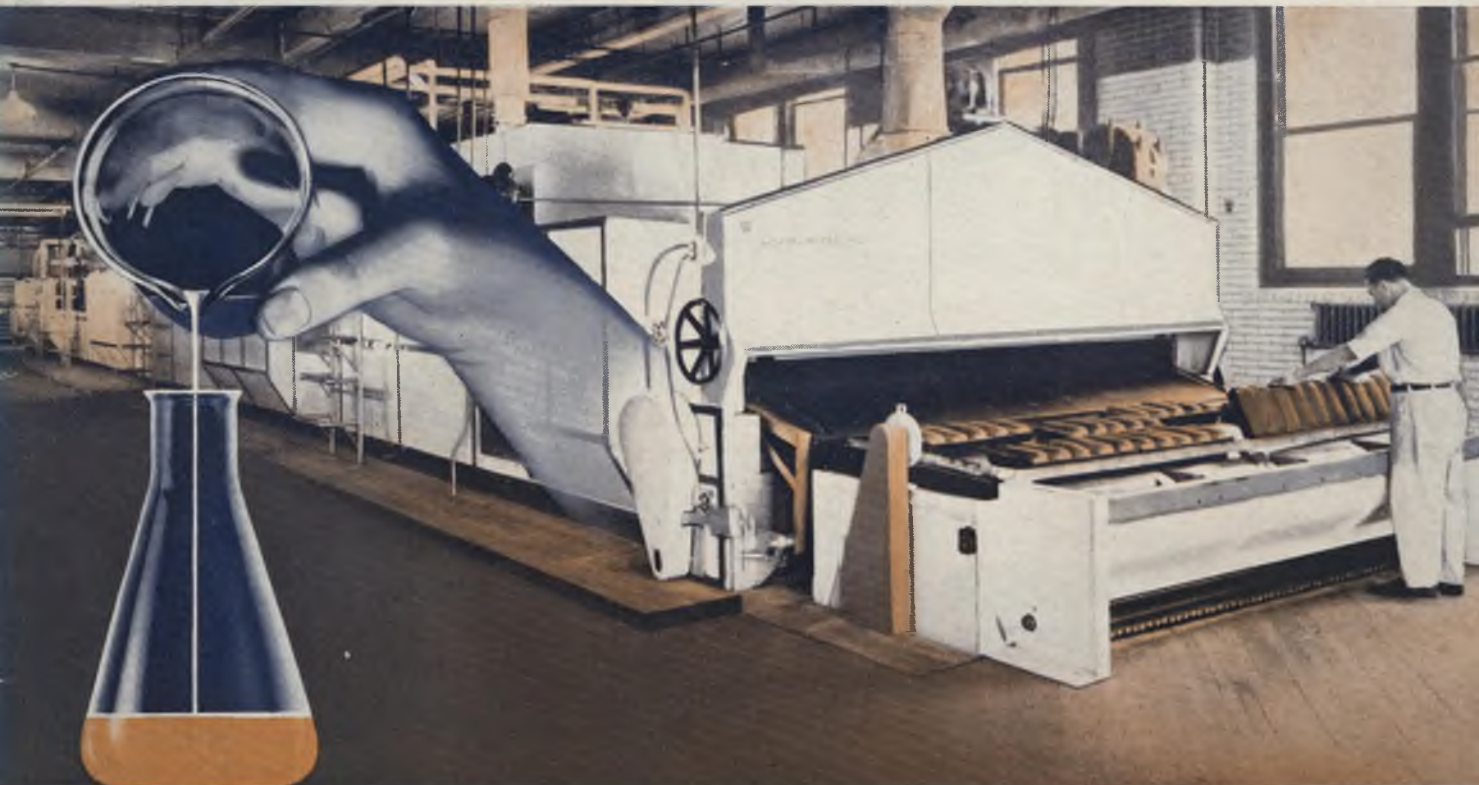


INDUSTRIAL AND ENGINEERING CHEMISTRY

SCIENCE IS POWER

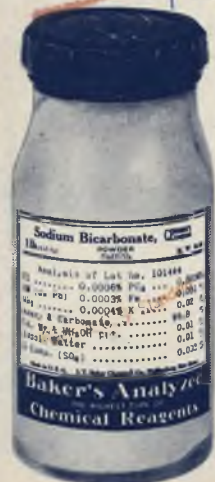


GOOD NUTRITION FOR AMERICA

P. 539/45

P. 1058/45

... starts in the laboratory!



Someone has said, "What we eat we are!" But few realize that good health frequently is charted in the laboratory!

Soils vary in chemical content and so do crops that are grown on them! The feed intake of livestock frequently determines the nutrient values of meat, eggs, milk, etc.

Vitamin and mineral fortification of food has been made possible through laboratory analysis. Laboratory analysis has indicated not only the need for but also the degree of enrichment necessary. Truly, America's good health starts in the laboratory.

In the laboratories (product control rooms) of many of the leading food and food processing manufacturers, you will find effective tools to measure good nutrition.

They are Baker's Analyzed C.P. Chemicals and Acids. The reason these Reagents have been selected is unique, for Baker's Analyzed C.P. Chemicals bear this distinction. Each bottle has the *actual lot analysis on the label*. The small percentages of impurities by lot analysis, as found by Baker's analysts, are printed on the label.

Chemists who work in terms of third and fourth decimal exactness know the value of the actual analysis rather than a statement of maximum limits of impurities.

So on your next order, be sure to specify Baker's Analyzed C.P. Chemicals and Acids. Your favorite laboratory supply house can supply you.



J. T. Baker Chemical Co., Executive Offices and Plant:
Phillipsburg, N. J.

Branch Offices: New York, Philadelphia and Chicago.

Purity defined — not to "maximum limits" — but to the decimal by actual lot analysis. That's the story of the Baker's Analyzed label.

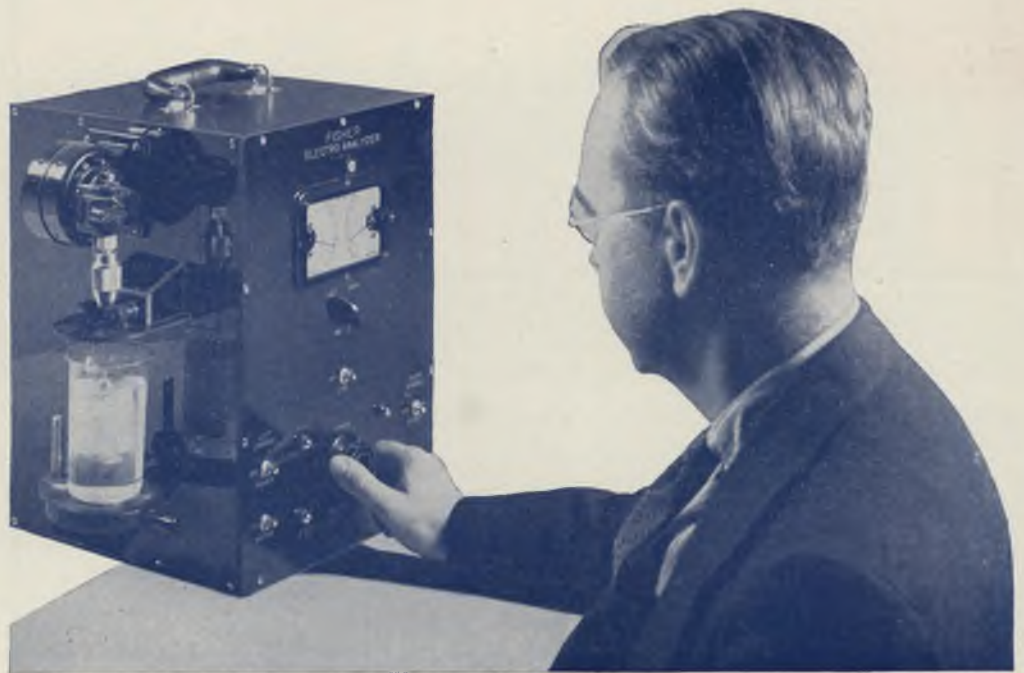
"Baker's Analyzed"

C P CHEMICALS AND ACIDS

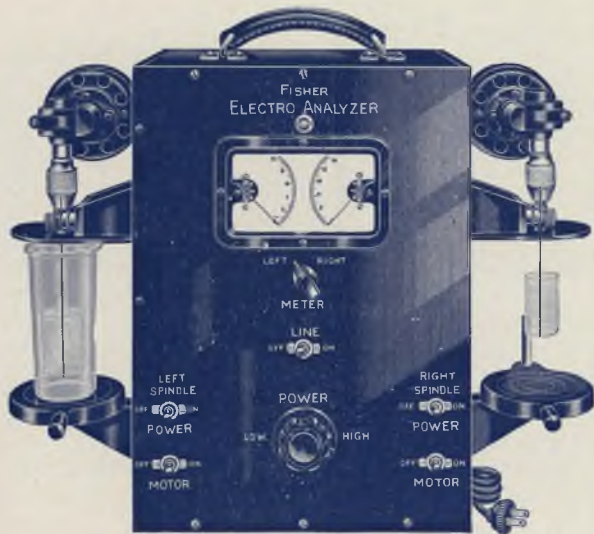
FOR RAPID, ACCURATE ANALYSES

FISHER Electro Analyzer

Operates Directly
on Alternating
Current



The Fisher Improved Electro Analyzer facilitates the rapid quantitative determination of metallic elements in solutions. It eliminates the need for expensive, cumbersome motor generators and rheostats, since it is a self-contained unit that operates directly from a 110 volt, 60 cycle, A.C. line.



The Fisher Electro Analyzer will make two similar determinations simultaneously. The voltage and amperage at the electrodes can be varied from zero to 36 watts (a maximum of six volts and six amperes), thus providing ample range to select the optimum current for each particular separation.

This new instrument is also an efficient source of power for electrolytic polishing, charging storage batteries, electroplating and many other applications where direct current within its capacity is required.

The bakelite panel of the Electro Analyzer is engraved and filled with permanent white. The sides of the case are also of bakelite to protect it from fumes and spattering.

Fisher Improved Electro Analyzer, for use with 110 volt, 50-60 cycle A.C., without electrodes or glass stirrer. **Each, \$150.00**

Glass Stirrer, for use with Electro Analyzer. Each, \$1.00

(Prices of platinum electrodes on request)

Manufacturers—Distributors

FISHER SCIENTIFIC CO.

717 Forbes St., Pittsburgh (19), Pa.
2109 Locust St., St. Louis (3), Mo.



EIMER AND AMEND

Greenwich and Morton Streets
New York (14), New York

Headquarters for Laboratory Supplies

22 4632
B
INDUSTRIAL AND ENGINEERING CHEMISTRY
ANALYTICAL EDITION

WALTER J. MURPHY, EDITOR • ISSUED MAY 19, 1945 • VOL. 17, NO. 5 • CONCESUTIVE NO. 10

Lawrence T. Hallett, Associate Editor

Manuscript Editor: G. GLADYS GORDON • Manuscript Assistant: STELLA ANDERSON • Make-up Assistant: CHARLOTTE C. SAYRE

Advisory Board

R. P. CHAPMAN
J. R. CHURCHILL
B. L. CLARKE

T. R. CUNNINGHAM
G. E. F. LUNDELL
M. G. MELLON

R. H. MÜLLER
B. L. OSER
H. H. WILLARD

ANALYTICAL CONTROL FOR AMMONIA SYNTHESIS

Control Requirements in TVA Plant
Earl H. Brown and Maurice M. Felger 273

Determination of Oxides of Carbon in Hydrogen-Nitrogen Mixtures
Earl H. Brown and Maurice M. Felger 277

Continuous Determination of Ammonia Activity in Ammoniacal Solutions . Earl H. Brown, James E. Cline, Maurice M. Felger, and R. Bowen Howard, Jr. 280

Continuous Determination of Carbon Dioxide by Electroconductivity in Concentrations Up to 2 Per Cent . Earl H. Brown and Maurice M. Felger 283

Continuous Photometric Determination of Bivalent Copper in Ammoniacal Solution
Earl H. Brown and James E. Cline 284

Determination of Argon in Ammonia-Synthesis Gases Earl H. Brown and James E. Cline 286

Continuous Determination of Carbon Monoxide in Concentrations Up to 3.5 Per Cent by Electroconductivity Earl H. Brown, Maurice M. Felger, and R. Bowen Howard, Jr. 287

Continuous Determination of Methyl Bromide in Atmosphere
Dwight Williams, George S. Haines, and F. D. Heindel 289

Determination of Low Concentrations of Methyl Bromide in Atmosphere Dwight Williams 295

Determination of Total Sulfur in Rubber
C. L. Luke 298

Laboratory Corrosion Tests R. M. Burns 299

Factors Causing Lubricating Oil Deterioration in Engines
R. E. Burk, E. C. Hughes, W. E. Scovill, and J. D. Bartleson 302

Analysis of Hydrofluoric-Nitric Acid Stainless Steel Pickling Bath
William E. McKee and William F. Hamilton 310

Determination of Water in Dry Food Materials
C. M. Johnson 312

Determination of Water in Liquid Petroleum Fractions O. T. Aeppli and W. S. W. McCarter 316

Fast Grating Spectrograph. Accessories and Techniques for Studying Raman Effect
Robert F. Stamm 318

Automatic Apparatus for Electrolysis at Controlled Potential James J. Lingane 332

BOOK REVIEW 333

MICROCHEMISTRY

Microdetermination of Acetyl Groups in Acetates of Sugars and Glycosides
Ray Clarke and Bert E. Christensen 334

Report of Committee on Analysis of Commercial Fats and Oils
E. W. Blank, E. W. Colt, F. G. Dollaar, J. L. Laing, J. Fitelson, C. P. Long, J. E. Maroney, R. T. Milner, L. B. Parsons, H. A. Schuette, S. O. Sorensen, L. M. Tolman, F. C. Woekel, V. C. Mehlenbacher, Chairman 336

The American Chemical Society assumes no responsibility for the statements and opinions advanced by contributors to its publications. Copyright 1945 by American Chemical Society.

Published by the American Chemical Society at Easton, Pa. Editorial Office: 1155 16th Street, N. W., Washington 6, D. C.; telephone, Republic 5301; cable, Jiechem (Washington). New York Editorial Branch: 60 East 42nd St., New York 17, N. Y.; telephone, Murray Hill 2-4682. Chicago Editorial Branch: 310 South Michigan Avenue, Chicago 4, Ill.; telephone, Wabash 7376. Business Office: American Chemical Society, 1155 16th Street, N. W., Washington 6, D. C. Advertising Office: 332 West 42nd Street, New York 18, N. Y.; telephone, Bryant 9-4430.

Entered as second-class matter at the Post Office at Easton, Pa., under the Act of March 3, 1879, as 24 times a year—Industrial Edition monthly on the 1st, Analytical Edition monthly on the 15th. Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918.

Remittances and orders for subscriptions and for single copies, notices of changes of address and new professional connections, and claims for missing numbers should be sent to the American Chemical Society, 1155 16th Street, N. W., Washington 6, D. C. Changes of address for the Industrial Edition

must be received on or before the 18th of the preceding month and for the Analytical Edition not later than the 30th of the preceding month. Claims for missing numbers will not be allowed (1) if received more than 60 days from date of issue (owing to the hazards of wartime delivery, no claims can be honored from subscribers outside of North America), (2) if loss was due to failure of notice of change of address to be received before the dates specified in the preceding sentence, or (3) if the reason for claim is "missing from files".

Annual subscription—Industrial Edition and Analytical Edition sold only as a unit, members \$3.00, nonmembers \$4.00. Postage to countries not in the Pan-American Union \$2.25; Canadian postage \$0.75. Single copies—current issues, Industrial Edition \$0.75, Analytical Edition \$0.50; back numbers, Industrial Edition \$0.80, Analytical Edition prices on request; special rates to members.

The American Chemical Society also publishes *Chemical and Engineering News*, *Chemical Abstracts*, and *Journal of the American Chemical Society*. Rates on request.



Reflecting the Integrity of the Maker :

Each time you see the Harshaw trademark, whether on tank car, package or small laboratory bottle, remember it identifies chemicals that will help to do a better job . . . truly reflecting the integrity of the maker. • Harshaw will always guard the quality of its chemicals . . . chemicals which you identify by the Harshaw trademark . . . and which you buy with confidence. For more than 50 years Harshaw has persevered in ceaseless research and field investigation. As a result, thousands of manufacturers have been supplied with hundreds of different chemicals which have helped them . . . and which in addition have proved a source of satisfaction to them and to us.

P. 374/59

★ ★ ★ ★ ★ ★ ★ ★ ★ ★ ★ ★ ★ ★ ★ ★

THE HARSHAW CHEMICAL CO.
 1945 East 97th Street, Cleveland 6, Ohio
 BRANCHES IN PRINCIPAL CITIES



On Sentry Duty

★ *A heavily armed soldier* guards a shipment of food for the hungry millions of devastated Europe . . .

★ *A laboratory technician* guards the quality of foods being processed.

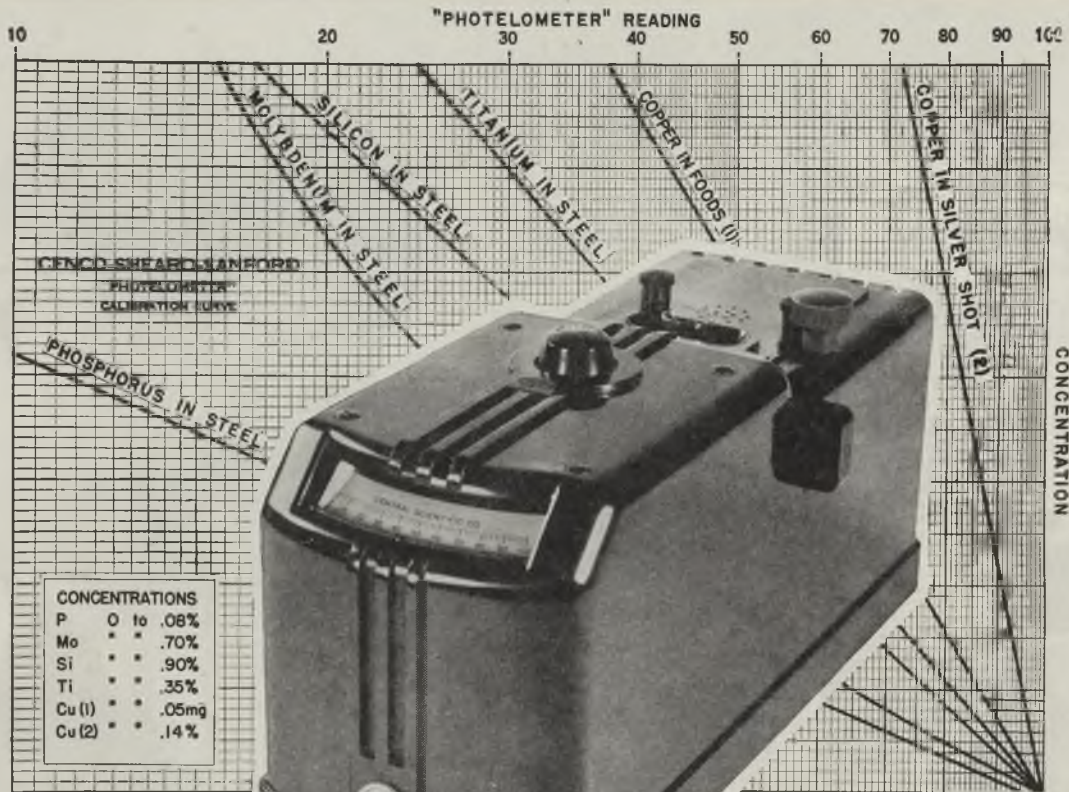
Both performing vital functions, both using the finest of equipment—equipment such as the Spencer Refractometer which is a standard laboratory control instrument of canners, dairymen, oleomargarine producers and others. Throughout these industries the refractometer is used to determine sugar content or total dissolved solids—to determine the times when condensation or hydrogenation

or other processes have progressed to the proper point.

For complete information about the many Spencer instruments which can help you maintain the quality of your product write Dept. P48.



Spencer LENS COMPANY
 BUFFALO, NEW YORK
 SCIENTIFIC INSTRUMENT DIVISION OF
 AMERICAN OPTICAL COMPANY



CONCENTRATIONS	
P	0 to .08%
Mo	.70%
Si	.90%
Ti	.35%
Cu (1)	.05mg
Cu (2)	.14%

RAPID ANALYSES

CENCO "PHOTELOMETER" Industrial Type B-2

This new compact filter photometer embodies the most recent improvements in design for efficiency, sensitiveness, attractiveness, and economy. Its use in the control or clinical laboratory for chemical analyses offers many advantages. Where speed, accuracy, and freedom from "human element" errors are desirable, the "Photometer" method of determining concentrations of colored solutions is rapidly replacing older, slower methods. Readings are now being applied to determinations such as molybdenum, titanium, vanadium, or manganese in steel; for lead, copper, iron or vitamins in foods; for hemoglobin and blood chemistry; and many other colorimetric procedures.

The New "Photometer" is a barrier-layer type instrument consisting of basically a low voltage light source, an adjustable light aperture, a three-color filter holder, receptacles for tubular or rectangular absorption cells, a single photoelectric cell, and a sensitive current-measuring instrument with a 2½-inch scale. The scale reads from 0-100 in 50 divisions.

The basic parts are mounted in an attractive plastic case measuring 4¾ inches high by 10¾ inches long by 4 inches wide. The 115-volt AC instruments are equipped with constant voltage transformers to supply constant intensity of light when operated on a controlled frequency power line.

No. 12346 "Photometer" Industrial Type B-2 Including a package of (12)
No. 12344G Cells and blue, green, and red filters:

No.	A	C
For volts	115 AC 60 cycles	6 DC
Price	\$110.00	\$100.00

CENTRAL SCIENTIFIC COMPANY

SCIENTIFIC INSTRUMENTS



LABORATORY APPARATUS

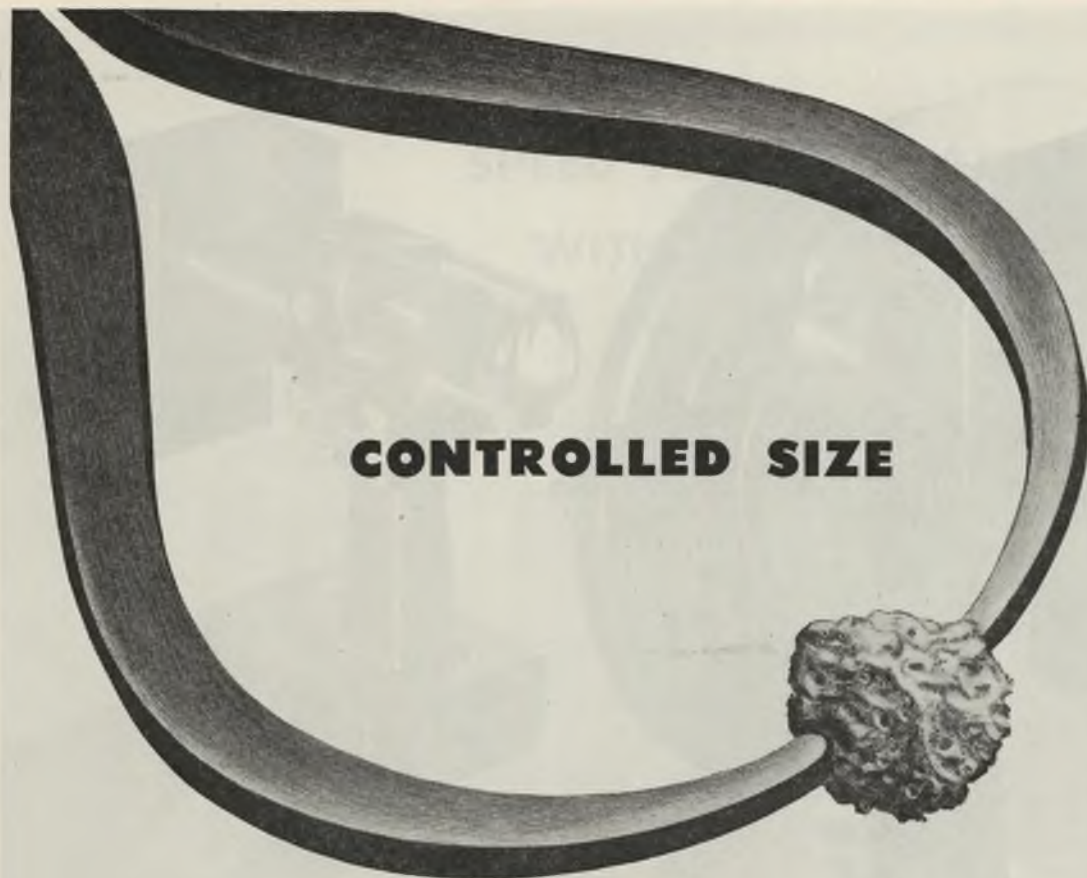
NEW YORK

TORONTO

CHICAGO

BOSTON

SAN FRANCISCO



CONTROLLED SIZE

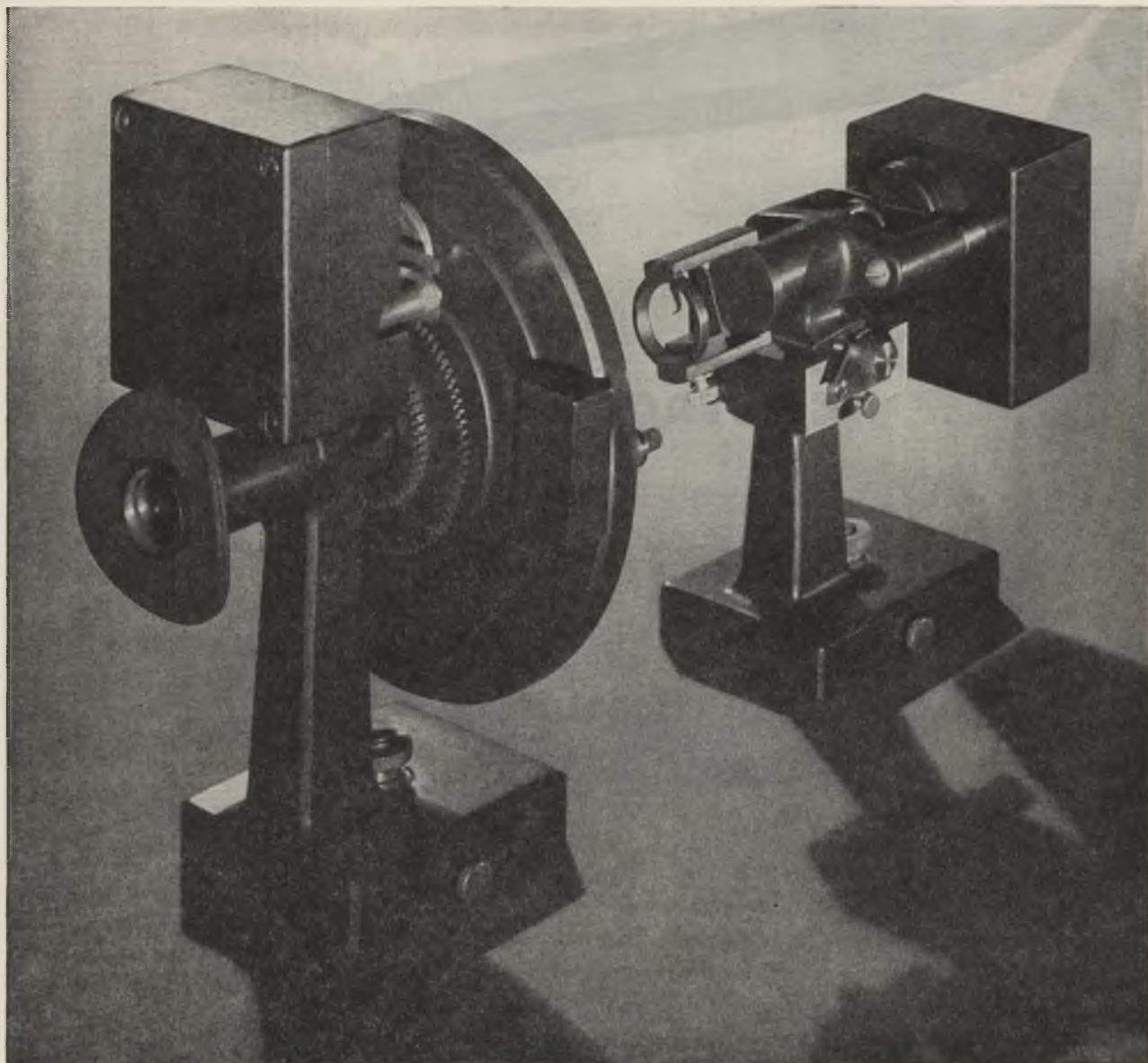
Rigidly controlled particle size is one of the factors which make Isocel a more acceptable catalyst than plain aluminum chloride. The bauxite used in Isocel as the carrier for aluminum chloride is prepared to uniform particle size, and control is maintained throughout the manufacture of Isocel. The aluminum chloride is thus presented in a lower concentration per unit of reactant space, yet uniformly dispersed. Isocel may be used with very sensitive or very active compounds, where reaction with finely powdered AlCl_3 is too rapid or severe, and in processes where lump AlCl_3 produces complications.

An important use of Isocel today is the conversion of normal butane to isobutane for the enrichment of alkylation feed stocks deficient in isobutane. Its value as an isomerization catalyst in refinery operations has been amply proved. Other reactions are constantly being studied. In many of them, the use of Isocel as a catalyst has unmistakable advantages, and it is safer to handle and less corrosive.

ISOCEL has a potential application in every field in which aluminum chloride is used as a catalyst. These seven fields are typical:

1. Reaction of organic halides with aromatic hydrocarbons.
2. Reaction of anhydrides of organic acids with aromatic hydrocarbons.
3. Reaction of oxygen, sulfur and sulfur dioxide with aromatic hydrocarbons.
4. Cracking of aliphatic and aromatic hydrocarbons.
5. Polymerization of unsaturated hydrocarbons.
6. Alkylation of aromatic hydrocarbons.
7. Isomerization of aliphatic hydrocarbons.

Our well-staffed laboratory and experienced engineers are available to help solve your special catalytic problems. Why not enlist their aid? There is no obligation. Write Attapulugus Clay Company (Sales Agent), 260 South Broad Street, Philadelphia 1, Pennsylvania.



Precision . . . **WITH PROVISION**

The G-E XRD Back Reflection Camera For X-Ray Diffraction Technics

When x-ray diffraction technics call for precision lattice parameter determination, here is a proved and invaluable instrument. The G-E XRD Back Reflection Camera incorporates ideally precise execution of the basic Sachs design . . . with provision for: oscillation and rotation of the film; eccentrically rotating the sample to permit integration of an area; assembling the camera for symmetrical focusing technics for minimum exposure. For full information about G-E X-Ray diffraction equipment for precision research and control—or to request the services of G-E's corps of experienced diffraction engineers in helping you apply x-ray diffraction to your individual problems—write or wire today, to Department N45.



GENERAL ELECTRIC
X-RAY CORPORATION

2012 JACKSON BLVD.

CHICAGO (12), ILL., U. S. A.

SPEED YOUR GAS ANALYSIS WITH THESE REAGENTS



LUSORBENT FOR ILLUMINANTS

Absorbs all the gases in the illuminants group, i.e., ethylene, propylene, butylene, acetylene, benzene and toluene. Requires fewer passes than fuming sulfuric acid, has no vapor pressure, absorbs less saturated hydrocarbons and does not attack rubber tubing.

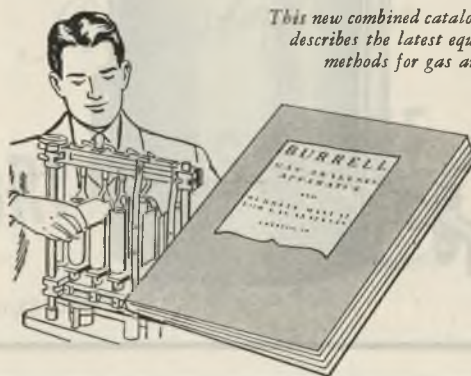
COSORBENT FOR CARBON MONOXIDE

Supplied in either liquid or powder form. Has no vapor tension, forms stable compound with carbon monoxide, is fast and active. Absorbs ethylene, propylene and acetylene, also oxygen slowly.

OXSORBENT FOR OXYGEN

Fast, clean and accurate, removes oxygen in a few passes and forms a stable compound with it. Absorbs four times its volume of oxygen. Rises cleanly in the capillary and is slightly acid — preventing sticking stopcocks.

This new combined catalog and manual describes the latest equipment and methods for gas analysis.



Complete information on reagents for gas analysis is given in the new Burrell Catalog 80. If you have not already received your copy, write to Burrell Technical Supply Co., 1936-42 Fifth Ave., Pittsburgh 19, Pa.

BURRELL

Improved Type PALO-MYERS WATER STILLS

**Assure Chemically Pure Water . . .
Available for EARLY DELIVERY**

Preference for Palo-Myers Water Stills is recognition of the fact that more and more careful consideration is being given today by chemists to the need for chemically pure water.

Basic improvements in design and operation achieved in Palo-Myers Water Stills include—

- **VERTICAL CONDENSER . . .** assures greater stability, easy release of gases and elimination of progens.
- **ECONOMY . . .** is effected by the most efficient method of heat exchange because the water enters at the lowest and hottest point of condenser.
- **MULTIPLE BAFFLES . . .** designed to prevent foaming and impurities entering condenser.
- **EASIER TO MOUNT . . .** due to compact construction, requires limited amount of space or can be supported on wall bracket.

Regular sizes $\frac{1}{2}$ to 10 Gallons per hour
—Stills 100 Gallons per hour if desired.

Inquiries invited — state capacity required per hour and method of heating.

CAPACITY G. P. HR.	PRICES		
	GAS	ELECTRIC	STEAM
$\frac{1}{2}$	\$49.50	\$56.00	\$
1	64.00	75.00	65.00
2	95.00	110.00	95.00
5	170.00	270.00	150.00
10	360.00	540.00	210.00

Prices subject to change

Other Palo-Myers apparatus available:

Partical size
measuring apparatus
pH equipment

Chemicals and solutions
for ASTM, AOAC, and
APHA analyses

Pumps—vacuum
Thermometers
Stirrers
Ovens
Electrolytic apparatus
Automatic burettes



PALO-MYERS INC.
81 READE STREET, NEW YORK 7, N. Y.



CONTROL...

Guides Modern Industry...

KIMBLE LABORATORY GLASSWARE

Serves Essential Control Laboratories

For Assurance

Consult Leading Laboratory Supply Houses Through
out the United States and Canada for Kimble
Laboratory Glassware to Meet YOUR Needs.



The Visible Guarantee of Invisible Quality

KIMBLE GLASS COMPANY . . . VINELAND, N. J.

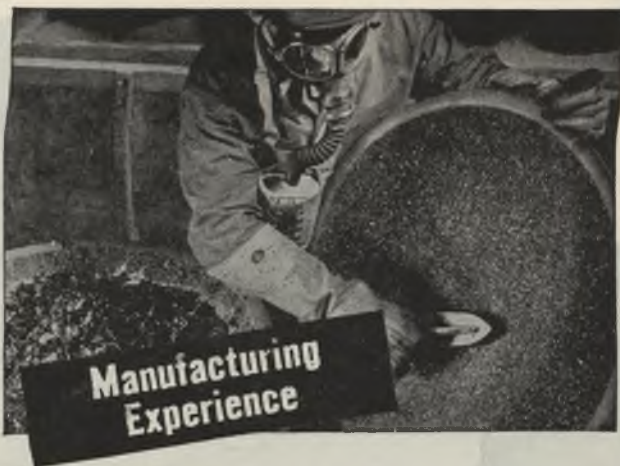
NEW YORK • CHICAGO • PHILADELPHIA • DETROIT • BOSTON • INDIANAPOLIS • SAN FRANCISCO





Constant Research

Determination of comparative melting points in the Merck Research Laboratories.



Manufacturing Experience

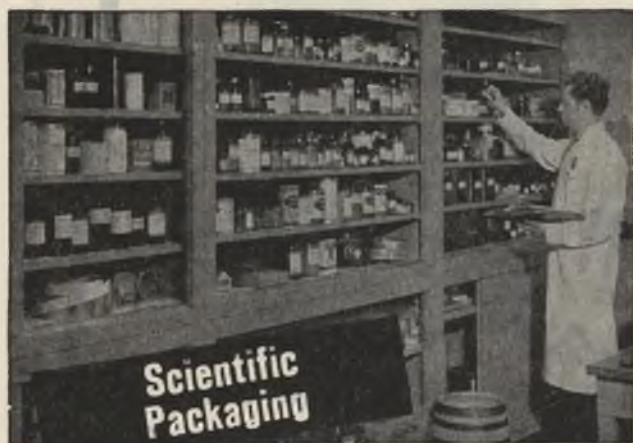
Fine chemicals for the professions and industry since 1818.

MERCK has
THE RIGHT
COMBINATION
for Laboratory Chemicals



Laboratory Control

One of the unique "Merck Cross Tables" in the Merck Analytical Laboratories.



