of the 12-stage multiplier phototubes are the specially designed dynodes which assure maximum electron collection, and a new basing in which all leads are widely separated, reducing leakage current, and hence noise.

Naturally, these new tubes provide the same excellent cathode-sensitivity, stability, and low dark current that characterize Du Mont's widely accepted 10-stage multiplier phototubes.

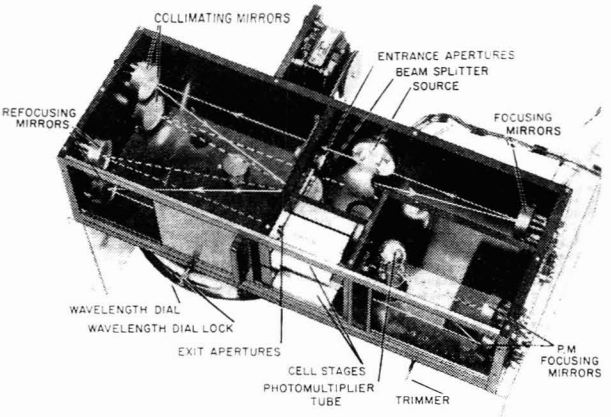
For additional information write to:

Technical Sales Department

Allen B. Du Mont Laboratories, Inc.

760 Bloomfield Ave., Clifton, N. J.

Circle no. 24 A on Readers' Service Card, page 49 A



Details of *Jarrell-Ash* Co.'s new double-beam spectrophotometer described at Kansas City by Frederick Brech, director of research. Further details in the Analyst's Column (page 13 A)

Constants for the complexes increased from 10^7 to 10^{24} for the following metals in the order named: barium, strontium, magnesium, calcium, manganese(II), lead(II), zinc, cadmium, cobalt(II), copper(II), and nickel(II).

CDTA complexing has been applied successfully also in the rapid and accurate analysis of brass and other copper-base alloys by Charles Goetz. A titrimetric technique is used following separation by gravimetric methods.

The presence of "catalyst poisoning" trace metals in petroleum may be determined quickly and accurately by a new acid-extraction technique described by J. E. Barney II, Standard Oil (Indiana), and G. P. Haight, Jr., University of Kansas.

Trace metals are often present in the original petroleum or may be introduced during early processing. Because small amounts of certain metals can "poison" the catalysts used in refining, the fact that they are present must be known.

The method calls for extractions with sulfuric acid followed by hydrochloric acid, acetone, and water. The metals are determined spectrographically using the evaporated extract. Use of aqueous solutions of metal salts as standards avoids need for oil-soluble metal compounds.

The authors reported that the method appears to give quantitative results. It avoids the losses by volatilization and entrainment involved in the standard combustion techniques. Results obtained compare favorably with the total sulfated ashing procedure and are more accurate than simple ashing, partial sulfated ashing, treatment with iodine, and extraction with a mixture of hydrobromic and acetic acids.

A practical and accurate method for analyzing gold-silver alloys has been developed by A. C. Shead and Norman W. Houghton of the University of Oklahoma. Results obtained by these coworkers compare favorably with those resulting from classical fire assaying methods. It has an advantage of not destroying the bead.

In the new technique, the diameter of a spherical gold-silver bead is determined using an ocular micrometer. The bead is weighed on a microbalance (assay balance). From these two figures, volume and density can be calculated. Percentage composition is determined by comparing the density of the sample with a table or graph of densities of alloys of known composition.

The quite different densities of gold and silver, 19.3 and 10.5, respectively, make this method practical. It cannot be applied to two-metal alloys where the constituents differ only slightly in density.

It is easier to teach engineering concepts to a chemist than to teach an engineer (not chemical) chemistry, H. H. Bliss, University of Oklahoma, said. For that reason instruction in analytical chemistry should incorporate factors of common concern to both chemists and engineers in both lecture material and demonstrations in a materials testing laboratory. Such instruction, Bliss feels, would improve relations between chemists and engineers when they are working side by side in industry.

Typical engineering concepts include the basic idea that, within the limits of economic availability, properties determine usage. Chemists should realize that, instead of seeking materials of high purity, engineers will seek the lowest grade material at the minimum cost which will do the job at hand. Chemists should also recognize that specifications are definitions of materials and that standards are widely accepted statements of specifications.

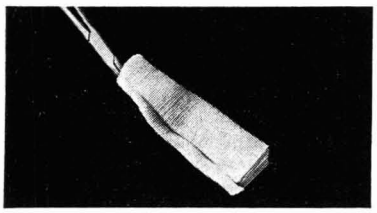
The chemist should be taught that sampling cannot be dissociated from analysis. He cannot ignore sampling and spend all his analytical time on composite samples. Finally, he must recognize that test methods resemble analyses in most major features and he should, therefore, learn to understand mechanical test equipment.

Kodak reports to laboratories on:

some things you can do with oxidized cellulose . . . an alien among our organics . . . making the selection of scientific photographic materials easier for you and us . . . how to find out more about cellulose acetate sheeting

Slightly degenerated cotton

Instead of oxidizing cellulose as man has done from time immemorial to take the chill out of his bones, cook his dinner, and dispel his gloom, we have a trick of oxidizing it only to a 10% to 22% carboxyl level. This we do by treatment with nitrogen dioxide. The product, called, surprisingly enough, "oxidized cellulose," looks like this:



It has the appearance and even some of the strength of ordinary cotton, along with some rather extraordinary properties. The most recent of these to come to light is its use in the diagnosis of congenital hyperplasia (enlargement) of the adrenal gland in children. This comes about from the remarkable affinity of oxidized cellulose for ACTH, which it absorbs quantitatively. ACTH is not detectable in the blood of normal children but does appear where this affliction exists. After cortisone treatment, no ACTH is detectable. One advantage of oxidized cellulose in ACTH assay is that the concentrates it yields are not toxic to the assay animal.

This is not the debut of the stuff as a tool in the healing art. Its first flush of prominence a few years ago was based on the surgically useful fact that it has the physical attributes of cotton gauze, yet is wholly absorbed in the blood stream after fulfilling its mechanical function.

Aside from its medical use, oxidized cellulose is an ion exchange medium, plucking cations out of aqueous solution to form metallic salts of cellulose. Plain cotton as far as the eye can see and the finger can feel, it bewitchedly vanishes into solution when popped into a 2% sodium hydroxide solution. When kept dry and cold, however, it survives indefinitely without change.

Trimming the cellulose chains with 10 to 22 percent of carboxyls drives the price of cotton up to $62.25 per pound, FOB Kingsport, Tenn. If you are interested in concentrating some ACTH, this may be a bargain for you right now, and, if you can develop some decent volume of demand for it, we'll probably drop the price. For the cold facts, write Eastman Chemical Products, Inc., Chemical Division, Kingsport, Tenn. (Subsidiary of Eastman Kodak Company).

Sale

As this is written, we find among our stocks of more than 3500 organic compounds a bottle containing 1,600 grams of indubitably inorganic *Cadmium Tungstoborate* (formerly borotungstate). We think its formula is $Cd_2B_2W_9O_{32}\cdot 18H_2O$, which would make its molecular weight 2738.03. We know that a saturated aqueous solution of it has a specific gravity of 3.28 and that it is probably less toxic than the thallium compounds sometimes used in the Klein's Solution Technique for gravity separation of minerals. You can find out all about this on page 521 of Johannsen's *Manual of Petrographic Methods.*

We're selling Cadmium Tungstoborate *off as Eastman 5931 at $2.50 for 10 grams, $5.50 for 25 grams. Orders may be placed with Distillation Products Industries, Eastman Organic Chemicals Department, Rochester 3, N. Y. (Division of Eastman Kodak Company).*

Catalog

There is a tradition in our sales department to encourage correspondence on business that looks like small potatoes to the average cost accountant. Unaware of the historical relationship between us and the scientific user of photographic materials, he might well question the exchange of two or three long letters leading up to a recommendation that an order be placed with a dealer for one dozen 1″ x 3″ *Kodak Autoradiographic Plates, Type No-Screen,* retailing at $1.66.

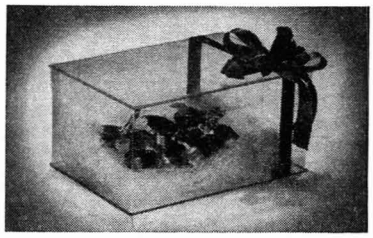
Noble as this outlook may be, we are now making an attempt to save time and stationery for the scientist and ourselves through the medium of a booklet that summarizes the facts about the various materials, familiar and obscure, which we offer for scientific photography. If it does nothing else, it should at least suggest useful questions to ask.

Covered are our offerings in the following categories: 1) for general photography and photomicrography, 2) for the specialized recording of radiation, 3) for general spectrochemistry, 4) for the deep ultraviolet, 5) for the infrared, 6) for autoradiography and nuclear particle tracks, 7) for electron imagery, 8) for the finest image detail, 9) for modifying spectral distribution, 10) for attenuating light, 11) for other photographic techniques.

"Kodak Photographic Materials and Light Filters for the Laboratory" is the title, and Eastman Kodak Company, Industrial Photographic Division, Rochester 4, N. Y., are the people who hope to lighten their correspondence load by sending a copy of it to you free.

Kodapak Sheet

Since plasticized cellulose ester sheeting finds use in many technologies even more complex than manufacturing the familiar orchid box,



we have just put out a newly revised pamphlet in which we tabulate a great many of the mechanical, optical, thermal, chemical, and electrical properties of the various forms of Kodapak Sheet. The gist of it is that Kodapak Sheet, which may be readily formed by means of heat and pressure, cemented, or high-frequency sealed, is quite a versatile material.

You can obtain a copy of "Properties of Kodapak Sheet" by writing Eastman Kodak Company, Cellulose Products Division, Rochester 4, N. Y.

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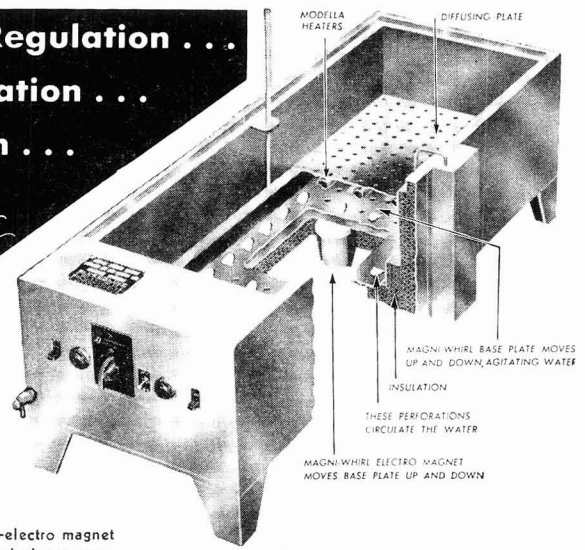

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ASTM Committee Week

Technical committees of the American Society for Testing Materials met in Washington, D. C., February 1 to 5, when new research work was discussed and new specifications and tests for materials and numerous revisions were completed. Most of the new specifications will be considered finally at the ASTM annual meeting in Chicago the week of June 13. Subjects discussed included the following:

Committee A-1 on Steel. A single table of chemical requirements for pipe and tubing covering the ranges now shown as check analysis will be substituted for the dual tables. Proposed specifications for high-strength electric fusion welded pipe for gas lines, and for forged and bored austenitic steel pipe for central station use, are under consideration. Impact test requirements covering plates for pressure vessels in low-temperature service are to be revised.

Committee A-10 on Iron-Chromium, Iron-Chromium-Nickel, and Related Alloys. A special compilation of chemical compositions and rupture properties of superstrength alloys has been submitted to the committee for comment, and is expected to serve as a basis for specifications for precipitation hardening, hot-cold worked, and cast superstrength alloys. Subject to confirming letter ballot, Emergency Alternate Specifications EA167, EA240, and EA276, which permit use of a columbium-tantalum combination in addition to straight columbium in columbium-modified steels, are continued.

Committee C-22 on Porcelain Enamel. Two existing tentatives were approved for advancement to standard: methods of test for resistance of porcelain-enameled utensils to boiling acid (C 283 T) and for sieve analysis of wet-milled and dry-milled porcelain enamel (C 285 T).

Committee D-1 on Paint, Varnish, Lacquer, and Related Products. Work on latex and emulsion paints is being undertaken through the organization of a new subcommittee. A sampling procedure for drying oils, two methods for determining total iodine value, proposed specifications or safflower oil, and analytical methods for fatty acids are under investigation. The group on foots and break of raw soybean oil has set up a collaborative testing program to determine proper specification ranges for degummed soybean oil. A new group is to be appointed to study tests for odor and methods for classifying odors. Groups were appointed to undertake work on yellowing of interior finishes and chemical resistance of appliance enamels. Two new groups will consider revision of the test for nonvolatile vehicles in the standard methods of chemical analysis of white linseed oil paints and preparation of a specific resistance method for soluble salts of iron oxide pigments. The Subcommittee on Shellac presented a new method for testing acid number of bleached lac and bleached lac varnishes.

Committee D-11 on Rubber and Rubberlike Materials. A comprehensive glossary of terms used in the rubber industry has just been completed. A new Subcommittee on Classification and Specifications of Rubber Compounds for General Use was organized. The Subcommittee on Chemical Analysis of Rubber Products presented a revision of the procedures for

determining copper and manganese in crude rubber (D 297). A revision of the procedure for analysis of ash was also recommended. The Subcommittee on Crude Natural Rubber voted to set up a task group to study methods for determining the vulcanization behavior of rubber by the Mooney viscometer.

Committee D-19 on Industrial Water. Revisions of the tests for carbon dioxide (D 513) and suspended and dissolved solids (D 1069) will be submitted in June. Studies of optical methods for turbidity in water have begun. The committee has nearly completed simplified methods for hardness, hydroxide, nitrite, and sulfite, to be recommended to the American Society of Mechanical Engineers for inclusion in the ASME Boiler Test Code.

Anachem Conference

The Second Annual Anachem Conference, sponsored by the Association of Analytical Chemists, Detroit, Mich., will be held May 3 at the University of Detroit.

Analytical Chemistry Fosters Progress in Steelmaking. Charles M. Parker, vice president, Iron and Steel Institute.

Induced Reactions, I. M. Kolthoff, University of Minnesota.

Organic Analytical Reagents, Their Structure and Property Prognosis. G. Frederick Smith, University of Illinois.

Nucleonics in Analytical Chemistry. G. W. Leddicotte, Oak Ridge National Laboratory.

The session will be concluded by an address on "Analysts and Analyses" by M. G. Mellon, recipient of the 1953 Anachem Award.

Advance registration, with $2.00 fee, should be sent to Paul G. Elsey, 16534 Beech Road, Detroit 10, Mich. Walter Wagner, University of Detroit, is general chairman of the Anachem Conference Committee. Paul K. Winter, Research Laboratories, Division General Motors Corp., is president of the association.

Symposium on Molecular Structure

A tentative program has been arranged for the Symposium on Molecular Structure and Spectroscopy to be held at Ohio State University, Columbus, Ohio, June 14 to 18.

Infrared Spectroscopy of the Solid State. D. Hornig, Brown University, Providence, R. I.

Optical Investigations of Energy Levels in Solids. Elias Burstein, Naval Research Laboratory, Washington, D. C.

Infrared Spectroscopy in the Millimeter Region. J. H. Rohrbaugh, New York University, New York, N. Y.

Microwave Spectroscopy. C. H. Townes, Columbia University, New York, N. Y.

Intensities of Infrared Bands. D. M. Dennison, University of Michigan, Ann Arbor, Mich.

Anomalous Intensities in Vibration-Rotation Bands. R. C. Herman, Applied Physics Laboratory, Silver Spring, Md.

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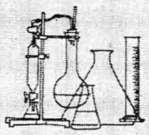

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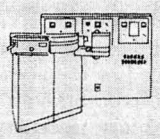

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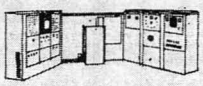

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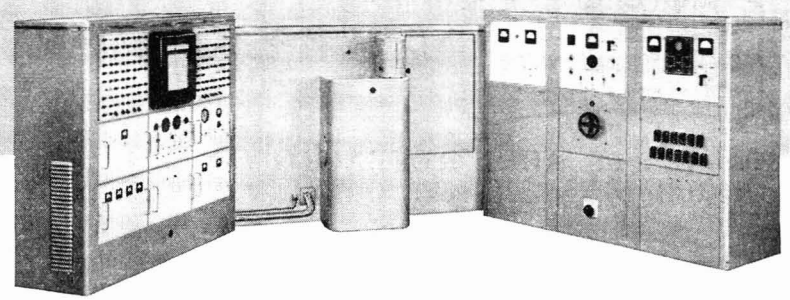

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Analyst's Calendar

American Chemical Society. 126th National Meeting. New York, N. Y., September 12 to 17.

Electrochemical Society. Electronics. La Salle Hotel, Chicago, Ill., May 2 to 6.

American Association of Spectrographers. Symposium on Direct Reading Emission Spectroscopy. Chicago, Ill., May 7.

American Petroleum Institute, Division of Refining. Rice Hotel, Houston, Tex., May 10 to 13.

Fourth Annual Research Equipment Exhibit. National Institutes of Health, Bethesda, Md., May 24 to 27.

Symposium on Molecular Structure and Spectroscopy. Ohio State University, June 14 to 18.

Committee on Vacuum Techniques. High Vacuum Symposium. Berkeley Carteret Hotel, Asbury Park, N. J., June 16 to 18.

Seventh Annual Analytical Symposium. Minneapolis, Minn., June 18 and 19.

Sixth Annual Conference on Electronics and Nucleonics in Medicine. American Institute of Electrical Engineers, Institute of Radio Engineers, and Instrument Society of America. Hotel New Yorker, New York, N. Y., November 19 and 20.

Interferometric Wave-Length Measurements in the Infrared. D. H. RANK, Pennsylvania State University, State College, Pa.

Diffraction Gratings for the Infrared. DAVID RICHARDSON, Bausch & Lomb Optical Co., Rochester, N. Y.

On June 18 discussion of the most effective technique for the solutions of a problem in industry will include talks on infrared spectroscopic technique, Raman spectroscopic technique (Eugene Rosenbaum, Sun Oil Co., Norwood, Pa.), ultraviolet spectroscopic technique (Robert C. Hirt, American Cyanamid Co., Stanford, Conn.), mass spectrographic technique, x-ray diffraction technique, and nuclear resonance technique.

H. C. Longuet-Higgins, Cambridge University, Cambridge, England, is tentatively scheduled as the speaker on June 14. Further information is available from H. H. Nielsen, Department of Physics and Astronomy, Ohio State University, Columbus 10, Ohio.

Oak Ridge Training Courses

The Oak Ridge Institute of Nuclear Studies will offer three basic courses in isotope techniques during the summer. A 2-week course on radioactivity, designed for teachers in secondary schools and teachers' colleges, beginning June 7, will consist of background lectures in physics and radioactivity, with demonstration of experiments outlined in the Atomic Energy Commission booklet, "Laboratory Experiments with Radioisotopes."

A 1-week advanced course in applied instrumentation, beginning June 28, will present lectures on instrumentation techniques and demonstrations of modern instruments by technical representatives of the manufacturers. An advanced course in radioisotope applications in biochemistry will be held September 6 to 17. Basic 1-month courses will begin June 14, July 12, and August 9.

Additional information may be obtained from the Special Training Division, Oak Ridge Institute of Nuclear Studies, P.O. Box 117, Oak Ridge, Tenn.

Workshops for Teachers

The Division of Chemical Education, AMERICAN CHEMICAL SOCIETY, will sponsor the Fifth General Chemistry and Fine Organic Chemistry Workshops at North Carolina State College, Raleigh, N. C., June 16 to 26, and at Kenyon College, Gambier, Ohio, June

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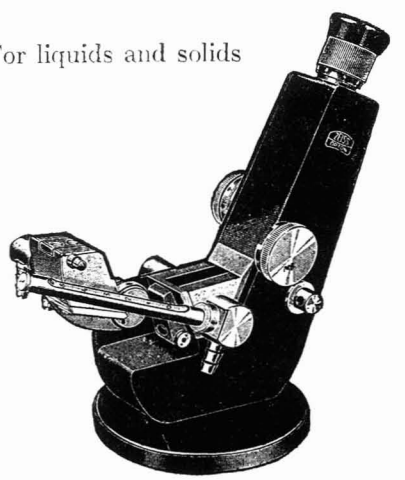

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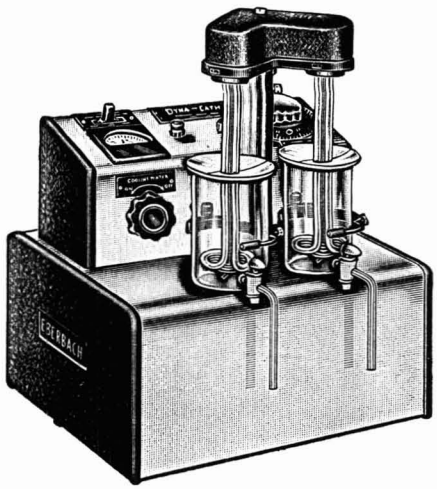

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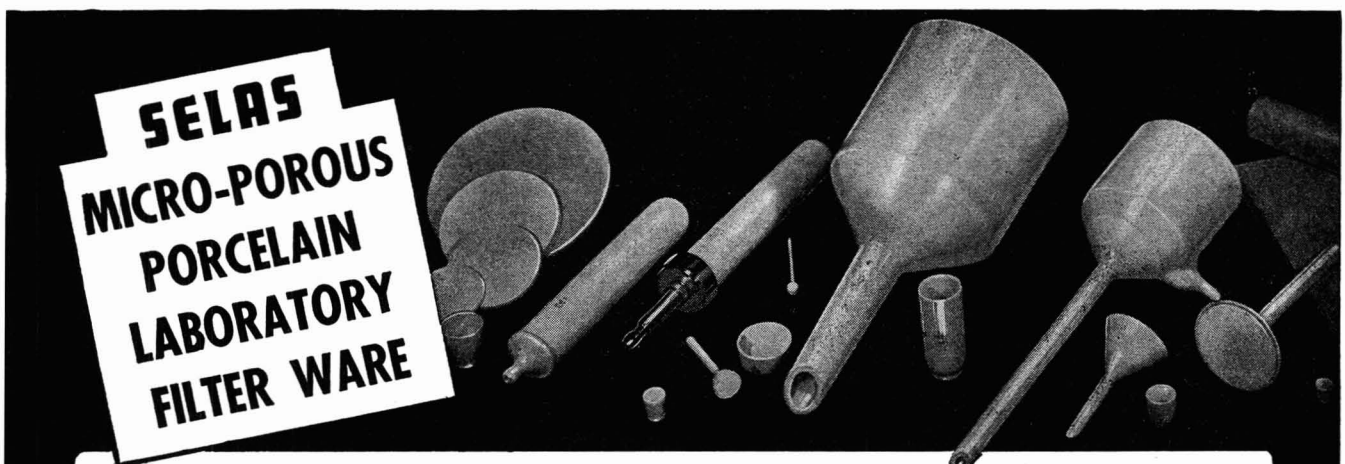

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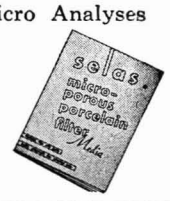

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26 to July 2. At the University of Wyoming, a 5-week institute, sponsored by the National Science Foundation, will be held July 19 to August 20, with particular attention to needs of teachers in junior and 4-year colleges, and problems of general, analytical, organic, and physical chemistry. Further information is available from E. H. Schierz, University of Wyoming, Laramie, Wyo.

Ottawa Symposium on Applied Spectroscopy

The Ottawa Symposium on Applied Spectroscopy will be held September 20 and 21. It will be concerned with emission spectroscopy.

Information may be obtained from J. K. Hurwitz, Physical Metallurgy Division, Department of Mines and Technical Surveys, 568 Booth St., Ottawa, Ontario, Canada.

International Colloquium for Spectroscopy

The Fifth International Colloquium for Spectroscopy will be held at Gmunden, Salzkammergut, Austria, from August 30 to September 3. The subdivision on absorption and emission spectroscopy plans to discuss the application of molecular spectroscopy to the examination of technical artificial fibers, and the analytical chemistry of nonconductors and alloys of copper. In addition to formal papers, evening sessions will be arranged for reporting personal experiences and engaging in free discussion.

The Arbeitsgruppe für Spektrochemie und Kolorimetrie of the Verein Österreichischer Chemiker, Vienna, Austria, is organizing the conference under the chairmanship of F. X. Mayer. K. H. Spitzy and H. Svejda are acting as secretaries.

Techniques of Electron Microscope

The annual Cornell summer laboratory course in techniques and applications of the electron microscope will be given June 14 to 26 by the Laboratory of Electron Microscopy in the Department of Engineering Physics. Under the direction of Benjamin M. Siegel, the course will have James Hillier, Melpar, Inc., Alexandria, Va., and C. E. Hall, Massachusetts Institute of Technology, Cambridge, Mass., as guest lecturers.

The course is designed for research workers who have recently entered the field of electron microscopy or are planning research problems involving applications of the instrument. Inquiries should be addressed to Benjamin M. Siegel, Department of Engineering Physics, Rockefeller Hall, Cornell University, Ithaca, N. Y.

Special Summer Courses at NYU

New York University has announced special summer courses in microtechniques in organic chemistry and electrical and electronic techniques in chemistry, from June 21 to July 30.

Information may be obtained from G. M. Murphy, Department of Chemistry, New York University, Washington Square 3, New York, N. Y.

Symposium on Analytical Chemistry

The Midlands Society for Analytical Chemistry is holding an 8-day Symposium on Analytical Chemistry at the University of Birmingham, Birmingham, England, August 25 to September 1.

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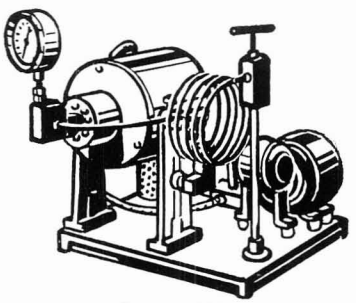

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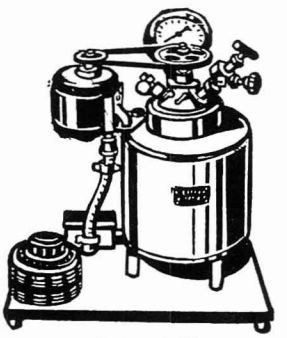

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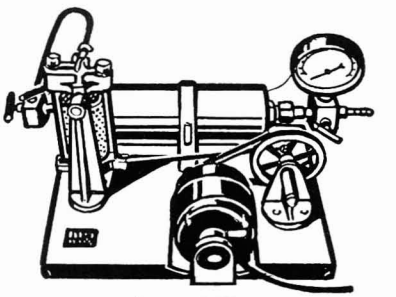

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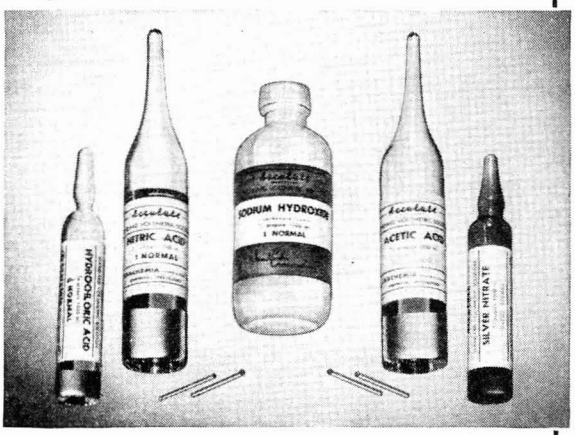

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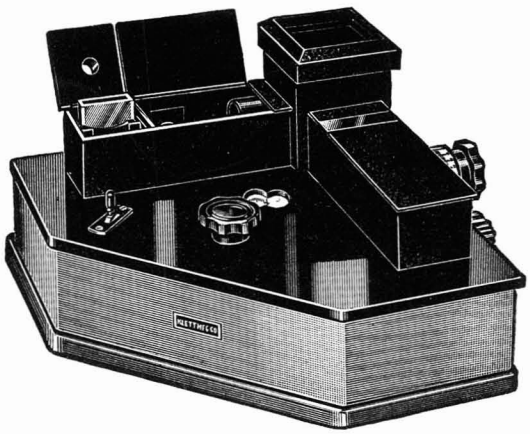

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literature embodying the latest developments in analytical chemistry, and demonstrations of new techniques will be features of the symposium. A special exhibition of historical chemical literature, including the Joseph Priestley Collection, will be on view in the Harding Library. A number of visits to local industrial establishments will be arranged.

In addition to a number of original papers, there will be reports on recent advances in selected branches of analysis.

Industrial Applications

Iron and Steel. B. BAGSHAWE.
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Plastics. J. HASLAM.

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Inorganic Chromatography. F. H. POLLARD.
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Spectrography. R. L. MITCHELL.
Absorptiometry. W. N. ALDRIDGE.
Biochemical Analysis. GARFIELD THOMAS.
Qualitative Analysis. H. HOLNESS.
Ion Exchangers. G. H. OSBORN.
The Quantometer. F. SLATER.

The symposium secretary is J. W. Robinson, 139 Stourport Road, Kidderminster, Wores., England.

International Instrument Congress

The Instrument Society of America and various other associations and societies will cooperate in putting on the First International Instrument Congress and Exposition in Philadelphia September 13 to 25. The congress will last two weeks but the exposition only one. Laboratory apparatus and equipment, as well as measuring and control instruments of every kind, will be available for inspection and discussion. The Dechema, Deutsche Gesellschaft für chemisches Apparatewesen, as one of the societies invited to participate, will organize two scientific journeys to the U. S. which will facilitate travel for all interested persons and societies in Europe.

Achema XI Chemical Apparatus Congress

At the Achema XI Chemical Apparatus and Equipment Congress and Exhibition, to be held in Frankfurt-am-Main, May 14 to 22, more than 600 firms from 12 countries will show regular lines and latest developments in apparatus and equipment. The exhibits are divided into laboratory technique and practice, measuring control and regulating technique and practice, materials, operation and production technique, and new chemical materials and products.

The space required is approximately 50% greater than for the exhibit of 1952.

Office Equipment Exposition

The National Office Management Association, Detroit, Mich., has planned an Office Machinery and Equipment Exposition to be held in the Kiel Auditorium, St. Louis, Mo., May 24 to 27, in connection with the association's 35th international conference.

In addition to talks on office management, a panel discussion on office practices, privileges, and problems is scheduled.

NEW BOOKS

Inorganic Syntheses. Vol. IV. Editor-in-Chief, *John C. Bailar.* xii + 218 pages. McGraw-Hill Book Co., 330 West 42nd St., New York 36, N. Y., 1953. $5.00. Reviewed by S. E. Q. ASHLEY, General Electric Co., Louisville, Ky.

Every true chemist who visits an unfamiliar laboratory and finds a collection of inorganic compounds assembled in a "museum" gets a thrill which is not diminished by the chastening disappointment he sometimes experiences when he has to use one of the neatly labeled preparations and finds that it is not what the label represents it to be. A book, such as this one, of recipes for preparing a wide variety of inorganic substances is as fascinating as the inspection of a museum collection. But this collection carries with it a certification that the apocryphal products in the museum often lack. A distinguished board of editors and advisers is a good guarantee of the quality of the contents. The preparations themselves are submitted to at least one referee for authentification. The names of many of the contributors and referees are guarantees of a high order of reliability.

The book is of considerable special interest to the analytical chemist in several regards. It has been said that analytical chemistry is the science of preparing compounds in a high degree of purity. Since the objective of inorganic preparations is to find procedures capable of high yields, the objectives of the analytical and inorganic chemists are similar. By these tokens the preparative methods described may in themselves suggest procedures which may be developed into processes of analysis. Furthermore, according to the preface, "If the analytical methods [used to establish the identity of the preparation] are sufficiently distinctive to warrant description, *they should* be presented in detail."

Data are reported by which the identity of the compounds described may be established. The data presented and the literature references on each compound often provide useful criteria for the establishment of the purity of a compound as well as its identity—a most important part of the analytical chemist's job. Unfortunately it is not always clear whether the data are for the product prepared by the authors or a mere recapitulation of information gleaned from the literature. This is important, as the analytical chemist attempting to establish the identity of inorganic compounds often finds such extraordinary discrepancies in data that the existence of even simple "well known" compounds may be called into question.

The preparation of standards and of reagents in a high state of purity are common activities in the analytical laboratory for which this collection may prove useful. A collective index by subject and by formula of the four published volumes in this series is an extremely useful part of the present volume.

Electroanalytical Chemistry. *James J. Lingane.* ix + 430 pages. Interscience Publishers, 250 Fifth Ave., New York, N. Y., 1953. $8.50. Reviewed by S. E. Q. ASHLEY, General Electric Co., Louisville, Ky.

Not every book that publishers add to the growing shelves of our technical libraries marks an advance in the literature of chemistry. Many are growths on rather than growths in the chemical literature. Lingane's "Electroanalytical Chemistry" is one of the rarer sort that marks a trail for the analytical chemist and provides him with something he has not had before.

The author makes clear in the introduction that it is his object to supplement existing works in the electroanalytical literature, and that his aim is not to make the work comprehensive. It becomes inappropriate, therefore, to note any omissions, such as the lack of any reference to so-called "micro" methods in the portions of the book devoted to methodology or in the bibliography of literature.