Scientific Packaging

A corner of the Merck Packaging Laboratory.



Nation-Wide Distribution

Stock points strategically located from coast to coast.

MERCK & CO., Inc. Manufacturing Chemists RAHWAY, N. J.

Ind. Eng. Chem.—5-15-45

Please send me the following charts:

- Sensitivity of Qualitative Reactions
- Periodic Chart of the Elements
- Sensitivity Chart

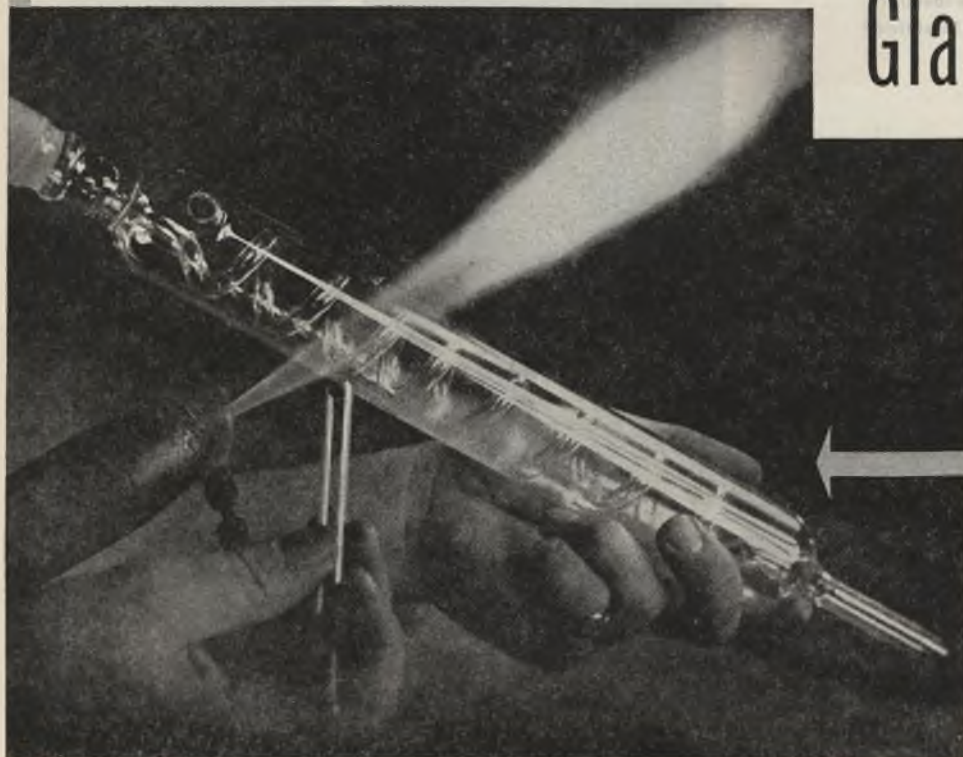
Name.....

Company..... Position.....

Street.....

City..... State.....

It Takes Years to Make a Glass Blower



There is no short course in glass blowing. You learn the long, hard way. For glass blowing is an art which requires special aptitude. In the past its secrets were handed down from father to son. Even today there are whole families of glass blowers at Corning.

All of which explains how a war can affect a lamp shop. Men and women can be taught to operate automatic machines—even lathes—overnight. But you cannot train a lamp shop craftsman in a day, a month or even a year.

War has made severe inroads on our lamp shops where the hand fabrication of laboratory glassware is performed. Well over twenty per cent of Corning's glass blowers are in military service. Few could be replaced.

However, despite such handicaps, lamp shop output has actually increased several fold. By working more shifts and longer hours, by adding new facilities and devising new ways of speeding production as much as is possible on hand work, the demands of the Armed Forces and war industries are being met.

Soon, heavy war demands may ease. Then, will you no longer have to wait, but also your requests for special apparatus can be met promptly. And to all this work, Corning can bring the new skill, the new techniques and the advanced methods, war production has added to Corning Research in Glass.

"Pyrex," "Vycor" and "Corning" are registered trade-marks and indicate manufacture by CORNING GLASS WORKS • CORNING, NEW YORK

PYREX brand LABORATORY GLASSWARE

BALANCED FOR ALL-AROUND USE

CORNING
—means—
Research in Glass



Heating Unit for Rubber Identification. Research by H. P. Burchfield*

"For Routine and Research"



Type MU-86 Crucible Furnace.

Multiple Unit Laboratory Furnaces are standard in most laboratories. In many cases, however, they are the active apparatus in industrial research programs being carried on in the search for better materials and improved processes. A case in point is the use of an MU-86 Crucible Furnace by H. P. Burchfield in his research on "Identification of Natural and Synthetic Rubbers." (*Ind. & Eng. Chem. Anly. 16,424,1944.)

*See Your Laboratory Supply Dealer
or send for Bulletin HD-639*

HEVI DUTY ELECTRIC COMPANY

LABORATORY FURNACES

TRADE MARK
MULTIPLE UNIT
 REG. U. S. PAT. OFF.

ELECTRIC EXCLUSIVELY

MILWAUKEE, WISCONSIN



**DOW CORNING, first in silicones,
is fully equipped with new plant and facilities for
the production and distribution of an expanding line of silicone products**

American industry has been quick to utilize the new Dow Corning Silicones—to see the potentialities inherent in their higher order of heat stability, chemical inertness, water resistance, and dielectric properties. Dow Corning is now supplying, directly or through selected distributors, the following silicone products:

DC FLUIDS Water-white, odorless, inert Silicone Liquids . . . notable for their low rate of viscosity change over a wide temperature range, low vapor pressure, water repellency, and good dielectric properties.

DC 993 Insulating Varnish . . . recommended because of its extreme heat stability for impregnating, coating and bonding, and waterproofing inorganic insulating materials such as asbestos, mica, and Fiberglas cloth, tape, and sleeving. Other special purpose silicone resins and compounds are available.

DC 4 Ignition Sealing Compound . . . an easily applied silicone waterproofing compound having excellent dielectric properties, corona resistance, and the consistency of petroleum jelly. It neither hardens nor melts at temperatures ranging from -40° F. to 400° F.

DC STOPCOCK GREASE A chemically resistant Silicone Grease for lubricating stopcocks and other ground glass joints.

DC 7 Special Low Temperature Compound . . . an oxidation resistant lubricant and sealing compound developed for use at temperatures as low as -70° F.

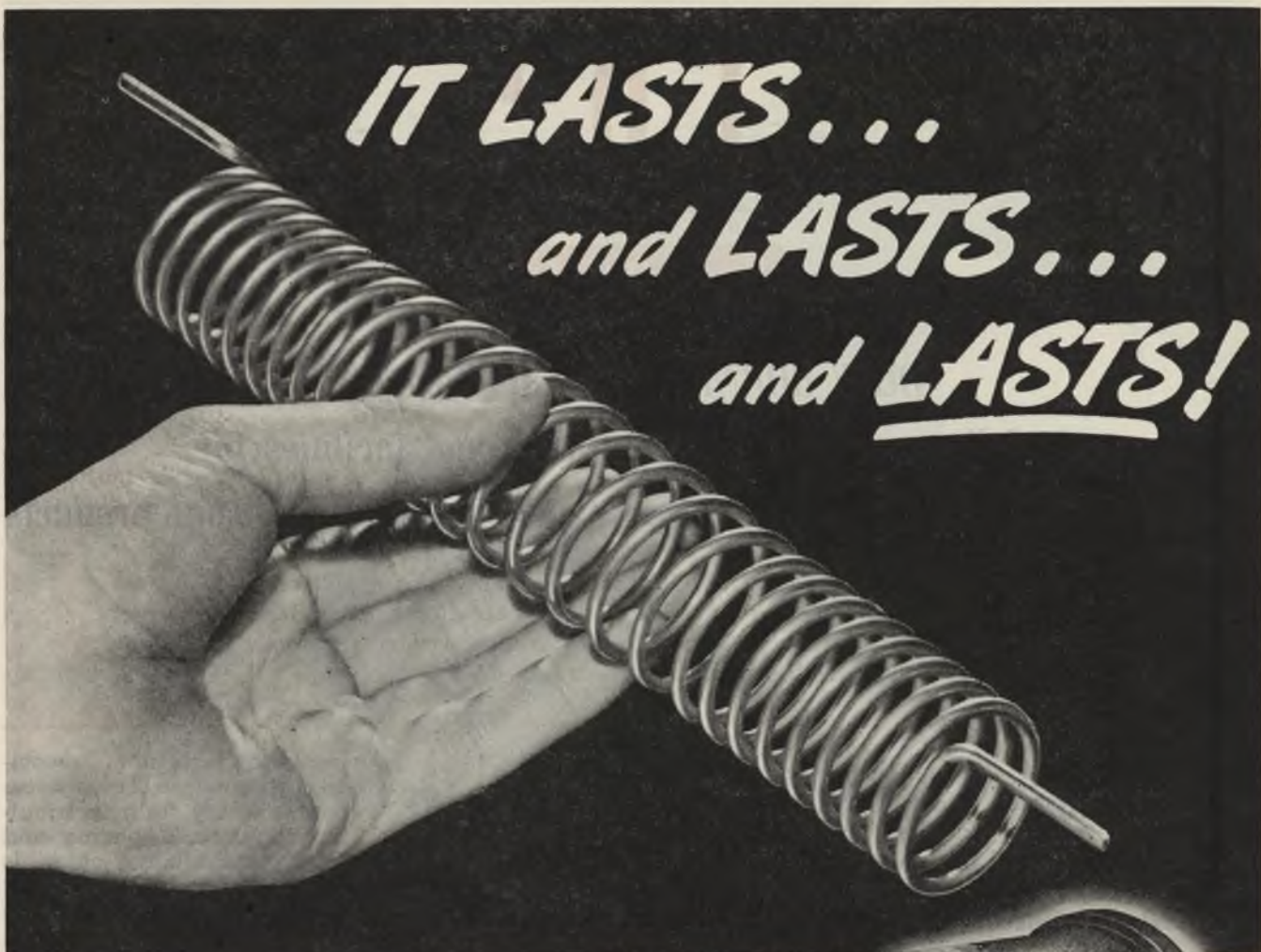
DC PLUG COCK GREASE A Silicone Grease that affords easy operation of lubricated plug valves over wide temperature ranges in most difficult services.

DC 31 A lubricating Silicone Grease for special applications in the temperature range of -70° F. to 190° F.

DC 41 A lubricating Silicone Grease for special applications where operating temperatures range from 0° F. to 400° F.

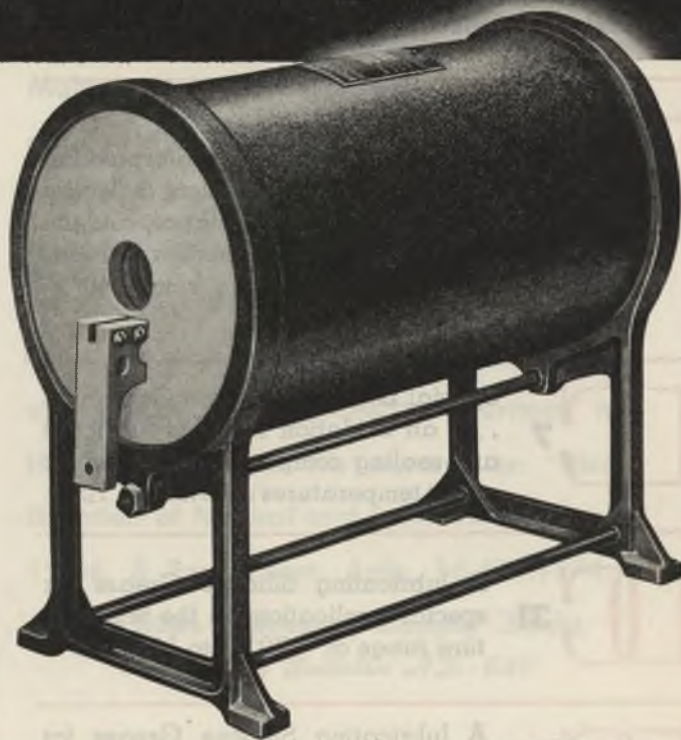
**DOW CORNING CORPORATION
MIDLAND, MICHIGAN
ADDRESS ALL INQUIRIES TO BOX 592**





IT LASTS...
and LASTS...
and LASTS!

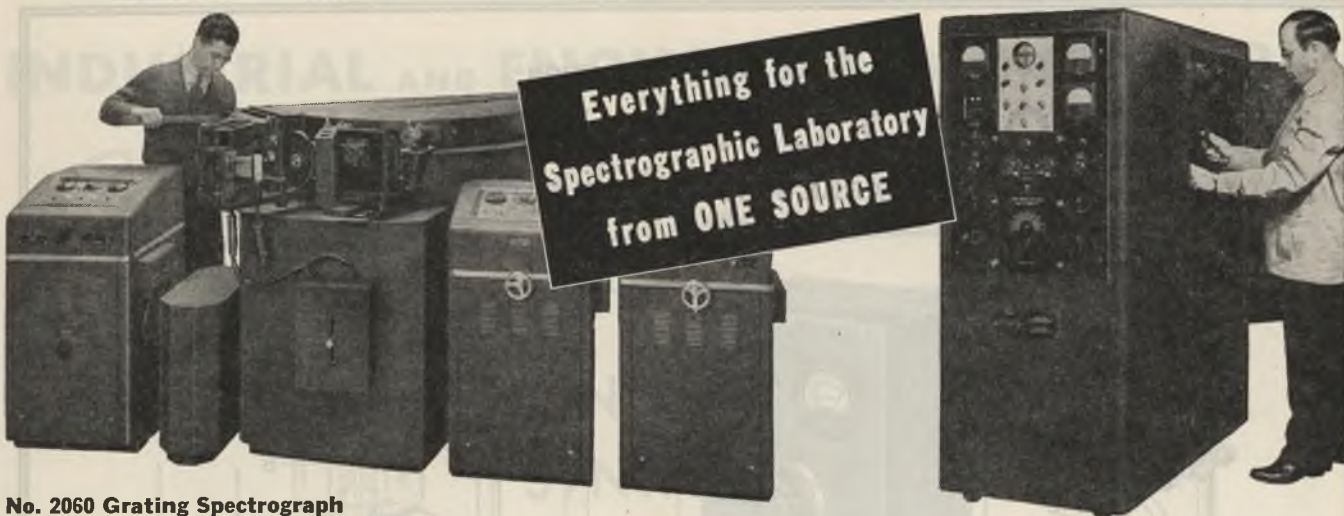
● The heating coil in this FH combustion furnace is made of 7 Gauge (.144") Chromel-A wire. That is to say, the unit is very heavy and is made of the most durable of the Nickel-Chromium alloys. In use, Chromel takes on a thin skin of oxide, which clings tenaciously to the metal, is virtually air tight—and thus acts as a protective coating for the wire against progressive oxidation. We make the wire and we make the furnace. They belong together—as a good team. A faithful combination that results in a Hoskins Combustion Furnace, that is more or less the standard, the world around. Write to your dealer or to us. . . . Hoskins Manufacturing Company, Detroit 8, Michigan.



HOSKINS PRODUCTS

ELECTRIC HEAT TREATING FURNACES • HEATING ELEMENT ALLOYS • THERMOCOUPLE AND LEAD WIRE • PYROMETERS • WELDING WIRE • HEAT RESISTANT CASTINGS • ENAMELING FIXTURES • SPARK PLUG ELECTRODE WIRE • SPECIAL ALLOYS OF NICKEL • PROTECTION TUBES





Everything for the Spectrographic Laboratory from ONE SOURCE

No. 2060 Grating Spectrograph

For unexcelled spectrum photography—available with either a 24,400 or a 36,600 line per inch original concave grating giving a linear dispersion of 6.95 and 4.64 A per mm in the first order and 3.48 and 2.32 A per mm in the second order respectively.

No. 2050 Multisource Unit

For exciting the spectra of samples and providing in one unit and in a superior manner, a virtually infinite variety of controlled types of excitation; ranging from the equivalent excitation of a high voltage spark, a high voltage A.C. arc or a D.C. arc and all intermediate cases.



No. 2380 Motor Driven Electrode Cutter and Saw

For machining carbon electrode tips to specific shapes.

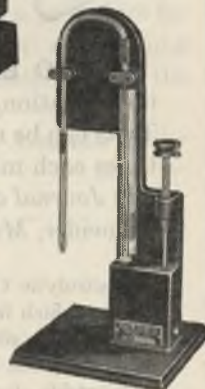


No. 2300 Developing Machine (above)

For rapid and consistent film and plate processing provided by agitation and accurate temperature control.

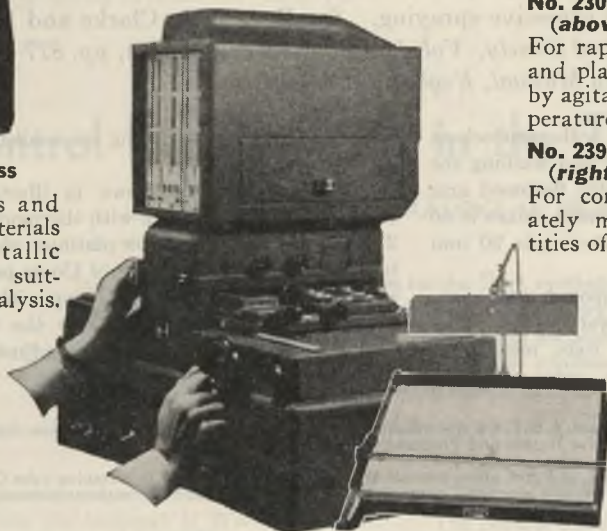
No. 2397 Micro-Pipette (right)

For conveniently and accurately measuring small quantities of solutions.



No. 3500 Briquetting Press

For briquetting borings and milled chips of metallic materials and powders of non-metallic materials into specimens suitable for spectrographic analysis.



No. 2250 Comparator-Densitometer

For convenient wavelength and density measurements—available for either film or plate spectrograms—wide range of master plates also available.

No. 2375 Calculating Board (right)

For the direct reading of sample composition from the transmission readings obtained from the Comparator-Densitometer.



No. 2351 Plate Dryer

For immediate drying of plates in from one to two minutes. Film Dryer also available.

The above spectrographic units are but a few of the many pieces of "mated" equipment offered by ARL-DIETERT. These accessories work very well not only with ARL-DIETERT Spectrographs, but also with spectrographs of other makes and types.

Whether a motor generator set is needed, a spectrograph for precise analysis, or just a few feet of graphite electrodes, ARL-DIETERT is prepared to take care of your spectrographic needs or problems in an efficient and prompt manner.



A.R.L. • DIETERT

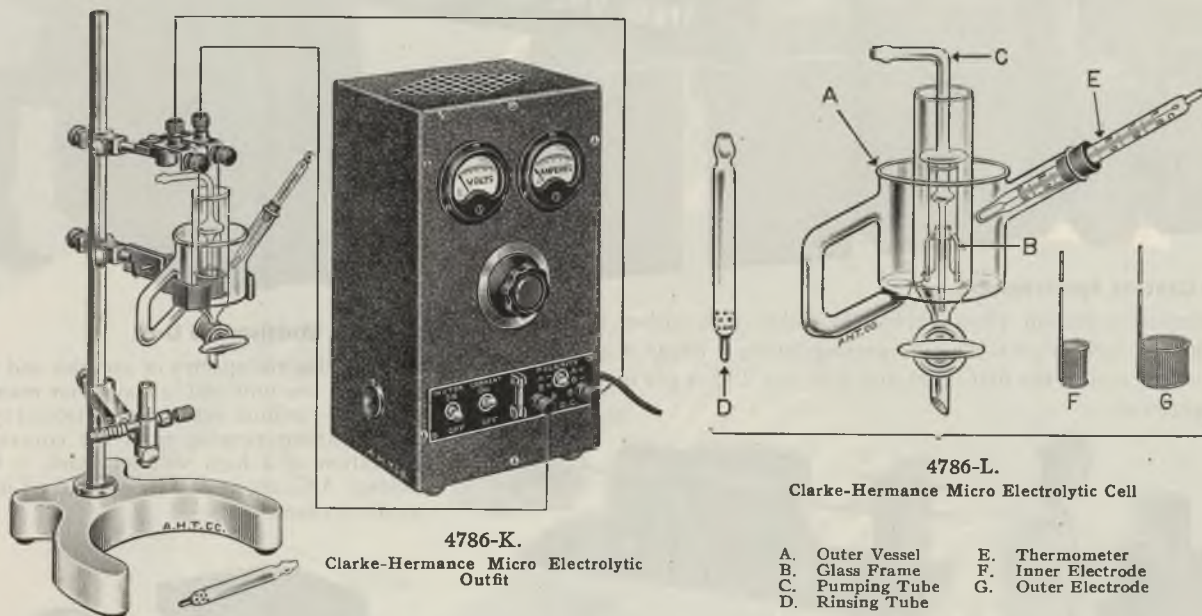
APPLIED RESEARCH LABORATORIES
4336 SAN FERNANDO RD., GLENDALE 4, CALIF.

HARRY W. DIETERT CO.
9330 ROSELAWN AVE., DETROIT 4, MICH.

A.H.T. CO. SPECIFICATION

MICRO ELECTROLYTIC OUTFIT

BASED ON CLARKE-HERMANCÉ ELECTROLYTIC CELL



4786-L.

Clarke-Hermance Micro Electrolytic Cell

4786-K.

Clarke-Hermance Micro Electrolytic Outfit

- | | |
|-----------------|--------------------|
| A. Outer Vessel | E. Thermometer |
| B. Glass Frame | F. Inner Electrode |
| C. Pumping Tube | G. Outer Electrode |
| D. Rinsing Tube | |

MICRO ELECTROLYTIC OUTFIT, CLARKE-HERMANCÉ, A.H.T. Co. Specification. For the identification, separation and determination of small quantities of metallic ions in liquid samples. Tests can be made with 4 to 5 ml of electrolyte, all of which can be forced between the electrodes several times each minute without causing excessive spraying. See Beverly L. Clarke and H. W. Hermance, *The Journal of the American Chemical Society*, Vol. 54, No. 3 (March, 1932), pp. 877-885; and Emich-Schneider, *Microchemical Laboratory Manual, English Ed. (1932)*, p. 152.

Electrolytic Cell A is water jacketed, with stopcock at bottom which facilitates draining the cell and washing the electrodes *in situ*. Jacket is supplied with flattened arm for heating the cell by a micro burner; water jacket is 50 mm outside diameter; electrode compartment is 90 mm deep \times 21 mm inside diameter.

Glass Frame B consists of superimposed and concentric glass tubes with cage-like lower section. In use the inner electrode fits inside the rods, resting on the flared base of the lower tube; the outer electrode

fits outside the rods, resting on small lugs attached to the rods.

Complete outfit as shown in illustration consists of: Electrolytic Cell complete with thermometer 0 to 110° C in 2° divisions, inner and outer platinum electrodes and rinsing tube D; Support with base of Coors porcelain and rod of aluminum alloy; Electrode Clamp with binding posts and holder; Spring-Grip Clamp for the Cell, with holder; Micro Burner with needle valve adjustment; and Power Unit complete with connecting leads.

- 4786-K. Micro Electrolytic Outfit, Clarke-Hermance, A.H.T. Co. Specification, complete outfit as shown in illustration, for use on 115 volts, a.c., but without rubber tubing connection for Burner and Pumping Tube..... 122.75
- 4786-L. Micro Electrolytic Cell, Clarke-Hermance, of Pyrex glass, consisting of Vessel A, glass frame B, pumping tube C, rinsing tube D, thermometer E, 0 to 110° C in 2° divisions, and inner and outer platinum electrodes F and G; without electrode clamp or connecting leads..... 41.25
- 4785-N. Power Unit, in ventilated sheet metal case 12 \times 7 \times 6 inches, containing dry disc rectifier, variable transformer for delivering stepless d.c. up to 5 amperes, voltmeter 0 to 10 volts, ammeter 0 to 5 amperes, extra safety fuse and switch for changing polarity of electrodes..... 70.00

More detailed information sent upon request.

ARTHUR H. THOMAS COMPANY

RETAIL—WHOLESALE—EXPORT

LABORATORY APPARATUS AND REAGENTS

WEST WASHINGTON SQUARE, PHILADELPHIA 5, U.S.A.

Cable Address "Balance," Philadelphia

ANALYTICAL CONTROL FOR AMMONIA SYNTHESIS

MODERN industry often automatically records pH, temperature, pressure, etc., for reasons of plant efficiency, and analysis of individual spot samples is commonly used in the control of an industrial process. Where process materials are gaseous or liquid, methods of continuous analysis are often possible, though these have not received the attention their importance justifies. Individual papers involving continuous analysis do not permit the analyst to include details which would enable readers to appreciate the over-all advantages and the limitations of continuous analysis.

It is for this reason that we take particular pleasure in publishing the following seven articles on "Analyti-

cal Control for Ammonia Synthesis", prepared by Earl H. Brown and co-workers at Tennessee Valley Authority, Wilson Dam, Ala. In these we have an excellent representation of development and application in this type of analysis for control of an important industrial process.

Further, to illustrate the conventional approach of the analyst in the determination of a specific compound and the compromises needed to develop a procedure for continuous recording, two articles on determining methyl bromide in air follow immediately after the group of seven.

L. T. HALLETT, *Associate Editor*

Control Requirements in the TVA Plant

EARL H. BROWN AND MAURICE M. FELGER¹

The analytical control requirements for the TVA synthetic ammonia plant are given. A description of the control laboratory and a flow sheet of the process showing the sample points are also included, with a table describing the samples analyzed, constituents determined, methods used, and frequency of determinations.

THERE has been a tremendous expansion in the production of synthetic ammonia since the outbreak of World War II. The synthetic ammonia plant of the Tennessee Valley Authority at Wilson Dam, Ala., one of the plants constructed since the beginning of the war, went into full production in September 1942. Miller and Junkins (1) have described the modern pressure-synthesis process employed and mentioned some of the methods developed for process control.

The successful operation of this process depends upon the maintenance of close, reliable analytical control. This paper describes the control laboratory and the analytical requirements for process control, while subsequent papers in this series describe methods and instruments for continuous analysis which have been developed by the TVA.

¹ Present address, Works Laboratory, General Electric Co., Fort Wayne, Ind.

DESCRIPTION OF CONTROL LABORATORY

The central control laboratory is a glass-walled room, 16 feet wide and 60 feet long, inside the main building, and is readily accessible to the plant operators. Samples for the more important determinations are brought directly to the laboratory by sample lines. There is a small laboratory in the gas plant in which analyses for the control of semi-water gas production are made.

Efficiency and convenience were emphasized in the layout and equipment of the laboratory in order to give the maximum use of the rather limited space available. The thermal conductivity cabinets and electroconductometric analyzers occupy about one third of the laboratory. One technician per shift operates and services these units. All analyses of the copper solution are made at a separate bench, and another bench is used for the preparation of reagents and for miscellaneous analyses. A bank

of three Orsat analyzers is located along one wall near the outlets of the sample lines. A bench with glass-blowing equipment is provided for the emergency repair of glass apparatus during periods when this regular service is not available. A small storeroom in the basement below the laboratory serves the immediate needs for chemicals and apparatus.

PLANT ANALYTICAL REQUIREMENTS

In the TVA ammonia plant the synthesis mixture is derived from semi-water gas by catalytic oxidation of most of the carbon monoxide with steam, and subsequent purification of the hydrogen-nitrogen mixture. In the purification process the concentration of carbon dioxide is reduced to about 0.7% by scrubbing with water at 17 atmospheres' pressure. The residual carbon monoxide and carbon dioxide are removed by scrubbing with cold ammoniacal copper solution at 121 atmospheres. The ammoniacal copper solution contains cupric ammino, cuprous ammino, ammonium, formate, and carbonate ions, and uncombined ammonia. The gas next passes through the caustic scrubbers where any remaining traces of carbon dioxide can be removed by scrubbing with sodium hydroxide solution. Actually, owing to the high efficiency of carbon dioxide removal in the water and copper scrubbers, the caustic scrubbers have not been operated. The purified hydrogen-nitrogen mixture is fed into the circulating gases of the synthesis system at a rate sufficient to replace the gas removed as ammonia and that discarded to control the concentration of inert gases.

The laboratory supplies analytical data for the control of: (1) the quality of the raw gas and of the finished product, (2) the steam-gas and hydrogen-nitrogen ratios, (3) the conversion in the water gas and synthesis converters, (4) the purification of the hydrogen-nitrogen mixture, and (5) the regeneration of the solution used for absorbing hydrogen sulfide from the semi-water gas and of the copper solution used in the final removal of oxides of carbon from the synthesis mixture.

A summary of the plant analytical requirements for the control of these factors follows. The numbers given in parentheses refer to the sample point designations shown in Figure 1. The sample points on train 1 have odd numbers while those on train 2 have even numbers, but this system does not apply where the sample point is common to the two trains comprising the TVA plant. Sample point designations, as well as the constituents determined and the methods used, are given in Table I. The determinations marked by an asterisk are made by special methods developed in the TVA research laboratories; these new developments are described in subsequent papers.

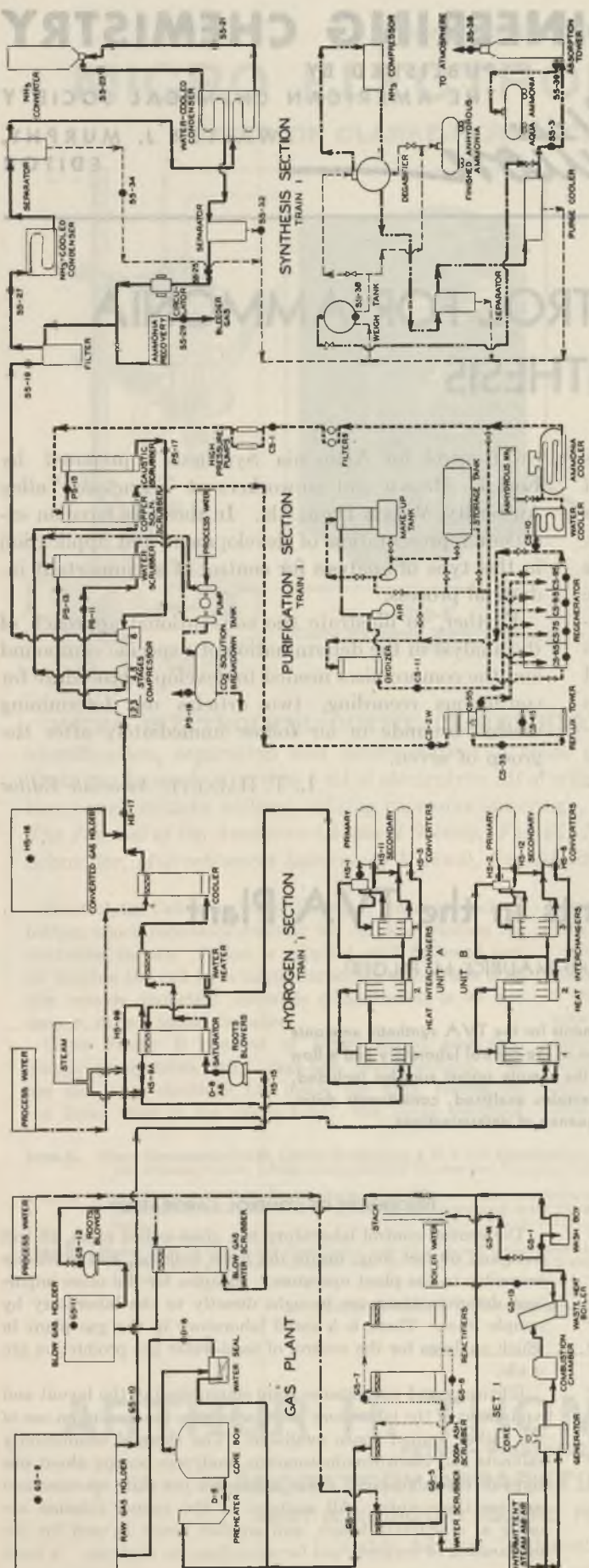


Figure 1. Process Flow Sheet Showing Location of Sample Points

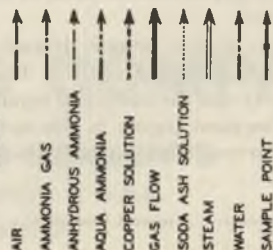


Table I. Sample Points and Analyses for Control of the Ammonia-Synthesis Process

Sample Point No.	Sample	Constituents Determined	Method	Frequency of Determination
Gas Plant				
GS-1, 2, 3, 4	Raw gas from generators Gas from blow run	N ₂ , H ₂ , CO ₂ , CO, CH ₄ , O ₂ O ₂	Orsat Orsat	Daily Every 8 hours or as required
GS-5	Raw gas to soda ash scrubber	H ₂ S	Tutweiler titration	Every 2 hours
GS-6	Raw gas from soda ash scrubber	H ₂ S	Tutweiler titration	Every 2 hours
GS-7	Soda ash solution to actifiers	HS ⁻ , SCN ⁻ , S ₂ O ₃ ⁻⁻ , total alkalinity, H ₂ S	Titration	Every week
GS-8	Soda ash solution from actifiers	Total alkalinity HS ⁻ , SCN ⁻ , HCO ₃ ⁻ , S ₂ O ₃ ⁻⁻ , CO ₃ ⁻⁻ , H ₂ S, total alkalinity	Titration	Every 2 hours
GS-9	Raw gas in holder	Specific gravity N ₂ , H ₂ , CO ₂ , CO, CH ₄ , O ₂	Hydrometer Orsat	Daily As required
GS-10	Raw gas from holder, before blow gas addition	N ₂ , H ₂ , CO ₂ , CO, CH ₄ , O ₂	Orsat	Daily (composite)
GS-11	Blow gas in holder	N ₂ , H ₂ , CO ₂ , CO, CH ₄ , O ₂	Orsat	As required
GS-12	Blow gas from holder	N ₂ , H ₂ , CO ₂ , CO, CH ₄ , O ₂	Orsat	Daily (composite)
GS-13	Boiler feed water	O ₂	Modified Winkler	Every 8 hours
GS-14, 15, 16, 17	Blast gas from stack	N ₂ , H ₂ , CO ₂ , CO, CH ₄ , O ₂	Orsat	As required
D-5	Raw gas to coke filter	Dust	Gravimetric	Daily
D-6	Raw gas from coke filter	Dust	Gravimetric	Daily
D-8AB	Raw gas, exit Roots blowers	Dust	Gravimetric	Daily
Hydrogen Section				
HS-1, 2, 3, 4	Raw gas to primary converters	Steam-gas ratio CO ₂ , CO, O ₂	Volumetric Orsat	Hourly Every 8 hours
HS-5, 6, 7, 8	Converted gas from secondary converters	H ₂ N ₂ , H ₂ , CO ₂ , CO, CH ₄ , O ₂	Thermal conductivity Orsat	Continuous Daily
HS-9, 10	Raw gas from saturator towers	Steam-gas ratio	Volumetric	Hourly
HS-11, 12, 13, 14	Gas from primary converters	CO ₂ , CO, O ₂	Orsat	Daily
HS-15	Raw gas to saturator, after blow gas addition	H ₂ N ₂ , H ₂ , CO ₂ , CO, CH ₄ , O ₂	Thermal conductivity Orsat	Continuous Every 3 days
HS-16	Converted gas in holder	N ₂ , H ₂ , CO ₂ , CO, CH ₄ , O ₂	Orsat	As required
HS-17	Converted gas to compressors	H ₂ N ₂ , H ₂ , CO ₂ , CO, CH ₄ , O ₂ N ₂ , H ₂ , CO ₂ , CO, CH ₄ , O ₂	Thermal conductivity Orsat Orsat	Continuous Every 3 days Daily (composite)
Purification Section				
PS-11, 12	Converted gas to water scrubbers	N ₂ , H ₂ , CO ₂ , CO, CH ₄ , O ₂	Orsat	As required
PS-13, 14	Gas from water scrubbers	CO, CO ₂ CO, CO ₂ , O ₂	Electrical conductivity* Orsat	Continuous Daily
PS-15, 16	Gas from copper scrubbers	CO	Electrical conductivity*	Continuous
PS-17, 18	Gas from caustic scrubbers	CO ₂	Electrical conductivity*	Continuous
PS-19	Vent gas from breakdown tank	N ₂ , H ₂ , CO ₂ , CO, CH ₄ , N ₂	Orsat	Daily (composite)
Synthesis System				
SS-19, 20	Make-up gas to synthesis	CO + CO ₂ H ₂ N ₂ , H ₂ , CH ₄	Electrical conductivity* Thermal conductivity Orsat	Continuous Continuous Every 3 days
SS-21, 22	Gas to ammonia converters	H ₂ , NH ₃ , A N ₂ + A, H ₂ , CH ₄	Thermal conductivity Orsat	Continuous Every 3 days
SS-23, 24	Gas from ammonia converters	NH ₃ NH ₃	Absorption and titration Thermal conductivity	Daily Continuous
SS-25, 26	Gas at circulators	NH ₃ , A NH ₃	Thermal conductivity* Absorption and titration	Continuous Daily
SS-27, 28	Gas to ammonia-cooled condenser	N ₂ + A, H ₂ , CH ₄ NH ₃	Orsat Absorption and titration	Daily As required
SS-29, 30	Bleeder gas	N ₂ + A, H ₂ , CH ₄ A	Orsat Thermal conductivity*	As required As required
SS-31	Purge gas from degasifier	NH ₃ N ₂ , H ₂	Absorption and titration Orsat	As required As required
SS-32, 33	Anhydrous ammonia, water-cooled condenser	NH ₃	Absorption and titration	As required
SS-34, 35	Anhydrous ammonia, ammonia-cooled condenser	Oil Water	Gravimetric Gravimetric Volumetric	As required Daily Daily
SS-36, 37	Anhydrous ammonia from weigh tanks	Oil, water	Same as SS-34, 35	As required
SS-38	Vent gas from absorption tower	NH ₃	Absorption and titration	As required
SS-39	Aqua ammonia	NH ₃	Specific gravity	As required
Copper Solution System				
CS-1	Copper solution at H.P. pump suction	NH ₃ activity Bivalent copper Cu ⁺⁺ , Cu ⁺ , CO ₂ , NH ₃ , HCOOH	Electrical conductivity* Photometric* Gravimetric and volumetric	Continuous Continuous Daily
CS-2W	Exit copper scrubber	Bivalent copper	Volumetric	As required
CS-3S	Base of reflux tower	Bivalent copper	Photometric*	Continuous
CS-4S	1st preheater, reflux tower	Bivalent copper	Volumetric	As required
CS-5S	2nd preheater, reflux tower	Bivalent copper	Photometric*	Continuous
CS-6S	1st section, regenerator	Bivalent copper	Volumetric	As required
CS-7S	2nd section, regenerator	Bivalent copper	Photometric*	Continuous
CS-8S	3rd section, regenerator	Bivalent copper	Volumetric	As required
CS-9S	4th section, regenerator	Bivalent copper	Volumetric	As required
CS-10	Low-pressure pump suction	Cu ⁺⁺ , Cu ⁺ , CO ₂ , NH ₃ , HCOOH	Gravimetric and volumetric	As required
CS-11	From oxidizing tower	Cu ⁺⁺ , Cu ⁺ , CO ₂ , NH ₃ , HCOOH	Gravimetric and volumetric	As required

* Special methods developed in TVA research laboratories.