On the other hand, the book is unique in attempting, for the first time in the reviewer's knowledge, to bring into a comprehensive relationship the principal methods of analytical chemistry which are called "electrical." The author presents the first "complete and systematic" account of coulometric

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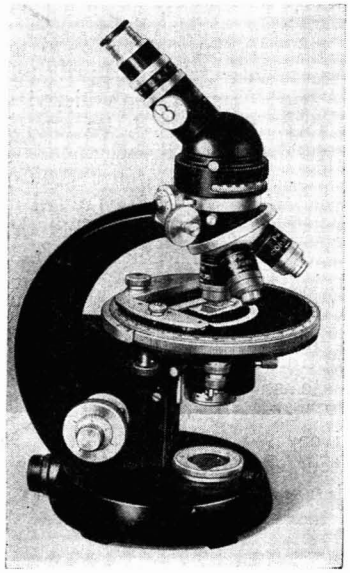

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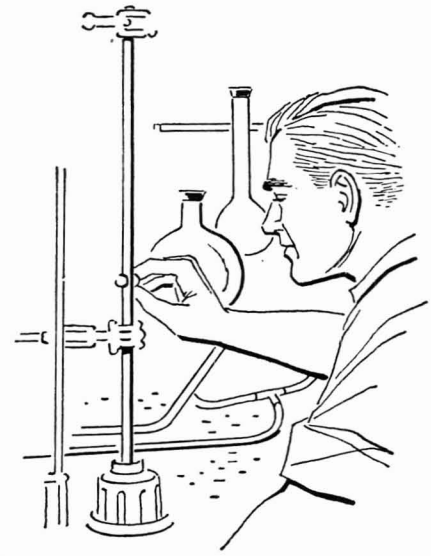

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analysis, to which he himself has contributed so substantially. The reader will find useful sections on modern instrumentation and laboratory techniques for the various forms of controlled potential electroanalysis. Key references are used to supplement the methods of analysis which are described, as the book carefully avoids the elaboration of procedures which are no more than recipes.

The success of the author will best be judged as the work is read, reread, studied for teaching purposes, and used as a reference book. One may question the author's enthusiasm in such a statement as (p. 182) the one that the Lewis and Randall conventions (for the use of + and − signs with standard potentials) are now most generally used, although the author will find strong champions. But the reviewer has no hesitancy in strongly recommending this individual, original work to practicing and teaching analytical chemists, as a pioneer effort from a recognized leader in this branch of science.

Industrial Inorganic Analysis. *Roland S. Young.* John Wiley & Sons, Inc., New York, N. Y., 1953. $5.75. Reviewed by ROBERT M. FOWLER, Metals Research Laboratories, Electro Metallurgical Co., Niagara Falls, N. Y.

Over the years the writer has accumulated a series of notes on analytical procedures, briefly outlining the theory, the separations necessary in a complex sample, frequently giving certain hints in manipulative technique which are extremely useful, and assessing the value of the method for universal or specialized work." The presentation of these notes in book form follows an alphabetical arrangement of chapters on the principal elements (over 50). Each chapter contains one or more general procedures for the determination of the particular element, a number of special procedures, and usually a dozen or more literature references. These special procedures, particularly in the area of nonferrous ore analyses, where the author has worked extensively are, in the opinion of this reviewer, the best part of the book.

The general procedures are all good, sound methods with a minimum of modern reagents and apparatus. The majority are old friends from Hillebrand and Lundell, Scott and Furman, or the ASTM "Chemical Analysis of Metals." Others have been collected from various industrial concerns over the past 15 years. It is unfortunate that the author did not request current methods from the latter source instead of publishing methods he may have received a decade or more ago. References to the literature are almost entirely to American and English journals published within the last 10 years.

To cover over 50 elements in 350 pages, the author has had to treat some of them briefly, while others are in very much detail. The chapters on cobalt, nickel, and copper are very good, but the general procedure for niobium and tantalum is esoteric. Lack of a chapter on the rare earths is an unfortunate omission.

There are many places in this book where we do not agree with the author on details, such as loss of manganese by volatilization from HF, $HClO_4$ solutions; "manganese is not precipitated by ammonia unless bromine is present. . . ."; α-benzoinoxime precipitation of molybdenum is incomplete in $HClO_4$ but complete in H_3PO_4 solutions; and the use of ferrous ammonium sulfate as a standard for iron determinations.

This book will be a valuable addition to the library of any industrial analytical chemist dealing with ores and metals. The sections on procedures for separating chemically the various compounds present in ores should prove particularly useful.

Analyse der Metalle. Herausgegeben von Chemikerausschuss der Gesellschaft Deutscher Metallhütten- und Bergleute e. V. *O. Proske, H. Blumenthal,* and *F. Ensslin.* Vol. 2. Betriebsanalysen. Part I. Aluminium bis Schwefel. xi + 716 pages. 174 illustrations. Part II. Selen bis Zirkonium. Physikalisch-chemische Verfahren. iv + 706 pages. 174 illustrations. Springer-Verlag, Berlin-Göttingen-Heidelberg, Germany, 1953. DM 114 for both volumes. Reviewed by RALEIGH GILCHRIST, National Bureau of Standards, Washington, D. C.

This comprehensive two-volume treatise, the united effort of 100 contributors, contains the present-day plant-control and commercial analytical chemical methods used in the nonferrous metallurgical industries of Germany.

Forty-five of the 60 chapters are devoted to the analytical methods for over 50 individual elements, arranged alphabetically for the sake of simplicity. Eight of the remaining chapters cover procedures for miscellaneous materials associated with metallurgical operations, such as those for metallic and nonmetallic coatings, oxide content of metals, refractory materials, solid fuels, fuel oils, industrial gases, and corrosive waste liquors. Four chapters describe methods of photometric, polarographic, potentiometric, and spectrochemical analysis. The remaining three chapters are devoted to the preparation and standardization of solutions, standard metals and alloys, and standard samples.

The general plan of the individual chapters includes a short discussion of the occurrence, qualitative detection, and refining of the metal, followed by methods for determining the element in question as well as impurities in the metal. In the sections on procedures a systematic scheme of presentation is followed—namely, the underlying principle of the method, its applicability and significance, its accuracy, the time for its completion, the procedure itself, sources of error, and a limited number of references to the original literature.

The degree of accuracy of a method is designated as 1, 2, or 3, depending on whether the procedure can be used for umpire analysis, is sufficient as a plant-control method, or serves for approximate assays.

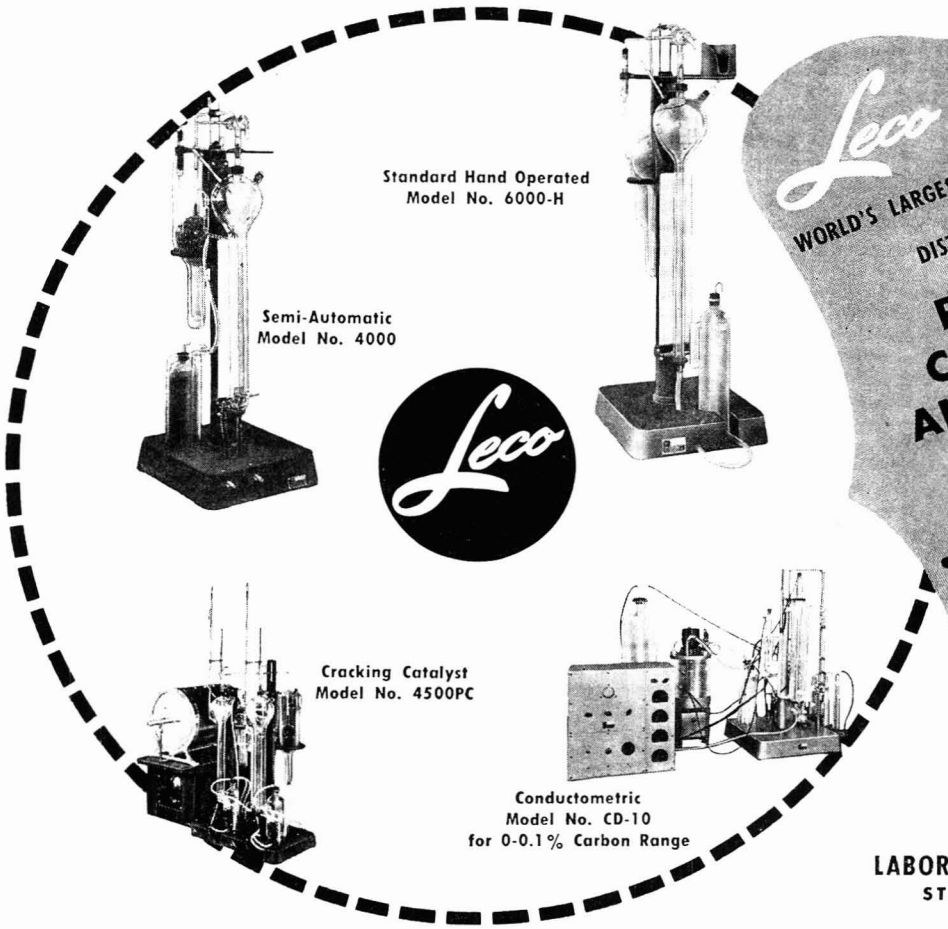
The essential feature of the procedures given is speed, rather than extreme accuracy. In view of this it is understandable why certain procedures—with the platinum metals, for example—appear a bit antique.

Since the procedures given represent the current practices in the German metallurgical industries, the treatise is of significant value to similar industries in other countries.

Applied Electron Microscopy. *Robert B. Fischer.* xiii + 231 pages. Indiana University Press, Bloomington, Ind., 1953. $4.85. Reviewed by F. A. HAMM, Eastman Kodak Co., Rochester, N. Y.

This book is a conglomeration of assorted bits of information, some of which is not accurate. The author has attempted to cover almost every conceivable aspect of electron microscopy, and, in fact, such topics as tracer micrography and the history of diffraction are presumed to be related to electron microscopy and are therefore included. By a similar token, there is no need to discuss the principles of vacuum gages or the photographic process in a book of this kind.

Treatment of any subject in a completely qualitative fashion often leads to inaccuracies. Clearly, only superficial thought was given to many of the subjects, discussed at times in sufficient length but with inadequate quantitativeness. For example, the discussions of resolution, useful magnification, depth of field, thermal effects of the electron beam on the specimen, reflection diffraction, etc., are not well done and doubtful conclusions are drawn. Specifically, the author's values of 33,000 diameters and 0.5 micron for useful magnification and depth of field, respectively, are not valid. Also, an



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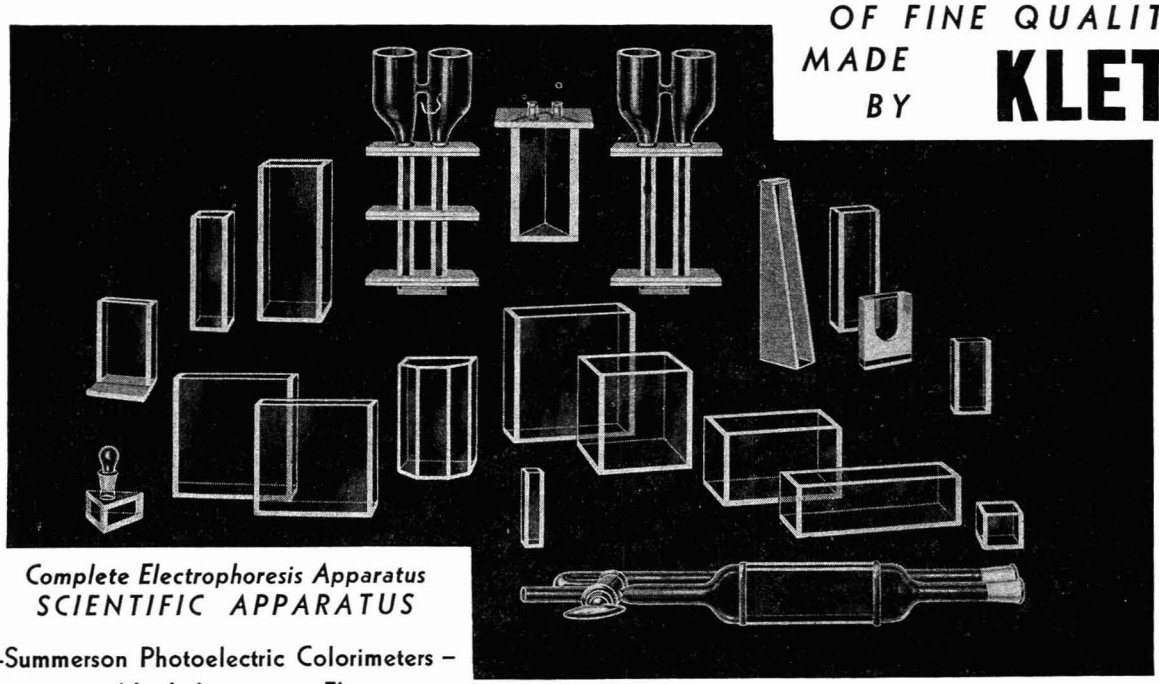

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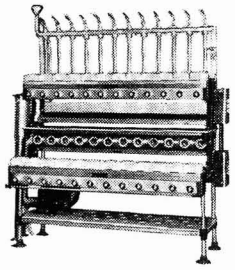

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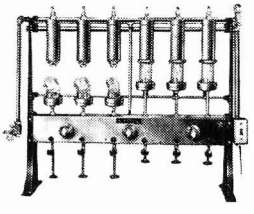

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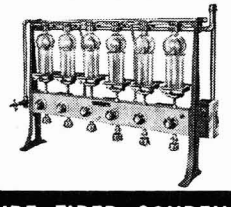

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electron micrograph of silver chloride is illustrated to show decomposition caused by the electron beam, presumably because of thermal effects. No distinction is made between melting and decomposition; the fact of the matter is that silver chloride melts in high vacuum without decomposition and the effect illustrated by the micrograph is one of photolysis or photographic printout due to the radiation-chemical effects of the electron.

Similarly, many of the diagrams have no value. A sketch designed to illustrate image formation includes only the optic axis or paraxial rays. Also, the choice of words and the construction of many sentences leave something to be desired. The author tends to convey the idea that the electron microscope is a panacea.

The book may be recommended to those who wish to acquire a cursory appreciation of electron microscopy.

Chemical Tissue Tests for Determining the Mineral Status of Plants in the Field. *D. J. D. Nicholas.* 33 pp. The Tintometer Ltd., Salisbury, England, 1953. Sold in U. S. by T. G. Walshe, Box 345, Oyster Bay, N. Y. $3.00. Reviewed by CORNELIA T. SNELL, Foster D. Snell, Inc., New York, N. Y.

A Lovibond Comparator, supplied with permanent glass color standards, calibrated sample tubes, etc., serves for semiquantitative determinations on plant tissues in the field. Methods are given for diagnosis of mineral disorders in plants by determination of nitrate nitrogen, phosphate, potassium, chloride, eight specific metals, and heavy metals as a group.

Organische Fallungsmittel in der Quantitativen Analyse. *Wilhelm Prodinger.* xv + 232 pages. Ferdinand Enke Verlag, Stuttgart, Germany, 1954. Paper-bound DM 32. Cloth-bound DM 34. Reviewed by P. O. POWERS, Pennsylvania Industrial Chemical Corp., Clairton, Pa.

Organic compounds are being produced in ever-increasing amounts and many new ones are synthesized each year. A few of these find application in the industrial field. It is of interest that materials used as rubber accelerators, growth promoters, and antiseptics have also found application in analytical chemistry. Organic reagents have frequently offered new methods for separation and for determination of metals, often yielding improvements over existing methods.

The second edition of "Organische Fallungsmittel" appeared over 15 years ago, and was soon translated into English. More recently Flagg has prepared a book in this same field. The earlier German edition has now been completely rewritten and much new material has been added. Among the added reagents are dipicrylamine, sodium tetraphenyl borate, Neocupferron, *N*-benzylphenylhydroxylamine, Oxin, *p*-hydroxyphenyl arsenious acid, Atoxyl, mandelic and bromomandelic acids, 3-toloxyacetic acid, *p*-aminoacetophenone, triphenyltin chloride, and tetraphenylarsonium chloride.

A chapter on principles opens the book. This is brief since the author feels this subject has been adequately handled by Flagg and not of prime importance to the analyst. Each reagent is considered separately; methods of preparation and of purification of the reagent are given in several instances. Conditions for the use of the reagents for various separations and determinations are given, often with considerable detail.

The subject is well organized and clearly presented. The methods are supported with frequent references to the literature. There is little attempt to compare efficiency of various methods. While the newer reagents are given careful consideration, the use of older reagents is given full treatment.

L'Analyse Chimique. *Clement Duval.* 126 pages. Presses Universitaires de France, 108 Boulevard Saint-Germain, Paris, France, 1953. 150 francs. Reviewed by F. E. BEAMISH, University of Toronto, Toronto, Canada.

This book is semipopular in character and of pocket size. The writer, conversant as he is with analytical techniques, aptly presents first the conventional processes used for the preparation of samples and subsequently in two separate sections deals in a most satisfying manner with the wide variety of physical and chemical methods of qualitative and quantitative analysis. Although not of great value to the academically trained analyst, the work will be enlightening to such groups as preuniversity students with an interest in science, junior university students who wish a comprehensive view of analytical techniques, and even experienced researchers who have a fringe interest in analytical chemistry. Written in French that is not difficult to read, it is a good book for the library shelves of any progressive chemist.

Manual on Industrial Water. ASTM Special Technical Publication No. 148. 333 pages. American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa. $4.25.

Crystal Growth and Dislocations. *A. R. Verma.* xii + 182 pages. Academic Press, Inc., 125 East 23rd St., New York 10, N. Y., 1953. $5.00.