GAS PLANT. Coke is analyzed for carbon, sulfur, and ash; the fusion point of the ash also is determined. Boiler water (GS-13) is analyzed in connection with the treatment to minimize boiler corrosion.

Raw gas is produced by blowing steam first up and then down through a hot bed of coke until the bed cools; air is then blown through the bed until the coke reaches the proper temperature for the repetition of the steam cycle. (A portion of the gas produced on the air blast is used to adjust the nitrogen content of the raw gas.) Gas samples from the various phases of the cycle, up-steam, back-steam, and blow runs, are analyzed (GS-1, 2, 3, and 4) for hydrogen, nitrogen, carbon dioxide, carbon monoxide, methane, and oxygen in order to check the quality of the gas produced.

The raw gas is passed through a water scrubber, where it is cooled and part of the dust and coke breeze is removed, and then

through a soda ash scrubber to remove the hydrogen sulfide produced as a by-product in the gas-production cycle. The gas entering (GS-5) and leaving (GS-6) the hydrogen sulfide absorber is analyzed for hydrogen sulfide to determine the completeness of removal. After absorption of the hydrogen sulfide, the soda ash solution is regenerated by blowing air through it in the two actifier towers. Adjustment of the composition of the solution is controlled by the analysis of samples taken at the entrance (GS-7) and the exit (GS-8) of the actifier towers.

The raw gas from the hydrogen sulfide absorbers contains considerable dust, most of which must be removed to prevent excessive clogging of the hydrogen plant catalyst beds. This dust is removed by passage through a coke filter. Samples taken at the entrance (D-5) and the exit (D-6) of the coke filter and at the entrance to the hydrogen system (D-8AB) are analyzed for dust as a check on the operation of the filter and of the gas generators.

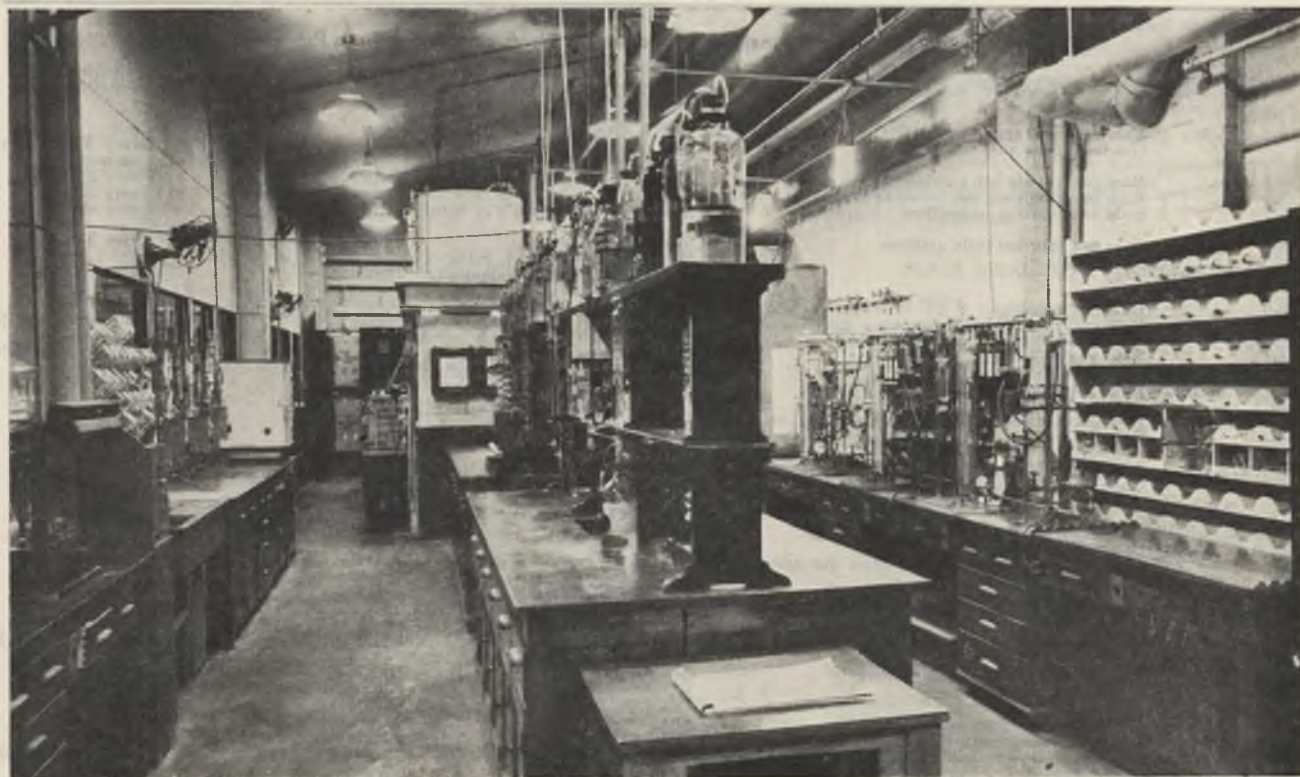


Figure 2. General View of Control Laboratory

HYDROGEN PLANT. The hydrogen-nitrogen ratio in the raw gas is maintained slightly above 3 to 1 by proper operation of the gas-production cycle at the gas plant. The final adjustment to a ratio of 3 to 1 is made after the gas has passed through the raw gas holder on its way to the hydrogen plant by adding the required amount of blow gas (GS-12), which is high in nitrogen. This blow gas is obtained from the blow gas holder in which part of the gas produced on the blow runs at the gas generators is stored. The amount of blow gas to be added is determined by continuous analyses for hydrogen at several points in the hydrogen and synthesis systems (HS-5, 6, 7, 8, 15, and 17; SS-19, 20, 21, and 22).

After adjustment of the hydrogen-nitrogen ratio, the raw gas is passed through hot water in the saturator tower where it is diluted by about one volume of steam per volume of gas (HS-9 and 10). The ratio of steam to gas is then further increased to about 3 to 1 by the addition of the proper amount of live steam. The steam-gas ratio is determined frequently (HS-1, 2, 3, and 4), since rapid fluctuations may result from changes in gas flow rate or steam pressure. The steam-gas mixture then passes successively through two catalyst chambers in which the steam and carbon monoxide react to form hydrogen and carbon dioxide. The converted gases leaving the primary (HS-11, 12, 13, and 14) and the secondary (HS-5, 6, 7, and 8) converters are analyzed for carbon monoxide and carbon dioxide to determine the operating efficiency of the catalyst.

PURIFICATION SYSTEM. The converted gas leaving the hydrogen plant contains large amounts of carbon dioxide and some unconverted carbon monoxide, both of which must be removed. Most of the carbon dioxide is removed by passing the gas under pressure through a water scrubber. The carbon dioxide content of the effluent gas (PS-13 and 14) is determined continuously, and the results are used in control of the amount of water pumped to the scrubbers. The water from the scrubbers is released to atmospheric pressure in a breakdown chamber, and the gas released (PS-19) is analyzed for carbon dioxide, hydrogen, and nitrogen to determine the amount of hydrogen and nitrogen lost by solution in the scrubbing water.

After passing through the water scrubber, the gas is further compressed and is passed through the copper scrubber, where the unconverted carbon monoxide and residual carbon dioxide are removed by absorption in ammoniacal copper solution. Since it is very important that no appreciable amount of the oxides of carbon enter the synthesis system, the gas from the copper scrubber is analyzed continuously for these oxides at several points (PS-15, 16, 17, and 18; SS-19 and 20). The gas entering the scrubber

is also analyzed continuously for carbon monoxide (PS-13 and 14); the results are used to determine the rate of circulation of copper solution necessary to ensure complete absorption.

SYNTHESIS SYSTEM. Gases in the synthesis system circulate through a converter, where part of the hydrogen-nitrogen mixture is converted to ammonia; through two condensers, where most of the ammonia produced is liquefied and removed from the system; and through a filter, where the make-up gas from the purification system is added. The circulating gas is analyzed continuously (SS-21, 22, 23, 24, 25, and 26) to check the efficiency of the converter and condensers.

Argon and methane, minor constituents of the raw gas, are not removed in any of the plant processes and their concentration builds up in the circulating synthesis gas. Therefore, sufficient gas is bled to the atmosphere to hold the concentration of these inert gases below a fixed value. Analyses for argon and methane are made (SS-21, 22, 25, 26, and 30) to determine the amount of gas to be bled.

The ammonia liquefied in the condensers collects in separators and goes into storage tanks. Analyses for oil and water are made (SS-32, 33, 34, and 35) to determine the quality of the product.

COPPER REGENERATION SYSTEM. The principal constituents of the copper solution used in the purification system are bivalent and monovalent copper, ammonia, formic acid, carbon dioxide, and water. The carbon dioxide and carbon monoxide absorbed in the scrubbers are removed by circulating the solution through a regeneration system at an elevated temperature. Some unavoidable loss of ammonia by evaporation and formic acid by decomposition also occurs. Periodic analyses of the copper solution are made (CS-1) to determine the magnitude of these changes in composition, so that proper adjustments can be made. The effective ammonia content (ammonia activity) is determined continuously (CS-1).

The copper in the solution is present both as cupric and cuprous amino complex ions. The cuprous complex ion absorbs carbon monoxide, and the cupric complex ion prevents precipitation of metallic copper. A continuous analysis for the bivalent copper content is made at four points in the regeneration system (CS-1, 3, 5, and 7). These analyses are used to determine the amount of air and the temperature to be used in the oxidation of the copper.

LITERATURE CITED

- (1) Miller, A. M., and Junkins, J. N., *Chem. & Met. Eng.*, 50, No. 11, 119-25, 152-5 (1943).

Determination of Oxides of Carbon in Hydrogen-Nitrogen Mixtures

Continuous Determination of Minute Concentrations by Electroconductivity

EARL H. BROWN AND MAURICE M. FELGER

An electroconductometric analyzer for the continuous, separate, or simultaneous determination of carbon dioxide and carbon monoxide in concentrations of 0 to 100 p.p.m. in hydrogen-nitrogen mixtures and the application of the analyzer to the analytical control of the TVA synthetic ammonia plant are described. An absorption-conductivity cell of new design and a recording alternating current Wheatstone bridge are employed. Carbon monoxide, after oxidation by an improved iodine pentoxide reagent, is determined as carbon dioxide. Full operating details are given.

THE gas-purification system of the TVA synthetic ammonia plant has been described by Miller and Junkins (13). The present paper describes in detail the method by which the purity of the synthesis mixture is controlled with respect to the oxides of carbon.

The hydrogen-nitrogen mixture produced by the catalytic reaction of semi-water gas with steam contains a large concentration of carbon dioxide and a small concentration of unconverted carbon monoxide. These oxides of carbon are removed by passing the converted semi-water gas through two scrubbing towers under pressure. In the first tower, water removes about 98% of the carbon dioxide, and in the second, ammoniacal copper solution reduces the concentration of each oxide to 5 p.p.m. or less. Since both carbon dioxide and carbon monoxide poison the synthesis catalyst, it is necessary to have a continuous and rapid indication of their concentrations, so that gas containing harmful concentrations may be vented and corrective measures taken. For analytical control purposes, an analyzer was desired for the

continuous, separate, or simultaneous determination of carbon dioxide and carbon monoxide in concentrations of 0 to 100 p.p.m.

Berger and Schrenk (4) described completely various methods for the detection and determination of carbon monoxide. Only two of these methods appear practical for the continuous determination of low concentrations of carbon monoxide in large concentrations of hydrogen. The Bureau of Mines (12) developed an analyzer for the determination of small concentrations of carbon monoxide in air by measurement of the temperature increase resulting from the oxidation of the carbon monoxide in the presence of the catalyst Hopealite. The analyzer was found suitable for the determination of carbon monoxide in hydrogen (12), provided the sample was diluted with a small, fixed proportion of air prior to its introduction into the apparatus. This method was not suitable for application to ammonia-synthesis gas, however, because it was not adaptable to the determination of carbon dioxide.

Methods based on the oxidation of carbon monoxide by iodine pentoxide are numerous (1, 3, 9, 10, 11, 14, 15, 17, 18). The concentration of carbon monoxide is calculated from the quantity of carbon dioxide formed or iodine liberated by a given volume of gas. The quantity of iodine liberated is determined by absorption in potassium iodide solution and titration with sodium thiosulfate. The carbon dioxide generally is absorbed in an alkaline solution and the quantity determined by titration or other methods.

In Baldewyns' method (2) the gas sample is passed through a purification and oxidation train in which the carbon monoxide is oxidized with iodine pentoxide. The resulting carbon dioxide is then passed into an electrolytic cell containing a definite volume of 0.005 *N* barium hydroxide solution. This cell and a reference cell containing barium hydroxide solution of the same concentration are made the arms of a Wheatstone bridge with a Kohlrausch slide-wire as the indicating instrument. The concentration of carbon monoxide is determined from the bridge readings and the volume of gas used. The instrument is calibrated empirically.

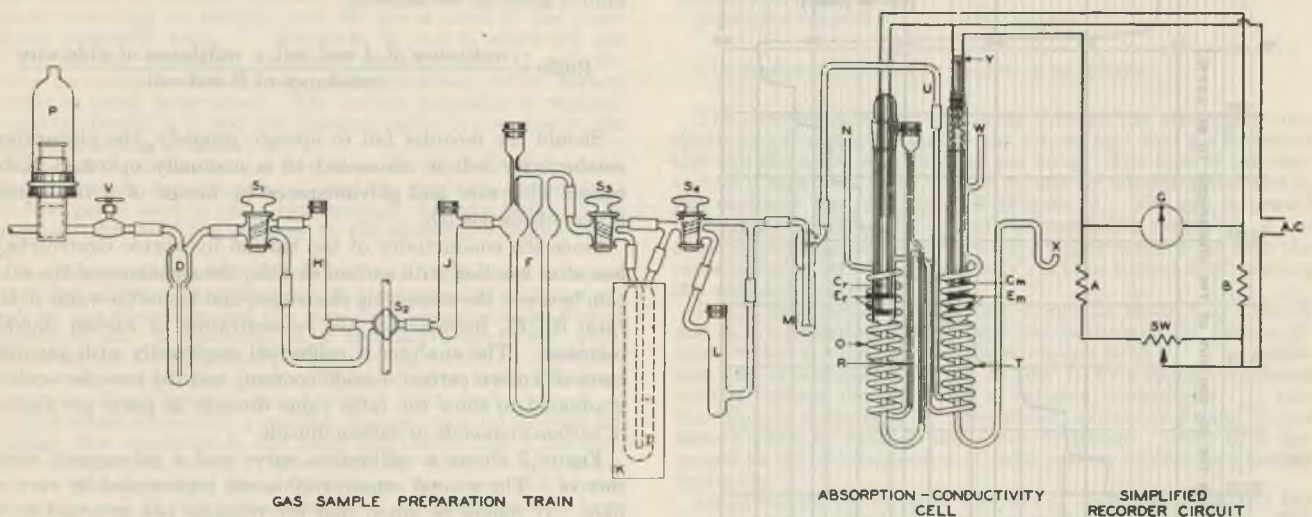


Figure 1. Carbon Monoxide Analyzer

- | | | | |
|--|--|--|--|
| A. A end coil | F. Flowmeter | M. KI scrubber | SW. Slide-wire |
| B. B end coil | G. Galvanometer | N. Electrolyte inlet | T. Gas absorption coil |
| C _m . Measuring electrode chamber | H. KOH-Ascarite tube | O. Temperature stabilizing coil | U. Gas inlet to cell |
| C _r . Reference electrode chamber | I. I ₂ O ₅ tube | P. Pressure stabilizer | V. Gas flow regulating valve |
| D. H ₂ SO ₄ scrubber | J. P ₂ O ₅ tube | R. Electrolyte flow regulator | W. Gas exit |
| E _m . Measuring electrodes | K. I ₂ O ₅ furnace | S ₁ , S ₂ , S ₄ . By-pass stopcocks | X. Constant-level electrolyte overflow |
| E _r . Reference electrodes | L. KOH-Ascarite tube | | Y. Electrode adjusting screw |

This electroconductivity method was adapted to the continuous determination of carbon monoxide in hydrogen-nitrogen mixtures in the production of synthetic ammonia (8). The train was modified by the addition of a by-pass arrangement, so that carbon monoxide and carbon dioxide could be determined singly or together. A recording alternating current Wheatstone bridge was used for indicating and recording the ratios of the resistance of the measuring cell to the resistance of the reference cell. This method has the obvious disadvantage that it does not give a direct indication of the concentration, because the continuous use of the same electrolyte gives a progressively higher bridge reading. The concentration of carbon monoxide at any given time is calculated from the slope of the curve drawn by the recorder.

An electroconductometric analyzer for the continuous determination of carbon dioxide in gas mixtures, which employs a continuous flow of both gas and electrolyte through the absorp-

tion-conductivity cell as well as a recording Wheatstone bridge, is described by Smith (16). The White (19) aspirator method is used to control the ratio of gas flow to electrolyte flow. This cell has two disadvantages: (1) it is neither rugged nor compact, and (2) the accuracy of the gas-electrolyte ratio is seriously impaired if the apparatus is subjected to vibration (16).

As none of these methods appeared entirely satisfactory for continuous control of the purity of the synthesis mixture in the ammonia plant, the method described below was developed and applied to the control of the TVA ammonia plant.

OPERATING PRINCIPLE

The analyzer developed consists of a preparation train, an absorption-conductivity cell, and an indicating and recording alternating current Wheatstone bridge. The preparation train removes traces of interfering gases and its construction is such that, by the proper adjustment of stopcocks, the analyzer may be used to determine carbon dioxide, carbon monoxide, or total carbon dioxide and carbon monoxide. The carbon monoxide is oxidized by an iodine pentoxide reagent and determined as carbon dioxide. In the absorption-conductivity cell the electrolyte, 0.001 *N* barium hydroxide, flows past a pair of reference electrodes, meets and reacts with the carbon dioxide in the gas, and then flows past a pair of measuring electrodes.

The rates of gas and electrolyte flow, as well as the temperature of the absorption-conductivity cell, are maintained constant. Thus, the resistance of the electrolyte between the reference electrodes, R_r , remains constant, while the resistance of the solution between the measuring electrodes, R_m , varies with the concentration of carbon dioxide. The electrode pairs are approximately the same size and shape. The distance between the measuring electrodes is adjusted so that the ratio R_m/R_r is 1.0 when the concentration of carbon dioxide is 0. The electrode pairs serve as the arms of a recording alternating current Wheatstone bridge, as shown in Figure 1. In this circuit the *A* and *B* end coils have the same resistance, and a jumper is connected between the alternating current source and the *B* end-coil end of the slide-wire. Thus the bridge gives a linear indication of the ratio R_m/R_r with the ratio 1.0 at the zero end of the recorder scale. The upper limit of the recorder indication depends on the relative resistances of the end coils and the slide-wire. This limit is given by the formula:

$$\text{Ratio} = \frac{\text{resistance of } A \text{ end coil} + \text{resistance of slide-wire}}{\text{resistance of } B \text{ end coil}}$$

Should the recorder fail to operate properly, the absorption-conductivity cell is connected to a manually operated Kohlrausch slide-wire and galvanometer by means of a triple-pole, double-throw switch.

Since the conductivity of the barium hydroxide electrolyte is less after reaction with carbon dioxide, the resistance of the solution between the measuring electrodes, and hence the value of the ratio R_m/R_r , increases as the concentration of carbon dioxide increases. The analyzer is calibrated empirically with gas mixtures of known carbon dioxide content, and the recorder scale is graduated to show the ratio value directly as parts per million of carbon monoxide or carbon dioxide.

Figure 2 shows a calibration curve and a subsequent check thereof. The several concentrations are represented by vertical lines. It should be noted that the recorder pen returned to its original position when the carbon dioxide of the test gas was reduced to zero.

The accuracy of the method depends on the accuracy of the accepted value for the carbon dioxide content of air which was employed for the calibration.

Frequent checks indicate a precision of at least 3 p.p.m. over the range indicated.

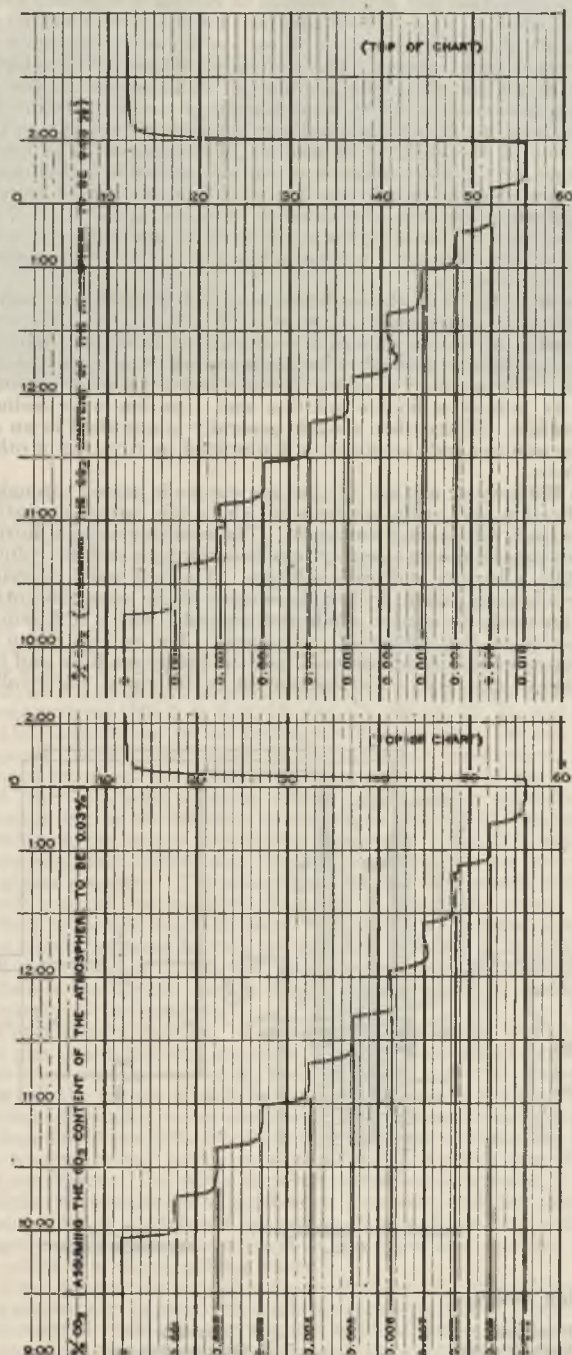


Figure 2. Calibration of Cell

Above. First run. Below. Check run. Test gas, mixtures of air and nitrogen. Electrolyte, 0.001 *N* barium hydroxide

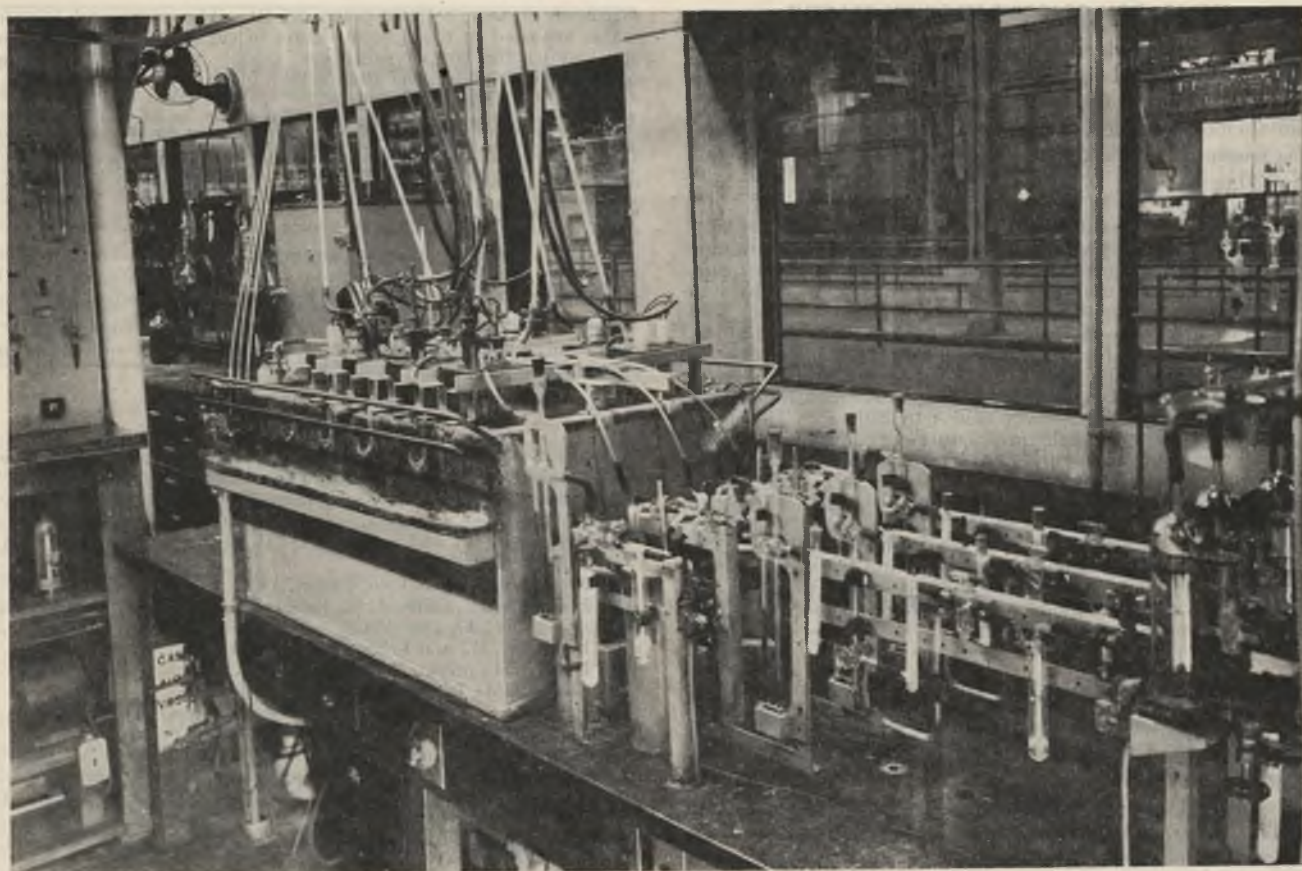


Figure 3. Electroconductometric Gas Analyzers

The complete analyzer is shown in Figure 1. The pressure stabilizer, *P* (6), gives a constant operating pressure and is adjusted so that the rate of leakage around the piston reduces the time lag in the sample line to 15 seconds or less. Valve *V* and flowmeter *F* are used to regulate the rate of gas flow through the train. The sulfuric acid scrubber, *D*, removes the ammonia picked up by the gas from the ammoniacal copper solution. The potassium hydroxide-Ascarite tube, *H*, removes any carbon dioxide that may be present, and the gas is dried in the phosphorus pentoxide tube, *J*. Stopcocks *S*₁ and *S*₂ allow the gas to by-pass the potassium hydroxide-Ascarite tube, *H*, and the iodine pentoxide oxidation tube, *I*, respectively, when carbon dioxide is being determined. The carbon monoxide is oxidized to carbon dioxide in *I*, and the liberated iodine is absorbed in the potassium iodide scrubber, *M*.

Stopcock *S*₄ allows the gas flow to be diverted through potassium hydroxide-Ascarite tube, *L*, and the resulting carbon dioxide-free gas is used in the adjustment of the zero point of the analyzer. From *M* the gas goes to the absorption-conductivity cell.

The absorption-conductivity cell is both rugged and compact and is not affected by vibration. It is constructed of Pyrex except for the electrodes and the wire used to regulate the flow of electrolyte and is operated in a constant-temperature bath. The electrodes are platinized platinum rings, 15 mm. in diameter, 5 mm. wide, and 0.2 mm. thick. The electrolyte, 0.001 *N* barium hydroxide, flows from a constant-head feed tank through *N* to coil *I* where it comes to a constant temperature, up through the capillary flow regulator, *R*, and down into the bottom of the electrode chamber, *C*_r, where it flows past the reference electrodes, *E*_r. As the electrolyte flows from *C*_r to the lower end of the absorption coil, *T*, it is joined through *U* by the gas stream from the preparation train. The carbon dioxide and electrolyte react while rising through *T* and pass into the electrode chamber, *C*_m. The gas leaves at the exit tube, *W*, and the electrolyte flows past the measuring electrodes, *E*_m, and leaves the cell through the overflow tip, *X*.

OPERATING PROCEDURE

Operating conditions for the analyzer for determination of minute concentrations of carbon monoxide and carbon dioxide are:

Electrolyte	0.001 <i>N</i> barium hydroxide
Electrolyte flow rate	15 ml. per minute
Gas flow rate	8 liters per hour
Electrode spacing	About 25 mm.
Cell temperature	Constant; between 28° and 32° C.
Bridge end-coil resistance	600 ohms
Bridge slide-wire resistance	60 ohms
Temperature of iodine pentoxide reagent	100° to 105° C.

The analyzer is placed in operation as follows:

The electrolyte is started flowing through the absorption-conductivity cell at approximately the correct rate, and gas is started through the analyzer at 8 liters per hour. The flow of the electrolyte is regulated to 15 ml. per minute by adjusting the wire in the capillary flow regulator, *R* (Figure 1). The gas is passed through absorption tube *L*, and the measuring electrodes of the absorption-conductivity cell are adjusted by screw *Y*, so that the recorder indicates zero. Stopcock *S*₁ is then turned 180°, placing the analyzer in operation.

In the determination of carbon monoxide alone, stopcocks *S*₁ and *S*₂ are turned so that the gas passes through the carbon dioxide-removal tube, *H*, and the oxidation tube, *I*. The oxidation tube is maintained at 100° to 105° C. by a small, cylindrical electric furnace controlled by a variable transformer. If carbon dioxide alone is to be determined, stopcocks *S*₁ and *S*₂ are turned 180°, so that *H* and *I* are by-passed. Only *H* is by-passed in the determination of total carbon dioxide and carbon monoxide.

Daily checks are made of the rate of electrolyte flow and the recorder zero, and adjustments are made when necessary. The activity of the iodine pentoxide reagent is checked daily by determining the response of the recorder to injections of known volumes of carbon monoxide; exit gas from the water scrubbers (about 2% carbon monoxide) is introduced into the analyzer by means of the special cross-bore stopcock, *S*₂ (5). The 10% potassium iodide solution requires replacement about every third day, but the reagents in the other units of the train retain their activity 3 to 4 weeks. The 0.001 *N* barium hydroxide electrolyte is standardized by electroconductance.

PREPARATION OF IODINE PENTOXIDE REAGENT

The iodine pentoxide reagent must completely oxidize low concentrations of carbon monoxide at comparatively low temperatures in the presence of about 75% hydrogen and in addition must maintain its activity for a long period. The following procedure, using reagent-grade chemicals, gives a reagent that has an active life of 30 to 40 days.

Seventy grams of calcined, crushed insulating brick (Armstrong A-25; -9 +14 mesh) are added to a solution containing 100 grams of iodine pentoxide and 4 grams of vanadium pentoxide. The mixture is evaporated to dryness over a steam bath, with frequent stirring during the latter part of the evaporation. This material is then oven-dried for several hours at 125° to 130° C. The oxidation tube, which holds about 50 grams, is filled with the oven-dried reagent and placed in the activation train. Activation is accomplished by passing purified air through the sample as the temperature is gradually raised to 220° C. The air is purified by passage through three scrubbers containing concentrated sulfuric acid, solid potassium hydroxide pellets, and phosphorus pentoxide, respectively. The reagent is maintained at 220° C. for about 8 hours and is allowed to cool in a current of purified air, after which it is ready for use or for temporary storage. The tube must be tightly sealed during storage. The activated reagent has a bright orange color and the spent reagent a brown color. The spent reagent is prepared for re-use by suspending it in water, evaporating to dryness, oven-drying, and activating as previously described.

APPLICATION TO PLANT CONTROL

Two complete analyzers are required to serve the two production trains in the TVA ammonia plant. Figure 3 shows the control laboratory installation of analyzers (except for control desk and recorders) for the determination of low concentrations of carbon dioxide, carbon monoxide, or mixtures of the two in the purified hydrogen-nitrogen mixture from one production train.

At the left is the constant-temperature bath containing the absorption-conductivity cells. To the right, at the end of the bath, are the preparation trains. The short (front) train is used in the determination of carbon dioxide in the gas from the caustic scrubber, sample point PS-17 (see flow sheet in 7 for specified sample points), and the second train is used to determine total carbon dioxide and carbon monoxide in the make-up gas to the

synthesis system, sample point SS-19. The third and fourth trains are used in the determination of carbon monoxide in the gas leaving the copper scrubbers, sample point PS-15; while one train is in service, the other is kept in stand-by condition.

This system of analytical control has been in operation for more than 2 years in the TVA ammonia plant and has proved very effective in preventing poisoning of the synthesis catalyst by oxides of carbon.

ACKNOWLEDGMENT

The authors express their appreciation to the staff of the control laboratory, especially to R. Bowen Howard, Jr., for the cooperation received in the installation and initial operation of these analyzers.

LITERATURE CITED

- (1) Am. Gas. Assoc., "Gas Chemists' Handbook", pp. 289-95, New York, Chemical Publishing Co., 1929.
- (2) Baldewyns, Joseph, *Congr. pharm. Liège*, 1935, 183-5 (1934).
- (3) Bech, A., *Ann. hyg. publ. ind. sociale*, 1933, 376-80.
- (4) Berger, L. B., and Schrenk, H. H., U. S. Bur. Mines, *Tech. Paper 582* (1938).
- (5) Brown, E. H., *IND. ENG. CHEM., ANAL. ED.*, 14, 551 (1942).
- (6) Brown, E. H., Cline, J. E., Felger, M. M., and Howard, R. B., Jr., *Ibid.*, 17, 280 (1945).
- (7) Brown, E. H., and Felger, M. M., *Ibid.*, 17, 273 (1945).
- (8) Dely, J. G., private communication.
- (9) Edell, G. M., *IND. ENG. CHEM.*, 20, 275 (1928).
- (10) Graham, J. I., and Winnill, T. F., *J. Chem. Soc.*, 105, 1996-2003 (1914).
- (11) Haldane, J. S., and Graham, J. J., "Methods of Air Analysis", pp. 116-29, London, J. B. Lippincott Co., 1935.
- (12) Katz, S. H., Reynolds, D. A., Frevert, H. W., and Bloomfield, J. J., U. S. Bur. Mines, *Tech. Paper 355* (1926).
- (13) Miller, A. M., and Junkins, J. N., *Chem. & Met. Eng.*, 50, No. 11, 119-25, 152-5 (1943).
- (14) Romashechenko, V. A., *Zavodskaya Lab.*, 9, 912-13 (1940); *Chem. Zentr.*, 1942, I, 2957.
- (15) Seidell, J. A., *J. IND. ENG. CHEM.*, 6, 321-3 (1914).
- (16) Smith, A. S., *IND. ENG. CHEM., ANAL. ED.*, 6, 293-5 (1934).
- (17) Teague, M. C., *J. IND. ENG. CHEM.*, 12, 964-8 (1920).
- (18) Vandaveer, F. E., and Gregg, R. C., *IND. ENG. CHEM., ANAL. ED.*, 1, 129-33 (1929).
- (19) White, E. C., *J. Am. Chem. Soc.*, 50, 2148-54 (1928).