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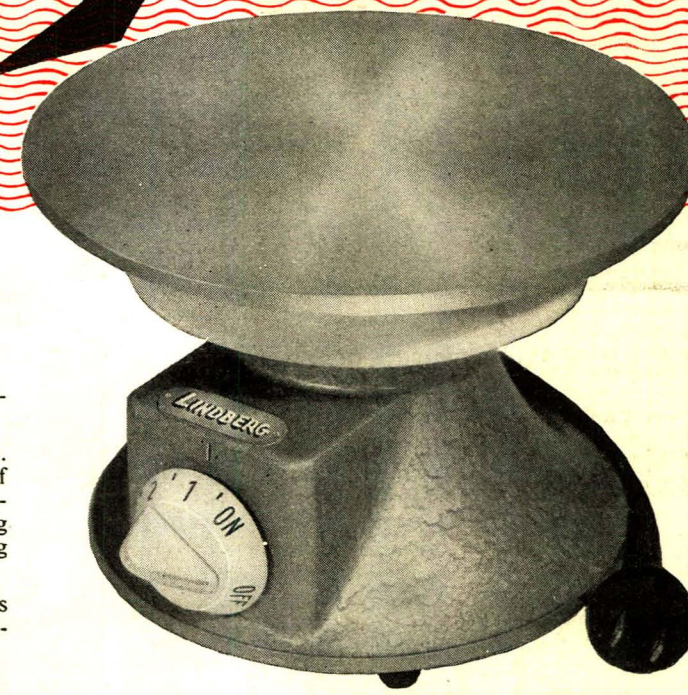

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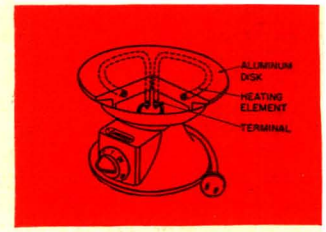

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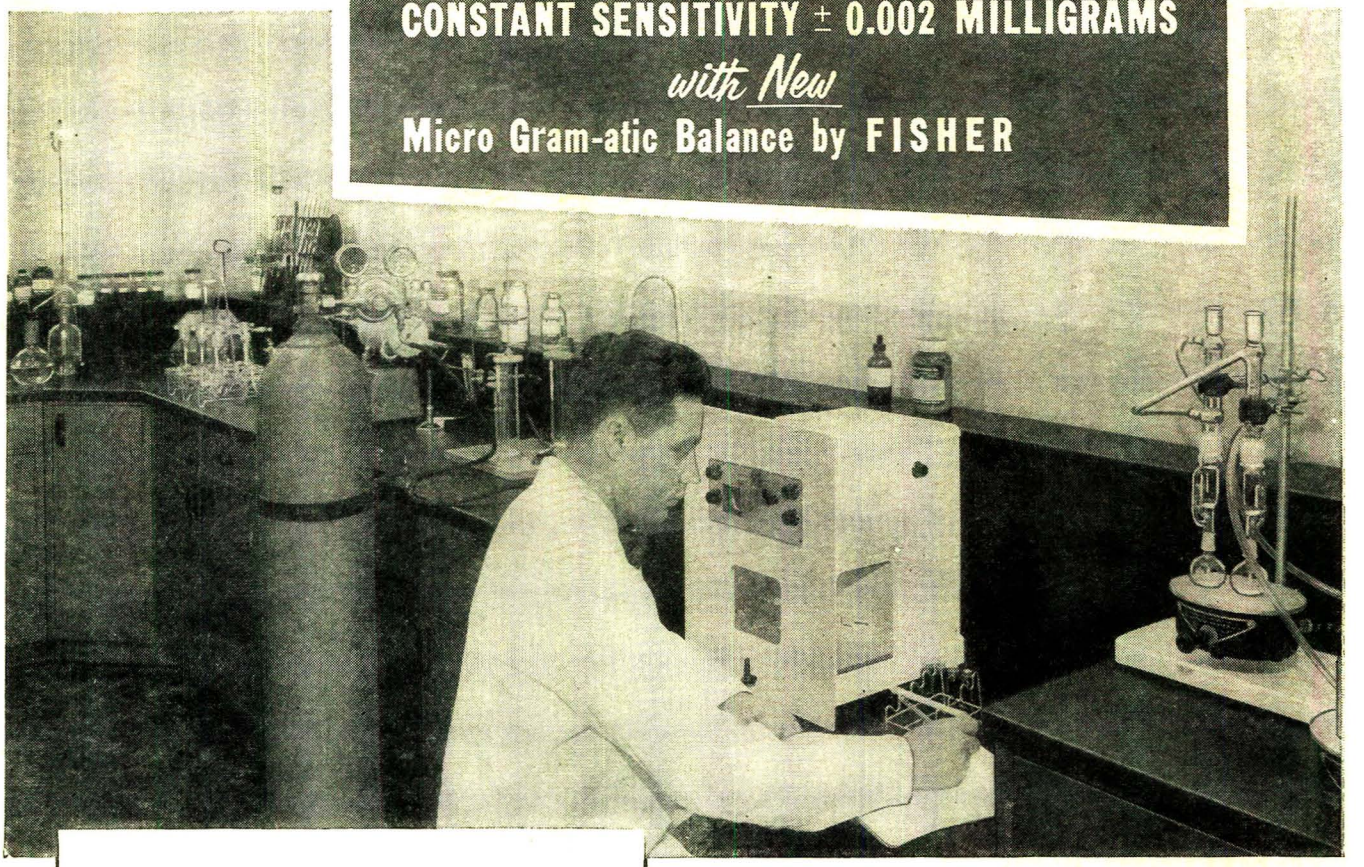

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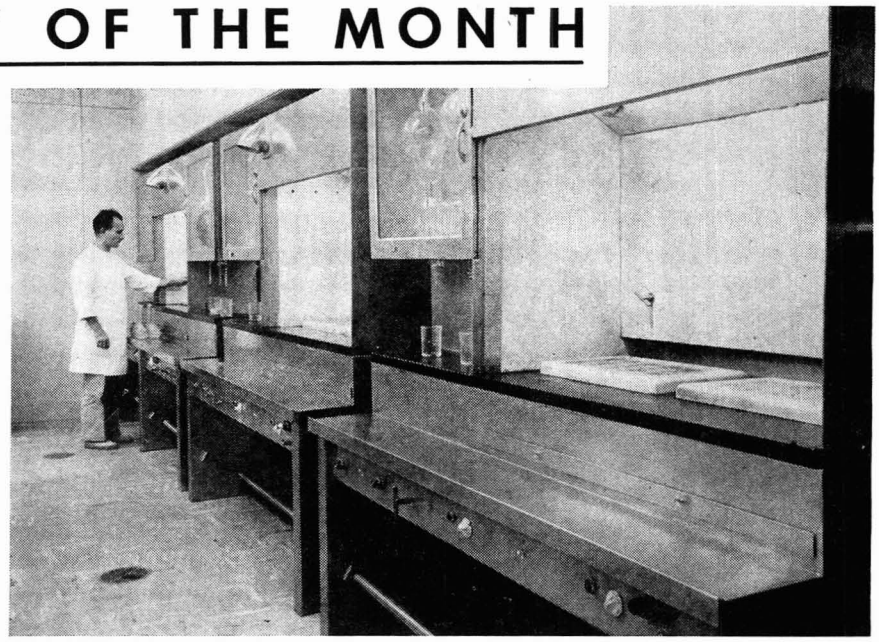
LABORATORY OF THE MONTH

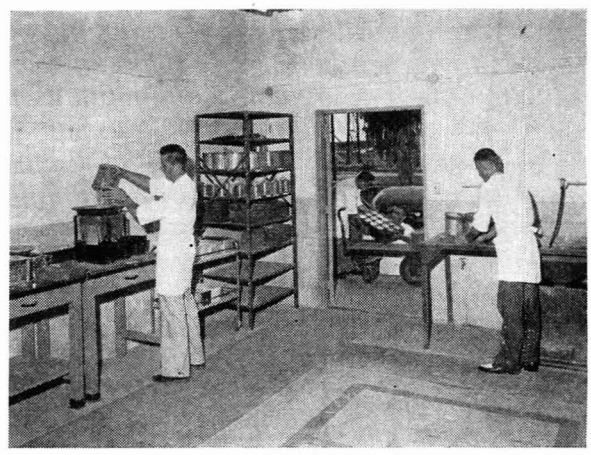
- *New International Minerals and Chemical Corp. analytical control lab to bring saving of over $40,000 annually*

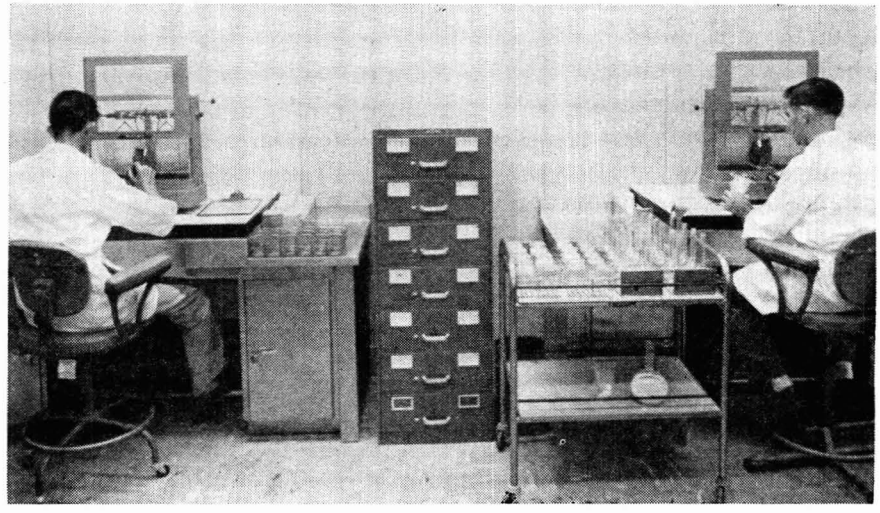
As the operations of International Minerals and Chemical Corp. expanded in the Florida phosphate fields, greater demands were put on the analytical control labs. So many determinations (328,000 in 1953) had to be made for process control, for customers, and for referees in cases of dispute that the several individual small laboratories attached to each plant became swamped and inefficient. After a thorough study of location and methods the company decided to establish a central control laboratory at the Noralyn, Fla., plant. As set up by the chemists and the engineering department, the specifications stated, "all work and materials used shall be of prime quality. No used, reconditioned, or inferior materials or products shall be employed in any of the items produced or installed as a part of this contract." The wisdom of this policy and the effectiveness of the layout and specially designed units are evident now after the lab has been tested in actual operation. The spick and span, air-conditioned atmosphere along with the high quality facilities, has had a marked beneficial effect on the staff and its work. According to the engineering study it was estimated that the new lab should save the company $40,000 to $50,000 a year as a result of improved efficiency.



Built to International's specification is this assembly of automatic dispensing burets, hot plates, and hoods used for digestion of samples. All controls are on panel below shelf. Acid carboys to supply burets are kept outside of building. They are embedded in several inches of plaster of Paris to prevent hazard of explosions. Teflon and polyethylene tubing connects carboys to dispensing burets and provides compressed air to top of carboys. When acid is wanted, a push button on panel is used to actuate solenoid valve thereby introducing compressed air into carboy and forcing acid into the automatic dispensing burets. Safety showers are provided in front of each unit

Sample receiving room. In spite of bulk and number of samples handled, good housekeeping prevails





A portion of the balance room where hundreds of thousands of weighings must be made each year. Conveniently located between sample preparation room and process room, the balance room is equipped with sit-stand furniture to provide for comfortable working position. High school graduates are specially trained as balance technicians and work under supervision of professionally trained chemists. They change stations throughout the lab during their shifts to minimize monotony

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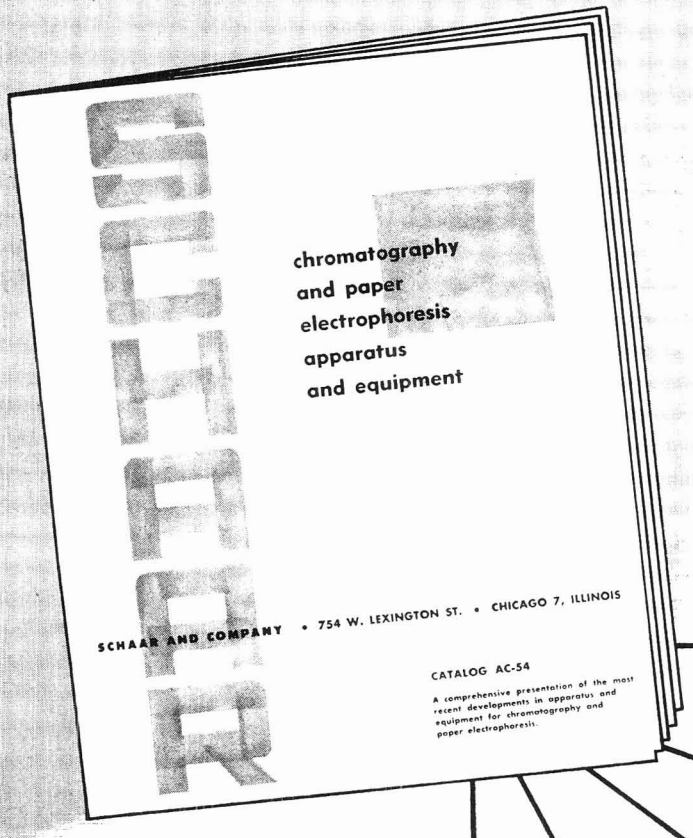

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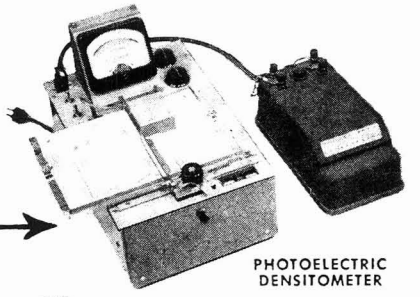

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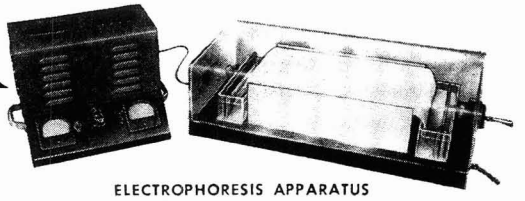

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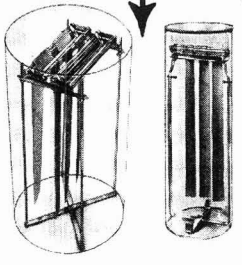

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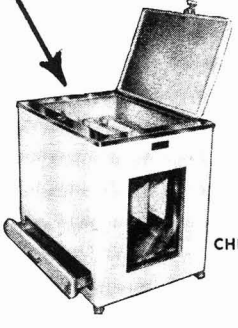

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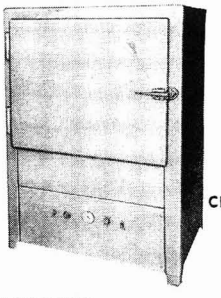

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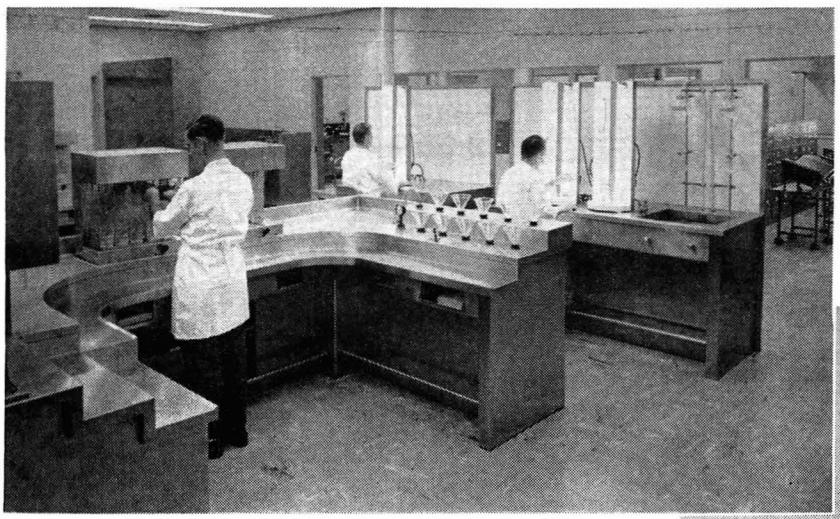
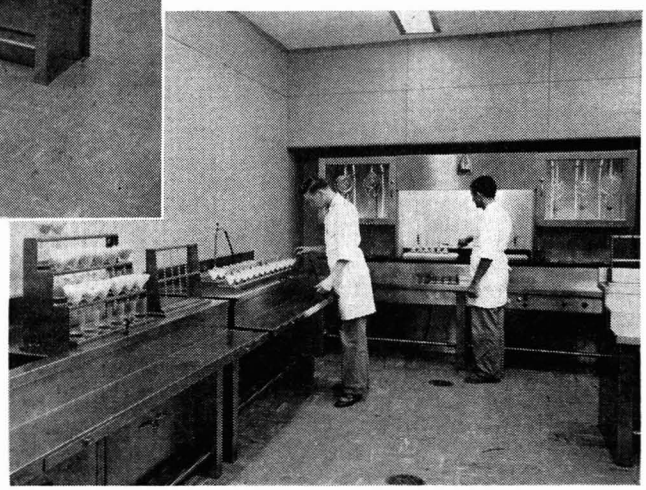
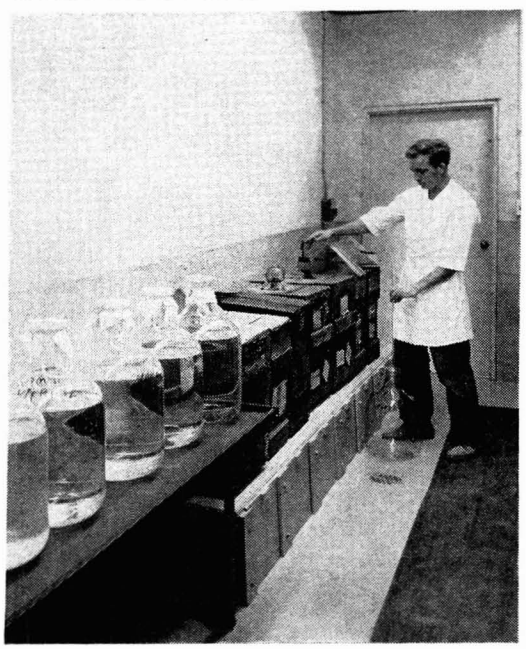