Continuous Determination of Ammonia Activity in Ammoniacal Solutions

EARL H. BROWN, JAMES E. CLINE, MAURICE M. FELGER, AND R. BOWEN HOWARD, JR.

IN THE TVA synthetic ammonia plant, an ammoniacal "copper solution" (3) is employed for the removal of harmful impurities, such as carbon monoxide, carbon dioxide, and oxygen, from the synthesis gas. The solution contains cupric ammino, cuprous ammino, ammonium, formate, and carbonate ions, as well as uncombined ammonia. There is a range of concentrations of uncombined ammonia below which the removal of carbon dioxide from the synthesis gas is incomplete and above which the loss of ammonia is excessive during regeneration of the copper solution. The uncombined ammonia is an important factor also in maintaining the copper complexes necessary for the complete removal of carbon monoxide. The concentration of uncombined ammonia cannot be calculated accurately from chemical determinations of the components in the copper solution, however, for there are several equilibria involved which have not yet been determined precisely.

An empirical formula based on five analytical determinations—total ammonia, formic acid, carbon dioxide, and monovalent and bivalent copper—was employed, prior to the development of the present method, to give a value related to uncombined ammonia for plant control. The utilization of the empirical formula had several disadvantages. Values with no strong theoretical foundation were obtained, many analytical determinations were necessary, and considerable time was required before the results could be reported to the plant operators. This paper describes the development and application of an instrument that gives rapid and continuous information regarding the uncombined ammonia in the copper solution.

THEORETICAL CONSIDERATIONS

The thermodynamic activity of ammonia was selected as the function of the uncombined ammonia to be determined, because

A method for the automatic, continuous determination of the thermodynamic activity of ammonia in ammoniacal solutions is based on the linear relationship between ammonia activity and vapor pressure of ammonia over the solution. A constant flow of inert gas is brought to equilibrium with the flowing solution at a given temperature and the concentration of ammonia in the saturated gas is determined. The ammonia activity is an important factor in maintaining the efficiency of the ammoniacal copper solution used in the TVA ammonia plant for absorbing the oxides of carbon and other harmful impurities from the synthesis gas.

The activity is easily measured and is directly related to the effect of the ammonia on any equilibrium of components in the copper solution. The concept of activity was introduced by Lewis and Randall (2). In an ideal solution the activity is equal to the concentration, and either can be used for calculating equilibrium constants, partial molal free energies, or other thermodynamic functions. In any solution, ideal or nonideal, at a given temperature the activity of a component is defined by the equation:

$$a = f/f^\circ \quad (1)$$

where a is the activity of the component in solution; f , the fugacity of the component in the vapor phase in equilibrium with the solution; and f° , the fugacity of the component in the vapor phase in equilibrium with the standard state. The standard state often is taken to be the pure liquid component. To simplify the calibration procedure, however, the ammonia activity in a normal ammonium hydroxide solution was set as unity in this work. Activity referred to any other standard state can be calculated from fugacity data.

With partial pressures of ammonia less than atmospheric, pressure can be substituted for fugacity in Equation 1 [for ammonia at 1 atmosphere and 25° C., the ratio of fugacity to pres-

sure is 0.99 (4)]. Using partial pressures and the chosen standard state, the following equation results:

$$a_{\text{NH}_3} = p/p^\circ \quad (2)$$

where a_{NH_3} is the ammonia activity of the solution; p , the partial pressure of ammonia over the solution; and p° , the partial pressure of ammonia over normal ammonium hydroxide at the same temperature. By means of Equation 2 the activity of ammonia in the copper solution can be determined directly by measurement of the partial pressure of ammonia in equilibrium with the solution.

DESCRIPTION OF APPARATUS

The basic design of the apparatus for continuous recording of the ammonia activity is shown in Figure 1. A gas, chemically inert to the copper solution, passes through a pressure stabilizer and a flowmeter at a constant rate, and becomes saturated with ammonia and other vapors as it bubbles through the copper solution in a gas saturator immersed in a thermostat. The copper solution flows through the gas saturator at a rate great enough to prevent significant alteration of the composition of the solution by loss of vapors to the gas stream. The saturated gas passes into an electroconductivity cell (1) where the ammonia is absorbed by dilute acid flowing at a constant rate. The ammonia content of the gas affects the conductivity of the acid, which is measured by a recording alternating current Wheatstone bridge (1).

The inert gas used to carry the ammonia vapor is purified synthesis gas, consisting of hydrogen, nitrogen, argon, and methane. This gas is used because of its ready availability in the control laboratory and because, by pressure scrubbing with the copper solution, it has been freed of impurities which react with the solution.

The piston-type pressure stabilizer used in this work to maintain a constant flow of inert gas operates more smoothly and reliably than the usual type, which allows gas to escape through a constant head of liquid. The piston of the stabilizer (Figure 2) fits into the cylinder with a clearance of about 0.075 mm. (0.003 inch) and is supported by the pressure of the gas within the chamber; excess gas leaks out between the piston and cylinder. Except for slight frictional losses, the pressure head of the gas in the chamber, under equilibrium conditions, is equal to the weight of the piston divided by the horizontal cross-sectional area of the chamber. When the flow of incoming gas varies, the vertical movement of the piston alters the resistance to gas leakage between the piston and cylinder and automatically stabilizes the pressure within the chamber. Because of piston inertia, a rapid change in gas flow will cause a momentary fluctuation in pressure until the piston reaches its new equilibrium position.

The shoulder on the piston serves to prevent its dropping low enough in the cylinder to interfere with the gas flow. Grooves may be placed in the piston to increase the rate of gas leakage or to enable the leaking gas to rotate the piston. Lubrication of the piston with graphite improves the operation of the stabilizer. The piston and cylinder should be made of the same metal, such as brass, to avoid variations in the fit due to difference of thermal expansion. The glass funnel connected to a vent collects the excess gas leaking past the piston. The pressure stabilizer, used in combination with a capillary flowmeter, proved satisfactory in maintaining a constant flow of inert gas through the apparatus.

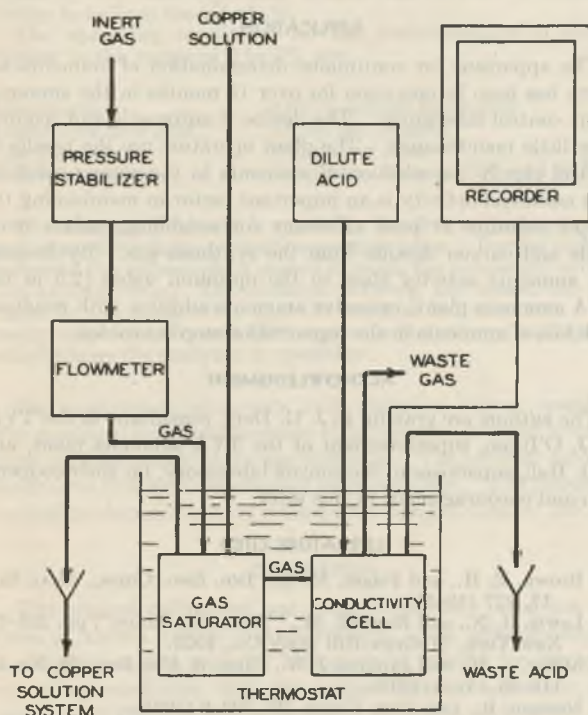


Figure 1. Schematic Diagram of Ammonia Activity Analyzer

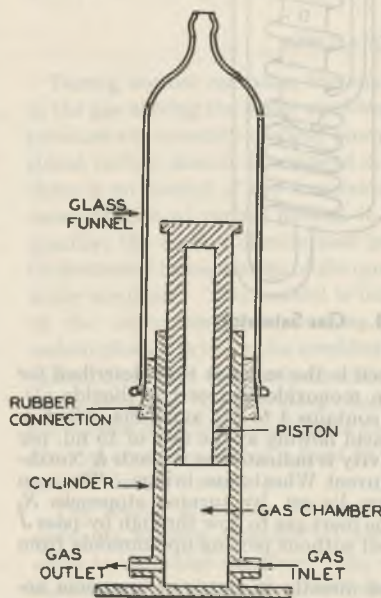


Figure 2. Pressure Stabilizer

The function of the gas saturator is to bring the gas stream and the flowing copper solution into contact long enough to establish a reproducible approach to equilibrium. The saturator must offer a constant resistance to the gas flow, in order that a constant rate of gas flow can be maintained. The type of gas saturator used is shown in Figure 3.

The copper solution flows into the apparatus at the inlet, *A*. Some of the copper solution constantly flows from *B* to an overflow tube that is set at a predetermined height to maintain a constant head.

The copper solution flows through stopcock *S*₁ at about 20 ml. per minute and is brought to the thermostat temperature in coil *C*. The solution enters the main body, *D*, of the saturator near the middle and flows out from the bottom through outlet *E*. The copper solution from *B* and *E* is returned to the plant regeneration system. The inert gas enters at *F* at about 100 ml. per minute and passes through stopcock *S*₂, through temperature stabilization coil *G*, and into the bottom of *D*. The gas becomes saturated with ammonia as it bubbles through the solution, and then passes through stopcock *S*₃ and tube *H* to the apparatus for determination of ammonia vapor. In an emergency the operator may close both *S*₂ and *S*₃ to avoid contamination of the electroconductivity cell connected to outlet *H*. The stopcocks are all above the level of the thermostat liquid to simplify the operation of the apparatus and to avoid danger of flooding the electroconductivity cell with copper solution.

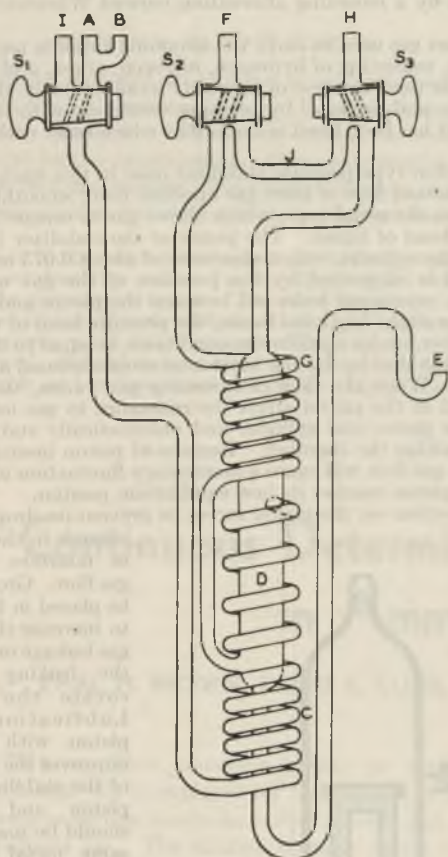


Figure 3. Gas Saturator

The electroconductivity cell is the same as that described for the determination of carbon monoxide and carbon dioxide (1). The gas from the saturator contains 4 to 5% ammonia, which is absorbed by 0.1 *N* sulfuric acid flowing at the rate of 15 ml. per minute. The ammonia activity is indicated on a Leeds & Northrup recording alternating current Wheatstone bridge. The zero point of the apparatus can be set by turning stopcocks *S*₂ and *S*₃ (Figure 3) to allow the inert gas to flow through by-pass *J* to the electroconductivity cell without picking up ammonia from the copper solution.

The recorder is calibrated directly in terms of ammonia activity. For calibration, solutions of ammonium hydroxide are allowed to flow through the calibration solution inlet, *I*, by turn-

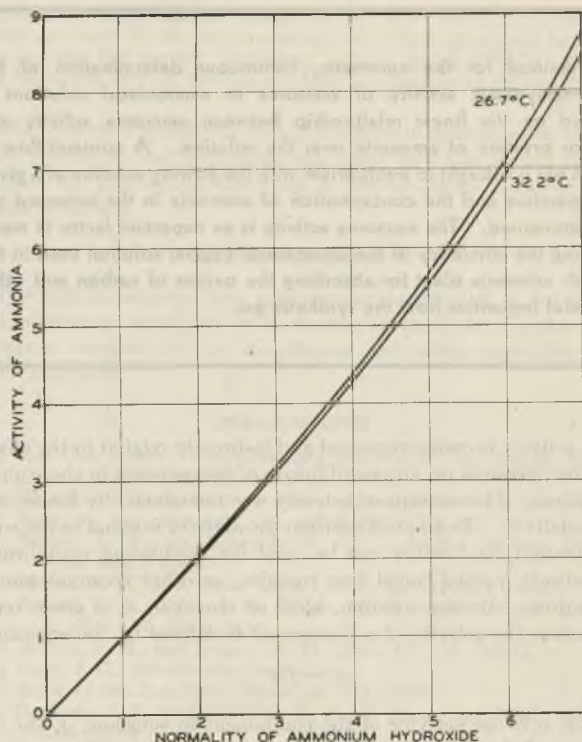


Figure 4. Activity of Ammonia in Ammonium Hydroxide Solutions

ing stopcock *S*₁ to the proper position. Using Equation 2 and ammonia vapor pressure data of Wilson (5) the activities of ammonium hydroxide solutions of normalities 0 to 7 were calculated at 26.7° and 32.2° C. and are plotted in Figure 4. Up to an ammonia activity of 3, the maximum found in the copper solution, there is no significant temperature effect on the ratio of activity to concentration. With this method of calibration the actual temperature of the thermostat (about 30° C.) is not a critical factor, provided the temperature is the same for both calibration and operation. Activity measurements in the range 0 to 3 are reproducible to within ± 0.05 with the apparatus.

APPLICATION

The apparatus for continuous determination of ammonia activity has been in operation for over 15 months in the ammonia plant control laboratory. The device is automatic and requires very little maintenance. The plant operators use the results to control closely the addition of ammonia to the copper solution. The ammonia activity is an important factor in maintaining the copper solution at peak efficiency for scrubbing carbon monoxide and carbon dioxide from the synthesis gas. By keeping the ammonia activity close to the optimum value (2.5 in the TVA ammonia plant) excessive ammonia addition with resultant high loss of ammonia in the regeneration step is avoided.

ACKNOWLEDGMENT

The authors are grateful to J. G. Dely, consultant to the TVA, E. J. O'Brien, superintendent of the TVA ammonia plant, and J. R. Hall, supervisor of the control laboratory, for their cooperation and encouragement in this work.

LITERATURE CITED

- (1) Brown, E. H., and Felger, M. M., *IND. ENG. CHEM., ANAL. ED.*, 17, 277 (1945).
- (2) Lewis, G. N., and Randall, M., "Thermodynamics", pp. 254-77, New York, McGraw-Hill Book Co., 1923.
- (3) Miller, A. M., and Junkins, J. N., *Chem. & Met. Eng.*, 50, No. 11, 119-25, 152-5 (1943).
- (4) Newton, R., *IND. ENG. CHEM.*, 27, 302-6 (1935).
- (5) Perry, J. H., "Chemical Engineers' Handbook", p. 352, New York, McGraw-Hill Book Co., 1934.

Continuous Determination of Carbon Dioxide by Electroconductivity

In Concentrations Up to 2 Per Cent

EARL H. BROWN AND MAURICE M. FELGER¹

An electroconductometric analyzer for the continuous determination of the carbon dioxide concentration in ammonia plant gases is described. The application of the results given by the analyzer to the operation of both the water and copper scrubbers of the gas-purification system of the TVA synthetic ammonia plant is given. The range of the analyzer described is 0 to 2%, but the analyzer is adaptable to other ranges.

THE converted semi-water gas entering the purification system of the TVA ammonia plant consists of hydrogen and nitrogen in the ratio of 3 to 1, together with about 29% carbon dioxide, about 2% carbon monoxide, and some inert gases (3). About 98% of the carbon dioxide is removed by scrubbing the gas with water, and the concentrations of both carbon dioxide and carbon monoxide are reduced to about 5 p.p.m. by scrubbing with ammoniacal copper solution. The analyzer described in this paper gives a continuous indication of the carbon dioxide content of the gas leaving the water scrubber.

DESCRIPTION AND OPERATION

The analyzer consists of a gas-control train, an absorption-conductivity cell, and a recording alternating current Wheatstone bridge. The gas-control train is shown in Figure 1. The pressure stabilizer (1) gives a uniform operating pressure; the grooved stopcock and flowmeter are used to regulate the rate of gas flow; and the potassium hydroxide-Ascarite tube removes carbon dioxide from the gas when the recorder zero is being checked. The principle and operation of the absorption-conductivity cell and recording alternating current Wheatstone bridge have been described (2).

The operating conditions for the determination of carbon dioxide in the range of 0 to 2% are:

Electrolyte	0.04 N sodium hydroxide
Electrolyte flow rate	15 ml. per minute
Gas flow rate	8 liters per hour
Cell temperature	Constant; between 28° and 32° C.

The analyzer is placed in operation by first adjusting the gas and electrolyte flows to their respective rates. During this adjustment the gas sample is passed through the potassium hydroxide-Ascarite tube. The distance between the measuring electrodes is then adjusted so that the recorder indicates zero. The 3-way stopcock is turned 180° to the position shown in Figure 1, which places the analyzer in operation.

The analyzer requires very little attention during operation. The combination of gas pressure stabilizer and grooved stopcock gives reliable control of the gas flow rate. The recorder zero and electrolyte flow rate are checked once each day. The potassium hydroxide-Ascarite tube is refilled after several months' use.

CALIBRATION

The original calibration was made empirically using gas mixtures of known carbon dioxide content. The relation between concentration and recorder indication is specific for the given operating conditions and the bridge circuit used—that is, a circuit with 220-ohm end coils and a 66.5-ohm slide-wire. The

R_m/R_r ratios (2) can be converted to recorder indications for any similar bridge by the relation which is shown herewith:

$$\frac{R_m}{R_r} = \frac{R_a + cR_s}{R_b}$$

where R_m = resistance of electrolyte between measuring electrodes

R_r = resistance of electrolyte between reference electrodes

R_a = resistance of A end coil

c = recorder indication, scale divisions

R_s = resistance of slide-wire per scale division

R_b = resistance of B end coil

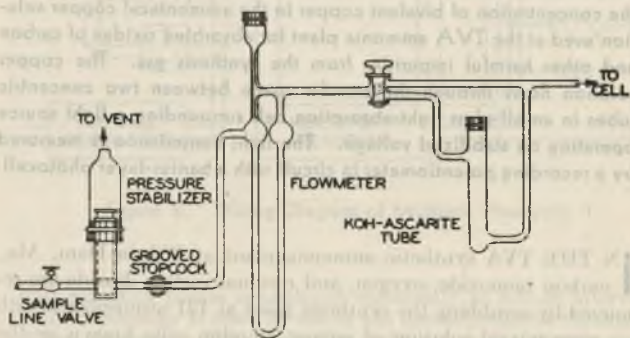


Figure 1. Gas-Control Train for Carbon Dioxide Analyzer

During the early operation of this analyzer, frequent gravimetric determinations were made of the carbon dioxide content of the gas being analyzed. It was established that the analyzer gave results that were accurate to about $\pm 0.03\%$.

APPLICATION

During normal operation the concentration of carbon dioxide in the gas leaving the water scrubber depends largely on the temperature and quantity of water pumped to the scrubber. This residual carbon dioxide is removed in the copper scrubber. Since there is no control of the temperature of the process water, the concentration of carbon dioxide in the effluent gas and, consequently, the carbon dioxide load on the copper scrubber, must be controlled by regulation of the quantity of water pumped to the water scrubber. This control is important because an overload on the copper scrubber resulting from insufficient removal of carbon dioxide in the water scrubber would lead to the presence of carbon dioxide in the synthesis system in concentrations harmful to the catalyst. On the other hand, the practical limit to which the carbon dioxide concentration may be decreased by increased flows of scrubbing water is fixed by the loss of hydrogen through solution in the water.

The results given by this carbon dioxide analyzer and the ammonia activity analyzer (1) are used to control the flow of water to the water scrubber. The carbon dioxide analyzer gives the load on the copper scrubber, and the ammonia activity ana-

lyzer gives a measure of the absorptive capacity of the copper solution for carbon dioxide. In actual practice the water to the scrubber is regulated so that the carbon dioxide concentration of the effluent gas is between 0.6 and 0.8%. The recorder is equipped with a high-low alarm system that warns the purification operators when the concentration is outside these limits. The application of this method to control the flow of water to the scrubber resulted in a significant decrease in the hydrogen loss by solution in the scrubbing water and a considerable decrease in the amount of process water used.

Continuous Photometric Determination of Bivalent Copper in Ammoniacal Solution

EARL H. BROWN AND JAMES E. CLINE

A photometric instrument was developed to record continuously the concentration of bivalent copper in the ammoniacal copper solution used at the TVA ammonia plant for absorbing oxides of carbon and other harmful impurities from the synthesis gas. The copper solution flows through the annular space between two concentric tubes in an all-glass light-absorption cell surrounding a light source operating on stabilized voltage. The light transmission is measured by a recording potentiometer in circuit with a barrier-layer photocell.

IN THE TVA synthetic ammonia plant at Wilson Dam, Ala., carbon monoxide, oxygen, and residual carbon dioxide are removed by scrubbing the synthesis gases at 121 atmospheres with an ammoniacal solution of copper amino salts known as the "copper solution" (2). The ratio of monovalent to bivalent copper in the copper solution is increased by reaction with the absorbed carbon monoxide and is subsequently decreased by regeneration of the copper solution with air. To facilitate close control of the regeneration by the plant operators and to reduce the number of chemical analyses required, a photometric instrument was developed to record continuously the concentration of bivalent copper in samples flowing from four different points in the copper solution system.

The copper solution contains cupric amino, cuprous amino, ammonium, formate, and carbonate ions, and uncombined ammonia. In the visible region the absorption of light by this solution is due exclusively to the deep blue cupric amino ion. The range of concentration of bivalent copper is from 10 to 70 grams per liter, with the optimum range (in plant operation) near 25 grams per liter. The low transparency of the copper solution was indicated by the absorption coefficients of cupric amino formate, as plotted in Figure 1 from data taken in the region of 390 to 700 millimicrons with a Cenco-Sheard spectrophotometer, using a 1.0-mm. slit and a 1-cm. absorption cell. The absorption coefficient, k , was calculated from the relationship:

$$k = (1/cd) \log (I_0/I)$$

where c = concentration of Cu^{++} , grams per liter
 d = depth of solution, cm.
 I_0 = intensity of incident light
 I = intensity of transmitted light

Because of the opacity of the copper solution, it was necessary to design a photometer capable of measuring the light transmission through a very thin layer of the solution. Dilution of the plant copper solution was considered impracticable, for the

ACKNOWLEDGMENT

The authors express their appreciation to the staff of the control laboratory, especially to R. Bowen Howard, Jr., for the cooperation received in the installation and initial operation of this analyzer.

LITERATURE CITED

- (1) Brown, E. H., Cline, J. E., Felger, M. M., and Howard, R. B., Jr., *IND. ENG. CHEM., ANAL. ED.*, **17**, 280 (1945).
- (2) Brown, E. H., and Felger, M. M., *Ibid.*, **17**, 277 (1945).
- (3) Miller, A. M., and Junkins, J. N., *Chem. & Met. Eng.*, **50**, No. 11, 119-25, 152-5 (1943).

maintenance of a diluting apparatus in continuous operation would be difficult, and dilution might change the monovalent-bivalent copper ratio.

DESCRIPTION OF APPARATUS

The absorption cell used is of all-glass construction and consists essentially of two concentric tubes surrounding the light source, as shown in Figure 2. The copper solution flows through the annular space, which is about 0.02 cm. wide. The cross section of the annular space, about 0.14 sq. cm., is sufficient to allow a copious flow of copper solution. The cells are rugged, are easily constructed, and are unaffected by hot acid cleaning solutions. They are made from 25- and 22-mm. Pyrex tubing, carefully selected so that the tubes fit together with the required clearance.

The light source used is a 6-c.p. 6-volt lamp operating at lower voltage to give it a long life. The lamp is mounted inside the concentric absorption cell, as shown in Figure 2. Both lamp and cell are supported by a brass tube fastened securely to the base of the photometer unit. The central terminal of the lamp is soldered to a wire leading to a 6-volt transformer, while the side terminal is soldered to the brass tube, which in turn is connected to the transformer. As shown in Figure 3, the voltage across the lamp is controlled by a variable transformer in the primary of the 6-volt transformer. The power to the four variable transformers in the system is supplied through a common voltage stabilizer from a 115-volt alternating current line.

The light transmitted through the copper solution is received by a barrier-layer photocell, Weston Model 594 G-B Type 3. The current from the photocell passes through a rheostat of about 100 ohms' resistance. The voltage across the rheostat is recorded on a four-point recording potentiometer with a range of 0 to 10 millivolts and a galvanometer coil resistance of 400 ohms (Leeds & Northrup Micromax).

The stability of the system was tested for continuous operation. During the initial period of illumination of the barrier-layer photocell, a copper screen was used to reduce the illumination to

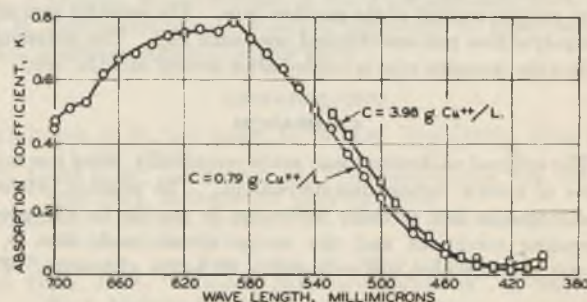


Figure 1. Spectral Absorption of Cupric Amino Formate

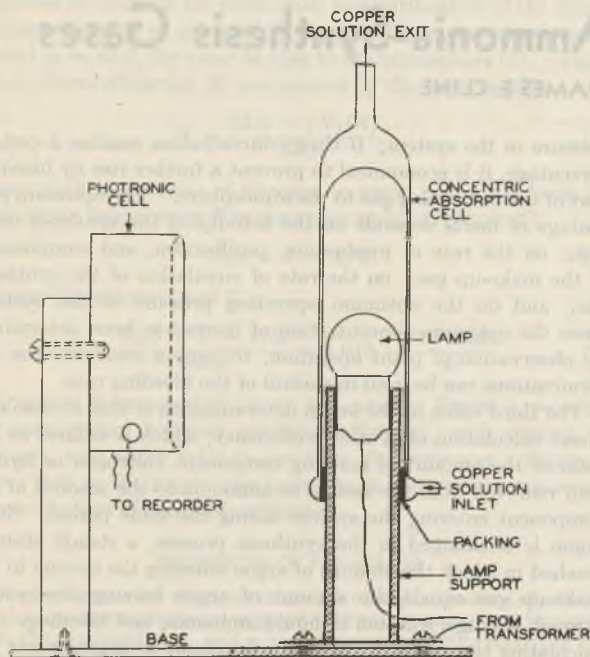


Figure 2. Vertical Section of Photometer Unit

40% of the full scale reading. During the first 30 minutes there was a gradual decrease in sensitivity, known as fatigue (1), after which the reading was practically constant for over 40 hours' continuous operation. When the illumination was increased from 40 to 100% by removal of the screen, a new fatigue effect was observed which again became constant within 30 minutes. When the illumination was diminished from 100 to 40% by replacement of the screen, the sensitivity of the photocell was found to be slightly lower than it had been with constant 40% illumination, but within 15 minutes the sensitivity had returned to the original value. The fatigue effect thus was shown to have a characteristic value for constant operation at each intensity of illumination. As the change in fatigue occurred only in the first 30 minutes after a change in illumination, the error introduced by fatigue was considered minor in the measurement of transmission through the copper solution in which the changes in concentration of bivalent copper are relatively slow. The constancy of the record over a 40-hour interval showed not only that the fatigue effect was constant but also that the illumination from the lamp was constant. The use of a second photocell to compensate for fluctuations in illumination therefore was considered unnecessary.

In the ammonia-synthesis plant four samples of copper solution flow continuously through the analyzer and then return to the plant system. The four photometer units (photocell, absorption cells, lamps, 6-volt and variable transformers) and the voltage stabilizer are mounted in a cabinet. The recorder and four fine-adjustment rheostats are mounted about 30 feet away from the photometer cabinet, at a place convenient for the plant operators. The scale on the recorder is calibrated directly in terms of grams of bivalent copper per liter, using chemical analysis as the standard. To avoid making a separate calibration for each absorption cell, the light transmission through each cell is assumed to be proportional to the same empirical function of concentration. This assumption permits a very simple procedure to be followed in reading and maintaining the instrument, and it causes no errors large enough to prevent satisfactory control of the plant operations.

The accumulation of precipitated material in the absorption cell during continuous operation is the greatest factor in causing a change in the calibration of the instrument. To correct for gradual changes, however, the copper solution from each of the

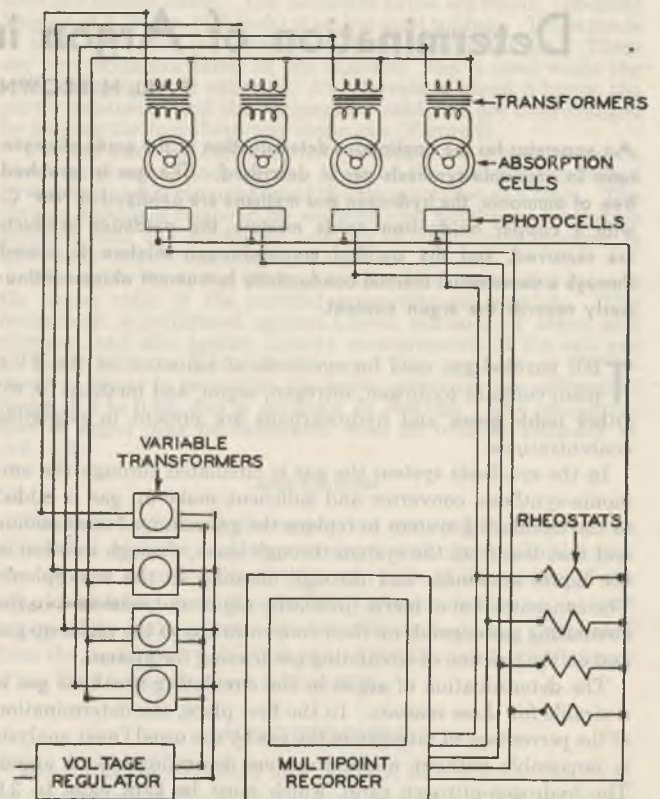


Figure 3. Wiring Diagram of Multiple Analyzer

four sampling points is analyzed chemically at 8-hour intervals and the recorder is reset by use of the fine-adjustment rheostats. When necessary, dirty absorption cells are replaced with clean cells and are cleaned with a hot mixture of chromic, sulfuric, and nitric acids. The use of filters to prevent solid material from entering the cells probably would entail greater maintenance requirements than the procedure outlined.

After the instrument is set to agree with a chemical analysis, the accuracy is ± 0.5 gram of bivalent copper per liter for a period of 8 to 100 hours, depending on the amount of sludge in the solution.

APPLICATION

In more than 2 years of continuous operation, the bivalent copper recorder has proved to be much more efficient, both technically and economically, than were the tedious chemical analyses previously employed for control over the regeneration of the copper solution. The trend of the bivalent copper concentration, as shown by the recorder chart, facilitates close control of plant operation.

The photometer and concentric absorption cell described may be useful in continuous transmission recording of the composition of other solutions, especially those of low transparency.

ACKNOWLEDGMENT

The authors are grateful to J. G. Dely, consultant to the TVA, whose suggestions initiated this work and to the staff of the control laboratory who devised the procedure for maintaining the instrument in continuous operation.

LITERATURE CITED

- (1) Lange, B., "Photoelements", tr. by A. St. John, New York, Reinhold Publishing Corp., 1938.
- (2) Miller, A. M., and Junkins, J. N., *Chem. & Met. Eng.*, 50, No. 11, 119-25, 152-5 (1943).

Determination of Argon in Ammonia-Synthesis Gases

EARL H. BROWN AND JAMES E. CLINE

An apparatus for the continuous determination of the argon-nitrogen ratio in ammonia-synthesis gas is described. The gas is scrubbed free of ammonia, the hydrogen and methane are oxidized at 700° C. with a copper oxide-iron oxide mixture, the oxidation products are removed, and the purified argon-nitrogen mixture is passed through a commercial thermal conductivity instrument which continuously records the argon content.

THE purified gas used for synthesis of ammonia at the TVA plant contains hydrogen, nitrogen, argon, and methane (3, 6). Other noble gases and hydrocarbons are present in negligible concentrations.

In the synthesis system the gas is circulated through the ammonia-synthesis converter and sufficient make-up gas is added to the circulating system to replace the gas removed as ammonia and that lost from the system through leaks, through solution in the liquid ammonia, and through bleeding to the atmosphere. The concentration of inerts (primarily argon and methane) in the circulating gas depends on their concentration in the make-up gas and on the fraction of circulating gas leaving the system.

The determination of argon in the circulating synthesis gas is desirable for three reasons. In the first place, the determination of the percentage of nitrogen in the gas by the usual Orsat analysis is impossible without a simultaneous determination of argon. The hydrogen-nitrogen ratio, which must be kept close to 3.0 for optimum ammonia production, is indeterminate to the extent to which the argon concentration is uncertain.

The determination of argon is necessary also for calculating the total percentage of inerts in the synthesis gas. The inerts act as a diluent and have approximately the same effect as a decrease of

pressure in the system; if their concentration reaches a certain percentage, it is economical to prevent a further rise by bleeding part of the circulating gas to the atmosphere. The optimum percentage of inerts depends on the activity of the synthesis catalyst; on the rate of production, purification, and compression of the make-up gas; on the rate of circulation of the synthesis gas; and on the optimum operating pressure of the system. Once the optimum concentration of inerts has been determined by observation of plant operation, the argon and methane determinations can be used in control of the bleeding rate.

The third value of the argon determination is that it enables a direct calculation of synthesis efficiency, which is defined as the ratio of the amount of reacting component (nitrogen or hydrogen) removed from the system as ammonia to the amount of the component entering the system during the same period. Since argon is unchanged in the synthesis process, a steady state is reached in which the amount of argon entering the system in the make-up gas equals the amount of argon leaving the system through leakage, solution in liquid ammonia, and bleeding. By calculating the ratios of reacting component to argon (parts per part argon) in both make-up gas and gas from the converter, the ratio of the amount of reacting component entering the system to that leaving the system in unsynthesized condition may be estimated. With normal gas compositions in the system, it was found that an error of less than 1% would be introduced into the calculation if the loss of gas by leakage occurred at a stage in the synthesis cycle other than that from which the sample was taken for analysis. Errors caused by differential solubility of the gases in liquid ammonia were considered negligible. The synthesis efficiency can thus be estimated from purely analytical data with no reference to production rates or gas flows.

For calculation of the synthesis efficiency with respect to hydrogen, determinations of the concentration of hydrogen, the sum of the concentrations of nitrogen and argon, and the argon ratio are required. (Argon ratio is defined here as the argon content divided by the sum of the argon and nitrogen contents.) For the synthesis efficiency with respect to nitrogen, however, only the argon ratio in the gas from the converter is needed. As neither the nitrogen nor the argon enter into any of the chemical

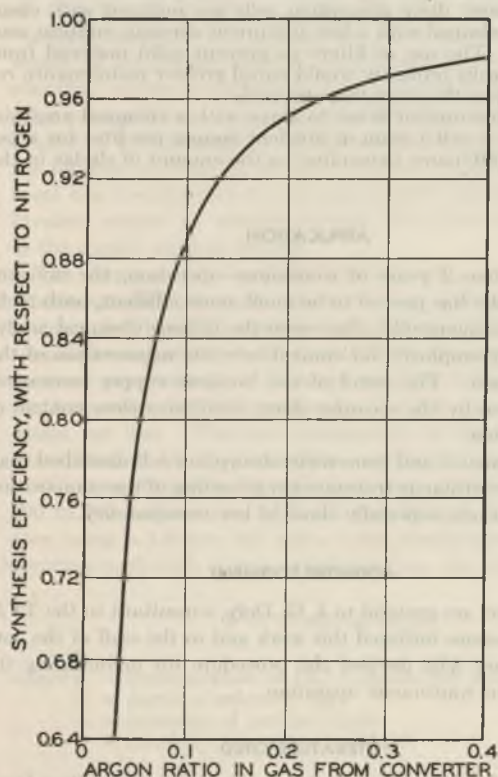


Figure 1. Relationship between Synthesis Efficiency, with respect to Nitrogen, and Argon Ratio in Gas from Converter

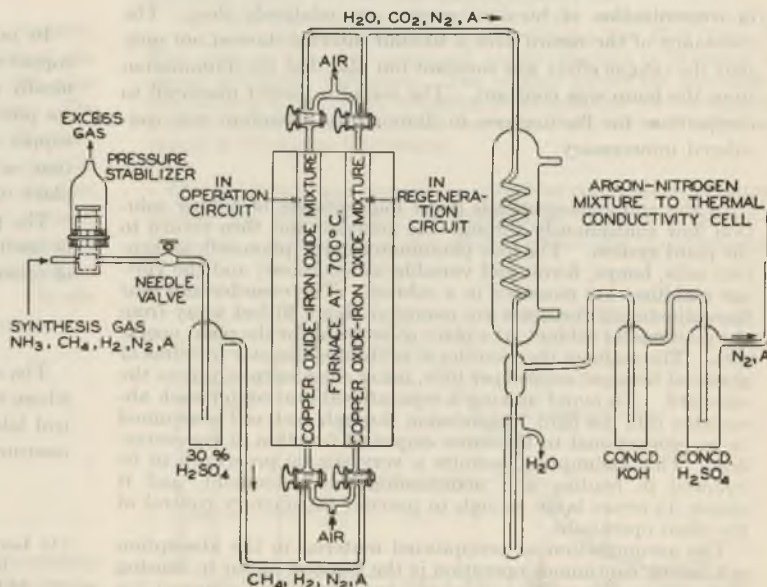


Figure 2. Train for Preparation of Argon-Nitrogen Mixture from Synthesis Gases

reactions involved in the production and purification of the make-up gas, the ratio of nitrogen to argon in the make-up gas is assumed to be 83.0, the same as that in the atmosphere (5). Thus, the synthesis efficiency, E , is expressed by the relationship:

$$E = \frac{83.0 - (N_2/A)}{83.0} \quad (1)$$

where N_2/A is the ratio of nitrogen to argon in the gas from the converter. Introducing R as the argon ratio, $A/(N_2 + A)$,

$$-N_2A = 1 - 1/R \quad (2)$$

From Equations 1 and 2,

$$E = \frac{83.0 + 1 - 1/R}{83.0} = 1.012 - \frac{0.01205}{R} \quad (3)$$

Equation 3 was used to obtain the curve in Figure 1, showing the relationship between synthesis efficiency, with respect to nitrogen, and argon ratio in gas from the converter. Figure 1 shows that as the argon ratio increases, it becomes a more sensitive indication of synthesis efficiency.