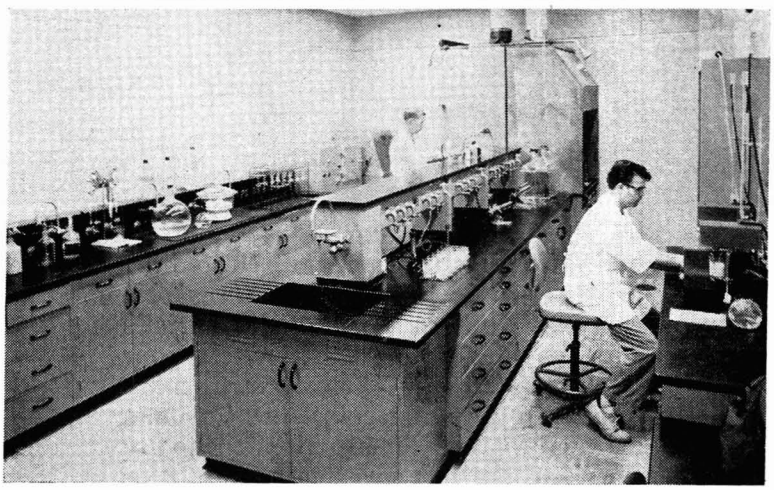
A process table especially designed for method of determining tricalcium phosphate. Conveniently located next to digestion bench, the table was built entirely of stainless steel. The stirring machine which handles twenty samples at a time was designed by International's chemists and engineers and built by the Florida Division of Food Machinery and Chemical Corp. A vacuum tank under bench is provided to speed up filtering and washing operation. From the process table the samples go to conveniently located titration tables

Additional process tables are provided for other standard tests—determination of iron and aluminum phosphates by dichromate method, and acid insolubles. Occasionally samples are also run for complete analysis. This involves methods for uranium, fluorine, lime, and trace metals such as vanadium, titanium, sulfur, sodium, potassium, etc.

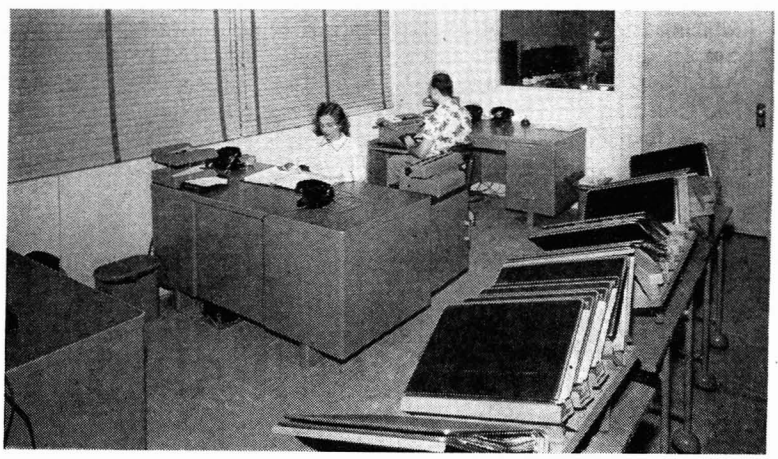




Acid and standard solution storage room. Underneath the acid carboys is an air duct. When transferring acid, a slide door in the hood next to the bottle is opened and the fumes are exhausted to the outside



Special lab of Chief Chemist H. H. Edwards is used for nonroutine work and research on improved methods of analysis. One of the hoods is designed especially for work with perchloric acid



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Information of analytical importance can be obtained by applications of nuclear physics and use of ultracentrifuge

by Ralph H. Müller

NUCLEAR physics has had great influence on chemistry, including analytical chemistry. The converse is also true because the preparation of radioisotopes, their separation, and purification for research purposes, involve many chemical operations. Heretofore, the analytical applications of radioisotopes have been considered to be those of labeling. With increasing availability and cheapness of radioisotopes, it may be expected that the labeling process could continue indefinitely and the whole business be relegated to the limited resourcefulness of a technician. As is true of the rest of nuclear physics, it is more than likely that the most profitable and versatile analytical applications will involve the distinctive electrical and physical characteristics of radioactive substances and the nature of their interaction with matter. This is evident in the case of activation analysis, in which samples can be exposed to radiation in a pile and thereafter examined on the basis of the induced radioactivity.

Applications of Nuclear Physics

Another example, described in this journal, is the determination of hydrogen in liquids with a beta-particle absorption apparatus [Smith, V. N., and Otvos, J. W., ANAL. CHEM., 26, 359 (1954)]. It has been known for some time that the density of samples can be determined by beta-particle absorption measurements, or, if the composition of the sample is known, beta-particle absorption can be recorded automatically to furnish a continuous thickness gage. The above-mentioned authors have shown that the hydrogen content of liquid samples can be determined to 0.1% if the density of the sample is measured independently to a comparable degree of precision. Apparatus for this type of work is already commercially available from the Central Scientific Co. and Hallikainen Instruments, Berkeley, Calif.

During the past spring, the writer observed what appears to be a perfectly general relationship between the back-scattering of beta particles from matter and its composition [Müller, R. H., *Phys. Rev.*, 93, No. 4, 891 (1954)]. It has been shown for 32 elements and some 40 compounds that the back-scattering of beta particles is a discontinuous function of the atomic number, but linear in Z within each period of the periodic system. In the case of compounds, an equivalent atomic number, $\bar{Z}$, is calculated which is equal to the atomic number of each element in the compound multiplied by the percentage of that element. This is summed for all elements in the compound. Hydrogen presents an anomaly, but its deviation is strictly proportional to the hydrogen content. Precision is limited only to the statistics of random counting and the technique requires a sample of infinite thickness for the beta particles in question.

From studies of this sort, it now seems fairly certain that the interaction of nuclear particles with matter may be sufficiently understood so that the analysis of chemical compounds in any state of aggregation can be accomplished rapidly and uniquely. One does not need gigantic "atom smashers" but rather moderate strength sources such as strontium-90 and none too expensive counting and scaling equipment.

Magnetic Suspension Ultracentrifuge

Information of analytical importance is forthcoming from the ultracentrifuge. This has been known for a long time, but it is not immediately apparent to the busy analyst what startling and unusual techniques are being evolved in the design of improved ultracentrifuges. J. W. Barnes, University of Virginia, has been one of the leading experts in this field for many years. He has recently given an account of the circuitry involved in magnetic suspension ultracentrifuges [Beams, J. W., *Electronics*, 27, No. 3, 152 (1954)].

In this type of instrument, the rotor is suspended in a magnetic field and rotated by either rotating magnetic fields or an air turbine. Appropriate electronic circuitry automatically maintains the rotor in suspension. Among the various ways in which this can be accomplished is by the use of a pickup coil in an oscillator circuit, whereby the most minute change in height of the rotor changes the frequency of the oscillator, and hence, the strength of the magnetic field which supports the rotor. Electronically, two signals can be derived in this manner, one proportional to the amplitude and another to its first derivative. In this manner, it is possible to support the rotor so that scratch marks on its surface exhibit no perceptible motion through a telescope of fiftyfold magnification. The rotational speeds which are attainable are limited only by the bursting strength of the rotor.

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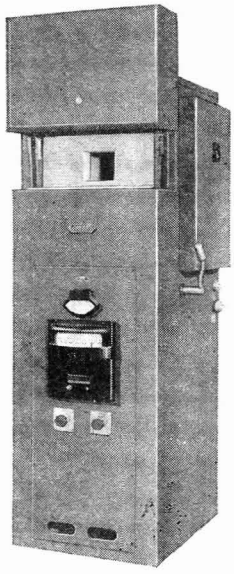

Model 30 (pictured) Automatic temperature control. From 600° F. to 2000° F., use for ashing, drawing, igniting, tempering, etc. Above 2000° F., for sintering, melting, clinkering, fusing and high speed hardening. For use with 230 volt, 50-60 cycle, single phase power supply; automatic controller for 115 volt, 50-60 cycle, single phase.

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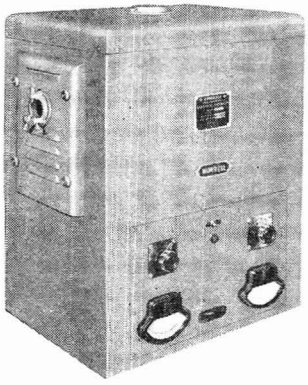

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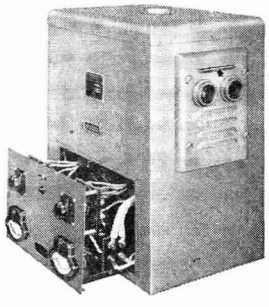
24-934	One Tube Furnace, Model H-1-9	585.00
24-944	Two Tube Furnace, Model H-2-9	600.00
24-954	Four Tube Furnace, Model H-4-9	850.00

For other models—ask for Bulletin No. 310

EASY ACCESS PANELS FOR EASE OF SERVICING

All current models of Burrell furnaces open from the front, for ease of inspection, parts replacement and servicing when necessary.



Prices listed are F.O.B. Pittsburgh, Pa.

BURRELL CORPORATION

Manufacturers and Distributors of
SCIENTIFIC APPARATUS and LABORATORY CHEMICALS
2223 Fifth Avenue, Pittsburgh 19, Pennsylvania

For further information, circle number 44 A-1, -2 on Readers' Service Card, page 49 A

could be driven to a bursting speed of 48,000,000 revolutions per minute, or peripheral speed of 100,000 cm. per second, and for which the maximum calculated stress was 454,000 pounds per square inch. Under these conditions, the centrifugal acceleration was 515,000,000 times gravity. This is a very tiny rotor; others weighing as much as 25,000 grams have been supported and driven in a like manner.

The essentially frictionless suspension, which is achieved by magnetic support, would be useless if the rotor were not maintained in a low pressure environment. It is fascinating to note what can be achieved by a magnetically suspended rotor in a very good vacuum. So, for example, an all-steel spherical rotor spinning at 300 revolutions per second decelerates at the rate of one revolution per second in 4 days when the air pressure surrounding the rotor is less than 10^{-5} mm. of mercury. In other words, when the rotor has been brought up to speed and the driving source is cut off, the rotor remains practically at constant speed or, more correctly, slows down at the extremely slow rate indicated above. It is interesting to calculate the Q for the magnetically suspended rotor under such circumstances, which equals 2π (total energy of rotor) divided by (energy lost per cycle) and which has a value of Q lying between 10^8 and 10^9.

The analyst, like other chemists, has been interested in these techniques almost exclusively to the extent that solutions or suspensions can be examined while they are rotated at these high speeds. Professor Beams has always been interested in the larger and more general problem of attaining higher speeds and extending these general techniques to a great variety of problems. For example, if a multifaceted rotor is spun at these prodigious speeds, it is possible to make speed of light measurements over comparatively short optical paths or to measure time intervals of extremely short duration. It is thus apparent that the rotating mirror technique is applicable to all phenomena; duration is of the order of microseconds or very small fractions thereof.

Unusually high precision in the measurement of the rotational speed is inherent in these techniques because the rotating mirror can be used to generate photoelectric impulses which are compared on an oscillograph with precision time or frequency signals from WWV. The attainable precision is of the order of 1 part in 10^7. It has been demonstrated that constancy of rotational speed of 1 part in 10^8 can be attained if the driving field is derived from a temperature-controlled quartz crystal oscillator.

Clinical Analyses

Clinical analysis has been utilizing microchemical techniques for the past

The BECKMAN Near-Infrared Quartz Recording SPECTROPHOTOMETER

New instrument covers the increasingly important near-infrared region.

The Beckman Model DK Spectrophotometer is the first commercially-available instrument designed specifically for the near-infrared region of the spectrum—filling an important gap in spectrochemical analysis. Its lead sulfide detector and quartz monochromator permit high-speed transmittance recording at cost and performance unmatched by conventional infrared instruments. Using a photomultiplier detector for ultraviolet work, the Model DK offers a guaranteed wavelength range of 220 to 2700 mμ—wider than that of comparable spectrophotometers twice the price.

The DK's "double-beam ratio" principle is a unique system for percent transmittance recording. (1) It provides the stability of double beam operation, with a single receiver. (2) The fast beam chopping (480 times per second) takes full advantage of the sensitive lead sulfide detector.

Resolution	0.1 mμ at 220 mμ; 2.5 mμ at 1000 mμ; 5 mμ at 2500 mμ—higher than any other instrument in its price range.
Scanning Speeds	For the entire 220 to 2700 mμ range, any of 5 speeds is selectable: 5, 15, 50, 150 or 500 minutes. At highest speed, the near-infrared is traversed in one minute, while very low speeds are available for extreme resolution.
Stray Light	Less than 0.2 percent 0.2 – 2.5μ
Recording Features	Ozalid-reproducible paper...adhesive strips for easy wavelength reference...chart speeds of ½, 1 and 2 inches per minute...

For additional information write for data file No. 98-15

Beckman *division*
BECKMAN INSTRUMENTS, INC.
FULLERTON 1, CALIFORNIA

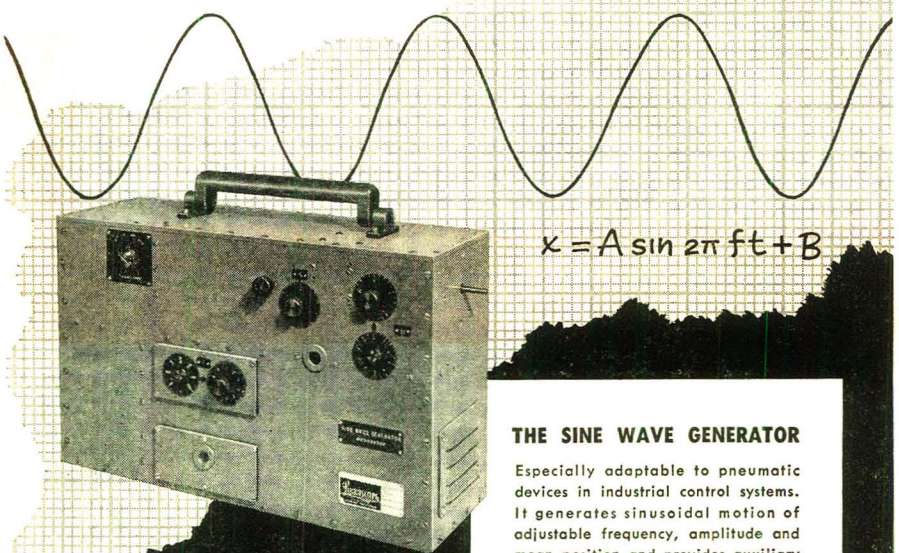
For further information, circle number 45 A on Readers' Service Card, page 49 A

frequency synthesis analysis simplified...

The Sine Wave Generator is designed as a convenient tool to determine transfer functions of components in automatic control systems and to define the physical properties of existing plants to which control systems are to be added. Data is acquired by the frequency synthesis method in which sinusoidal forcing functions are applied to the system and measurements taken of amplitude and phase shift of the output response. For further information on this or other special purpose devices, or assistance in solving your particular computing-controlling problems, consult LIBRASCOPE.

$$\frac{1}{S(S+T)}$$

$$\alpha\left[\frac{1+TS}{1+\alpha T_1 S}\right]$$



$$x = A \sin 2\pi ft + B$$

THE SINE WAVE GENERATOR

Especially adaptable to pneumatic devices in industrial control systems. It generates sinusoidal motion of adjustable frequency, amplitude and mean position and provides auxiliary electrical signals for phase reference.

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For further information, circle number 46 A on Readers' Service Card, page 49 A

three or four decades. In most instances, the methods still require the drawing of blood samples, although a moderate sample is sufficient for a great many quantitative determinations. It is a continuing challenge to instrumentation to increase the number of useful analyses that can be made without withdrawing any sample whatsoever. The modern photoelectric oximeter and the apparatus for determining basal metabolism are among the few instruments which come within this category and permit one to obtain essentially chemical information of clinical importance. The modern clinical laboratory does, indeed, use a variety of instruments, among which are the colorimeter, spectrophotometer, flame photometer, nephelometer, Van Slyke gas analysis equipment, etc. Future developments, we believe, will be concerned with devices which can give clinical information without drawing samples.

A striking illustration of additional clinical information which can be obtained by existing instruments is to be found in *Life Magazine* for March 22, 1954. The facilities are those of the Southwestern Poliomyelitis Respiratory Center in Houston, Tex. An integrated assembly of instruments affords nine quantitative tests to be recorded automatically within 10 minutes. The total amount of air breathed is shown by volume changes in inhalation and exhalation reservoirs. The amounts of carbon dioxide, oxygen, and nitrogen used are measured by gas analyzers. Study of the circulation includes the heart beat, amplified by a loud speaker; the heart's electrical impulses, recorded by an electrocardiograph; the blood pressure, measured with an automatically inflated arm cuff and analyzer; and the oxygen content of the blood, detected with an oximeter. The readings of all these instruments are combined electronically and recorded on a single chart for direct intercomparison.

Additional equipment is also shown, including a fluoroscope with an image amplifier. It is not too generally known, even in medical circles, that the image amplifier tube has attained a degree of perfection which enables radiologists to make examinations over more or less indefinite periods of time, without fear of harmful or excessive exposure. The editors of *Life*, in presenting this interesting and well illustrated information, cannot escape the layman's temptation to say that the scene suggests the lair of a mad medico out of science fiction. In all probability, there has never been a fatality arising from too much clinical information. As for the converse, it is perhaps better not to dwell upon the subject but to count our blessings and feel that we are living in an enlightened and reasonably progressive age.

Rapid centrifugal preparation

with the *Spinco* Model L ULTRACENTRIFUGE

- VACUUM
- 162 ml – 40,000 rpm
- REFRIGERATED

FULLY-AUTOMATIC features make the Spinco Model L Preparative Ultracentrifuge operationally self-supervising. Simple speed- and time-controls are preset by operator and electronic unit brings rotor to speed, times run, and decelerates with smoothly operating automatic brake.

Various sizes and types of interchangeable rotors mount in operating chamber with instantaneous coupling. Time between runs, using pre-loaded rotors, is less than a minute. Speed and vacuum are established almost simultaneously. Acceleration time for the 40,000-rpm rotor is only four minutes.

SAFETY FEATURES include automatic overspeed cutout; interlocks to prevent running at high speeds without vacuum in chamber and prevent breaking vacuum or opening chamber while running at high speeds. Rotor chamber is encased in thick double steel guard.

UNIT IS SELF-CONTAINED, of worktable height, and requires only electric connection for installation. Spinco electric drive and gearing system are of types proved in more than 100,000 hours of actual field operation. Self-balancing feature eliminates weighing of loaded tubes. Controllable refrigeration holds rotors and contents at any temperature down to -5 C.

In operation, the Model L applies forces up to 144,000 times gravity on 162 ml of material at a maximum speed of 40,000 rpm. Individual rotor tubes have sealing caps—are available in plastic or metal. Rotors provide second vacuum seal in quickly-detachable cover with integral lifting device. Wide selection of rotors is available with largest holding 1700 ml—

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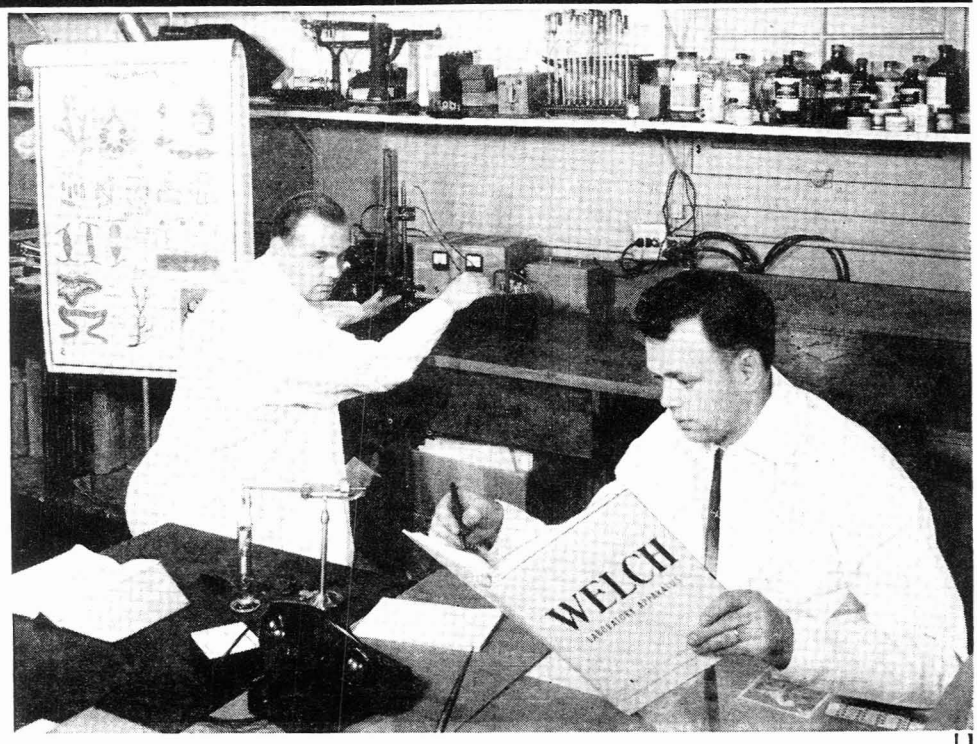

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ANALYTICAL CHEMISTRY

APRIL 1954

Readers' Information Service

These handy cards will bring information of value to chemists, engineers, and other technologists in laboratory, pilot plant, and production

Circle desired items: For further information about items mentioned on the advertising pages or listed under NEW PRODUCTS and MANUFACTURERS' LITERATURE, circle the corresponding key number on the adjoining tear-out cards and mail. ADVERTISED PRODUCTS INDEX numbers are keyed to the ad pages and to the index below. Numbers refer to the page on which an ad appears. Numbers following the letter A refer to specific items on pages where more than one ad and/or product is indexed. Where these latter numbers are used, consult the ad and INDEX to determine the keyed item.

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NEW PRODUCTS

Timers

Two repeat cycle electronic timers that provide on-intervals ranging from 0.01 to 150 seconds and off-intervals of from 0.01 to 900 seconds have been announced by G. C. Wilson & Co. They are suitable for controls where the timing device must be stable and accurate over nominal changes of line voltage and temperature.

The timers are housed in steel cabinets of 9 × 10 × 5 inches with external settings. They utilize one radio type tube and a voltage regulator to charge two resistance-capacitance networks. During operation, one cycle automatically initiates the next without moving parts or external operation. **1**

Magnetic Amplifier

The output of a low level d.c. device such as a thermocouple, phototube, strain gage, or thermistor bridge, can be amplified sufficiently to operate an insensitive meter or relay through use of a low level magnetic amplifier designed by Polytechnic Research & Development Co., Inc.

The company's Type 806 amplifier will operate from input signals as low as 200 micromicrowatts and will provide an output of 0.05 watts of reversible polarity to a 50 ohm load. A power gain of approximately 300,000 can be obtained. The unit is self-contained and requires no additional rectifiers or power supply. It operates from 115 volts, 60 cycles, single phase. **2**

Humidity Cabinets

A line of humidity-temperature test cabinets has been announced by Hudson Bay Division of Refrigeration Systems, Inc. Weather-Lab units are available in standard 20- and 30-cubic foot sizes for simulation of conditions between 35° and 200° F. and 20 to 95% humidity.

Access to the test space is through two front-opening doors. All cooling, heating, humidifying, dehumidifying, and air moving equipment is located in an enclosed portion of the test space. The refrigeration condensing unit is placed within a machine compartment beneath the chamber.

The basic unit is equipped with an exterior-mounted control panel with adjustable wet and dry bulb thermostats, switches, and pilot lights. Optional controllers provide programming of the wet and dry bulb functions on a predetermined time cycle. **3**

Hydrogen Sulfide Analyzer

For continuous and automatic detection and recording of the concentration of hydrogen sulfide in vehicle gas in industrial applications, Viking Instruments, Inc., has brought out the Type SU detector. The apparatus consists of a sensitive chart recorder for panel mounting, a sampling and detecting unit with photocells and controls, and a glass tube flowmeter. Audible and visual alarms can be furnished, if desired.

In operation, the instrument produces a series of stains on a test strip and compares the density of these stains to the

(*Continued on page 52 A*)

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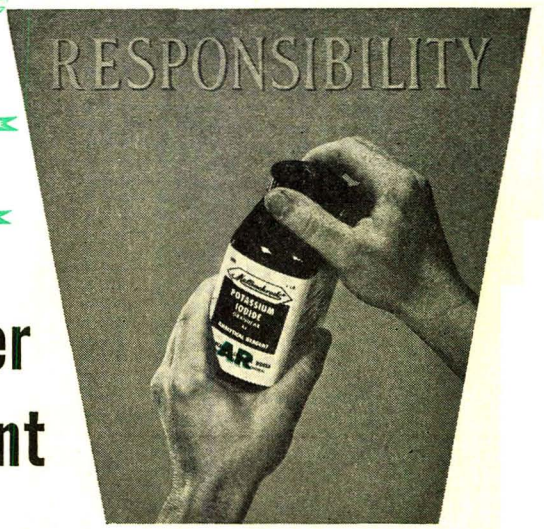

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There are 85 Mallinckrodt AR dealers in 57 cities. They were not picked at random. They were picked because of their long record of outstanding service. These dealers proved through the years that they are dedicated to serving the chemical and scientific professions — with *trained personnel, ample stocks* and a *conscientious choice of suppliers.*

When you call your AR dealer, you can *expect to be satisfied,* whether you need chemicals or other dependable supplies or apparatus — for three good reasons:

Mallinckrodt dealers maintain more than 2,500,000 square feet of floor space given over to well-chosen stocks — to make sure that *what you want* is available *when you want it.*

They have over 500 trained and specialized men at your service — to give you intelligent attention and technical guidance.

And they distribute for the best known and the most dependable suppliers in the field — *their* responsibility to you is backed by the long-established responsibility of the manufacturers.

Mallinckrodt backs up their dealers with a staff of 2,500 people, an 87-year-long reputation for service, and standards of quality and purity not exceeded by any other chemical manufacturer. Your AR dealer has a strong sense of responsibility. The more you deal with him, the more you will come to realize it.

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Mallinckrodt® AR's* always pure always available always dependable

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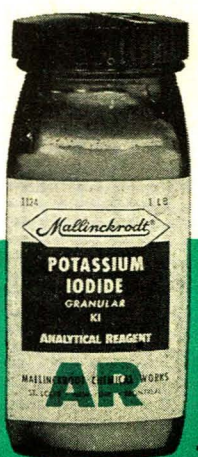

available in 1 lb. and many ¼ lb. sizes, excluding liquids

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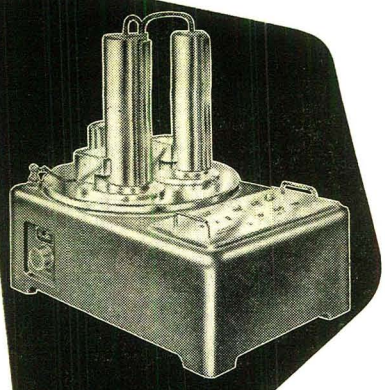


First
AUTOMATIC
FLOW COUNTER

Here is the first commercially practicable, completely sealed flow counter for automatic radioassays either in the Geiger or proportional region. The instrument accepts 25 samples of any size up to 1 7/8" D by 5/16" high, with choice of appropriate chamber sizes. Each sample may be counted from one to four times in cyclical order, or the unit may be set so that the cycles are repeated indefinitely. The SC-50 may be used either with the Superscaler or Autoscaler and results are printed on a tape by the Printing Interval Timer, a unit designed *specifically* for nuclear use.

- Completely automatic Geiger or Proportional counting.
- 2 pi geometry.
- 25 samples up to 1 7/8" D in size.
- Automatic sample recycling.
- Overall accuracy of 1%.
- Elapsed time printed for each sample or cumulatively.

Please request Tracerlog No. 57, for complete details.

Tracerlab® inc.
130 HIGH ST., BOSTON
2030 WRIGHT AVE., RICHMOND, CAL.

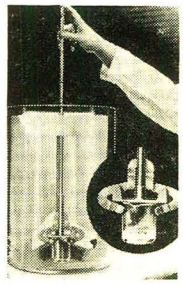
Circle No. 52 A on Readers' Service Card, page 49 A

density of unstained test strips. To form a stain, the test gas is permitted to enter the sampling chamber at a predetermined and adjustable rate. Stain density is a function of rate of gas flow, time of strip exposure, and hydrogen sulfide concentration in the test gas. When a series of stains is produced while flow rate and exposure time are held constant, the difference in density between the stained test strip and a clean strip is directly related to hydrogen sulfide concentration.

Density of each stain is electronically measured constantly during the exposure period, and the relative density shown on the indicator or recorder. Full scale ranges from 200 p.p.m. to 0.05 p.p.m. are provided. **4**

Beaker Holder

BeekurGrip has been designed by The Nalge Co. for convenient handling



of beakers in descending type chromatographic apparatus containing corrosive or irritating solvents. The device is of lightweight aluminum construction.

Spring tension grips are controlled from the top of the handle and are adjustable to accommodate 50- to 250-ml. beakers. A built-in platform acts to prevent contamination or spillage. **5**

Gravity-Weight-Volume Chart

Revised American Petroleum Institute gravity-temperature correction tables have been published by Fisher Scientific Co. in a 45 × 35-inch chart for use in petroleum control and inspection laboratories.

The chart presents an abridgement of three tables needed to convert API gravity readings observed with a glass hydrometer at any temperature to API gravity at 60° F. and then to volume and pounds per U. S. gallon at 60° F. Price is $1.00. **6**

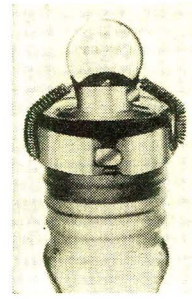
Filter

Carl Schleicher & Schuell Co. has announced a flexible membrane filter for use in the determination of numbers and types of bacteria and other microbes in water, sewage, milk, foods, beverages, air, and soil or for filtration of fine particles from suspensions.

The Bac-T-Flex filter is said to be flexible, durable, and easy to handle and sterilize. A green grid makes counting of colonies easy and accurate. The grid is of large size to facilitate counting at magnifications up to 15×. **7**

Hooks for Glassware

To provide a method of securing two ground glass joints together by means



of metal hooks and springs, Metzkier Metal Products Co. is offering Tension Hooks. The hooks are sturdy and not so easily broken as the conventional glass hooks used on glass equipment for this purpose.

The metal adapters are made of stainless steel, 0.01 inch thick, and are easily bent around glass necks or tubes and fastened by means of a replaceable metal tab. They can be used on any type of glass for holding together automatic burets, wash bottles, stirring assemblies, or other equipment and for securing stoppers or thermometers. **8**

Gas Analyzer

A radiological gas analyzer developed by Shell Development Co. is now being manufactured by Hallikainen Instruments. It is designed for continuous analysis of binary gas mixtures by measurement of ionization produced in the gas by beta radiation from a strontium-90 source.

The instrument is available in standard or explosionproof models. First installations have been for the measurement of argon in converter gas in an ammonia plant. **9**

Microscope Attachment

An English-made microscope attachment that minimizes space restriction between objective lens and specimen by providing 12.8 mm. working distance is being distributed by Edmund Scientific Corp. The device, which is available in 20× and 40× models, also erects the image viewed.

The system is particularly suitable for dissection work or for viewing surface defects, indentations, and specimens at high temperature, according to the distributor. The erect-image feature is said to eliminate awkwardness in manipulation of specimens, as movements of the hand need not be reversed in relation to the image.

The attachment replaces one of the

For further information, see coupon on page 49 A

objective lenses of any standard microscope and revolves along with the other objectives in the nose piece. Heart of the system is a half-aluminized plate which first passes light rays and then, when they are reflected back to it by a surface mirror, reflects the rays correctly positioned for viewing by the objective. **10**

Hot Plate

Thermo Electric Mfg. Co. is producing a hot plate measuring 9 inches square and 6 inches high for heavy duty service. It has a cast iron top plate and a stainless steel body. The body is in two sections separated by an insulating plate, and the heating plate itself is insulated and suspended in the top section with ventilating air channels underneath and on all four sides.

Temperatures are regulated by a four-way switch providing surface temperatures of 400°, 535°, 710°, and 930° F. Units operate on 115 or 230 volts a.c. **11**

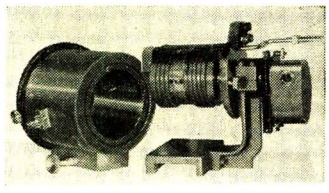
Electrophoresis Apparatus

E-C Apparatus Co. is marketing an electrophoresis apparatus that can analyze up to 12 samples simultaneously under identical conditions of temperature and ionic strength. It can be used to determine mobilities of mixture components at three pH levels at the same time.

The unit is constructed of Plexiglas, with permanently attached platinum electrodes. The migration chamber will accommodate paper sheets or starch columns up to 4 cm. thick and provides water cooled surfaces in contact with the paper or starch column. Unit operates at 1000 volts d.c. or less. **12**

X-Ray Diffraction Camera

Designed for general purpose investigations of substances at controlled temperatures up to 1000° C. is the Model HC-101 high temperature x-ray diffraction powder camera of Central Research Laboratories, Inc.