DESCRIPTION OF APPARATUS

The apparatus for the determination of argon consists of a train for the continuous removal of gases other than argon and nitrogen from the synthesis gas, and a thermal conductivity analyzer for recording the argon ratio in the purified mixture. Since the Orsat analyses regularly performed in the laboratory furnish the sum of argon and nitrogen, the argon ratio enables calculation of both argon and nitrogen.

A diagram of the purification train is shown in Figure 2. The flow of synthesis gas into the purification train is maintained at about 8 liters per hour by means of a piston-type pressure stabilizer (2) and a needle valve. Accurate control of the rate of flow is unnecessary; the rate affects the time lag and reagent consumption, but not the analytical results. Ammonia is removed by 30% sulfuric acid, leaving methane, hydrogen, nitrogen, and argon.

Campbell and Gray (4) stated that methane was oxidized completely by copper oxide in 7 minutes at 700° C. and that, in the presence of hydrogen, the oxidation of methane proceeded more easily. Arneil (1) found that ferric oxide catalyzed the reaction and lowered the temperature of complete oxidation of methane to 500° C. In the apparatus shown in Figure 2, both hydrogen and methane are oxidized at 700° C. by copper oxide containing 1 to 10% iron oxide to catalyze the oxidation. The temperature is regulated by a Brown controlling pyrometer. Channel formation in the oxidant as a result of sintering of metallic copper is minimized by mixing crushed refractory, such as alumina brick,

with the copper oxide. The oxidation tubes are 90-cm. (36-inch) lengths of 3.75-cm. (1.5-inch) stainless steel tubing. Tubes made of silica or of iron are unsatisfactory for continuous use. There are two oxidation tubes in the furnace; one is used while the other is regenerated with air. At intervals of about 8 hours, the partly exhausted and the regenerated oxidizers are interchanged by turning the four three-way stopcocks (Figure 2).

The gas from the oxidation tube contains water vapor, carbon dioxide, nitrogen, and argon. Most of the water is condensed by cooling and is removed from the system through a trap. The carbon dioxide is removed by concentrated potassium hydroxide solution, and the remaining mixture of argon and nitrogen is dried with concentrated sulfuric acid.

A Leeds & Northrup thermal conductivity apparatus records the argon ratio in the purified argon-nitrogen mixture. The instrument is calibrated against known mixtures of argon and nitrogen, and also against density measurements of the exit gas as made with an Edwards balance. The response of the recorder is linear in respect to the argon ratio over the calibration range of 0 to 0.33, and is accurate to ± 0.005 . The concentration of argon may be calculated with an over-all accuracy of $\pm 0.15\%$.

APPLICATION

The results given by the apparatus are used in combination with Orsat analyses to determine argon and nitrogen in the synthesis gases. Application of the argon ratio to the control of the rate of bleeding from the synthesis system facilitates maintenance of the optimum rate of ammonia production. Calculated from the argon ratio (usually 0.25 to 0.30), the synthesis efficiency of the TVA ammonia plant is 96 to 97%.

ACKNOWLEDGMENT

The authors are indebted to J. G. Dely, consultant to the TVA, for proposing that this work be undertaken, and to the staff of the control laboratory, supervised by J. R. Hall, for modifying the apparatus to simplify its maintenance in continuous operation.

LITERATURE CITED

- (1) Arneil, A., *J. Soc. Chem. Ind.*, 53, 89-92T (1934).
- (2) Brown, E. H., Cline, J. E., Felger, M. M., and Howard, R. B., Jr., *IND. ENG. CHEM., ANAL. ED.*, 17, 280 (1945).
- (3) Brown, E. H., and Felger, M. M., *Ibid.*, 17, 273 (1945).
- (4) Campbell, J. R., and Gray, T., *J. Soc. Chem. Ind.*, 49, 432-7T, 447-50T (1930).
- (5) International Critical Tables, Vol. I, p. 393, New York, McGraw-Hill Book Co., 1926.
- (6) Miller, A. M., and Junkins, J. N., *Chem. & Met. Eng.*, 50, No. 11, 119-25, 152-5 (1943).

Continuous Determination of Carbon Monoxide in Concentrations Up to 3.5 Per Cent by Electroconductivity

EARL H. BROWN, MAURICE M. FELGER, AND R. BOWEN HOWARD, JR.

THE production of the hydrogen-nitrogen mixture for the synthesis of ammonia in the TVA plant was described by Miller and Junkins (4). In one step of the process, semi-water gas is enriched with hydrogen by catalytic oxidation of the carbon monoxide with steam. Most of the resulting carbon dioxide is removed from the gas by pressure scrubbing with water, and the remainder, together with residual carbon monoxide from the catalytic oxidation step, is removed by pressure scrubbing with an ammoniacal copper solution.

A continuous indication and record of the unreacted carbon monoxide in the converted semi-water gas are desirable for plant control. The continuous indication, along with the rate of gas flow, gives the carbon monoxide load on the copper scrubber and thus aids in both the operation of the scrubber and the re-

generation of the copper solution. An indication of high concentrations of carbon monoxide warns the plant operators of unsatisfactory operation in the catalytic oxidation step. Data taken from the continuous record are used in the preparation of material balances. In actual practice the gas leaving the water scrubber is analyzed, because the excess steam and most of the carbon dioxide present in the gas leaving the converters have been removed at this stage of the process. The carbon monoxide concentration of this gas is about 2%.

The use of neither iodine pentoxide for selective oxidation of the carbon monoxide nor of other solid oxidants, such as copper oxide, for the direct oxidation of both the carbon monoxide and the hydrogen was considered practicable in the continuous analysis of this gas because of the inordinate amount of time required

in the frequent reactivation of the oxidant. A method was devised, therefore, in which the gas is diluted with air in a predetermined ratio, the carbon monoxide and hydrogen are oxidized over a hot copper oxide catalyst, and the resulting carbon dioxide is determined by an electroconductometric method.

DESCRIPTION

Small portions of the gas undergoing analysis are injected intermittently into a stream of air by means of a sampling stopcock (1). The stopcock (Figure 1) has a stainless steel barrel and a tapered brass plug. The plug encloses two coaxial, cylindrical compartments of equal volume; each compartment communicates with either of two pairs of diametric openings in the barrel through oblique bores that meet the periphery of the plug on a common circumference. The gas containing carbon monoxide

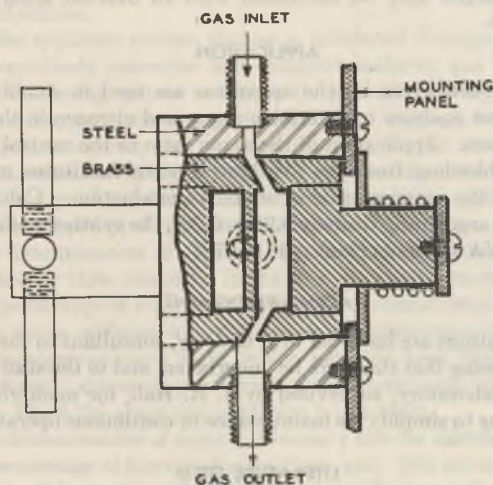


Figure 1. Sampling Stopcock of Carbon Monoxide Analyzer

flows through one compartment, while the air flows through the other. The larger projecting end of the plug has four studs equally spaced on its circumference. By engagement of these studs with a rotating crank geared to a synchronous motor, the plug is turned through 90° at regular intervals, and the gas being analyzed thus is injected into the air stream in successive portions of equal volume. A uniform mass for the successive portions is ensured by the incorporation of a temperature and pressure compensator in the gas sample line to compensate for changes in room temperature and atmospheric pressure.

The sample metering and preparation system in which the gas is prepared for introduction into the absorption-conductivity cell is shown in Figure 2. Air enters the system through a piston-type pressure stabilizer (2) and flows through grooved stopcock S_1 , a flowmeter, and the sampling stopcock, where it picks up the carbon monoxide sample. The diluted sample then passes through a scrubber containing potassium hydroxide solution, which removes carbon dioxide; through a heated tube containing copper oxide for the catalytic oxidation of the carbon monoxide and hydrogen; through a condensate trap where water produced by the oxidation of hydrogen is removed; and finally to an absorption-conductivity cell where the carbon dioxide produced by the oxidation of carbon monoxide is measured (3). The gas from the sample line enters the system through a piston-type pressure stabilizer and flows through the sampling stopcock, a temperature and pressure compensator, a gas pressure safety trap, and grooved stopcock S_2 for the regulation of the line pressure.

The principle and operation of the absorption-conductivity cell, as well as the electrical circuit, have been described (3).

An analyzer for the continuous determination of carbon monoxide in the range 0 to 3.5% and in the presence of a large concentration of hydrogen is described. The sample is diluted with air, the carbon monoxide oxidized to carbon dioxide over hot copper oxide, and the carbon dioxide determined by an electroconductometric method.

OPERATION

The operating conditions for the determination of carbon monoxide in concentrations up to 3.5% are:

Electrolyte	0.04 N sodium hydroxide
Electrolyte flow rate	15 ml. per minute
Cell temperature	Constant; between 28° and 32° C.
Temperature of copper oxide	300° to 350° C.
Air flow rate	10 liters per hour
Volume of each sample injection	4.8 cc.
Frequency of injections	6 per minute
Bridge slide-wire resistance	60 ohms
Bridge end-coil resistance	600 ohms

Although specific rates of flow of air and gas sample through the analyzer are not required, the rates should be constant and must be sufficient to replace entirely the gas in the compartments of the sampling stopcock in the 10-second intervals between sampling.

In starting the analyzer, the air and electrolyte flows are first adjusted to their proper rates. The distance between the meas-

Table I. Comparison of Carbon Monoxide Concentrations Determined by Orsat and Electroconductometric Analyses

Time Hours	CO by Orsat (Fisher) %	CO by Analyzer %
0	2.4	2.45
4	2.5	2.45
8	2.1	2.05
12	2.1	2.05
16	2.2	2.25
20	2.2	2.25
24	2.3	2.20
28	2.3	2.15
32	2.2	2.20
36	2.3	2.20
40	2.5	2.25
44	2.2	2.25
48	2.1	2.20
52	2.1	2.25
56	2.2	2.25
60	2.3	2.30
64	2.3	
68	2.4	2.30
72	2.3	2.30
76	2.1	2.20
80	2.2	2.15

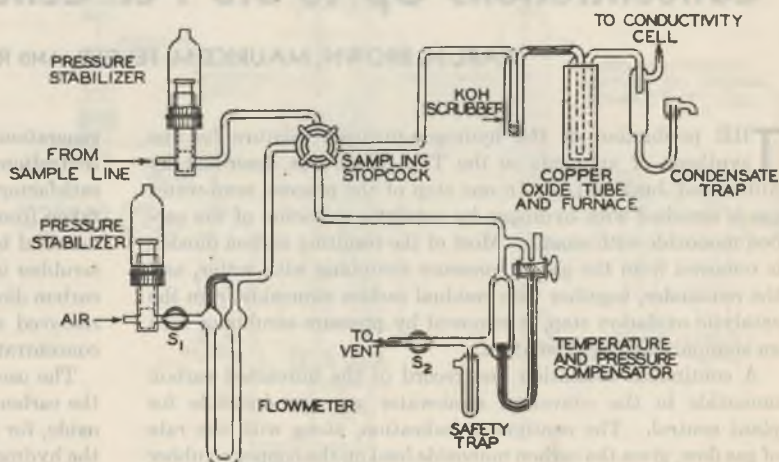


Figure 2. Sample Metering and Preparation System

uring electrodes is then adjusted so that the recorder indicates zero. The gas flow from the sample line is started, and grooved stopcock S_2 is adjusted so that the top of the mercury column of the temperature and pressure compensator is at the calibration mark. The sampling stopcock is started and the analyzer is in operation.

The analyzer is calibrated with gas mixtures of known composition.

The accuracy of the calibration was checked during regular plant operation by comparison with analyses obtained by means of a Fisher precision gas analysis unit over a 3-day period (Table I).

There is good reason for believing that the accuracy of the electroconductometric method is better than that of the Orsat method.

MAINTENANCE

The sample metering and preparation train is so mounted that the pressure stabilizers, flowmeter, and compensator are readily visible. The gas sample and air flows seldom require adjustment, but the pressure in the gas sample line must be adjusted at S_2 (Figure 2) when significant changes in temperature or atmospheric pressure occur. The rate of flow of electrolyte and the zero setting of the recorder are checked daily. The zero setting

of the recorder is obtained by stopping the rotation of the sampling stopcock for sufficient time for all the carbon dioxide to be flushed from the train leading to the absorption-conductivity cell. The solution in the potassium hydroxide scrubber is changed once each week, and the sampling stopcock is lubricated as required. The catalytic unit in which the carbon monoxide and hydrogen are oxidized requires no attention other than the maintenance of its temperature. The original charge of copper oxide catalyst has shown no decrease in activity in more than a year of continuous use.

ACKNOWLEDGMENT

The authors express their appreciation to the staff of the ammonia plant control laboratory for their cooperation in the installation and initial operation of the analyzer.

LITERATURE CITED

- (1) Brown, E. H., *IND. ENG. CHEM., ANAL. ED.*, **14**, 551 (1942).
- (2) Brown, E. H., Cline, J. E., Felger, M. M., and Howard, R. B., Jr., *Ibid.*, **17**, 280 (1945).
- (3) Brown, E. H., and Felger, M. M., *Ibid.*, **17**, 277 (1945).
- (4) Miller, A. M., and Junkins, J. N., *Chem. & Met. Eng.*, **50**, No. 11, 119-25, 152-5 (1943).

[End of Symposium]

Continuous Determination of Methyl Bromide in the Atmosphere

DWIGHT WILLIAMS, GEORGE S. HAINES, AND F. D. HEINDEL

Research Department, Westvaco Chlorine Products Corporation, South Charleston, W. Va.

A method and apparatus for the continuous determination of the concentration of methyl bromide at several points in the atmosphere are described. The methyl bromide is converted to hydrogen bromide by adding hydrogen to the sample and passing the mixture through a quartz tube which is maintained at a temperature above 800° C. The hydrogen bromide is continuously absorbed in a stream of water and the electrical conductivity of the water solution measured by means of a recording conductivity meter. Concentrations as

low as 1 part per million may be detected and concentrations up to 600 parts per million have been determined with a precision of $\pm 5\%$ of the amount present. The method is not specific for methyl bromide but gives the total chlorine and bromine compounds in the air. A similar apparatus in which the hydrogen is omitted and the air stream is saturated with water vapor is used for the determination of chlorinated hydrocarbons when brominated hydrocarbons are absent.

THE determination of low concentrations of methyl bromide in the atmosphere by combustion on passage through a quartz tube followed by titration of the bromine by the Kolthoff-Yutzy (1) procedure has been described (5). This method has numerous disadvantages when considering the safety of personnel exposed to the vapors. The most serious of these is the time lag between the sampling operation and the completion of the analysis.

Since the methyl bromide was converted on combustion either to hydrogen bromide or to free bromine, which could presumably be readily converted to hydrogen bromide, it appeared that electrical conductivity offered a ready means for the continuous determination of methyl bromide. The possibility of determining carbon tetrachloride in air continuously and automatically by measuring the electrical conductivity has been suggested by Olsen, Smyth, Ferguson, and Scheffan (2). Thomas, Ivie, Abersold, and Hendricks (4) have described an automatic apparatus suitable for determining volatile chlorine compounds by combustion and conductivity measurements. However, they absorbed the combustion products batchwise and obtained their quantitative results from the rate of change of conductivity. It appeared that this procedure could be improved if the combus-

tion products could be absorbed in a continuous flow of water. This would involve the continuous passage of a constant stream of the air sample through the furnace and the continuous pumping of a constant stream of water through the absorber. Obviously this method is not specific for bromide, as is the Kolthoff-Yutzy procedure, but it should prove useful where methyl bromide is the most probable atmospheric contaminant and will in any case give results on the high side, which is in the interest of safety.

A consideration of the concentration of methyl bromide which it was desired to detect and of the probable optimum air and liquid flows indicated that a conductivity cell having a cell constant of about 0.1 reciprocal centimeter was required. The conductivity cell was designed to permit the complete absorption of the combustion products, reduce holdup to a minimum, and permit the compact assembly of the apparatus.

Low and erratic recoveries of methyl bromide were obtained in early tests based on the assumption that the methyl bromide was quantitatively converted to hydrogen bromide. This was traced to the formation of free bromine. The addition of hydrogen to the air stream eliminated this source of error.

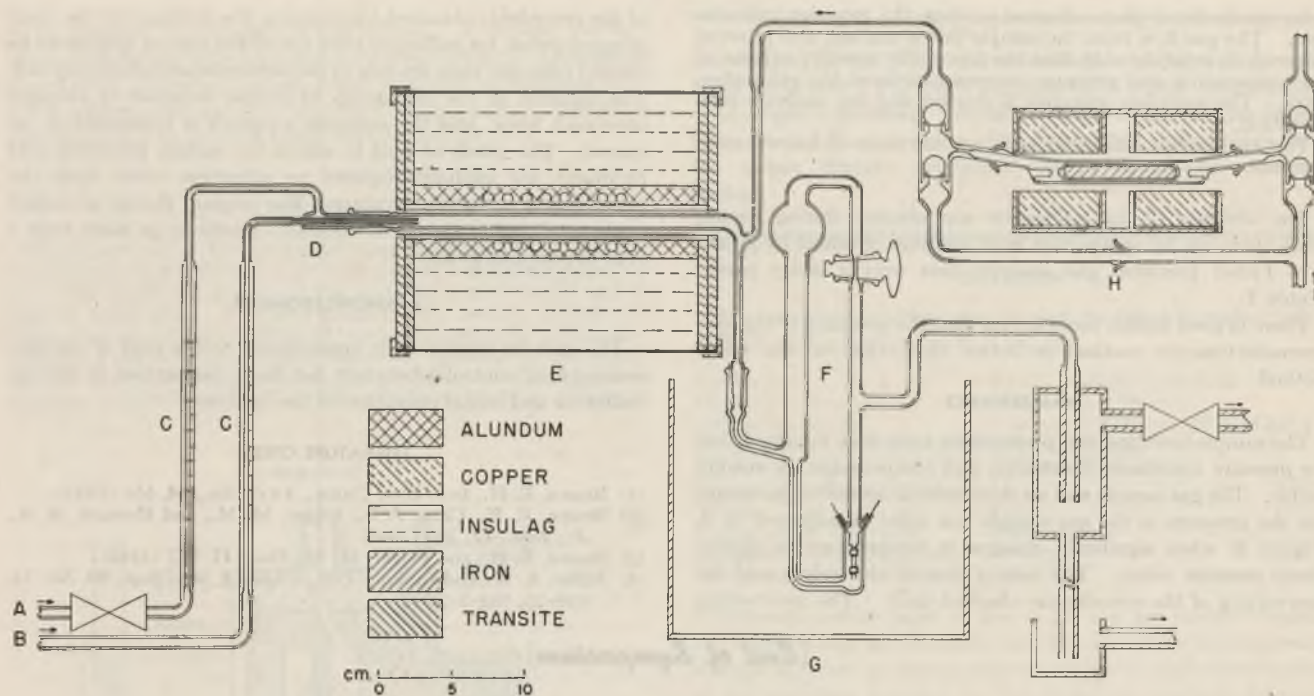


Figure 1. Diagram of Analyzer

A. Hydrogen inlet
B. Air inlet
C. Rotameter

D. Burner
E. Furnace
F. Absorber conductivity cell

G. Water bath
H. Water pump
I. Water inlet

APPARATUS¹

A scale diagram of an individual system of the analyzer is shown in Figure 1. Details of construction of the parts and the flow of water and gases through the system are indicated.

WATER PUMP. The piston and cylinder are made from a 5-ml. Pyrex hypodermic syringe. The stops are adjusted to give a stroke of about 1 ml. The hollow core of the piston is filled with iron wire (No. 22 B. and S. lacquered iron wire was used) and the glass sealed together again. The check valves are made by grinding glass marbles into the preformed valve seats before assembly. The authors found single-colored marbles superior to the varicolored variety. Hand grinding on a stationary rubber plate using 240-, 400-, and 600-mesh Carborundum powder, in that order, and then rouge gave good results. Each valve seat is tested individually and, if found defective, is reground before assembly. The test is made under a 150-cm. (5-foot) head of water using a 20-mm. head tube. A drop of 30 cm. (12 inches) in the water level in the head during 24 hours is cause for regrinding the valve. This all-glass pump assembly provides a small, precise flow of water without danger of contamination which would affect the conductivity of the water.

All pump-valve assemblies were tested for constancy of delivery with variation in head. In some cases variations in delivery were observed which could not be traced to leaky valves or cylinders. Leaks resulted in deliveries less than the displacement of the piston but deliveries greater than the displacement, sometimes as much as 2.5 times, were observed in these anomalous cases. It was observed that all four valves moved at each stroke of the piston, two during the stroke and the other two just at the end of the stroke. It was concluded that this was caused by the inertia imparted to the water by the rapid motion of the piston, which tended to force water through the inlet valves at the end of the stroke. This source of error was eliminated by inserting short lengths of capillary at either end of the cylinder. This slowed the motion of the piston, reduced the inertia, and gave the rated delivery.

The piston is driven by two electromagnets which are actuated alternately by means of an automatic electric timer having a speed of about 1 r.p.m. (Automatic Electric Manufacturing Co., Mankato, Minn., Catalog No. 1005). The timer is set at 10 cycles per minute. The solenoids are made by winding 2500 turns of No. 22 enameled copper wire on an arbor 6.25 cm. (2.25 inches) long by 2.5 cm. (1 inch) in diameter. A perforated steel shell 7.8 cm. (3.125 inches) inside diameter by 14 cm. (5.625 inches) long encloses the two solenoids which are required to drive a single pump assembly. There is a 2.19-cm. (0.875-inch) gap between the two solenoids. The length of this gap is fixed by means of two washers 7.8 cm. (3.125 inches) in diameter which are machined to fit the inside of the shell, to which they are welded. The syringe passes through a 2.5-cm. (1-inch) hole in the center of the washers.

Water is pumped alternately to each of two conductivity cells by means of a single pump. Water passes from the conductivity cell to a water separator from which it is discharged through a 90-cm. (3-foot) standleg to a small reservoir having an overflow to the sewer.

HYDROGEN SUPPLY SYSTEM. Hydrogen is supplied by means of a cylinder or other source at about 2.3 kg. (5 pounds) pressure. The flow to the analyzer is controlled by means of a 0.3-cm. (0.125-inch) V-point needle valve (Hoke, Inc., New York, N. Y., Catalog No. 341). The hydrogen flow rate is measured by means of a rotameter, having a range 0 to 1000 ml. per minute.

AIR FLOW SYSTEM. The air sample is conducted continuously through Saran tubing to the analyzer. A rotameter having a range of 0 to 1500 ml. per minute is used for measuring the air flow rate. The hydrogen and air flows are combined by means of the Pyrex burner. The gas streams should not combine until inside the furnace. Otherwise, burning may be erratic. Clear quartz ground joints (Thermal Syndicate, Ltd., New York) are used on the combustion tubes. One complete 10/30 $\frac{1}{8}$ quartz joint is required for each combustion tube, the outer member being at the inlet end of the furnace and the inner member at the outlet end. The burner and the conductivity cell, to which the combustion tube is attached by means of these standard taper quartz joints, are made of Pyrex.

The air stream passes through the furnace and conductivity cell to the water separator and from there to a needle valve of the same type as that which is used to control the hydrogen flow. The needle valve is connected to a manifold which is evacuated continuously by means of a Cenco-Pressovac pump.

CONDUCTIVITY CELL. The electrodes are made of two 1 × 2 cm. sheets of 0.013-cm. (0.005-inch) platinum foil held approxi-

¹ Patent applied for

mately 2 mm. apart by means of glass spacers. It is convenient to adjust all the cells for a given analyzer to the same cell constant which should be approximately 0.1 reciprocal centimeter. With this cell constant the authors' laboratory-distilled water showed resistances of from 35,000 to 38,000 ohms corresponding to about 1 p.p.m. of methyl bromide. The exact cell constant is not important, since the range can be more readily adjusted by changing either the air or water flow rates. To adjust the cells to a constant value, the electrodes are lightly platinized by the procedure outlined by Reilly and Rae (3), and placed inside a 14-mm. outside diameter glass tube. Using 0.0001 *N* hydrobromic acid as the electrolyte, the platinum is trimmed from the low-resistance electrode pairs until all match the electrode pair having the highest resistance.

The platinum black is then removed by electrolysis in aqua regia for a few minutes and the electrodes are permanently mounted in 14-mm. outside diameter tubes by sealing the platinum lead wires through the glass. Sections of appropriate tubing are sealed to each end of the electrode envelope to permit subsequent attachment to the balance of the cell. These extended tubes should be of length to permit the final sealing without heating or drying the electrodes.

The electrode assemblies are then replatinized and calibrated with several concentrations of hydrobromic acid before final assembly. This calibration should be carried out at 25° C., since Micromax conductivity recorders are calibrated to show the correct resistance at this temperature.

The concentrations of hydrobromic acid are calculated to correspond to the proper methyl bromide concentrations according to the following formula:

$$\frac{N \text{ HBr} \times (\text{ml. per minute of H}_2\text{O}) \times 22.4 \times 1,000,000}{\text{ml. per minute of air}} = \text{p.p.m. of methyl bromide}$$

Thus a hydrobromic acid concentration of 0.0001 *N* corresponds to 22.4 p.p.m. in the atmosphere when using an air flow

rate of 1000 ml. per minute and a water rate of 10 ml. per minute. The cell has a resistance of 1000 to 1500 ohms at this concentration and 25° C. The range of the Micromax recorder which was used in conjunction with the analyzer was 250 to 50,000 ohms. It was possible by means of this combination to detect 1 p.p.m. and the top of the range corresponded to 100 to 200 p.p.m. The maximum safe working concentration, which was considered to be 30 p.p.m., was easily read from the recorder chart. A scale reading in parts per million of methyl bromide was provided for the recorder as shown in Figure 7, in order to permit the instantaneous reading of the methyl bromide concentration.

The stopcock in the conductivity cell is open during the operation of the analyzer to permit escape of the air through this leg of the cell. When the analyzer is shut down, the stopcock is closed and most of the water is drawn out of the cell to prevent back-pressure from forcing water into the furnace.

The conductivity cells are immersed in a water bath equipped with a thermoregulator, flexible-type immersion heater, and electric stirrer. Water is added to the bath continuously to maintain its level and prevent the temperature from rising above 40° C. Without the cooling effect of the added water, the bath temperature rises, even when the heater is off, owing to the heating effect of the pyrolysis furnace and the hot gases emerging from it to the conductivity cells.

FURNACE. The pyrolysis furnace may be constructed to accommodate four, six, or more combustion tubes. Furnaces accommodating four and six tubes have actually been constructed. The latter was built as follows: Six 1.31-cm. (0.625-inch) inside diameter Alundum tubes 20 cm. (8 inches) long were arranged adjacently in a horizontal position and held in place by Transite end plates, 28.1 × 17.19 cm. (11.25 × 6.875 inches), each containing six holes to fit over the tubes. The crevices between the tubes were filled with a paste made of Alundum cement No. 1055 and water. The center 10-cm. (4-inch) section of the tubes was wound with a helical coil of resistance wire

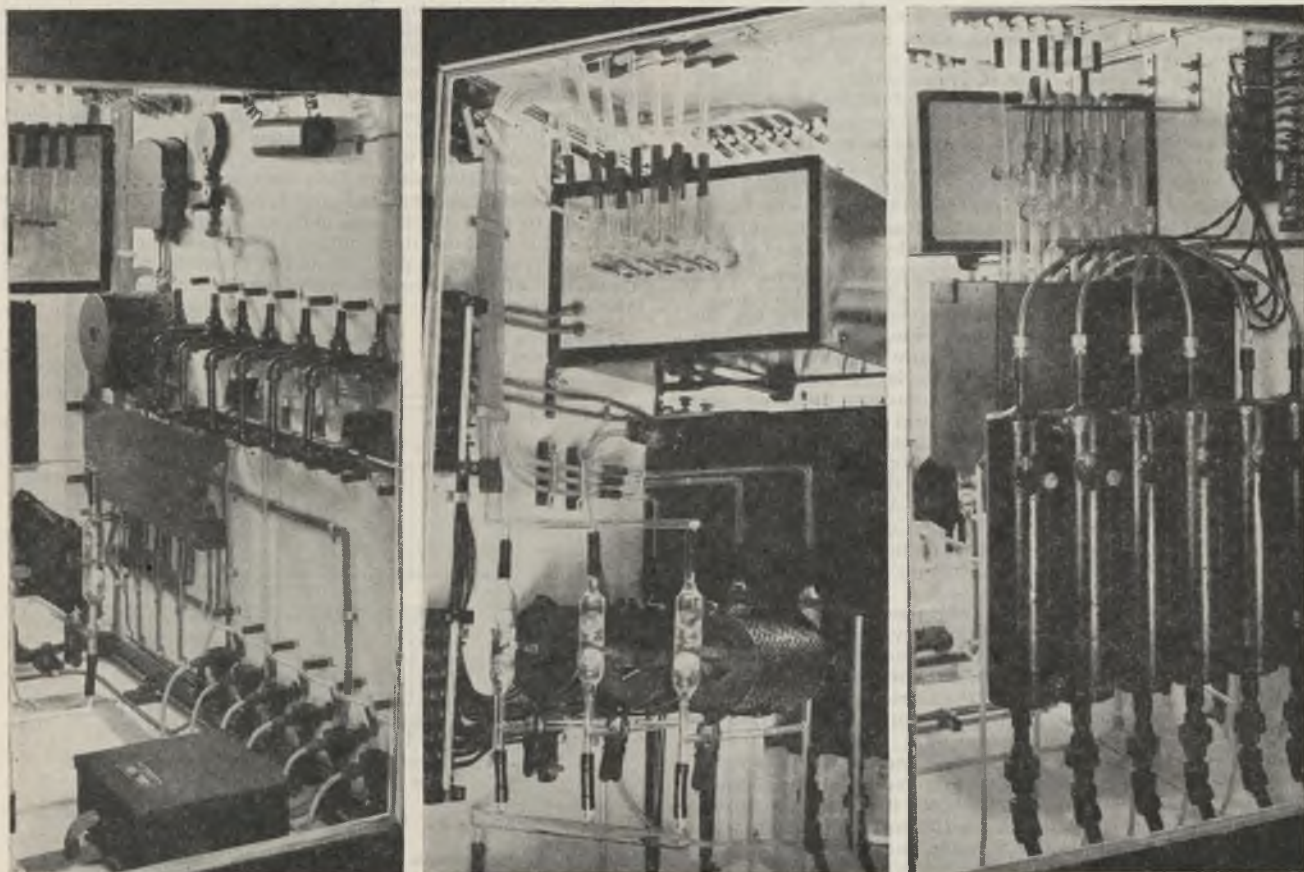


Figure 2. Interior of Analyzer

A. Front panel from left side

B. Rear panel from left side

C. Rear panel from right side

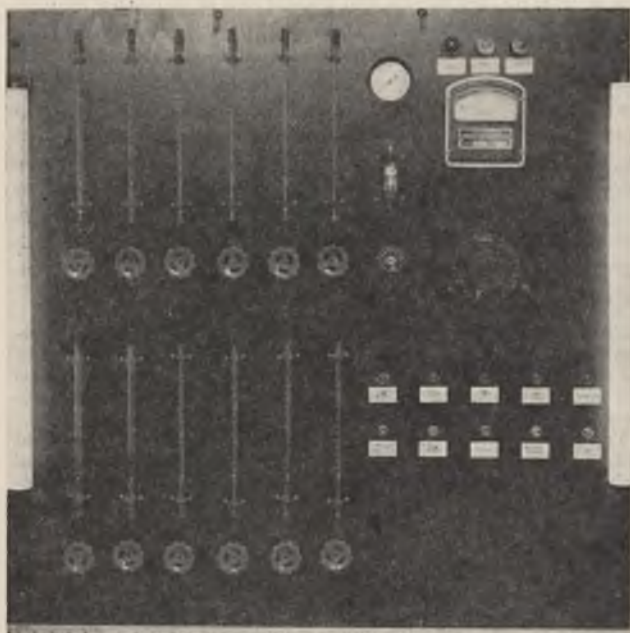


Figure 3. Front of Analyzer

formed by winding 960 cm. (32 feet) of No. 20 Chromel A wire on a 0.3-cm. (0.125-inch) arbor. This helix was stretched to cover the desired center section of the tubes and was covered with a 0.6-cm. (0.25-inch) layer of Alundum cement. One Transite end plate was removed and the heating unit was inserted into a rectangular sheet iron shell. The shell covered the front, back, top, and bottom of the furnace. The remaining space inside this shell was filled with loose Insulag insulation and the second end plate replaced. An additional end plate, having six 1.31-cm. (0.625-inch) holes, was installed at either end of the heater to keep the tubes in place. The entire assembly was held together by two rectangular frames made of 1.25-cm. (0.5-inch) angle iron made to fit over each end of the furnace and held together by two tie bolts, one on top and one on the bottom, and running lengthwise of the furnace. The furnace was mounted on a panel by means of angle irons welded to the end frames.

The voltage to the furnace was controlled by means of a Variac autotransformer, type 200 CM (General Radio Co., Cambridge, Mass.). The temperature was measured by a chromel-alumel thermocouple and a high-resistance pyrometer (Model No. 30, 0° to 1200° C., Wheelco Instruments Co., Chicago, Ill.).

The six systems comprising the six-point analyzer are installed in a cabinet 95 cm. (38 inches) wide, 65 cm. (26 inches) deep, and 92.5 cm. (37 inches) high. Figure 2 shows three interior views of the analyzer cabinet. At the left is the rear of the front panel, including the hydrogen and vacuum manifolds and the rear of the Variac autotransformer and the pyrometer. In the center is shown the inside of the rear panel, on which is mounted the pyrolysis furnace near the top and the constant-temperature bath in the background. In the lower foreground are the three pump and valve assemblies. At the right is shown the interior of the rear panel from the right side with the pyrolysis tubes leading from the furnace to the conductivity cells which are immersed in the constant-temperature bath. In the foreground are the air-water separators.

Figure 3 shows the outside of the front panel containing all the necessary electrical switches, adjusting devices, and indicating instruments except the water bath thermometer, which is inside. At the upper left of the panel are the hydrogen rotameters and needle valves. At the lower left are the air rotameters and needle valves. At the upper center are the vacuum gage, water flow indicator for the constant-temperature bath, and the water-controlling valve. At the upper right of the panel are the pilot lights for the various electrical circuits, the pyrometer for the furnace, and the autotransformer for controlling the furnace temperature. At the lower right are the switches for the water pumps, pyrometer, vacuum pump, bath heater, furnace, and lights.

In Figure 4 is shown a wiring diagram of the analyzer. The solenoid coils must be wired so that the switches will break the connection in both wires, as shown. Otherwise, when one or two pumps are off the other one or two will operate at about twice the wattage and only one half the power.

Saran tubing has been found useful in the construction of the analyzer for conducting water, air, and hydrogen flows. Saran is connected to glass or other tubing by means of short lengths of rubber tubing, as may be seen in Figure 2.