The camera has a movable film carrier that allows five 7-mm. diffraction pat-

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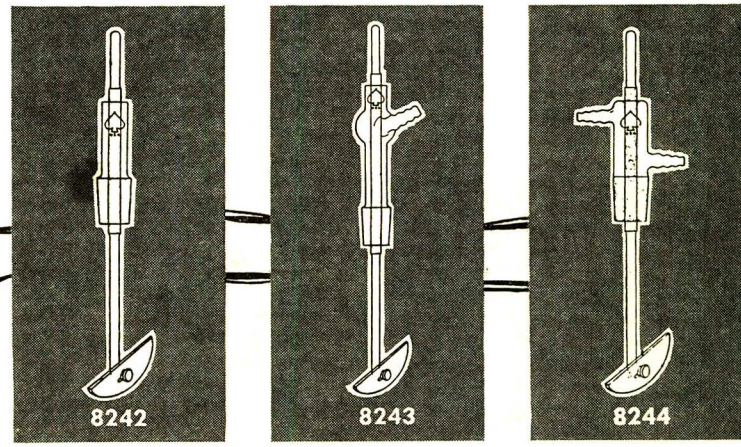

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terns to be made on the same film, facilitating the determination of phase diagrams and registering comparison patterns of different substances at selected temperatures. The carrier, which is 114.6 mm. in diameter, may be removed from the furnace assembly at any stage of the investigation without disturbing the thermal environment of the powder sample. Standard 35-mm. x-ray film may be used for single exposures.

Two concave ceramic bodies, separated by a 3-mm. spacing which allows the diffraction to pass to the film, support coiled helix furnace heating elements of platinum-rhodium. Intervening barriers of low heat capacity minimize radiation and convection losses. The temperature of the specimen can be changed from one thermal level to another with equilibrium being rapidly obtained.

Thermocouple for temperature determinations can be positioned in the heating cavity where the x-ray beam intersects the sample or in a retracted position in line with the specimen axis. Samples may be mounted and aligned externally on a ball bearing spindle which is rotated by a 1 r.p.m. motor. Both the aligning fixture and film punch are included as standard equipment. **13**

Grease Worker

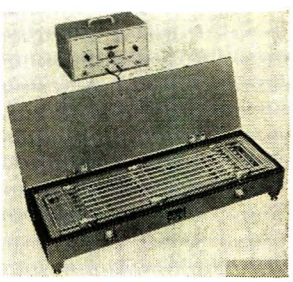
An automatic grease working machine suitable for testing the shear stability of greases and other colloidal and plastic solids and liquids under prolonged isothermal mechanical working is offered by Technical Equipment Co.

The worker contains a built-in thermocouple and water jacket for maintenance of constant temperature and measuring the temperature of material being worked. A constant temperature bath provides liquid to the worker jacket and controls and indicates temperature to ±0.1° F. The apparatus has a temperature range from −65° to 300° F.

A preset counter totals strokes of the worker and shuts off the machine at a predetermined number of strokes. The equipment is motor driven. It is suitable for ASTM D-217 test for cone penetration of lubricating greases, as well as for various government specification tests. **14**

Electrophoresis Apparatus

For separation and identification of mixtures of biological materials, such as amino acids and proteins, by electrophoresis on wet filter paper, Precision Scientific Co. offers the Junior Ionograph. The unit is a modification of an older Precision model.



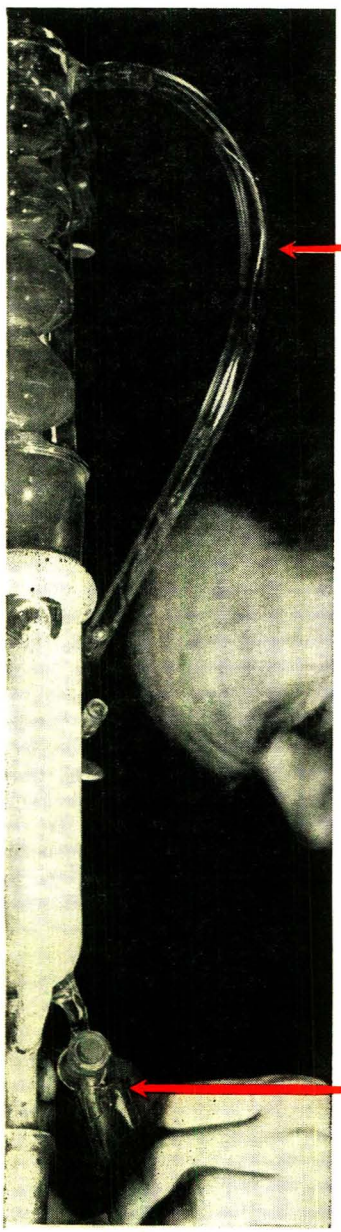
It accommodates seven filter paper strips or a single sheet for two-dimensional electromigrations. The apparatus consists of a single-wall, nonconducting cabinet which holds a paper strip frame and electrode vessels, and a separate power supply system containing voltmeter, ammeter, and controls. Range of potential is 150 to 500 volts of regulated current.

Up to 0.5 mg. of test material may be used. The instrument is portable and may be placed in an incubator or low temperature chamber. **15**

Metallurgical Polishing Table

For the production of metallurgical specimens, Buehler, Ltd., is manufacturing a cabinet type polishing table with companion mounted and floor storage cabinets. The two-unit polishing table has a Formica top and is approximately 60 inches long, 27 inches

For further information, see coupon on page 49 A



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deep, and 30 inches high to table top. It includes two 12-inch swing spouts, an 8-inch diameter wash bowl with drain, plumbing, and wiring. **16**

Saybolt Viscometer

A constant temperature Saybolt viscometer available from Labline, Inc., employs an electronic circuit with a mercury thermostat. It is of double-wall insulated construction with stainless steel exterior and Bakelite cover.

Stirring is accomplished by an external induction motor with turbine type impeller. Immersion heaters provide temperatures to 450° F. and a mercury thermoregulator is adjustable through the full temperature range. Two- and four-tube models are available. **17**

p-Xylene

For use as a flash point test standard for closed-cup devices, Fisher Scientific Co. has a special grade of *p*-xylene. The chemical meets ASTM specifications for specific gravity, boiling range, and purity. It is offered in quart lots. **18**

Power Supply

An adjustable a.c. regulated power supply for operation from a 60-cycle a.c. line has been designed by Summit Electronics, Inc. The apparatus is suitable for industrial production and inspection use as well as laboratory work. Several models are available for varying output requirements ranging from 0.1 to 100 amperes. Output voltages are varied by a front panel control. Intended for panel mounting, the equipment measures $12^1/_4 \times 19 \times 6^1/_2$ inches. **19**

Diphenylamine

Fisher Scientific Co. is selling a special indicator grade of pure diphenylamine for spectrographic analysis of nitrate and nitrite in a variety of materials, detection of chromium, iron, manganese, uranium, or zinc, and glycerol titrations.

The material is a white solid that yields almost colorless solutions in concentrated sulfuric acid, and therefore provides low blanks. **20**

Freeze Drying Apparatus

A standard glass lyophilizing unit for quick drying and freezing of organic tissues and other materials is being produced by Wakefield Industries, Inc. Lyophilizing time for the equipment's capacity of 400 cc. is within 6 hours.

The unit is made of borosilicate glass tubing, 4 inches o.d. by 3 inches i.d., and is 300 mm. in length. It has four outlets and a tube at the bottom for drainage, and is furnished with four receiving flasks. **21**

MANUFACTURERS' LITERATURE

Oscillograph. Bulletin of 16 pages describes features and specifications of a recording oscillograph for static or dynamic data, as well as accessories and associated equipment. Consolidated Engineering Corp. **22**

Moisture Determination. Four-page leaflet lists features of an apparatus for moisture determinations by xylene and toluene distillation methods. Hafco Scientific Instruments & Development Co. (*Moisturscope*). **23**

Environmental Test Equipment. Brochure of 4 pages describes line of equipment for simulating various conditions of altitude, temperature, humidity, sunshine, and dust. American Research Corp. **24**

Resistors. Four-page folder describes and gives specifications for precision wire-wound resistors. International Resistance Co. (*Bull. D-1*). **25**

Phthalic Anhydride. Booklet of 24 pages discusses properties, uses, handling, and analysis of phthalic anhydride. American Cyanamid Co. **26**

Volt-Ammeter. Design and use of an a.c. multirange instrument with an accuracy of 0.05% through a frequency range from 20 to 20,000 cycles per second described in 4-page bulletin. Charles Engelhard, Inc. **27**

Hydrogen Analyzer. Four-page folder on features and operation of instrument for continuous determination of hydrogen concentration in mixtures with air or hydrocarbons. Taller & Cooper, Inc. (*Bull. 301*). **28**

Flame Photometer. Four-page bulletin describes features and operation of instrument for sodium, potassium, calcium, or lithium determinations. Baird Associates, Inc. (*Bull. 37*). **29**

Spectrophotometer Recorder. Operating and design features of a continuous recording instrument for ultraviolet and visual spectra presented in

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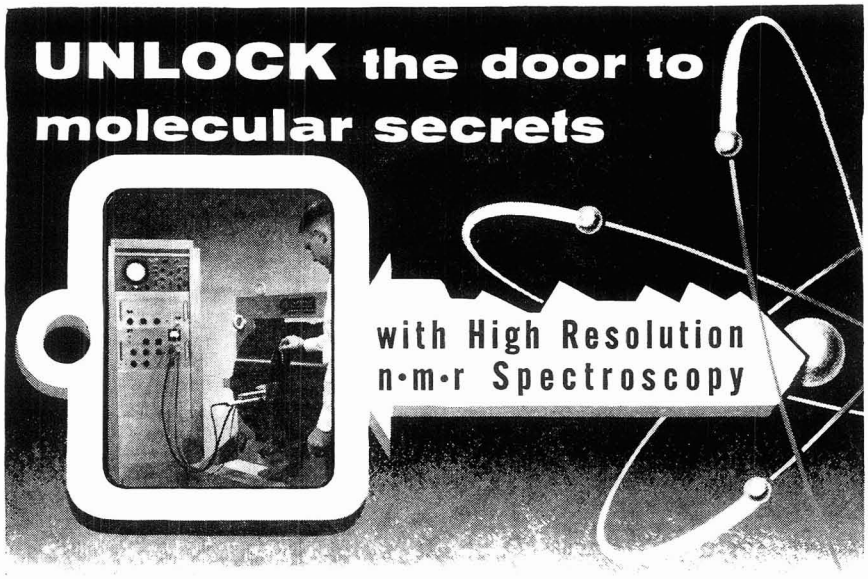

The Varian Model V-4300 High Resolution n·m·r (nuclear magnetic resonance) Spectrometer has stirred the imagination of chemists everywhere. With this new instrument, signals from H^1, F^{19}, P^{31}, B^{11}, C^{13} and several other nuclei can be detected, revealing the occurrence of identical nuclei in different chemical environments.

High Resolution n·m·r techniques permit rapid and completely non-destructive study of small liquid samples, including melted solids and liquefied gases.

Outstanding applications include:

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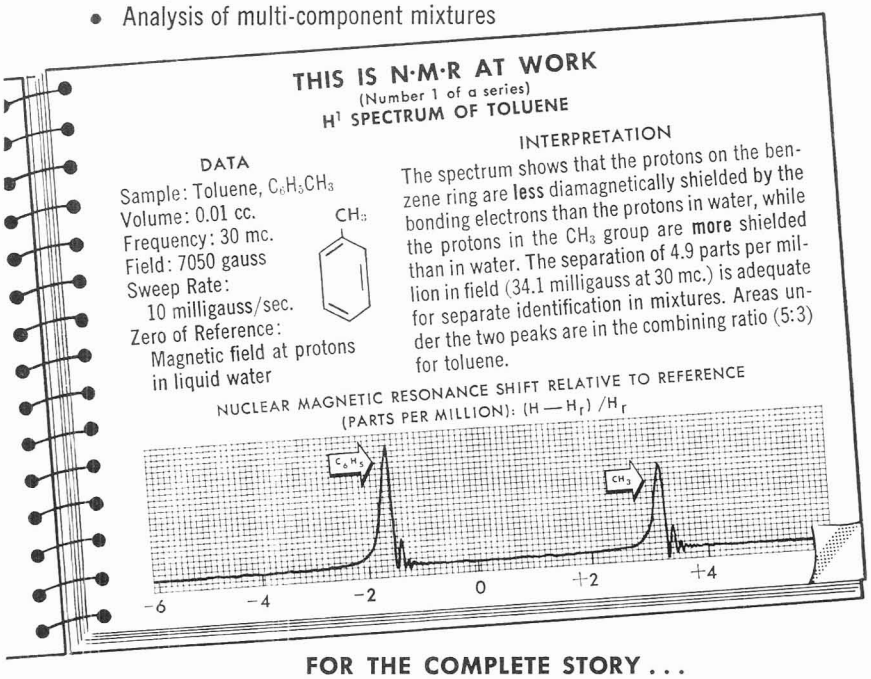
- Analysis of multi-component mixtures



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- Data Sheets
- n·m·r Table

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LITERATURE, continued

12-page bulletin. Warren Electronics, Inc. (*Spectracord*). **30**

Ion Exchangers. A catalog of 20 pages covering mixed-bed, two-bed, and four-bed demineralizers with capacities from 5 to 2500 gallons per hour for laboratory and industrial use. Barnstead Still & Sterilizer Co. (*Cat. 127*). **31**

Laboratory Furniture. A 24-page catalog presents information on a variety of laboratory furniture and utility equipment. Schaar and Co. (*Cat. AK-54*). **32**

Salicylamide. Seven-page bulletin lists properties of analgesic material and presents literature abstracts concerning its pharmacology and toxicology. Monsanto Chemical Co. (*Tech. Bull. 0-112*). **33**

Recording Densitometer. Two-page sheet describes a manually operated recorder for rapid photometric analysis of light-absorbing materials on dry paper strips obtained in electrophoresis and chromatography. Arthur H. Thomas Co. (*Bull. 117*). **34**

Electronic Computers. Booklet of 30 pages on electronic data processing equipment discusses functional principles and components of digital computers and new developments in their design. International Business Machines Corp. (*Light on the Future*). **35**

Organic Chemicals. Catalog and price list of over three dozen compounds offered by Arapahoe Chemicals, Inc. **36**

Melamine. A 56-page booklet contains sections on applications, specifications, properties, chemistry, toxicity, test methods, and bibliography for melamine. American Cyanamid Co. **37**

Oscillographic Recording Systems. A 38-page catalog presents technical data and specifications for 1-, 2-, and 4-channel systems for industrial research and production. Sanborn Co. **38**

Pharmaceuticals. Ten-page bulletin gives abstracts of patent applications and manufacturing processes of German pharmaceutical manufacturers available in translation from Research Information Service (*Bull. 83*). **39**

Creep Testing Machines. Five types of creep testing machines for standard size metal specimens described and illustrated in 12-page bulletin. Baldwin-Lima-Hamilton Corp. (*Bull. 4208*). **40**

Oscillograph. Specifications and circuit diagrams for wide-band cathode ray oscillograph for general laboratory ap-

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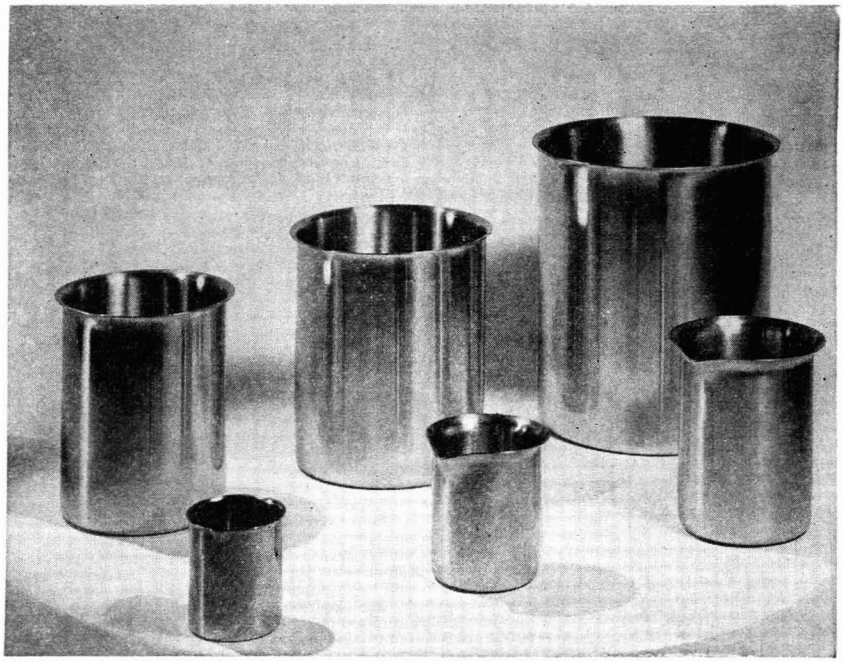
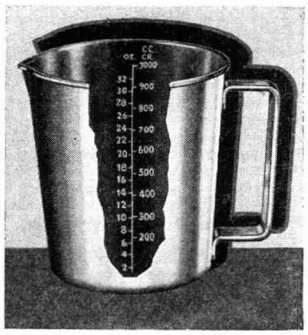
STAINLESS STEEL Laboratory Ware



JL9420—Beakers



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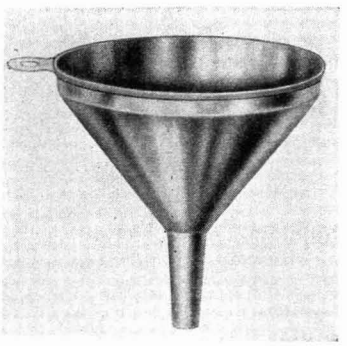

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Organic Analysis
Biochemistry
General Technique and Laboratory Apparatus

the last two sections being sub-divided for convenience.