EXPERIMENTAL

The apparatus used in the experimental work consisted of three main sections—namely, air purification, sample addition, and analysis section. The air used in the experimental work was purified of any material which would affect the electrical conductivity of the pyrolyzed product, by passing it through a quartz tube which was maintained at a temperature of about 1000° C. The air feed to this pyrolysis tube was saturated with water vapor to ensure complete pyrolysis. The air leaving the pyrolysis tube was bubbled through 6 *N* sodium hydroxide to remove any acidic gases.

Addition of methyl bromide to the air stream was accomplished by two means. The more satisfactory consisted of adding a small flow of highly concentrated methyl bromide vapor.

A weighed capsule of methyl bromide was introduced into a 250-ml. graduated separatory funnel. After breaking the capsule of methyl bromide inside the evacuated separatory funnel, the top of the funnel was connected to the analysis section of the apparatus and purified air allowed to enter. Mercury was passed from an elevated reservoir through an orifice-type flowmeter into the bottom of the separatory funnel, displacing the air-methyl bromide mixture into the purified air stream. The mercury rate was controlled by means of an adjustable-flow stopcock. Thus the rate at which the methyl bromide-air mixture entered the gas stream was read on the mercury flowmeter. This was checked against the graduations on the separatory funnel and the time required for delivery.

The second method of methyl bromide addition was based on the displacement of a more dilute air-methyl bromide mixture into the analyzer at a high rate by means of acidified, saturated sodium chloride solution. The brine was passed from an elevated reservoir through a calibrated rotameter into the sample container, which was a 20-liter Pyrex bottle. The brine rate was controlled by means of a screw clamp on the rubber tubing leading to the sample container.

In operation, air passed through the air flowmeter, humidifier, pyrolysis tube, and absorber. The methyl bromide-air mixture of known composition was added to the purified air stream at a known rate and the mixture thus obtained was passed into the analysis section. A portable Leeds & Northrup resistivity meter was used to measure the conductivity during the experimental work. This instrument permitted the measurement of concentrations beyond 200 p.p.m. of methyl bromide, which was the upper limit of the Micromax recorder with the authors' particular conductivity cells.

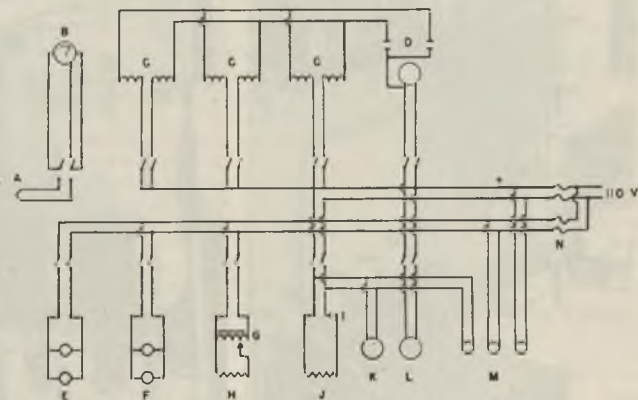


Figure 4. Wiring Diagram of Analyzer

A. Thermocouple	H. Furnace
B. Pyrometer	I. Thermoregulator
C. Solenoid coils	J. Bath heater
D. Timer	K. Stirrer
E. Panel lights	L. Vacuum pump
F. Interior lights	M. Pilot lights
G. Autotransformer	N. Fuses

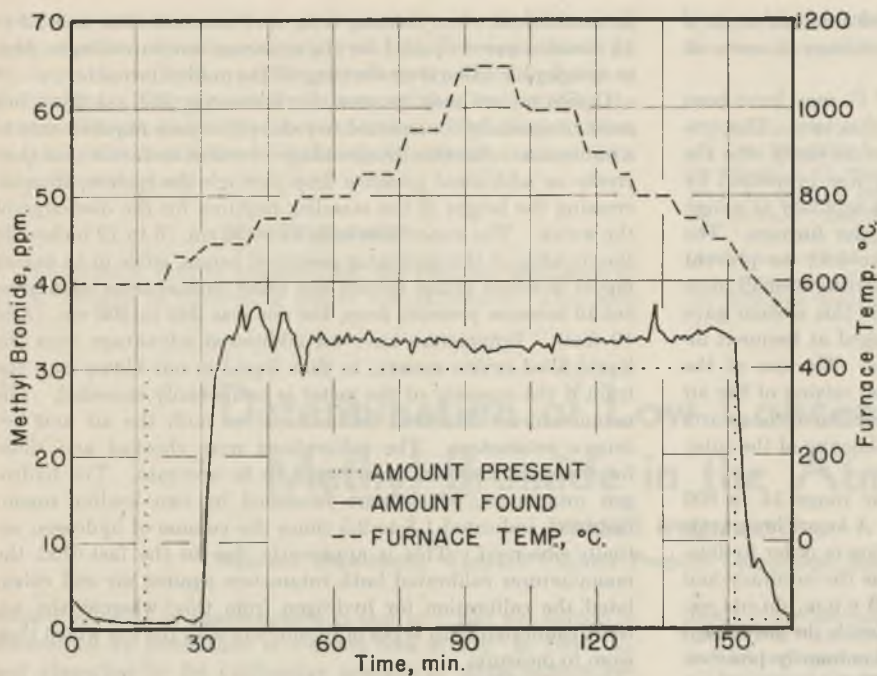


Figure 5. Effect of Furnace Temperature

In the initial work, before hydrogen was added to the air stream, recoveries were low and erratic, varying from 20 to 80% of the amount taken. The relatively high dissociation constant of hydrogen bromide at elevated temperatures suggested that the formation of free bromine might account for the erroneous results. To test this possibility, a second absorber charged with dilute sodium hydroxide was placed in the train. A substantial amount of free bromine was found in this absorber. Prevention of bromine formation or its reduction to hydrogen bromide after it is formed is essential to the utilization of the conductivity method for methyl bromide. Olsen, Smyth, Ferguson, and Scheflan (2) have shown that the formation of free chlorine during the thermal decomposition of carbon tetrachloride in air can be prevented if a sufficiently high humidity is maintained. However, humidification of the air did not appear promising in this application. Addition of large amounts of moisture in the train resulted in a slight increase in recovery of added methyl bromide, but caused complications due to condensation of the moisture in cooler parts of the train.

The use of hydrogen appeared to be a good possibility in preventing the formation of bromine or in reducing it to hydrogen bromide after it is once formed. The hydrogen could presumably be regulated to provide the desired excess of oxygen or of hydrogen in the furnace. Quantitative recovery of methyl bromide required the addition of sufficient hydrogen to react with all the oxygen of the air. The use of 30% excess hydrogen caused no deleterious effects and, accordingly, a slight excess of hydrogen was adopted.

In order to ensure complete absorption of the hydrogen bromide the first conductivity cell contained a built-in

absorber consisting of an Alundum extraction thimble through which the air stream diffused into the water in the cell. In this system water was fed directly to the cell at the top of the spray bulb, rather than into the quartz tube near the furnace. Erratic results were obtained with this system. Calculation showed that the dew point of the air stream leaving the furnace was 70° or 80° C., owing to the combustion of hydrogen. The cell was thermostated at 40° C., thus causing condensation of moisture inside the air line as it entered the bath. Drops of water were observed to form at intervals in the air line and to run down into the diffuser. Raising the temperature of the bath above the dew point eliminated condensation and gave uniform results but equilibrium was attained only very slowly under these conditions. The cause of this lag is not well understood, but it appeared to be associated with the diffuser. Accordingly, this unit was eliminated and the water was added as near the furnace

as possible, before any condensation is likely. Thus that portion of the air line in which condensation does occur is continually flushed with water into the conductivity cell. This system gave concordant results and rapid response to changes in concentration.

Upon bringing the furnace up to operating temperature, no methyl bromide was recovered below 690° C. Reaction between hydrogen and oxygen started at 690° C. but was somewhat erratic until the temperature reached 800° C. Recovery of methyl bromide during this temperature interval was approximately quantitative although somewhat erratic. Burning was smooth as the temperature was raised to 1100° C. and again reduced to 670° C. and recovery of methyl bromide was precise over this interval as shown in Figure 5. These data indicate that a mini-

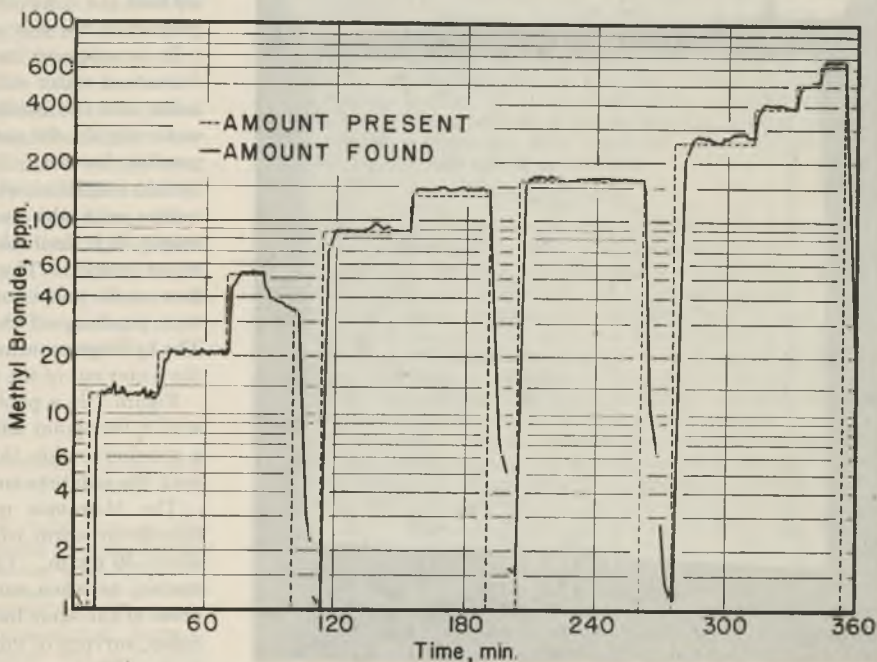


Figure 6. Range and Accuracy of Method

imum furnace temperature of 800° C. is desirable, although if burning has already been initiated, it may continue to occur at lower temperatures.

The erratic results between 690° and 800° C. may have been associated with the type of burner used for this test. The system of burning involved mixing the gases before entry into the furnace. Backfiring to the point of mixing was prevented by passing the mixed gas through a small quartz capillary at a high velocity. The capillary ended just inside the furnace. The capillary alone did not provide sufficient velocity to prevent backfiring, which was finally prevented by inserting a small piece of platinum wire inside the capillary. While this system gave satisfactory burning, the small capillary plugged at frequent intervals, causing excessive maintenance costs. The use of the burner, which is shown in Figure 1, prevented mixing of the air and hydrogen until they had entered the hot section of the quartz tube, successfully prevented backfiring and plugging of the tube, and reduced maintenance on the apparatus.

The recovery of methyl bromide over the range 14 to 600 p.p.m. is illustrated graphically in Figure 6. A logarithmic scale is utilized for the methyl bromide concentration in order to illustrate the wide range of the method as well as the accuracy and precision at low levels. The errors up to 50 p.p.m. do not exceed 1 or 2 p.p.m. and the errors at higher levels do not exceed 10% of the amount taken. Errors are predominantly positive. This suggests a slight error in calibration. This constant error could be eliminated and a precision of $\pm 5\%$ obtained by empirical calibration.

From Figure 6 it is seen that the apparatus responds rapidly to changes in the composition of the atmosphere. Equilibrium after a change in composition was established in 4 to 5 minutes and about 80% of the change took place in 1 to 2 minutes. A somewhat longer time, up to 8 minutes, was required for equilibrium to

be established when starting from zero concentration and 12 to 15 minutes were required for the apparent concentration to drop to a negligible value after shutting off the methyl bromide.

Orifice meters may be used for measuring the gas flows but must be specially constructed to reduce the space requirements to a minimum. Another disadvantage of orifice meters is that they create an additional pressure drop through the system, thus increasing the height of the standleg required for the discharge of the water. The water rises only 15 to 30 cm. (6 to 12 inches) in the standleg of the apparatus described herein, while in an earlier model in which orifice meters and other constrictions were present to increase pressure drop, the rise was 240 to 300 cm. (8 to 10 feet). Rotameters have an additional advantage over the liquid-filled orifice meters, in that liquid is not blown into the train if the capacity of the meter is temporarily exceeded. The manufacturers furnished calibrations for both the air and hydrogen rotameters. The calibrations were checked and those for the air flowmeters were found to be accurate. The hydrogen rotameters, which were furnished by two leading manufacturers, indicated 1.5 to 2.5 times the volume of hydrogen actually observed. This is apparently due to the fact that the manufacturer calibrated both rotameters against air and calculated the calibration for hydrogen from this, whereas the authors calibrated both types of rotameters with the gas which they were to measure.

Several different types of solenoids were tested during the course of the experimental work. A number of commercial solenoids overheated, causing the water to boil out of the pump. The solenoid assembly which was finally adopted is one of several experimental models. The pump using this solenoid assembly will pump accurately under a 240-cm. (8-foot) head of water at a rate of 10 cycles (20 strokes) per minute. It will pump under a higher head but does not make a complete stroke.

An aspirator was used as the vacuum source during the experimental work. Fluctuations in water pressure caused fluctuations in the air-flow rate. A throttling air-flow rate controller was built to eliminate this irregularity. The vacuum was turned on at a rate greater than the desired air rate and the excess air was bled in through the controller. Experience showed that a vacuum pump, such as a Cenco-Pressovac, is a far more satisfactory source of vacuum. A constant vacuum can be obtained in this manner and precise control of the air flow is possible even without the controller, provided good needle valves are used to proportion the flow among the several systems.

It is necessary to use a good grade of distilled water. A Barnstead water still was used and no special precautions were taken with the distilled water supply. The blank on the distilled water supply did not exceed 2 p.p.m. of methyl bromide. It is possible, however, that distilled water might be obtained under certain conditions which would contain sufficient electrolyte to interfere with the measurement of the conductivity. For this reason, it is desirable to run an occasional blank on the distilled water supply. This can be accomplished by closing the air-flow needle valve until the air flow is reduced to a minimum and then pinching off the air flow entirely at the furnace entrance. The hydrogen continues to bubble through the train and to sweep the water out of the system.

Figure 7 is a photograph of a portion of the record obtained with a four-point analyzer. The various points are indicated by a number beside the recorded dot. In the six-point analyzer both the numbers and dots have distinctive colors.

The Micromax recorder is equipped with a contact which sounds an alarm when the methyl bromide concentration rises above 30 p.p.m. This protects personnel not in view of the recorder, as when sampling in different buildings or in remote areas of the same building. By means of long, flexible sampling tubes, surveys of vapor concentrations in different areas can be made. This same system has proved very valuable in detecting and locating leaks in equipment and containers. A similar

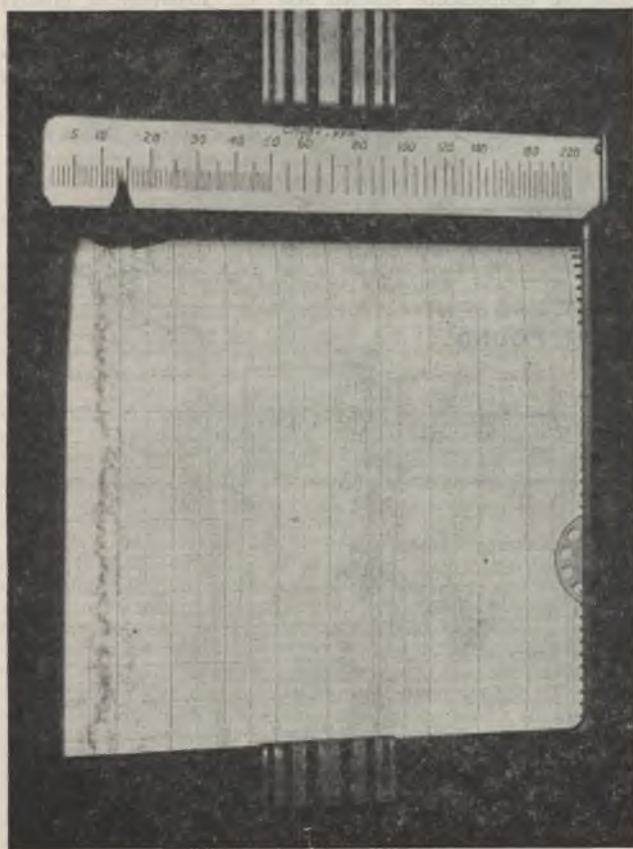


Figure 7. Recorder Scale and Record

apparatus has been used very successfully in the continuous determination of carbon tetrachloride. In this application, no hydrogen is required, providing a relatively high humidity is maintained. This can readily be accomplished by bubbling the sample through water prior to combustion. The determination of other volatile chlorinated hydrocarbons could presumably be determined similarly.

ACKNOWLEDGMENT

The authors wish to acknowledge the valuable assistance of L. A. Bedwell in fabricating quartz and glassware. They also

wish to express thanks for the permission of Westvaco Chlorine Products Corporation to publish this paper.

LITERATURE CITED

- (1) Kolthoff, I. M., and Yutzy, H. C., *IND. ENG. CHEM., ANAL. ED.*, **9**, 75 (1937).
- (2) Olsen, J. C., Smyth, H. F., Jr., Ferguson, G. E., and Scheffan, L., *Ibid.*, **8**, 260-3 (1936).
- (3) Reilly, J., and Rae, W. N., "Physico-Chemical Methods", 2nd ed., New York, D. Van Nostrand Co., 1933.
- (4) Thomas, M. D., Ivie, J. O., Abersold, J. N., and Hendricks, R. H., *IND. ENG. CHEM., ANAL. ED.*, **15**, 287-90 (1943).
- (5) Williams, Dwight. *Ibid.*, **17**, 295 (1945).

Determination of Low Concentrations of Methyl Bromide in the Atmosphere

DWIGHT WILLIAMS

Research Department, Westvaco Chlorine Products Corporation, South Charleston, W. Va.

Methyl bromide in concentrations as low as 1 part per million is determined by combustion in a quartz tube at 950° to 1000° C. and absorption of the combustion products in dilute sodium hydroxide. The bromine content of the sodium hydroxide solution is determined by the Kolthoff-Yutzy procedure. The method is readily adjusted to any concentration level by adjusting the sample size. Recovery of larger amounts is 98% complete.

A METHOD for the determination of methyl bromide in the atmosphere in low concentrations was desired to detect the presence of hazardous concentrations when manufacturing and handling this compound. Stenger, Shrader, and Beshgetoor (2) recommended hydrolysis of methyl bromide with monoethanolamine followed by titration of the bromides formed by hydrolysis. They applied this method to the determination of methyl bromide at relatively high concentrations. Preliminary tests indicated that the method was useful at high concentrations where the bromides could be titrated by the Volhard method. However, at low concentrations, it was necessary to titrate the bromide by the procedure of Kolthoff and Yutzy (1) and to remove the monoethanolamine before applying this latter method. The removal of the monoethanolamine proved troublesome and other means for analysis were sought.

Combustion (or pyrolysis) at high temperatures in a quartz tube has been widely applied to the determination of the chlorine content of chlorinated hydrocarbons in the atmosphere. Apparently no attempt has been made to apply this principle to brominated hydrocarbon vapors. While somewhat more elaborate apparatus would be required than in a hydrolysis procedure, no foreign substance need be introduced and the sample size could be varied more readily. In addition, experience showed that at low concentrations where it was necessary to apply the Kolthoff-Yutzy titration procedure, combustion was more rapid than hydrolysis.

APPARATUS AND REAGENTS

The sample bottle, combustion tube and furnace, diffuser and absorber, flowmeter, and needle valve illustrated in Figure 1 are required.

COMBUSTION FURNACE. A 20-cm. (8-inch) tube furnace was made by winding resistance wire around a 20-cm. (8-inch) length of 2.5-cm. (1-inch) quartz tubing and insulating with Alundum cement and magnesia pipe lagging. The voltage to the furnace was controlled by means of a Variac, type 200-CM. The temperature was measured by means of a chromel-alumel thermocouple and a milliammeter. The milliammeter was calibrated against an L. & N. portable potentiometer.

COMBUSTION TUBE. A 50-cm. (20-inch) length of 4-mm.

inside diameter quartz tubing was bent at a 90° angle 2.5 cm. (1 inch) from the exit end. This tube should extend 15 cm. (6 inches) beyond the furnace on the exit side to permit dissipation of the heat of the exit gases.

DIFFUSER AND ABSORBER. The diffuser is a 6 × 37 mm. Alundum extraction thimble No. RA98 sealed to the end of a 32-mm. length of 7-mm. glass tubing. The absorber is made from a 14-cm. length of 14-mm. glass tubing.

Flowmeter, Scientific Glass Apparatus Co., Catalog No. J-1912.

Needle valve, Hoke, straight, 0.3 cm. (0.125 inch), V-point, No. 341.

Sodium hydroxide, approximately 0.1 N.

Sodium hypochlorite about 5%. A commercial bleaching agent (Clorox) was used.

Sodium dihydrogen phosphate, NaH₂PO₄·H₂O, 200 grams per liter.

Sodium formate, 500 grams per liter. This solution is usually turbid and is filtered before using.

Ammonium molybdate, 50 grams per liter of MoO₃.

Potassium iodide, 300 grams per liter.

Sulfuric acid, 6 N.

Sodium thiosulfate, 0.01 N containing 0.4 gram per liter of sodium carbonate.

Starch, 10 grams per liter.

The sodium phosphate, sodium formate, potassium iodide, and sulfuric acid are added by means of dispensers consisting of pipets cut off at the bottom of the bulb. The pipet is fitted in a one-hole rubber stopper, so that the bulb is at the bottom of the reagent bottle. A notch is cut in the stopper to permit equalization. When dispensing the reagent the analyst closes the top of the filled dispenser with his finger, raises the dispenser, and discharges it into the reaction flask.

PROCEDURE

Set up the combustion furnace, absorber, flowmeter, and needle valve shown in Figure 1. Charge the absorber with 10 ml. of 0.1 N sodium hydroxide. If the sample is to be taken directly, connect the inlet side of the furnace by rubber or Saran tubing directly to the point at which the sample is to be taken. Turn on the needle valve and adjust the air flow to 500 ml. per minute. Start the stop watch simultaneously. Continue the air flow for 4 minutes or longer, depending on the sensitivity which is required. If the sample is taken in a bottle, connect it to the furnace through an L-tube at F and attach a bottle containing acidified saturated sodium chloride at E. Open stopcock D. Turn on the needle valve until an air rate of about 500 ml. per minute is obtained. When the sample bottle has been filled with brine, stop the brine flow by closing stopcock D, then turn off the needle valve. Disconnect the sample bottle from the furnace to allow the air pressure to equalize.

Disconnect the absorber, first from the quartz tube, then from the flowmeter. Pour the liquid from the absorber into a 250-ml. conical flask. Pipet 5 ml. of distilled water into the diffuser and force it through the diffuser into the absorber by means of a rubber bulb. Combine this washing with the absorber liquid and wash three more times in the same manner, transferring each washing separately to the flask.

To the combined absorber liquid and washings add 5 ml. of sodium hypochlorite solution by means of a pipet. Add 8 to 10 ml. of sodium dihydrogen phosphate and heat the solution just to boiling. Add 3 to 4 ml. of sodium formate and again bring to a boil. Cool to room temperature in a stream of water. To the cooled solution add 100 ml. of cold water (about 10° C.). Add 2 drops of ammonium molybdate solution, 8 to 10 ml. of potassium iodide solution, and 20 to 25 ml. of 6 *N* sulfuric acid. Titrate promptly with 0.01 *N* sodium thiosulfate solution. Add 3 to 4 ml. of starch solution just before the end point is reached and titrate until the last visible trace of pink or blue color just disappears.

A reagent blank containing all the reagents including the 0.1 *N* sodium hydroxide is prepared and carried through the titration procedure and is subtracted from the sample titration.

$$\frac{\text{Ml. of } 0.010 \text{ } N \text{ Na}_2\text{S}_2\text{O}_3 \times 41.5}{\text{liters of sample}} = \text{p.p.m. of methyl bromide}$$

EXPERIMENTAL

The sampling apparatus shown in Figure 1 was employed to obtain the small concentrations required for this work.

A weighed quantity of methyl bromide is sealed in a glass capsule following the procedure employed by Stenger, Shrader, and Beshgetoor (2). The sealed capsule is placed in the 9-liter bottle, *G*, the bottle is closed by means of the standard-taper joint assembly, and the capsule broken by shaking the bottle. The 2-liter bottle, *H*, is partially evacuated to a predetermined pressure, depending on the concentration desired in *H*, by applying suction at *E*. The pressure in *G* is measured by means of the Zimmer-type manometer with stopcock *A* open and *B* closed; *A* is now closed and *B* opened to obtain the pressure in *H*. Both *A* and *B* are now opened (*C* is kept closed throughout these manipulations) and the pressure again measured. The concentration of methyl bromide in *G* in parts per million is given by the following formula, calculated at 27° C. and 750 mm. pressure:

$$C_1 = \frac{\text{grams of } \text{CH}_3\text{Br} \times 263,000}{L}$$

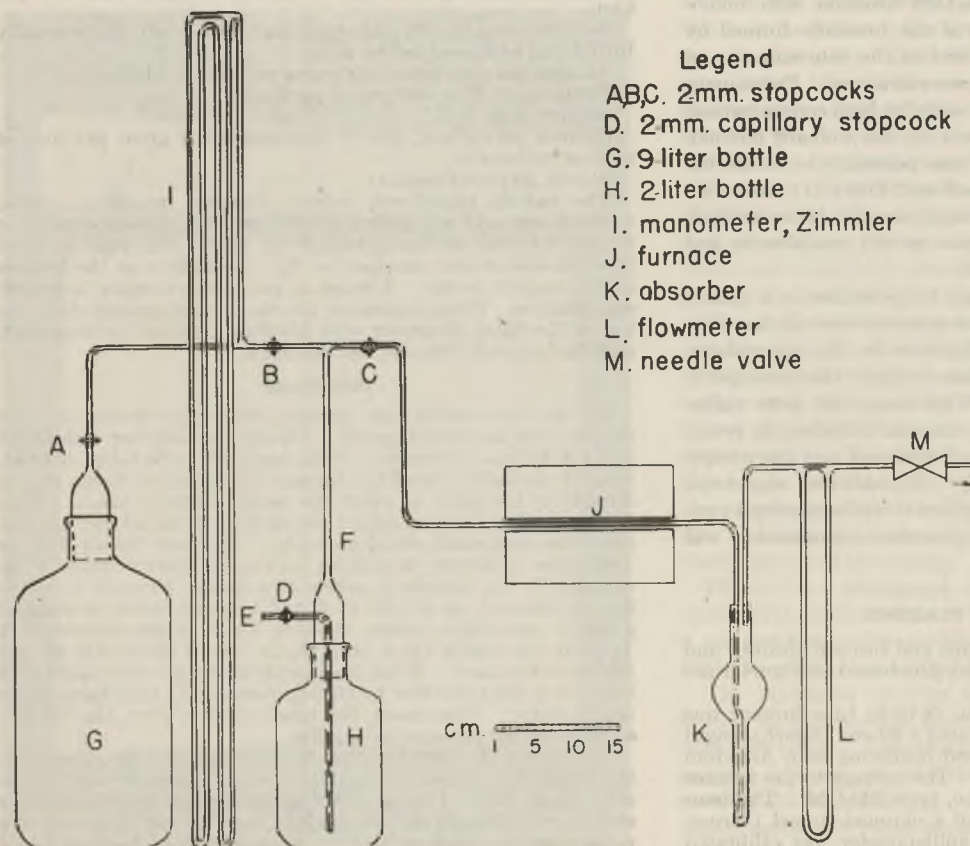


Figure 1. Sampling, Combustion, and Absorption Apparatus

The volume, *L*, of *G* in liters is determined approximately by filling with water from a graduate.

The concentration in *H* is calculated as follows:

$$c = \frac{(P_2 - p_1)C_1}{P_1}$$

where P_1 is pressure in *G* before adjustment

p_1 is pressure in *H* before adjustment

P_2 is pressure in both *G* and *H* after adjustment

To determine the volume of air which must be passed through the system to recover all the methyl bromide, approximately 500 p.p.m. of methyl bromide were introduced into *H* and air was swept through the system at the rate of 1000 ml. per minute for 2.5-minute intervals. The air flow was stopped after each interval and fresh caustic introduced into the absorber. Each portion of caustic was titrated separately for bromides. The data obtained (Table I) indicate that a minimum of 17.5 liters of air must be passed through the system for maximum recovery. A 20-liter air sweep was used in subsequent tests.

The Kolthoff-Yutzy procedure is best applied to small volumes. It appeared that some care might have to be exercised in the design of the absorber and in the manipulations to avoid a subsequent evaporation prior to the oxidation and titration. Several portions of sodium bromide, equivalent to 460 micrograms of methyl bromide, were diluted to various volumes and analyzed in the usual manner. Negative errors were obtained at all dilutions and the magnitude of the errors increased sharply above 80 ml. (Figure 2). These data indicate that the volume should be kept as small as possible for the best results.

The absorber (Figure 1) requires about 10 ml. of fluid to fill to the bottom of the spray bulb. To determine the minimum volume of water required for washing the diffuser a 2-liter sample containing 500 p.p.m. of methyl bromide was analyzed in the usual manner except for the washing. The diffuser was washed with six 5-ml. portions of water. The caustic in the diffuser, the first and second, the third and fourth, and the fifth and sixth washings were oxidized and titrated separately. The data obtained (Table II) indicate that even six washings may not remove all of the bromides. However, since in the final procedure each washing is transferred separately, fewer washings would be required and, since excessive dilution introduces an error, the use of four separate 5-ml. washes was adopted.

A study of the effect of furnace temperature indicated that satisfactory results were obtained above approximately 900° C. Recovery broke sharply below this temperature and no recovery was obtained below a temperature of about 700° C. Tebbens (3) reported that platinum reduces the minimum temperature required for the decomposition of carbon tetrachloride in the air. No change was observed in the minimum temperature required for complete combustion of methyl bromide when 2 grams of scrap platinum wire were introduced into the combustion tube. Subsequent work was done at a temperature of 950° to 1000° C.

The data in Table III show that the recovery decreases with

Table I. Volume of Air Required to Sweep Methyl Bromide from 2-Liter Bottles

Cumulative Volume Ml.	Recovery		Cumulative Volume Ml.	Recovery	
	Incremental %	Cumulative %		Incremental %	Cumulative %
2,500	54.3	54.3	12,500	1.0	93.3
5,000	28.0	82.3	15,000	1.0	94.3
7,500	7.0	89.3	17,500	0.3	94.6
10,000	3.0	92.3	20,000	0.0	94.6

Table II. Effect of Washing Diffuser

	Recovery, %
Absorber	53.1
First and second washing	28.8
Third and fourth washing	5.4
Fifth and sixth washing	2.7

increasing air flow rate. White vapors were observed above the absorber liquid at the highest air flow rate (2000 ml. per minute), suggesting incomplete absorption of hydrogen bromide. However, no significant amount of hydrogen bromide was recovered in a second absorber and white vapors were observed there also. No satisfactory explanation can be advanced for this phenomenon. While recovery at the lowest rate (500 ml. per minute) was not quantitative, it appears that further reduction in flow rate is not likely to improve recovery further.

The accuracy of the method was determined using the sampling apparatus shown in Figure 1. In each case 20 liters of air were drawn through the 2-liter bottle, *H*, at a rate of 500 ml. per minute. An average recovery of about 98% of the amount taken was obtained at the higher concentrations (Table IV). A possible explanation for these slightly low recoveries at high concentrations is suggested below. Errors at lower concentrations tend to be positive and do not exceed 2 p.p.m. The positive errors may be due to the presence of a small amount of methyl bromide in the laboratory atmosphere. Since the volume of air which was passed through the furnace was 10 times the volume of the sample bottle, a concentration of 0.2 p.p.m. of methyl bromide in the atmosphere would account for this error.

These data show that this method will detect methyl bromide in concentrations as low as 1 or 2 p.p.m. when using a 2-liter sample. The sensitivity of the method may readily be increased several-fold by increasing the sample size. The technique of sweeping air through a sample bottle until free of methyl bromide is not practical for routine work, owing to the long time required to complete the air sweep. Two methods of sampling may be used. The easiest method, where feasible, is to pass air directly from the point which it is desired to sample to the combustion furnace. In case this method is not feasible the air can be swept from the sample bottle into the furnace by filling the bottle with acidified saturated sodium chloride solution. The solubility of methyl bromide in water is substantial, between 1 and 2% by weight at 760-mm. pressure, and that in brine is probably of the same order of magnitude. However, the solubility would be slight when only a few parts per million were present in the air and experimentation which was carried out in connection with a continuous method (4) indicates that there is no significant error from this source. An analysis of a 2-liter sample could be completed in 15 to 20 minutes if either of these sampling techniques were used.

Dilute sodium hydroxide was used as the absorbent for the combustion products in this work. In an investigation of a continuous method for methyl bromide (4) it was found that part and perhaps all of the methyl bromide is converted to free bromine on passing through the combustion furnace and that the bromine is only partially absorbed in water. The recoveries obtained by absorption in 0.1 *N* sodium hydroxide indicate that a higher concentration of sodium hydroxide is not necessary.

In several applications of the Kolthoff-Yutzy procedure in this laboratory departures from the conventional procedure have been

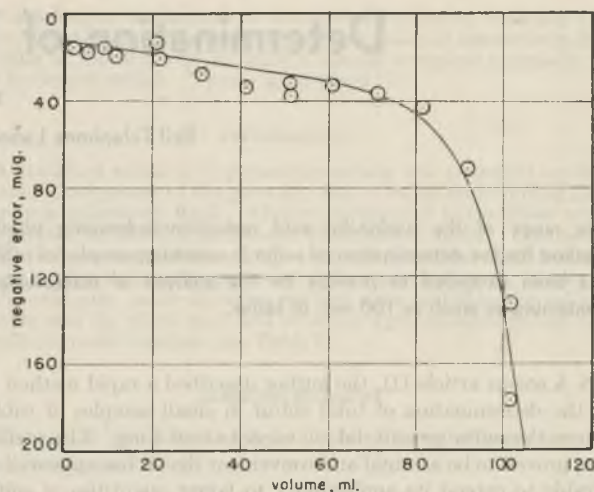


Figure 2. Volume vs. Error in Titration of Bromide

made. These departures have been incorporated into the present procedure. For convenience, some commercial bleaching agent, usually Clorox, has been used as a source of hypochlorite. The small bromine content of the bleaching agent is corrected for by means of the blank. Commercial bleaching agents almost always contain some chlorate and the chlorate may increase the magnitude of the blank slightly. However, the chlorate content is usually many times the magnitude of the blank. The solution is diluted with 100 ml. of cold water prior to the titration. This gives a dilution having a temperature a little below 20° C., even in the summer, which is ideal for the subsequent iodometric titration. In this application, no sodium chloride was added prior to oxidizing the bromide. This last factor may have contributed to the low results at higher concentrations noted in Table IV but, since the method was intended primarily for low concentrations, this point was not investigated.

Table III. Effect of Air Flow Rate

Air Flow Ml./min.	Recovery %
2000	81
2000	81
2000	81
1000	92
500	94

Table IV. Range and Accuracy of Method

Methyl Bromide			Methyl Bromide		
Added P.p.m.	Found P.p.m.	Error P.p.m.	Added P.p.m.	Found P.p.m.	Error P.p.m.
0.7	1.6	+0.9	18.0	18.0	0.0
1.9	3.4	+1.5	24.5	23.5	-1.0
2.2	3.5	+1.3	40.3	40.3	0.0
3.6	5.3	+1.7	90.0	87.0	-3.0
5.4	6.3	+0.9	132.0	129.4	-2.6
5.9	6.3	+0.4	213.0	213.0	0.0
9.2	8.3	-0.9	286.9	283.5	-3.4
11.2	11.4	+0.2	356.4	348.4	-8.0
11.8	11.3	-0.5	439.0	426.0	-13.0
17.0	17.0	0.0	486.0	476.0	-10.0

ACKNOWLEDGMENT

The writer wishes to acknowledge the assistance of Mary P. Brevoort, George S. Haines, and Frank D. Heindel in performing the experimental work.

LITERATURE CITED

- (1) Kolthoff, I. M., and Yutzy, C. H., *IND. ENG. CHEM., ANAL. ED.*, 9, 75-6 (1937).
- (2) Stenger, V. A., Shrader, S. A., and Beshgetoor, A. W., *Ibid.*, 11, 121-4 (1939).
- (3) Tebbens, B. D., *J. Ind. Hyg. Toxicol.*, 19, 204-11 (1937).
- (4) Williams, Dwight, Haines, G. S., and Heindel, F. D., *IND. ENG. CHEM., ANAL. ED.*, 17, 289 (1945).

Determination of Total Sulfur in Rubber

C. L. LUKE

Bell Telephone Laboratories, Inc., New York, N. Y.

The range of the hydriodic acid reduction-iodometric titration method for the determination of sulfur in semimicrosamples of rubber has been extended to provide for the analysis of macrosamples containing as much as 100 mg. of sulfur.