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LITERATURE, continued

plications contained in 12-page bulletin. *Allen B. Du Mont Laboratories, Inc. (Type 323).* **41**

Thermocouple and Extension Wires. Technical data on thermocouple and extension wires for pyrometric work. Thermo Electric Co., Inc. (*Bull. 31*). **42**

Centrifuges. Four-page folder gives information on small-size angle centrifuges and accessories. Ivan Sorvall, Inc. (*Types SS-1 and SS-1a*). **43**

Electrophoresis Apparatus. Leaflet of 3 pages with specifications and price information for apparatus with platinum foil electrodes for preparing horizontal paper strip electrophorograms. Arthur H. Thomas Co. **44**

Textile Microscopes. Four-page brochure with information on microscopes and accessories for use in textile studies. American Optical Co. **45**

Carbon Monoxide Analyzer. Folder of 4 pages briefly describes a compact detector with a range from 0 to 10 parts of carbon monoxide per 10,000. Taller & Cooper, Inc. (*Portoco*). **46**

Laboratory Planning. Revised publication of 24 pages discusses the planning of industrial and school laboratory layouts. Scientific Apparatus Makers Assoc. (*Better Laboratory Planning*). **47**

Spectrographic Equipment. An 8-page price list of spectrographic equipment and supplies available from National Spectrographic Sales Corp. **48**

Crucibles. Brochure of 4 pages describes porous-bottom porcelain crucibles and microfiltersticks. Coors Porcelain Co. **49**

Laboratory Apparatus. Catalog of 17 pages describes laboratory furnaces and controls, hot plates, combustion units, and sulfur and carbon analysis equipment manufactured by Lindberg Engineering Co. (*Bull. 1001*). **50**

Quantometers. Pamphlet of 8 pages describes features of optical emission quantometers for analytical production control applications. Applied Research Laboratories. **51**

Electrophoresis Apparatus. Design and operating information for micro electrophoresis apparatus presented in 4-page folder. Ivan Sorvall, Inc. **52**

Flame Spectra. Pocket-size card carries emission spectra for 36 typical elements that can be determined by flame spectrophotometry. Beckman Instruments, Inc. (*FC-15*). **53**

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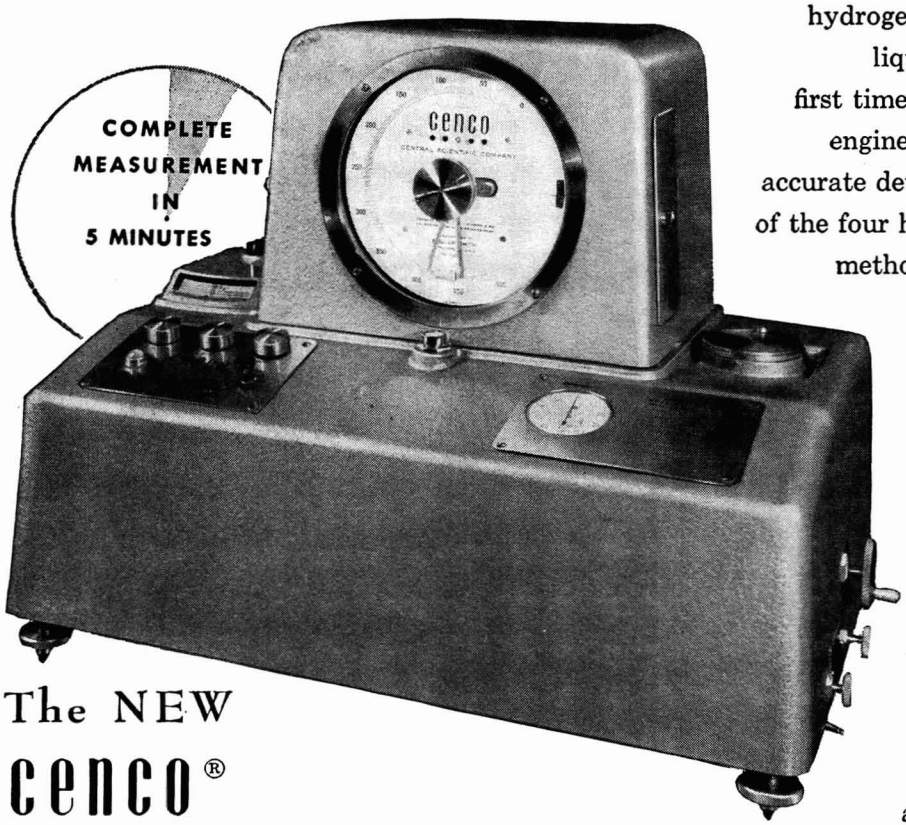

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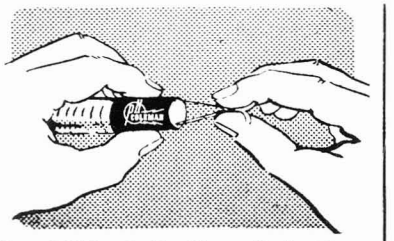

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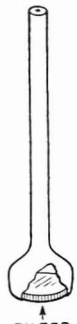

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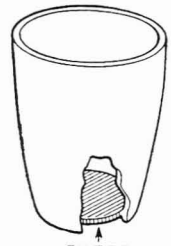

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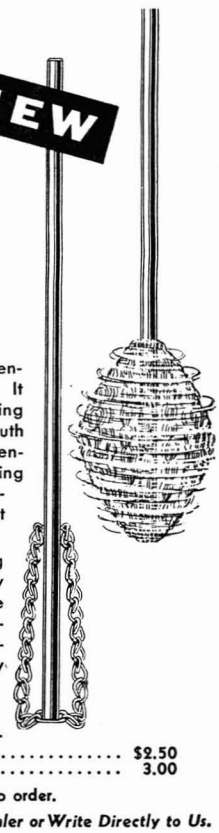

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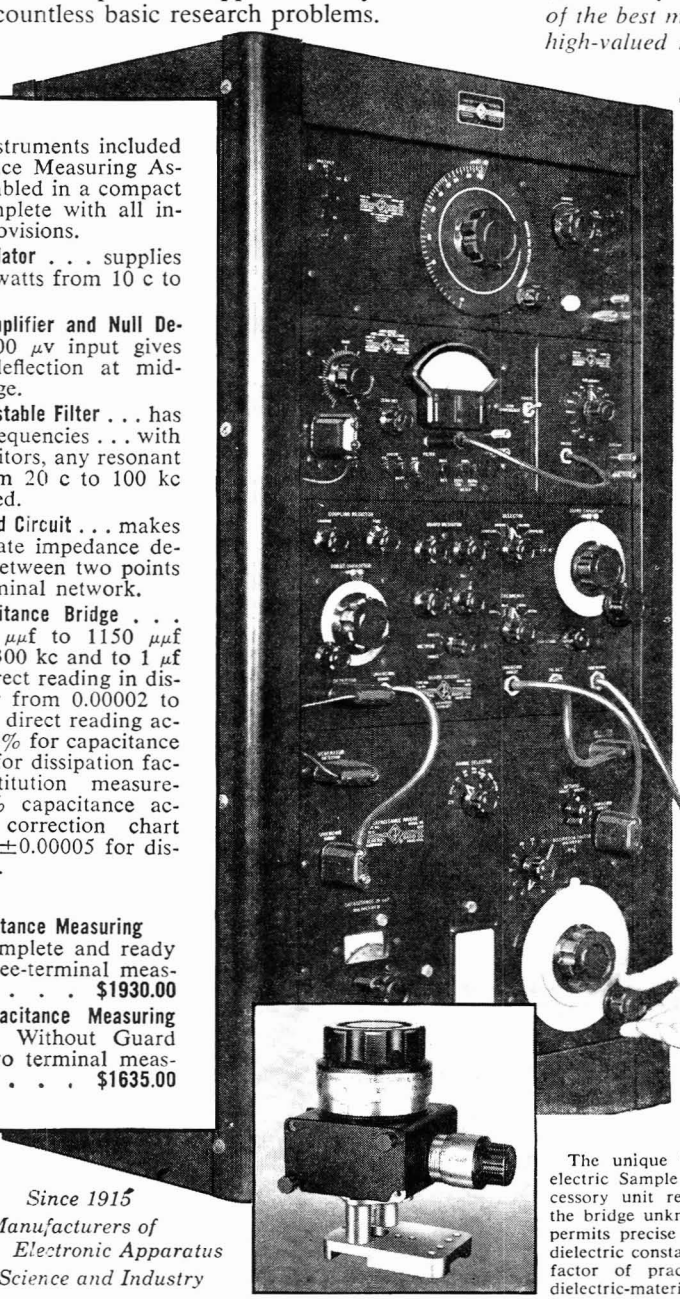

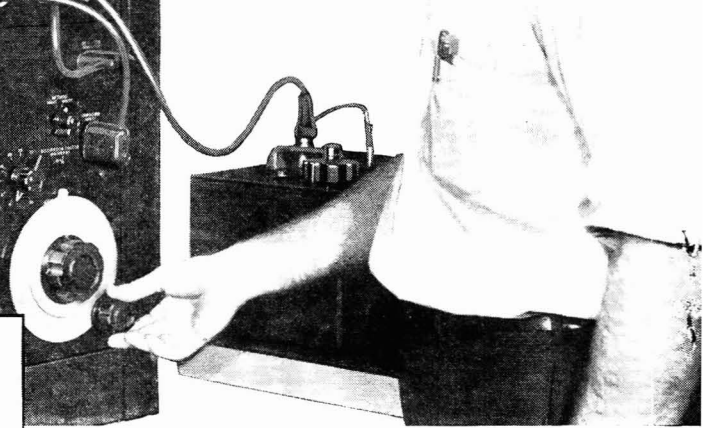

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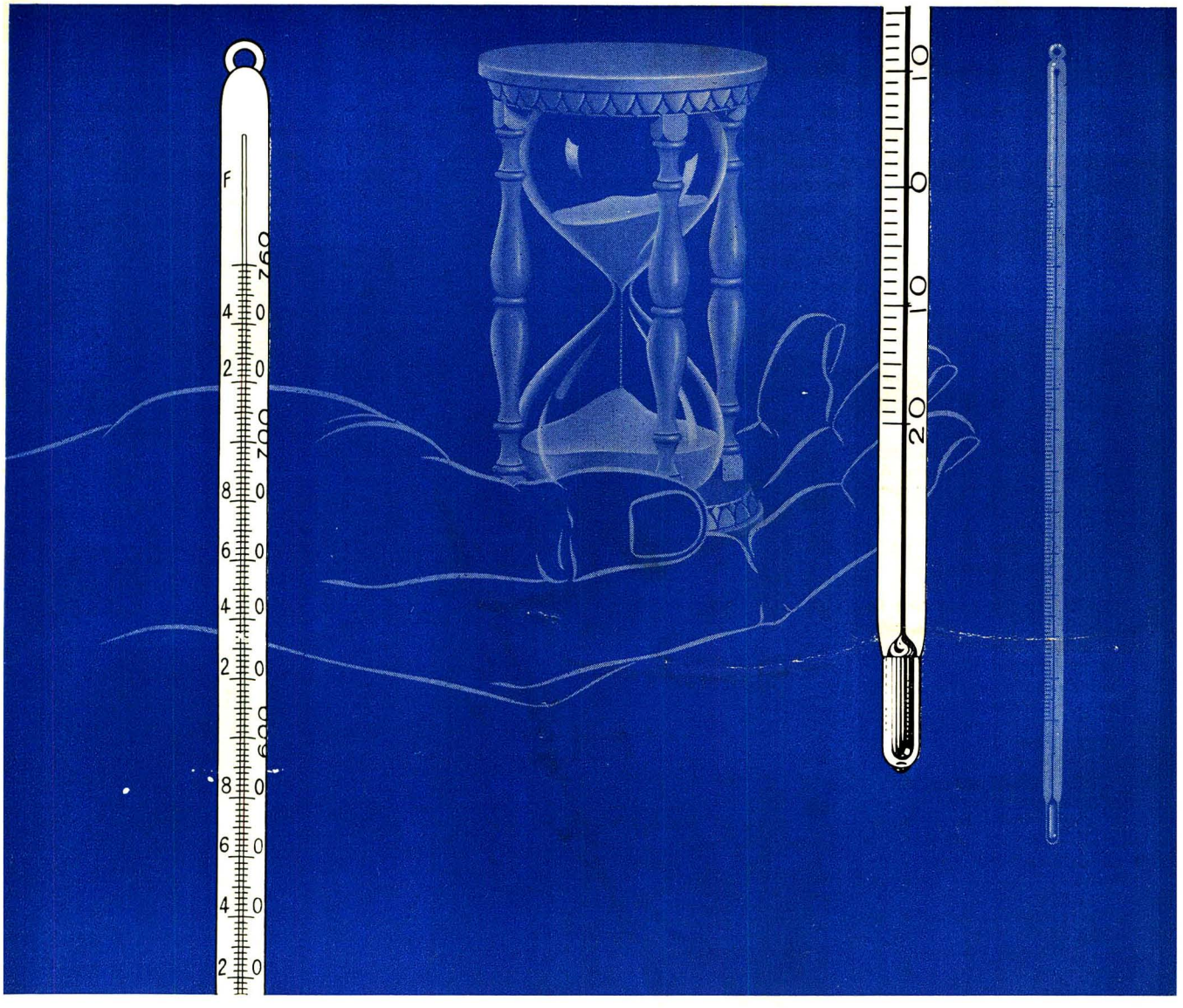

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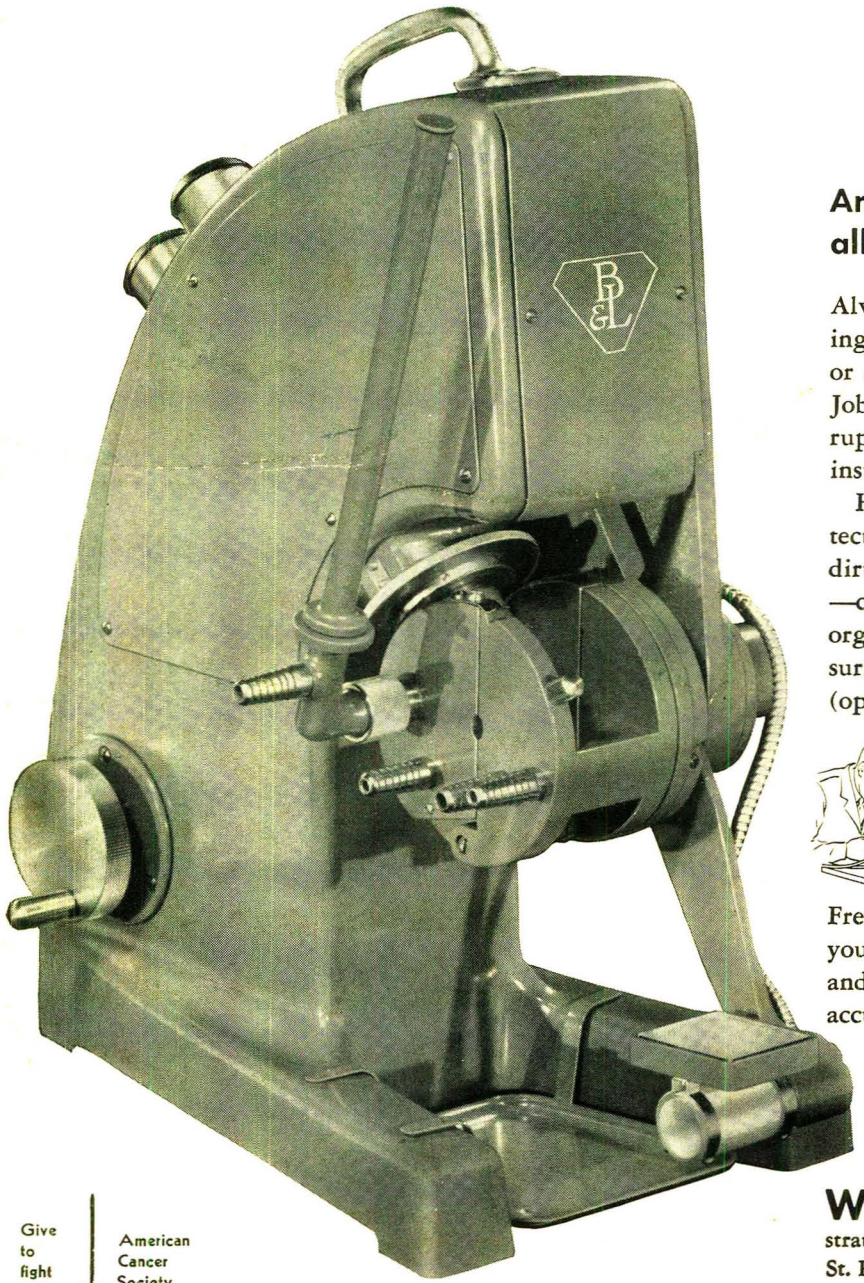

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