IN A recent article (1), the author described a rapid method for the determination of total sulfur in small samples of rubber where the sulfur present did not exceed about 5 mg. This method has proved to be so rapid and convenient that it has appeared desirable to extend its applicability to larger quantities of sulfur. Experiments have shown that this can be done very easily by making a few simple changes in technique.

REAGENTS

NITRIC ACID-ZINC OXIDE-BROMINE MIXTURE. Dissolve 20 grams of zinc oxide in 100 ml. of nitric acid and saturate with bromine.

ACID MIXTURE FOR DISTILLATION. Place 320 ml. of hydriodic acid (specific gravity 1.70), 320 ml. of hydrochloric acid, and 90 ml. of hypophosphorous acid (50%) in a 1-liter Erlenmeyer flask. Add a few grains of silicon carbide and boil vigorously without cover for 5 minutes. Cool in an ice bath to room temperature. Keep stoppered in a brown glass-stoppered bottle to avoid oxidation of the hydriodic acid.

AMMONIACAL CADMIUM CHLORIDE SOLUTION. Dissolve 20 grams of cadmium chloride dihydrate in water. Add 200 ml. of ammonium hydroxide and 150 ml. of 1% starch solution and dilute to 2 liters.

NITROGEN. Commercial "prepurified" lecture bottle tank nitrogen.

STANDARD POTASSIUM IODATE SOLUTION (0.1 N). Recrystallize c.p. potassium iodate from water twice and dry at 180° C. to constant weight. Weigh 7.134 grams of the pure potassium iodate and dissolve in water. Add 2 grams of sodium hydroxide and then 50 grams of potassium iodide (free from potassium iodate). After complete solution of all salts adjust to room temperature and dilute to 2 liters in a volumetric flask.

STANDARD SODIUM THIOSULFATE SOLUTION (0.1 N). Dissolve about 50 grams of sodium thiosulfate pentahydrate in 2 liters of freshly boiled and cooled distilled water. Store in a clean Pyrex bottle. To standardize this solution, pipet 25 ml. of the standard potassium iodate solution into a 300-ml. Erlenmeyer flask. Add 150 ml. of water and 20 ml. of hydrochloric acid and then titrate with the thiosulfate solution. As the end point is approached add 2 ml. of 1% starch solution and titrate carefully until the solution is colorless.

STARCH SOLUTION. Add a cold aqueous suspension of 10 grams of soluble starch to 1 liter of boiling water. Cool to room temperature and store in a clean bottle.

PROCEDURE

Dissolve 0.5 gram of the rubber sample (containing 5 to 100 mg. of sulfur) in 10 ml. of nitric acid-zinc oxide-bromine mixture and 15 ml. of fuming nitric acid in a 200-ml. Erlenmeyer flask as described (1). After destruction of the organic matter and conversion of zinc nitrate to oxide add 10 ml. of hydrochloric acid and boil down to near dryness to expel all oxides of nitrogen. Repeat if necessary. Add 35 ml. of hydriodic acid mixture, and immediately cap with the distillation head. Place on a hot plate with surface temperature of 170° to 200° C. with the condenser tube dipping to within about 0.5 cm. from the bottom of a 300-ml. tall-form beaker containing 150 ml. of ammoniacal cadmium chloride solution. Pass a slow stream of pure nitrogen through the solution by way of the capillary pressure regulator tube. Adjust the flow of nitrogen so that it escapes from the receiver solution at a rate of about 3 bubbles per second. (The rate of flow is not critical, providing it is not so fast as to prevent complete absorption of the hydrogen sulfide by the receiver solution; or so slow as to permit the ammoniacal solution to be sucked back into the acid solution.)

Heat the acid solution until fumes of ammonium chloride begin to appear over the ammoniacal solution and then continue for 10 minutes longer. Remove the distilling flask and detach the distillation head at once. Transfer the traces of cadmium sulfide from the condenser tube of the distillation head to the ammoniacal solution with the aid of a policeman and wash bottle.

Buret or pipet enough standard 0.1 N potassium iodate solution to provide a 5- to 25-ml. excess over that required for oxidation of the sulfide, to a 500-ml. iodine flask. Add 25 ml. of hydrochloric acid to the iodate in the flask and wash down the sides with water. Immediately pour the ammoniacal solution into the flask and transfer all the sulfide with the aid of a policeman and wash bottle. (If the starch-iodine color disappears, showing that too little iodate has been used, immediately add more iodate from a buret to provide about a 5-ml. excess.) Immediately stopper and shake vigorously to entrap any sulfide in the atmosphere in the flask. Titrate with standard 0.1 N sodium thiosulfate solution. Run a blank through the whole procedure, using 5 ml. of potassium iodate solution for the oxidation of the sulfide.

If (ml. of KIO_3 - ml. of $Na_2S_2O_3 \times KIO_3$ factor) = A and (ml. of KIO_3 for blank - ml. $Na_2S_2O_3$ for blank $\times KIO_3$ factor) = B,

$$\frac{0.1603(A - B)}{\text{sample weight in grams}} = \text{per cent sulfur}$$
then

Table I. Determination of Sulfur in Potassium Sulfate by the Proposed Method

No.	Sulfur Present Mg.	KIO_3 Used Ml.	Sulfur Found Mg.	Error Mg.
1	5.0	5	5.1	+0.1
2	5.0	5	5.0	±0.0
3 ^a	5.0	25	5.1	+0.1
4	10.0	50	10.0	±0.0
5	10.0	10	10.0	±0.0
6 ^b	10.0	10	9.9	-0.1
7	10.0	10	10.0	±0.0
8 ^a	25.0	25	25.0	±0.0
9	50.0	50	50.0	±0.0
10 ^a	50.0	50	49.8	-0.2
11	100.0	75	100.2	+0.2
12 ^b	100.0	75	99.9	-0.1
13 ^a	100.0	75	99.8	-0.2

^a HNO_3 -ZnO-Br₂ mixture used.

^b Distillate containing CdS cooled to 10° C. before titration.

DISCUSSION

In the above method the distillation is performed at a much lower temperature than that previously used and gaseous nitrogen is used to sweep the hydrogen sulfide out of the flask. This procedure eliminates the danger of loss of sulfide caused by incomplete absorption in ammoniacal cadmium chloride solution when large quantities of hydrogen sulfide are suddenly distilled over.

The method cannot be used on samples which contain barium (and presumably lead and calcium) because the insoluble sulfate is but slowly decomposed.

The iodometric titration of large amounts of hydrogen sulfide suggested in the previous publication is not very sound, since the loss of a certain amount of iodine can hardly be avoided. Attempts to titrate the sulfide by addition of a measured excess of a standard Wijs solution (iodine monochloride in glacial acetic acid), followed by back-titration of the excess iodine, failed because high results were obtained, due presumably to partial oxidation of the sulfide to sulfate.

When large amounts of sulfide are titrated iodometrically the precipitated sulfur may occlude appreciable amounts of iodine.

This error can be eliminated by dissolving the sulfur in carbon disulfide, but a better procedure is to keep the sulfur colloiddally dispersed with the aid of starch.

It is essential that nitrogen acids be completely expelled before the distillation with hydriodic acid, otherwise sulfide will be oxidized to sulfur during the distillation and unstable end points will be encountered in the titrations with thiosulfate.

APPLICATION OF THE METHOD TO INORGANIC ANALYSIS

The new method for the determination of sulfate (1) has proved very useful in the analysis for sulfur in chemicals and alloys where the usual methods fail. Following is an outline of the method used in these laboratories for the determination of 0.0005 to 0.05% sulfur in molybdenum permalloy—i.e., 79% nickel, 17% iron, and 4% molybdenum.

Dissolve 10 grams of the metal in 80 ml. of aqua regia. Evaporate to moist dryness to expel most of the excess acid. Add 35 ml. of hydrochloric acid and heat to dissolve all soluble salts. Add 25 ml. of formic acid and heat to destroy the nitric acid. Transfer the solution to a 200-ml. flask and reduce the volume to 50 to 60 ml. by boiling. Add 35 ml. of acid mixture and perform

the distillation as directed in the procedure above, doubling the time of distillation (and also the concentration of ammonium hydroxide in the receiver) in order to assure complete expulsion of the hydrogen sulfide. Titrate as directed (1).

EXPERIMENTAL

A standard solution of potassium sulfate was prepared by dissolving 27.18 grams of the pure dry salt in water and diluting to 1 liter in a volumetric flask. Aliquot portions of the solution were evaporated to dryness in 200-ml. Erlenmeyer flasks. Hydriodic acid mixture was added and the samples were then analyzed for sulfur as directed in the procedure. In some instances, 10 ml. of nitric acid-zinc oxide-bromine mixture were added to the sulfate sample and the nitric acid and bromine were expelled before the distillation and titration (see Table I).

ACKNOWLEDGMENT

The author is indebted to B. L. Clarke of these laboratories who read the manuscript.

LITERATURE CITED

- (1) Luke, C. L., *IND. ENG. CHEM., ANAL. ED.*, 15, 602 (1943).

Laboratory Corrosion Tests

R. M. BURNS

Bell Telephone Laboratories, Inc., New York, N. Y.

A critical review of laboratory corrosion tests is presented, with description of methods of measurement, preparation of test specimens, and discussion of tests and testing facilities.

A CORROSION test is a procedure for determining the rate of reaction between a metallic material and a nonmetallic element of the surrounding environment. The primary electrolytic reactions of the process consist in the anodic dissolution of metallic ions and the cathodic reduction of hydrogen ions, other metallic ions, or nonmetallic elements. These reactions occur at high velocity. Secondary reactions which depend upon composition, diffusion, convection, and solubility of components of the system proceed much more slowly and usually control the rate of the corrosion process.

Most environments present a multiplicity of factors which may affect corrosion reactions and it becomes necessary to recognize those which are of significance in a given instance. Of compositional components there are two classes, those which retard and those which accelerate corrosion. When these co-exist in a natural environment, as is usually the case, their relative proportions or activities may determine the character as well as the rate of corrosion. For example, when the ratio of retardant to accelerator is high there may be no corrosive attack; when it is low there may be general corrosion over the metal surface, while for intermediate values of this ratio severe pitting action may develop. Practical corrosion tests are often more concerned with the determination of rate of corrosion in localized areas than in the over-all corrosion rate of the metallic specimens. For example, tests are designed to measure pitting, loss of tensile strength, etc.

The purposes for which laboratory corrosion tests are to be used may determine their general character. If a test is intended to be used as a control test to ascertain the degree of uniformity of successive lots of a given material it is desirable to provide close control and standardization of conditions and procedures. If on the other hand the purpose of a test is to determine the relative suitability of materials for a certain application, then the test conditions should be patterned as closely as possible after the conditions of service.

It is obvious that there can be no universal corrosion test—

that is, no single test by means of which the corrodibility of a metal in all environments can be determined. To appraise corrosion resistance it is first necessary to know precisely the character of environments to which the metal is to be exposed. With this knowledge it becomes possible to devise laboratory corrosion tests in which the variables are known and can be controlled. These tests may then be used to obtain preliminary information concerning the corrodibility of metallic materials or the efficacy of protective coatings which, if confirmed by extensive exposure tests in natural environments, may be assumed to be dependable for engineering purposes.

Laboratory corrosion tests in simulating natural environmental conditions are designed to provide for the exposure of metallic materials to controlled atmospheric or liquid media. Commonly both gaseous and liquid phases and even contact with solids are included in a single test. Changes in temperature, humidity, or other variables experienced in natural environments may be provided in the laboratory. It is the usual practice to increase the rapidity and to some extent the severity of the so-called weathering cycles in an effort to accelerate corrosion rate. While this is permissible within reason, it must be emphasized that the reliability of the result is inversely proportional to the amount of acceleration which is induced. Corrosion tests which employ severe conditions may produce a degree of disintegration of metals or protective coatings which bears no relationship to corrodibility under conditions of service. It is preferable to carry out corrosion studies under nearly natural conditions and to use sensitive measuring techniques to determine rate of reaction rather than to depend upon highly accelerated tests to furnish the larger effects which can be detected by less precise methods of measurement.

METHODS OF MEASUREMENT

The rate of corrosion may be measured by a variety of means, most common of which is change in weight of the metallic specimen under study. In laboratory atmospheric tests the products of corrosion are usually adherent and produce a gain in weight, while in immersion tests in liquids in which the corrosion products are soluble, the course of reaction is accompanied by loss of weight. Observation of rate of consumption of corroding reagent

or of increase in concentration of corrosion products may be employed to determine corrosion rate. Where corrosion is characterized by pitting, measurement of pitting density and depth furnishes significant data on corrodibility. Intergranular as well as surface corrosion rate may be determined in terms of tensile strength or elongation loss of specimens of the appropriate shape and dimensions. Among electrical methods of following rate of reaction are the determination of (1) the contact resistance of corrosion product-coated metal surfaces and (2) the rate of increase of electrical resistance of small wires of the metal under study as their cross-sectional size is reduced by corrosive action (4). Finally, considerable information concerning corrosion rate as well as mechanism of corrosion reactions may be obtained from studies of electrode potential and polarization in controlled environments.

Where the purpose of a corrosion test is to determine the quality of protective coatings—a common use of corrosion tests—the effectiveness of a coating may be judged by the appearance of corrosion, the rate of enlargement of corroded area, and depth of penetration of corrosive attack in the underlying metal. In the case of coatings which are cathodic to the basis metal, porosity is an index of quality and this may be determined readily by the extent of pinhole rusting produced by immersion of test specimen in hot water (15) or in a sodium chloride solution containing hydrogen peroxide (3). A more recent and more general method which may be used for the detection of pinholes in any metal coating on any basis metal consists in the anodic dissolution of the surface of the coated metal into a paper moistened with a solution of a reagent which will react with ions of the basis metal to give a compound of distinctive color at points corresponding to the location of pinholes. This is the so-called electrographic method (6, 14).

PREPARATION OF TEST SPECIMENS

Test specimens are usually made from sheet material, since this affords the largest ratio of surface to mass. It is desirable to apply a paint coating to the sheared edges after the surface of the specimen has been prepared for test unless the effect of cut edges is to be studied.

Oil, grease, and other extraneous materials which interfere with the purpose of the test are removed from the surface of the specimen. This includes mill scale and other corrosion products with the exception of superficial oxide films which form immediately upon any exposed metal surface. However, when tests are made for engineering purposes it is the usual practice to employ specimens with surfaces representative of the material as it would be used. Grease is removed by organic solvents or by alkali dips and corrosion products by abrasion, sand blasting, or acids or other chemical reagents. Nonferrous metals are usually only degreased, and specimens of protective coated metals are tested as finished without further treatment.

DESCRIPTION OF TESTS AND TESTING FACILITIES

The present discussion is concerned with a brief description of the essential facilities and principal features of typical tests commonly used in determining the corrodibility of metals and the quality of protective coatings in atmospheric and liquid media. The corrosion literature furnishes descriptions of numerous and ingenious special property tests, the description of which does not fall within the scope of the present paper.

TOTAL IMMERSION TEST. The susceptibility of metals to corrosion in liquids may be tested most simply by complete immersion in sufficient volume of testing solution to minimize concentration changes resulting from depletion of initial components or accumulation of corrosion products. A recommended ratio is 250 ml. per sq. inch of specimen area (1). It is common practice to support test specimens by means of stirrups or hooks made from glass or other nonmetallic materials. The supports, the test jar,

and apparatus should not be attacked by the test solution. A suitable temperature for routine testing is 95° F. It is essential that provision be made for temperature control of the test within $\pm 2^\circ$ F. This may be accomplished by placing the test jar in a thermostatically controlled water bath.

Since corrosion reaction rates are markedly affected by dissolved oxygen (which acts as a cathodic depolarizer) and by the relative movement between test specimens and liquid, it becomes necessary to devise means of controlling these variables. It has been found that saturation of the solution with air provides satisfactory control of oxygen concentration and that this can be done practically by introducing air through the pores of an Alundum thimble (13). Care is taken to prevent impingement of air bubbles on the specimens. Pure oxygen or nitrogen or mixtures of the two may be employed when it is desired to determine the influence of oxygen on rate of corrosion in a given system. The effect of velocity may be satisfactorily controlled and studied by providing mechanical movement of the specimen in the solution or of flowing the solution by specimens in fixed position. Tests are often carried out in stagnant solutions but it is usually difficult to avoid convection currents which influence reaction rate. The apparatus used for moving the specimens in the solution is usually designed for variable speeds and it becomes necessary to determine by experiment the optimum speed to give reproducible results.

ALTERNATE IMMERSION TEST. Alternate or intermittent corrosion tests have been widely used for many years (7, 12, 16, 18). In principle this test consists in periodic immersion of test specimens in the test solution. The interval between successive immersions varies in different tests over a range of 1 to 15 minutes, the latter period being sufficient to permit drying the surface of the specimens. The period of immersion is usually 1 or 2 minutes. Immersion may be accomplished either by lowering the specimens into the solution or by raising the solution to cover the specimens. As in the total immersion test temperature is maintained constant within $\pm 2^\circ$ F.

ATMOSPHERIC TEST. The objective of atmospheric tests carried out in the laboratory is to determine the performance of metallic materials under conditions which simulate the corrosive atmospheres which are experienced in service. Formerly some attention was given to the provision of industrial-type atmospheres by the introduction of small concentrations of sulfur dioxide into atmospheric test chambers. Much more attention has been given to the use of the prevailing natural atmosphere highly humidified at elevated temperatures and it has become common practice to equip small rooms or cabinets for the maintenance of these conditions. Wider experience with tropical exposures since the beginning of the war has led to the conclusion that the highly corrosive nature of tropical atmospheres is due to moisture condensation. As a consequence, test rooms are now employed in which condensation is induced by means of temperature or humidity cycles or both. The temperatures and humidities employed in these rooms and the means of obtaining condensation have not been standardized as yet. The increasing attention given to simulation of stratospheric conditions has been reflected in the use of wider ranges of temperature and humidity—for example, some use has been made in so-called stratospheric chambers of a range from -77° to 150° F. Considerations other than mere condensation of moisture have of course dictated selection of this range.

A reasonable range of temperature cycle for inducing condensation is at least from 80° to 120° F. During the change from low to high temperature, which should be accomplished in about 30 minutes, it is customary to maintain the relative humidity above 90%, while during the reverse part of the temperature cycle, requiring about 1 hour, humidity control is not required until after the minimum temperature is attained. The humidity chamber is provided with rapid air circulation and with sufficient additional moisture to compensate for that removed by condensation on the specimens. It is desirable that condensed moisture remain on the surface of the specimen for at least 2 hours.

It has been found difficult to control by this means the period of retention of condensed moisture on specimens, and consequently one alternative practice is to induce condensation by chilling the specimens outside the humidity room in a separate chamber which is maintained at a lower temperature. Here again there has been no general agreement as to the proper temperature

and it may not be critical. The heat capacity of the specimens and the amount of condensation desired are factors which may bear on the selection of the "chilling" temperature. Actually temperatures from -40° to 60° F. are used. In this method the humidity room is usually held at 90 to 95% relative humidity and the temperature from 95° to 120° F. It is the usual practice in any case to subject the specimens to the condensation process at least twice daily.

SALT SPRAY TEST. The salt spray test, originally proposed as a laboratory corrosion test simulating marine atmospheres, has become widely used and specified as an inspection test for protective coatings. It is employed also as an accelerated corrosion test for metallic materials and while it may be useful for comparing the quality or uniformity of different samples of a given material, it is unreliable for evaluating corrosion resistance of metals unless some correlation has been established between test results and service performance. In its use as a quality test for metallic coatings it is more dependable when applied to coatings which are cathodic (or noble) than to those which are anodic (or electronegative) toward the basis metal. It has been pointed out that the duration of exposure to the salt spray test required to reveal a given degree of coating porosity varies with the electrode potential relationship between coating and basis metal and should be correlated with actual exposure tests (19).

The salt spray test apparatus consists essentially of a box or chamber into which is introduced behind a baffle plate a mist of an atomized solution of sodium chloride. The specimens are supported so as to permit free access to this mist. Details as to dimensions and construction of the chamber are available elsewhere (11, 17). Recently (at an informal committee meeting held at the National Bureau of Standards May 19, 1944) it was proposed to standardize the salt spray test conditions and procedure along the following lines (8, 20): The concentration of the salt solution should be maintained at $20 \pm 2\%$, the pH between 6.5 and 7.2, the temperature of the solution in the range 92° and 97° F., and the temperature of the chamber at $95^{\circ} + 2^{\circ}$ or -3° F. It is proposed that the atomization of the solution be such as to permit the collection in the exposure zone of the chamber of 0.5 to 3 ml. of solution per hour in a vessel 10 cm. in diameter.

In the specification use of the salt spray test for quality control, interpretation of the requirements is sometimes difficult. In view of the serious limitations of the test the requirements should be stated in specific terms which can be interpreted fairly and intelligently by those who may not have had the benefit of wide corrosion experience.

SOIL TEST. Metals used in direct contact with soils are subject to an environment of great diversity and complexity which it is difficult to simulate in the laboratory. Only by numerous burial tests in many soil types in many climates can the corrosion resistance of metals toward soils be appraised reliably. There are a number of laboratory tests, however, which are useful for the exploration of soil corrosivity and three of these representing important factors in soil exposure will be described. These are tests to determine the influence of (1) contact with inert particles, (2) soil waters or extracts, and (3) corrosion cell polarization.

The effect of contact of soils upon corrosion may be studied by burying metallic specimens at a given depth in trays of ground quartz maintained at constant temperature and humidity (5). Some acceleration in corrosion rate is permissible and may be obtained by operating at about 100° F. and near 100% humidity. The influence of soil texture may be studied by employing in separate tests quartz representing a series of particle sizes from fine gravel down to silt.

The relative corrosivity of soil waters may be determined by performing immersion tests in extracts made by leaching given quantities of soils with given volumes of water. For example, in tests on cable sheath alloys a ratio of soil to water of 250 grams of soil to 2 liters of water has provided extracts which are believed to be fairly representative of soil waters which seep into cable conduit. The extract is prepared by thoroughly stirring mixtures of soil and water for half an hour and separating by filtration.

A suitable apparatus (9, 10) for studying the polarization characteristics of corrosion cells which develop in soil exposures consists essentially of a test cell employing two steel electrodes separated by a layer of moist soil prepared in an arbitrary fashion. One electrode in the form of a steel screen is buried in the soil and becomes cathodic to the steel electrode at the top of the soil. The single electrode potentials of the anode and cathode are measured with respect to a calomel reference electrode and these values plotted against the applied current. From the curve so obtained the current required to bring the anode and cathode to the same potential is recorded as the measure of the rate of corrosion. This value corresponds to the current which would flow if the resistance of the soil were zero and is therefore somewhat greater than the actual corrosion current. Studies employing a number of soils have shown a correlation between the current at the corrosion potential and the loss of weight of the anode. Further amplification of the role of polarization in corrosion processes is given below.

ELECTROCHEMICAL TECHNIQUES. Previous reference has been made to the marked difference in rate of the primary and secondary reactions which occur in corrosion processes. As a consequence, concentration gradients develop at the electrode areas on the metal surface which may be measured in terms of anodic and cathodic polarization. Since corrosion is dependent upon current flow in the electrolytic cells at the metal-environment interface, it is evident that the state and degree of polarization determine corrosion rate. Factors which influence rate do so largely through their effect upon corrosion cell polarization.

The technique of measuring the characteristics of individual corrosion cells is difficult but it is feasible to determine experimentally the polarization behavior of metal surfaces in known surroundings and by this means to obtain information concerning mechanism and rate of reaction. This knowledge is often more useful in predicting or explaining corrosion behavior than the more quantitative results of the foregoing corrosion tests.

The measurement of polarization consists in the determination, by means of a standard reference electrode, of the change in potential of a metal when it is made the anode in one case and the cathode in another in an electrolytic cell in which there are provided as electrolyte the significant components of a given environment. From studies of this kind upon metals in electrolytes representative of a variety of environments, a body of information may be accumulated by means of which it becomes possible to predict the degree of corrosion resistance to be expected in a given instance. From an inspection of these experimental data, usually plotted in the form of potential-current density curves, it is possible to identify the factors which accelerate or retard corrosion and to observe which electrode is influenced—that is, to determine whether the process is anodically or cathodically controlled (2). Once this is known the probability of corrosive attack and the need and effectiveness of protective measures can be estimated.

The laboratory tests described in the present discussion provide means for appraising the corrosion resistance of metallic materials and for investigating corrosion problems which occur in the use of metals. In addition to the typical test methods which have been referred to, it is common practice to employ in corrosion studies many of the varied experimental techniques and procedures commonly used in chemical and metallurgical laboratories.

LITERATURE CITED

- (1) Am. Soc. Testing Materials, Tentative Method of Total Immersion Testing of Non-ferrous Metals, *Preprint* 14, 1943.
- (2) Burns, R. M., *J. Applied Physics*, 8, 398 (1937); Am. Soc. Testing Materials, *Bull.* 126, 17-20 (Jan., 1944).
- (3) Burns, R. M., *Trans. Am. Electrochem. Soc.*, 52, 284 (1927).
- (4) Burns, R. M., and Campbell, W. E., *Ibid.*, 55, 271 (1929).
- (5) Burns, R. M., and Salley, D. J., *IND. ENG. CHEM.*, 22, 293 (1930).
- (6) Burns, R. M., and Schuh, A. E., "Protective Coatings for Metals", A.C.S. Monograph 79, pp. 252-3, New York, Reinhold Publishing Corp., 1939.
- (7) Crampton, D. K., and Mitchell, N. W., Symposium on Corro-

- sion Testing Procedures, Am. Soc. Testing Materials, p. 74 (1937).
- (8) Darsey, V. M., Am. Soc. Testing Materials, *Bull.* 128, 31-4 (May, 1944).
- (9) Denison, I. A., *Trans. Electrochem. Soc.*, 81, 435 (1942).
- (10) Denison, I. A., and Darnielle, R. B., *Ibid.*, 76, 199 (1939).
- (11) Dix, E. H., Jr., and Bowman, J. J., Symposium on Corrosion Testing Procedures, Am. Soc. Testing Materials, p. 57 (1937).
- (12) Farnsworth, F. F., and Hoeker, C. D., *Trans. Am. Electrochem. Soc.*, 45, 281 (1924).
- (13) Fraser, O. B. J., Ackerman, D. E., and Sands, J. W., *IND. ENG. CHEM.*, 19, 332-8 (1927).
- (14) Hermance, H. W., *Bell Lab. Record*, 18, 269 (1940).
- (15) Hothersall, A. W., and Hammond, R. A. F., *Trans. Electrochem. Soc.*, 73, 449 (1938).
- (16) Mears, R. B., Walton, C. J., and Eldredge, G. G., Am. Soc. Testing Materials, *Preprint* 29 (1944).
- (17) Mutchler, W. H., Buzzard, R. W., and Strausser, P. W. C., Natl. Bur. Standards, *Letter Circ.* 530 (July 1, 1938).
- (18) Rawdon, H. S., Krynsky, A. I., and Finkeldey, W. H., *Proc. Am. Soc. Testing Materials*, 24, Pt. 2, 717 (1924).
- (19) Sample, C. H., Am. Soc. Testing Materials, *Bull.* 123, 19-24 (August, 1943).
- (20) Waldron, L. J., June 1944 Meeting, Am. Soc. Testing Materials.

PRESENTED before the Division of Petroleum Chemistry, Symposium on Bench Scale Technique, at the 108th Meeting of the AMERICAN CHEMICAL SOCIETY, New York, N. Y.

Factors Causing Lubricating Oil Deterioration in Engines Laboratory Evaluation

R. E. BURK¹, E. C. HUGHES, W. E. SCOVILL, AND J. D. BARTLESON
Research Laboratory, Standard Oil Company of Ohio, Cleveland, Ohio

The deterioration of lubricating oil in internal combustion engines is due largely to oxidation reactions. It is shown that these reactions are primarily catalytic at the engine temperatures in question, the catalysts being metals and metal compounds such as iron, copper, lead, and their compounds. The effects of other possible catalytic materials, such as blow-by gas components, are considered. These observations are applied to a laboratory test procedure for evaluating the service stability of oils in which an attempt was made to develop a set of conditions and catalysts which duplicate those of the present Chevrolet engine test. The degrees of reproducibility and of correlation with engine results are shown in detail. Correlation of the test with four B oils has been found to be good except upon the point of bearing corrosion. Additional procedures are described for determining the tolerance of oils to more severe conditions, since the results indicated that the above conditions and catalysts are not universally suitable.

THE complexity of factors causing the deterioration of lubricating oils in an engine has necessitated a widespread use of engine tests for oil evaluation. The obvious desirability of providing a laboratory method has led to the proposal of a large number of procedures. Excellent reviews of these methods have appeared recently (10, 11). However, the correlation of the laboratory procedures with engine operation has not been adequately demonstrated, possibly because it is but recently that standard engine tests have been developed.

The results of many investigations (5, 6, 9-12), as well as the work described herein, provide a basis for understanding the important factors causing the deterioration of oil. The utilization of this knowledge should ultimately enable the chemist to conduct laboratory evaluations with confidence. As a step in this direction some of the relevant variables and factors have been combined in a laboratory procedure which will correlate in most respects with a certain well-established engine performance for a series of oils. The selection of factors responsible for the deterioration was made to correspond as closely as possible, in a quantitative fashion, to the engine with which correlation was desired. Nevertheless, the state of knowledge is still such that it is considered desirable to augment the results of this procedure with one or more "tolerance" tests in which the resistance of the oil to possible increases in the severity of certain

factors can be observed. This procedure often is very desirable in the study of additives.

MECHANICAL CONSTRUCTION OF TEST EQUIPMENT

A schematic diagram of the apparatus used in this investigation is shown in Figure 1. A 160-cc. sample of oil was used in a glass tube, A, 45 mm. in outside diameter and 42 cm. long. A piece of steel tubing, B, 1.3 cm. in outside diameter by 1 cm. in inside diameter and 14 cm. long was centered in the glass tube and was held in place on the glass support, C, attached to the air-inlet tube, D. This support was spaced from the bottom of tube A by 2-mm. glass tabs to allow oil and suspended solids to pass into the support and up the air lift. The air-inlet tube and steel tube supports may also be made of steel, which is more rugged but a little more difficult to clean.

In the upper end of steel tube B a flat piece of bearing metal, G, was inserted and was held in place by a copper pin, H. The size of each of these two pieces was adjusted to give the ratio of

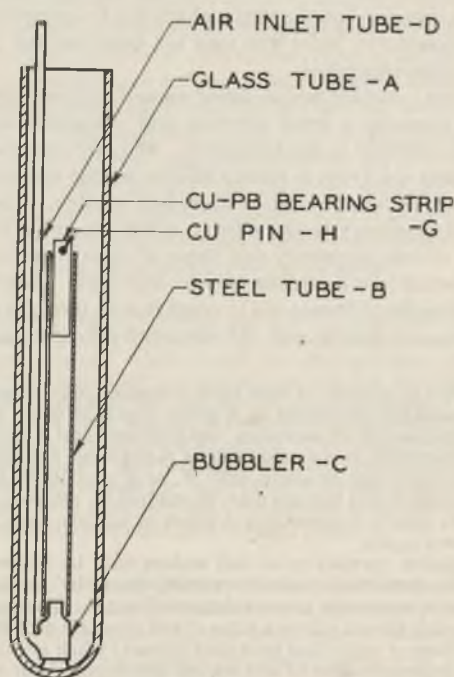


Figure 1. Oil Deterioration Cell for Suspending Solids

¹ Present address, Plastics Division, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

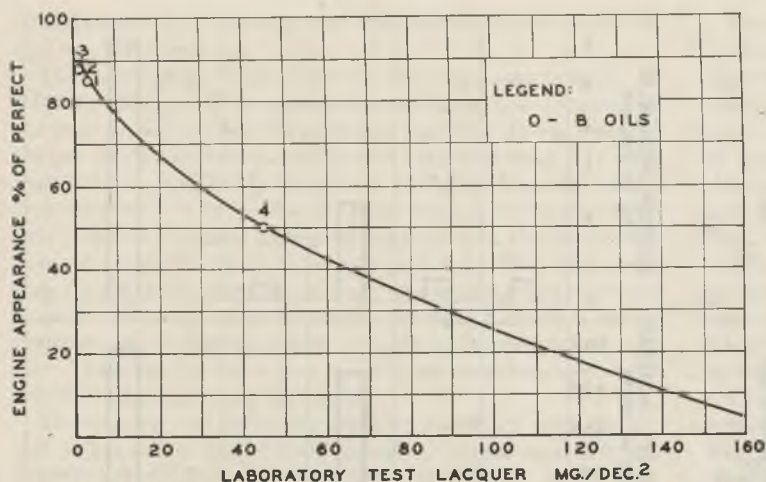


Figure 2. Conversion Chart of Lacquer to Engine Appearance

corresponding metal to oil volume found in the engine with which comparison was sought. Numerous other arrangements have been tested but that shown was preferred. A glass wool plug was placed in the top of the glass tube to minimize oil loss by splashing.

The assembly was placed in a thermostat which in the authors' case comprised an electrically heated aluminum block (16) with 14 holes for the test units. It weighed 185 pounds, and was 48.4 cm. (19 inches) long, 24.5 cm. (9.625 inches) wide, and 29.6 cm. (11.625 inches) high. The electrical energy consumption ran 6.33 kw.-hr. per 36-hour test. Air under constant pressure was passed through a porous clay filter to remove dust and then through concentrated sulfuric acid containing chromic acid to remove water and sulfur dioxide. The air rate was indicated by calibrated orifice-type flowmeters and was controlled by 0.6-cm. (0.25-inch) needle valves.

OPERATION OF THE TEST

The glass parts were cleaned by the usual chromic acid method, rinsed, and dried. The steel and copper parts were washed with chloroform or methyl ethyl ketone, or both, and polished until bright with No. 925 emery cloth or steel wool. The steel tube was, in most cases, rotated for polishing purposes with a motor and chuck. New bearing pieces were used each time. The copper and bearing metal parts were weighed before and after the test to ascertain corrosion. After assembly with the oil in the test block, the oil was brought to temperature, the soluble catalyst added, the air flow started, and the lead bromide added immediately. This procedure required 0.5 to 1 hour, and the period before the air was started was not included in the recorded duration of the test.

A study of test conditions has been made and the following were used when correlation was desired for the B oils with the present "standard" Chevrolet test:

- Temperature 280° F. for heavy-duty oils
- Oil sample 160 cc.
- Air flow rate 70 liters per hour
- Time 36 hours
- Catalysts Steel, 100 sq. cm. (tube B, Figure 1)
- Copper, 1 sq. cm.
- Copper-lead bearing, 4.4 sq. cm.
- Ferric 2-ethyl hexoate, 0.012% as Fe₂O₃ in c.p. benzene
- Lead bromide, 0.1% as precipitated powder

The ferric 2-ethyl hexoate was prepared by reacting sodium 2-ethyl hexoate with ferric nitrate solution, followed by washing by decantation. The solution in benzene was prepared by Soxhlet extraction of the precipitate with benzene, followed by analysis of the solution for iron. The 2-ethylhexoic acid was obtained from the Carbide and Carbon Chemicals Corporation.

The lead bromide was prepared by reacting calcium bromide in absolute alcohol (1 molar) with alcoholic lead acetate at 32° F. followed by filtering and washing with absolute ethanol. This was vacuum-dried to constant weight. The surface area (Emmett method) of the lead bromide was 1.0 sq. meter per gram.

At the close of the test the lacquer deposition on B (1 sq. dm. area) was determined as the difference in weights after washing with a light naphtha and scrubbing with chloroform, methyl ethyl ketone, or both. After each wash the tube was air-dried to constant weight.

Figure 2 shows a tentative relationship between the weight of lacquer as determined by this procedure and the visual rating system used in engine testing. The form for this curve with the vertex at zero lacquer was chosen because this form was found to relate the actual weight of lacquer to the visual rating on a single-cylinder engine piston. The weight of lacquer on a piston for a given visual rating will not be necessarily the same weight obtained in the laboratory procedure. The approximate relationship in Figure 2 is used in correlating engine tests with the laboratory procedure.

The copper and bearing metal pieces, after an oxidation test were scrubbed with chloroform or methyl ethyl ketone, or both, before reweighing. The change in weight was a rough indication of corrosion.

The used oil was sufficient in volume to enable determination of all the usual oil tests. The oil-insoluble sludge remaining in the glass tube was thought to be related to similar sludge deposits in engines. It was rated visually against color photographic standards and a scale ranging from F (worst) through A (best) has been used for recording.

Figure 3 shows a relationship between the visual ratings of sludge in the engine tests and in the laboratory procedure. The derivation of the curve was largely empirical from the B oils. It is used for correlating engine data with those from the laboratory procedure.

DEVELOPMENT OF THE TEST

The effects of the following variables on the deterioration of oils in the laboratory apparatus were considered in developing this test:

1. Catalytic factors
2. Effect of blow-by materials
3. Temperature
4. Duration of test
5. Volume of oil
6. Rate of air flow
7. Procedure for addition of catalyst and oil

CATALYTIC FACTORS. In Figure 4 typical results are presented showing that the catalytic factors predominate in causing oil deterioration in the relevant temperature range. In any engine the metal catalysts are present initially in the massive

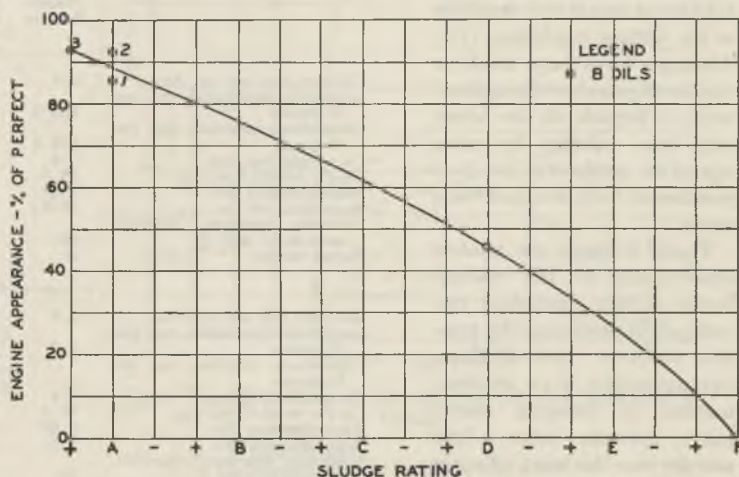


Figure 3. Conversion Chart of Appearance to Engine Appearance

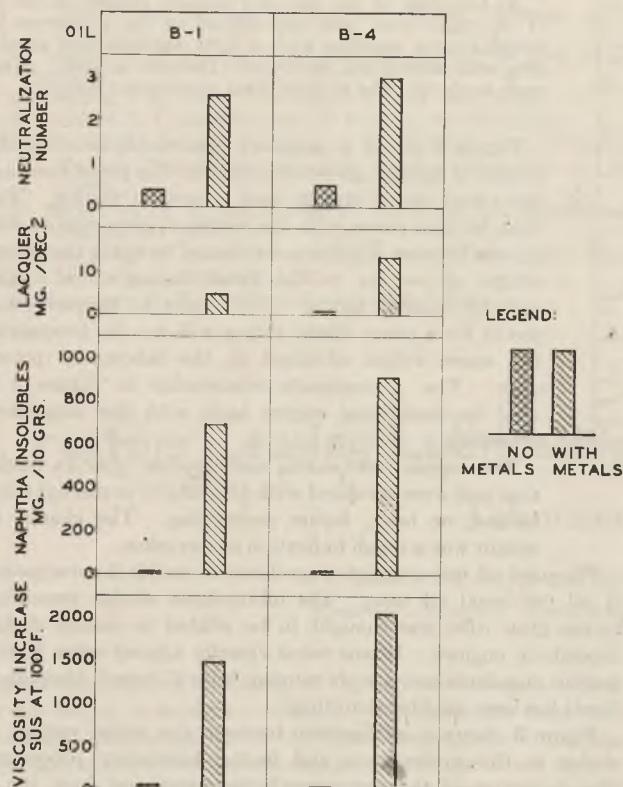


Figure 4. Effect of Metals on Deterioration of Oils in Laboratory Procedure

condition and it is not known with certainty whether catalytic action is on the surface, or due to formation of oil-soluble soaps from the metals, or both. It is clear that the latter are powerful catalysts (5). Since the soaps are formed in an engine by reaction of metals, or metal compounds, with acidic constituents formed by oxidation of the oil, it would be desirable in a laboratory test to have only massive metals present.

Iron is the most abundant potential catalyst in an engine, although it is often relatively less active in the massive condition than other metals. It appears, moreover, that the activity of iron is very sensitive to its surface conditions (10). Attempts have been made in the development of the authors' work to furnish all the necessary iron catalyst by using massive surfaces, or fine powders of both iron and ferric oxide.

Figure 5 shows the relative effectiveness of the various forms of iron, including two methods of preparing the massive surfaces. One of these, electrocleaning, is a common method of cleaning engine parts between tests. Iron powder was the most effective type, and by using large quantities it was possible to obtain

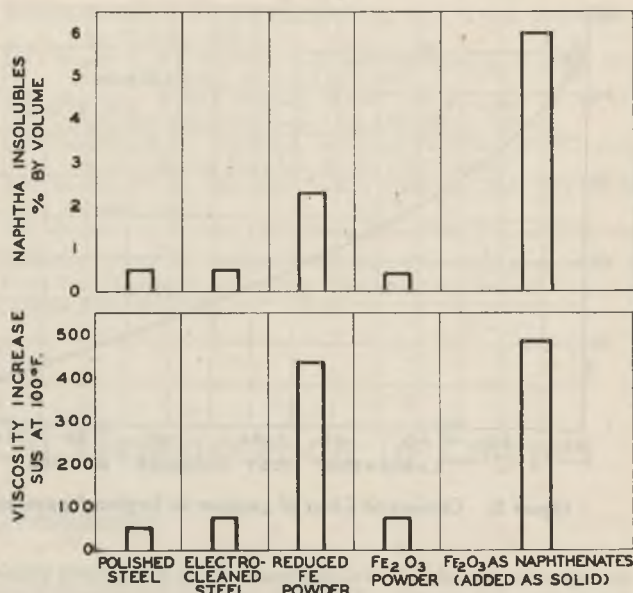


Figure 5. Effect of Various Types of Iron

Oil B-1. Temperature, 310° F. Air rate, 70 liters per hour. Time, 36 hours. Metals. Steel as specified. Cu, 1.0 sq. cm. Cu-Pb, 4.4 sq. cm.

extensive deterioration in 36 hours, if the temperature of the test was 310° F. However, good correlation with engine results could not be obtained under these conditions and reproducibility was poor. Since the iron powder was prepared by reduction of the oxide with hydrogen, it was pyrophoric to a certain extent. This often led to considerable difficulty in handling. Finally attempts were made to prepare a composite catalyst containing all the principal active components occurring in the practice. However, if reasonable amounts of lead bromide, copper-lead, and copper were employed in the laboratory procedure and, in addition, sufficient iron were taken to increase the rate of oxidation to that of the engine, so large a quantity of massive iron—e.g., tubes, powder, wool—would be required as to

Table I. Comparison of Ferric Soaps in the Laboratory Procedure

(Time, 36 hours. Temperature, 280° F. Air rate, 70 liters per hour. Metals, 100 sq. cm. of steel, 4.4 sq. cm. of Cu-Pb, 1.0 sq. cm. of Cu. Catalyst, 0.02% Fe₂O₃ as naphthenate, propionate, or 2-ethyl hexoate in benzene as specified. Oil, 160 ml.)

	Sohio Laboratory Test, FeO ₃ as:			36 Hours Chevrolet	Sohio Laboratory Test, FeO ₃ as:			36 Hours Chevrolet
	Naphthenate	2-Ethyl hexoate	Propionate		Naphthenate	2-Ethyl hexoate	Propionate	
	Oil B-1				Oil B-2			
Lacquer, mg. per sq. dm.	2.6	0	0.9	...	3.2	0	1.1	...
Isopentane insolubles, mg. per 10 grams	150.7	201.6	12.9	130.4	0.1	2.8	2.0	57.3
Chloroform solubles, mg. per 10 grams	148.0	198.8	10.4	102.6	17.6
Cu weight loss, mg.	0.4	1.4	0.4	...	1.9	3.4	0.5	...
Cu-Pb weight loss, mg.	16.5	23.5	9.0	9.3	12.7	19.1	19.3	32.0
Neutralization No.	1.33	2.06	0.75	2.40	3.07	1.64	1.93	5.41
Saponification No.	16.8	16.6	11.6	...	26.9	28.9	38.7	...
Viscosity increase, Saybolt, seconds at 100° F.	460	669	230	489	1546	675	691	389
Sludge rating	B	B-	A+	...	B+	A	B	...
	Oil B-3				Oil B-4			
Lacquer, mg. per sq. dm.	1.9	0	1.1	...	52.7	31.4	26.1	...
Isopentane insolubles, mg. per 10 grams	4.0	2.8	4.4	39.7	623.5	732.5	491	235.6
Chloroform solubles, mg. per 10 grams	8.1	620.0	731.3	462.0	216.6
Cu weight loss, mg.	1.4	1.4	1.1	...	0.2	2.0	0.2	...
Cu-Pb weight loss, mg.	13.2	5.2	6.0	8.0	10.5	9.3	6.0	3.12
Neutralization No.	0.83	0.53	0.33	1.36	3.82	4.09	1.87	4.99
Saponification No.	2.3	4.0	5.95	...	25.4	28.9	31.9	...
Viscosity increase, Saybolt, seconds at 100° F.	35	20	34	86	5838	4740	1958	904
Sludge rating	A+	A+	A+	...	D	D	D	...

be impracticable. Consequently the applicability of dissolved iron was investigated.

The relatively powerful effect of soluble iron soap is shown in Table I. The net effect on oil deterioration has been found to be the same as massive iron catalysis (see also 10). It was a simple matter to obtain reproducibility with the iron soap. It was, therefore, the preferable method of providing the bulk of the iron catalysis. It is possible in engine testing that much of the iron catalysis is caused by iron soaps formed in the hotter ring belt zone from freshly abraded iron particles. The time available for oxidation per unit of oil in this zone is relatively very limited. Thus the soaps formed in this zone will return to the crankcase and there contribute strongly to deterioration of the oil. Therefore, the use of iron soaps in the laboratory test might simulate the situation in the engine.

The choice of the particular iron soap was based upon the desire to provide a reproducible material. Iron 2-ethyl hexoate appeared to satisfy the requirements. As shown in Table I, the results differ somewhat depending upon the acid radical used with the iron, although they are of the same order of magnitude. Hydroxy acids are prominent in the products of oxidation of oil but have not been examined as an iron carrier.

A certain amount of iron catalysis may occur as a result of contact of the oil with the iron surface of the crankcase, although this may vary greatly between oils. Moreover, the steel surface was desired in order to determine lacquer deposition. Therefore some massive iron was retained in the test equipment, and Figure 6 shows, in the case of certain oils, the effect of omitting it. The amount of iron catalyst available in an engine under a given set of conditions is difficult to determine by direct measurement. Analysis of the used oil will show only what is left in solution; further amounts may have passed through and into the sludge, etc. Therefore, the amount contributing to the oil deterioration over that available from the massive iron in the test was determined by adding iron soaps until breakdown equivalent to that in the engine was obtained for a series of oils.

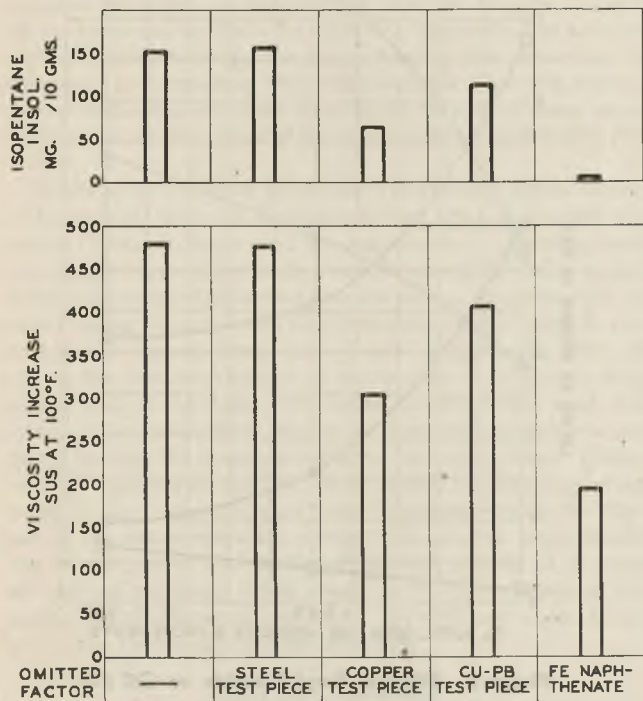


Figure 6. Effect of Individual Metallic Components

Oil B-1. Temperature, 280° F. Air rate, 70 liters per hour. Time, 36 hours.
 Catalyst. 0.02% Fe₂O₃ as naphthenate in benzene solutions.
 Metals. 100 sq. cm. of steel, 1.0 sq. cm. of Cu, 4.4 sq. cm. of Cu-Pb.

The catalytic effects of the copper and copper-lead bearing metal can both be supplied by the massive metal without resorting to the use of soluble salts. Figure 6 shows how each of these catalysts contributed to the deterioration of oil B-1. By omitting one catalytic factor at a time it was found that all the catalysts in the test except massive iron were active catalysts for the deterioration of the oil. With some oils, one of the catalysts may be more effective than the others but all these catalysts, at least, must be present to reproduce engine catalysis faithfully.

The only other metal present in the Chevrolet engine in appreciable quantity is Babbitt but this has been found by the authors to have no appreciable effect. While not present in the Chevrolet engine, aluminum has also been found by the authors and others to be without action (3).

EFFECT OF BLOW-BY MATERIALS. Other catalysts could enter the oil from the combustion space with the blow-by gases. The end products from the ethyl fluid are among the most important of these and are usually lead bromide and sulfate. It was reported (2) that these have little or no effect upon the oil; later investigations have shown that lead bromide can have a powerful catalytic effect upon some oils but that lead sulfate does not (3, 10). Ethyl fluid itself has an analogous affect (3)—for example, both ethyl fluid and lead bromide were harmful to a Pennsylvania oil but not to an acid-treated mid-continent oil. It is well established that lead halides, particularly the bromide, are present in the blow-by in an engine (10). Therefore, it was considered essential that lead bromide be included as a catalyst in a laboratory test. The quantity to be used was deduced from the volume of blow-by and average lead content of the gasolines. This corresponded well with the lead content of typical oils from several Chevrolet oil test engines and amounted to 0.10 weight % of the oil. Figure 7 shows the effect of various amounts of lead

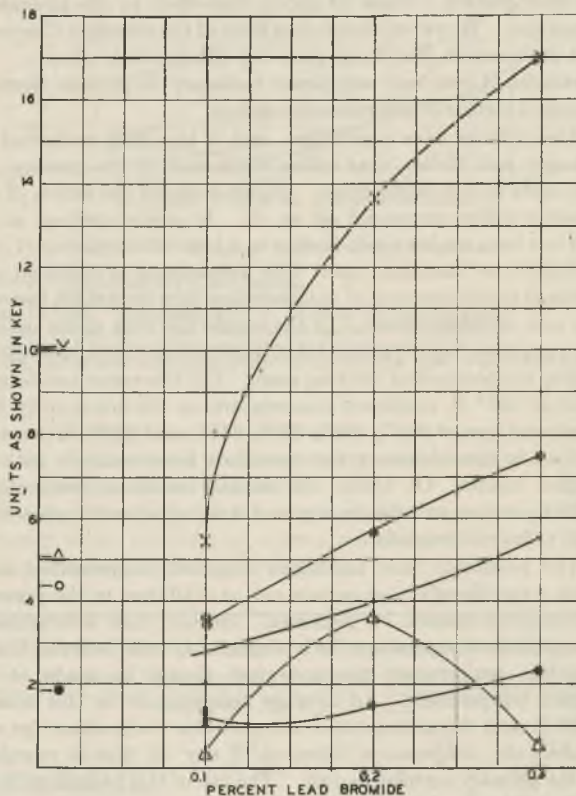


Figure 7. Effect of Lead Bromide on Oil B-1 with 0.01% Fe₂O₃

• Lacquer, mg.
 ○ Viscosity increase, Saybolt seconds at 100° F.
 ● Neutralization No.
 △ Cu-Pb weight loss, mg. per 10 sq. cm.
 X CHCl₃-solubles, mg. per 10 sq. cm.

Table II. Effect of Blow-by Materials Peculiar to Rich Mixture Operations

Blow-by material	5% CO in air	3% H ₂ in air
Oil, SAE 20	Inhibited mid-continent	Inhibited mid-continent	B-2	B-2
Time, hours	20	20	36	36
Temperature, ° F.	310	310	280	280
Air rate, liter per hour	30	30	70	70
Metals (area per 160 cc. of oil)				
Steel, sq. cm.	300	300	100	100
Cu, sq. cm.	20	20	4.4	4.4
Cu-Pb, sq. cm.	---	---	1.0	1.0
Soluble catalyst, % Fe ₂ O ₃ as naphthenate (in benzene solution)	---	---	0.03	0.03
Lacquer, mg. per sq. dm.	10.5	5.2	0.0	0.2
Cu weight loss, mg. per 10 sq. cm.	6.1	5.2	17.0	13.0
Cu-Pb weight loss, mg. per 10 sq. cm.	---	---	56.3	30.5
Neutralization No.	---	---	4.50	3.80
Viscosity increase, Saybolt seconds at 100° F.	178	119	2317	797
Sludge rating	B+	B+	B+	A
Naphtha-insolubles	4.8 vol. %	4.0 vol. %	0.2 mg. per 10 grams	1.2 mg. per 10 grams

bromide upon oil B-1 in the laboratory test. This was typical of an oil which was influenced substantially by lead bromide catalysis.

Gaseous blow-by material can also have an effect. The oxides of nitrogen were shown to be pro-oxidants (8), but in normal non-knocking operation and at moderate compression ratios their concentration in the blow-by gases is not thought to exceed 0.01% (7). This quantity of oxides of nitrogen failed to affect the results in the authors' laboratory procedure. Two of the gaseous components peculiar to rich mixture operation are carbon monoxide and hydrogen, which have been found by the present authors (3) and by Mougey and Moller (14) to act as inhibitors for oil deterioration. Table II shows this effect in the laboratory procedure. However, the air-fuel ratio of the standard Chevrolet test is chosen so that these gases are substantially absent. Accordingly, it was not considered necessary to include them as standard factors in laboratory procedure.

The authors have also found, and it has been confirmed by Mougey and Moller, that sulfur compounds in the gasoline can also have an inhibiting effect. Figure 8 shows the action of one possible sulfur compound on an oil. In engine testing, an effort has been made to standardize on a low-sulfur gasoline (14).

EFFECT OF TEMPERATURE. The temperature at which an oil is oxidized in the presence of catalysts is a very important factor in the rate of deterioration. In the engine the bulk of the oil is at the crankcase temperature, but a small amount is exposed to the higher temperature of the ring zone. The Chevrolet test is operated at 280° F. crankcase temperature on the heavy-duty test. Temperatures of 265°, 280°, 300°, 315°, and 330° F. were examined in the laboratory test procedure for correlation with the engine results. Of these, the actual crankcase temperature, 280° F., was as suitable as any and was consequently chosen for heavy-duty correlation.

The possibility that the higher ring belt temperatures could have a specific effect on certain oils or inhibitors in the presence of catalysts cannot be neglected. Rather than attempting a compromise temperature for a single test, it is believed that a separate temperature tolerance test should be made at the higher temperature. An average temperature in this zone is 350° F. and the authors have adopted this temperature for estimating the temperature tolerance of any oil that is promising in the primary correlating test. The use of this procedure is discussed below under tolerance tests.

EFFECT OF DURATION OF TEST. A large number of these tests can be made at once and consequently for most work it is not essential that the rate of deterioration be accelerated over that obtained in engine testing. It is possible to decrease the duration of a test by increasing the temperature, as in the temperature-

tolerance test. However, this might increase the uncertainties of an already complex field.

VOLUME OF OIL. The usual procedure was to use a 160-ml. sample of oil. However, tests have been made on 35-ml. samples in which the metal areas, air rate, and size of the container were adjusted in each case to the same ratio with respect to the volume of oil used as in the case of the larger sample. The results were substantially the same and the small-scale test may be of considerable value for research work. With an Ostwald type of viscometer for measuring viscosity, a 35-ml. sample is sufficient to determine all the usual used oil properties.

RATE OF AIR FLOW. In accordance with the authors' basic thought on the testing of oil, the rate of air flow was chosen so that the ratio of this rate to the volume of oil was the same as that existing in the engine with which correlation was desired. Information from the manufacturers of 10 cars showed that the air flow plus the blow-by through the crankcase on the road varies from 30 to 350 liters per hour per 160 ml. of oil. The main gaseous flow through the crankcase of an engine on the test stand is the result of blow-by. In the standard Chevrolet test this is said (13) to be about 1 cu. foot per minute or 70 liters per hour per 160 ml. of oil. This quantity has, therefore, been used. Table III shows that air rates substantially less than 70 liters per hour result in appreciably less breakdown in the authors' particular apparatus. However, other studies showed that the effect of air rate reached a maximum at about 70 liters per hour. Dry air was used in this investigation, but probably wet air is to be preferred because it will disclose hydrolyzable additives.

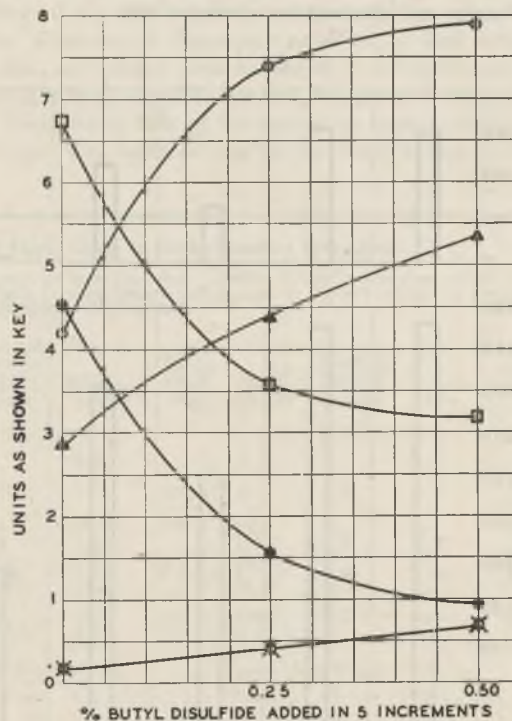


Figure 8. Effect of Butyl Disulfide on Oil B-2

● Viscosity increase, Saybolt seconds at 100° F./1000.
○ Cu corrosion, mg.
□ Neutralization No.
△ Cu-Pb corrosion, mg per 10 sq. cm.
⊗ Lacquer, mg. per sq. dm.
Standard conditions except temperature is 300° F. and iron naphthenate concentration is 0.04% as Fe₂O₃.

Table III. Comparison of 30 vs. 70 Liters per Hour Air Rate

(Temperature, 300° F. Time, 36 hours. Cu, 1.0 sq. cm. Cu-Pb, 4.4 sq. cm. Oil and catalyst added in 5 increments. 160 ml. of oil)

Air rate, liters per hour	Oil B-1		Oil B-2		Oil B-3	
	30	70	30	70	30	70
Fe ₂ O ₃ as naphthenate (added as solid), %	0.04	0.035	0.04	0.035	0.04	0.035
Lacquer, mg. per sq. dm.	0.5	2.8	1.2	4.9	0.5	7.3
Naphtha-insolubles, % by volume	0	2.5	0	0	Trace	0
Cu weight loss, mg. per sq. dm.	0.7	0.0	1.5	1.9	0.1	0.2
Cu-Pb weight loss, mg. per 10 sq. cm.	2.2	4.3	4.9	18.7	22.3	33.5
Neutralization No.	1.2	1.28	3.4	3.42	2.7	2.19
Viscosity increase, Saybolt seconds at 100° F.	197	266	264	480	122	160
Sludge rating	A+	B+	A+	B+	A	A-

Table IV. Stepwise Addition of Ferric Naphthenate vs. Addition of the Total at Start

(Time, 36 hours. Temperature, 300° F. Air rate, 70 liters per hour. Metals, 100 sq. cm. of steel, 4.4 sq. cm. of Cu-Pb, 1.0 sq. cm. of Cu)

Fe ₂ O ₃ as naphthenate (added as solid), %	Method of Addition					
	5 Increments			All at Start		
Average concentration	0.035			0.010		
	0.022			0.010		
Oil No.	B-1	B-2	B-3	B-1	B-2	B-3
Lacquer, mg. per sq. dm.	2.8	4.9	2.3	1.8	3.8	2.2
Isopentane-insolubles, mg. per 10 grams		4.0		18.0	6.5	2.7
Cu weight loss, mg.	0.0	1.9	0.2	0.3	4.9	0.3
Cu-Pb weight loss, mg.	4.3	18.7	33.5	7.3	37.7	13.1
Neutralization No.	1.28	3.42	2.19	1.08	4.40	1.29
Viscosity increase, Saybolt seconds at 100° F.	266	480	160	235	1452	68
Sludge rating	B+	B+	A-	A+	A-	A+

One factor which can be affected seriously by air rate is the concentration of organic acids, since some of them are volatile. It was found that acetic and propionic acids were carried away substantially completely by 30 liters per hour of air without affecting the oxidation. It is well known that acidic products do come off in oil oxidation. However, lauric, stearic, and cerotic (C₂₆) acids, when added to an oil on an equimolar basis, had roughly an equal and powerful effect. All were very corrosive to copper and copper-lead and the metal soaps thus formed were powerful catalysts. It was thought that the removal of acids by the air would be about the same in a laboratory test as in an engine, if the air rates were proportional to the respective oil volumes. In correlating work with reported Chevrolet results, the neutralization numbers were equal to and in some cases slightly greater than those of the used engine oil, supporting this concept.

METHODS OF ADDITION OF OIL AND IRON SOAP. In life testing oil in engines, some oil is consumed and some is removed for testing, fresh oil being used for replacement. Likewise, fresh iron catalyst is probably made available during the entire course of the run instead of all at once near the start. The fresh oil to be added during the run in the Chevrolet test is about equal in volume to the original charge (1). Table IV shows the effect of adding the iron naphthenate in increments as compared with adding it all at the start. The former procedure was much less severe and at least 40 to 50% more iron naphthenate was required to bring the deterioration up to that of the latter. Otherwise, the results were similar. Wear studies (4) have shown that much of the "wear-produced" iron is formed during the first part of the engine operation, so that this catalytic factor might best be reproduced by bringing all the iron soap in, at, or near, the start of the test. There seems to be no advantage in replacing the oil during the laboratory test with new oil and it detracts from the simplicity of the procedure.

APPLICATION TO B OILS

Table V shows check tests on the four B oils and deviation of each property. The reproducibility was very good for oils in which the deterioration was not excessive. The larger deviations are found in oil B-4, which was so unstable that the useful life

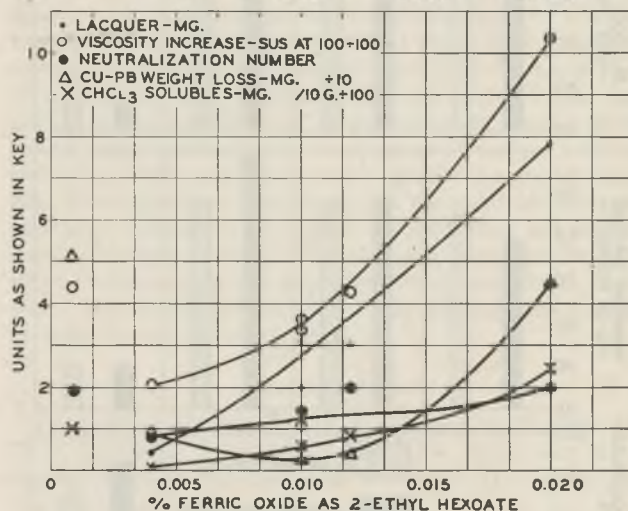
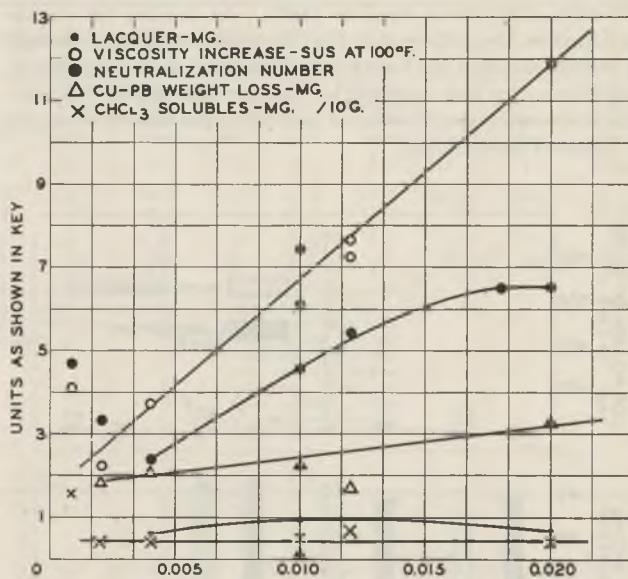


Figure 9. Effect of Ferric 2-Ethyl Hexoate

Above. Oil B-2 with 0.1% lead bromide.
Below. Oil B-1 with 0.1% lead bromide.
 Time, 36 hours. Temperature, 280° F. Air rate, 70 liters per hour. Metals, 100 sq. cm. of steel, 4.4 sq. cm. of Cu-Pb, 1.0 sq. cm. of Cu. Ferric 2-ethyl hexoate added as solution in C.P. benzene. 0.10% lead bromide with surface area of 1.0 sq. meter per gram. Passed 250 mesh.

was considerably short of the 36 hours of the test. In a large number of other check tests the reproducibility was as good or better than that shown in Table V.

The reproducibility of the results depends largely upon the accuracy of the temperature control, which should be ±1° F. or better, and the addition of the iron soap.

Table V. Reproducibility of Test as Measured on B Oils

(Time, 36 hours. Temperature, 280° F. Air rate, 70 liters per hour. Metals, 100 sq. cm. of Cu-Pb, 4.4 sq. cm. of Cu. Catalysts, 0.012% Fe₂O₃ as 2-ethyl hexoate, 0.10% PbBr₂)

	Oil B-1	Oil B-2	Oil B-3	Oil B-4
Lacquer, mg. per sq. dm.	3.0	8.0	0.8	0.7
Isopentane-insolubles, mg. per 10 grams	85.9	119.7	8.8	4.5
Cu weight loss, mg. per 1.0 sq. cm.	0.6	0.8	2.5	0.7
Cu-Pb weight loss, mg. per 4.4 sq. cm.	3.6	4.7	16.7	10.7
Neutralization No.	2.0	2.3	5.4	4.6
Viscosity increase, Saybolt seconds at 100° F.	426	317	721	761
Sludge rating	A	B+	A	A+

CORRELATION WITH ENGINE TESTS. As a basis for engine performance, the authors took the Chevrolet test work sponsored by Subdivision B of the Lubricants Division of the S.A.E. Standards Committee and reported by Mougey and Moller (13, 14). This work involved the testing of four oils in the Chevrolet engine by fourteen laboratories.

All the factors entering the oil test except that of iron soap content were selected to correspond to the respective values of those factors in the engine test. Figure 9 shows that the iron soap concentration was also a very important factor. The selection of a correlating concentration, 0.012% (as Fe_2O_3), was based on the results of studies on B oils of which Figures 9 and 10 are typical. The reported results of the 14 participating laboratories have been averaged and compared with the laboratory results in Figure 10. The relative correlation of laboratory and engine sludge rating was also good with one exception, oil B-3, which was rated better than the engine tests. Recent engine data of several laboratories have given it a higher rating than before, as shown in the shaded area of this bar. This was more in accord with the laboratory results.

The isopentane-insoluble material in the used oils from this test were usually completely soluble in chloroform. However, in the used oils from the engine tests a substantial part was insoluble in chloroform. This was probably due to materials entering the oil from the combustion zone and the breather pipe of the engine.

The correlation with all the oils was good on viscosity increase.

The corrosion of the pieces of copper-lead bearings, Figure 9, in the laboratory procedure was usually considerably less than in the engine, probably because of the absence of vigorous mechanical action. It is not felt that the present procedure will evaluate corrosion quantitatively.

VARIATIONS OF TEST PROCEDURE

Once it has been established that an oil shows promise in the above standard test, which was based to a large extent on the particular composition of the B oils, it becomes important to know whether it would tolerate excessive amounts of a particular catalyst or the higher temperatures in the ring zone. For this purpose a series of tolerance tests has been employed. The operating factors of the primary test save one were retained and separate tests were made in which one of the variables was changed as follows:

Type of Tolerance Test	Change in Concentration or Condition
Iron	Increased from 0.012 to 0.05%
Lead bromide	Increased from 0.1 to 0.4%
Temperature	Increased from 280° to 350° F. and time reduced from 36 to 10 hours
Copper	Increased from 1 to 4 sq. cm.

In general, the iron and temperature tolerance tests are of greatest importance, as is illustrated below. The results of the tolerance tests on the B oils which were correlated by the standard test procedure are shown in Figure 11. Except for oil B-3, the temperature tolerance data were better or equal to the standard test data. This indicates a low-temperature sensitivity of these oils. In contrast, excess iron was deleterious in some way to each of the oils, although some were affected more than others. The engine appearance on B-4 was improved somewhat, possibly owing to some detergent action of the iron soap. Everything considered, B-3 remained the best oil and B-4 the poorest. On the other hand, studies have been made on a certain type of inhibitor-oil combination, which was not affected by the standard or the iron tolerance tests but was seriously harmed by the temperature tolerance conditions. This was reflected in poorer results from the Chevrolet tests than from the "standard" laboratory test. The prediction based upon the temperature tolerance test was that increased concentrations of inhibitor would be necessary for a successful Chevrolet test. This proved to be the case.

RESULTS ON SOME OTHER KNOWN OILS. The utility of any laboratory test rests in its application to the evaluation of an

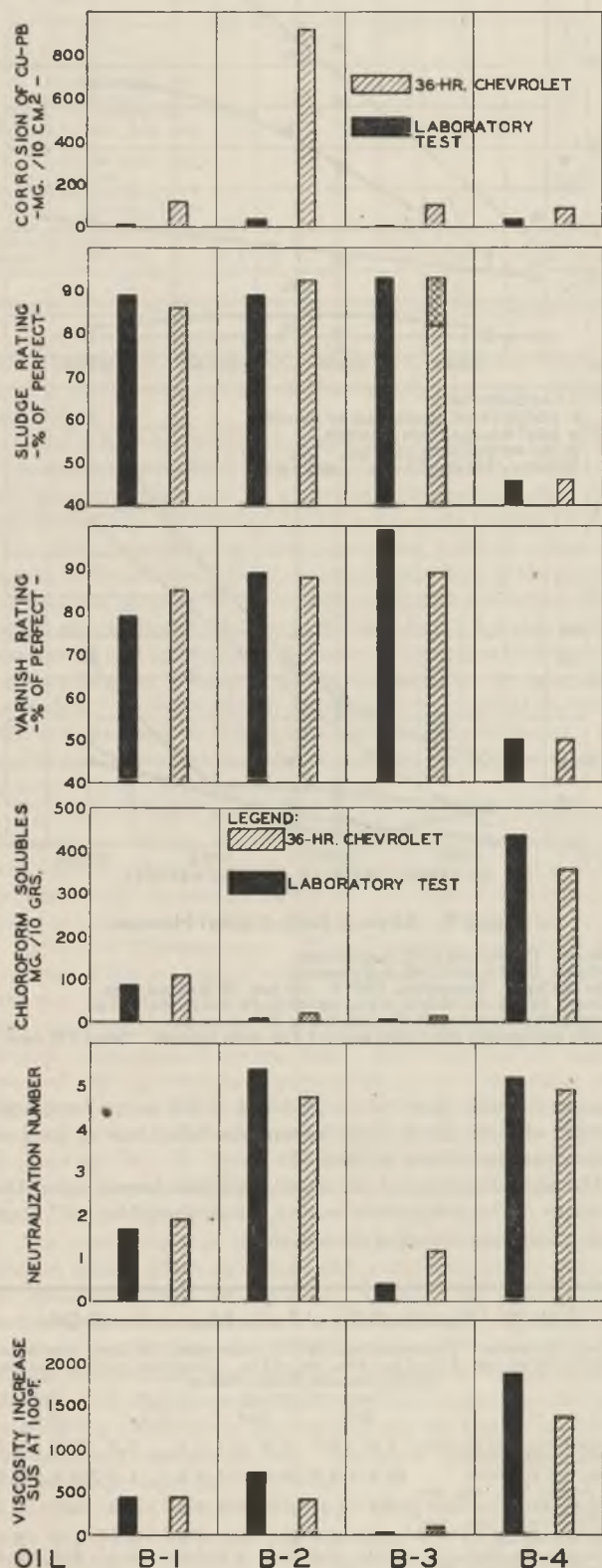


Figure 10. Correlation between Average Chevrolet Test and Standard Laboratory Test

Table VI. Oxidation Test on X Oil and Penn 30

Type of Test	Oil AX			Oil BX			Oil CX			Oil DX			Penn Oil 30		
	Stand-ard	Iron toler-ance	Temper-ature toler-ance	Stand-ard	Iron toler-ance	Temper-ature toler-ance	Stand-ard	Iron toler-ance	Temper-ature toler-ance	Stand-ard	Iron toler-ance	Temper-ature toler-ance	Stand-ard	Iron toler-ance	Temper-ature toler-ance
Lacquer	0.0	5.0	1.2	7.6	8.6	3.5	19.5 ^a	2.0	1.7	11.3	1.4	2.8	15.6	1.5	10.4
Isopentane-insoluble	355.7	336.0	177.3	222.2	830.6	320.6	1.2	193.7	58.8	0.9	23.3	22.8	201.9	228.0	72.7
Cu-Pb weight loss	1.0	0.8	0.5	6.2	66.5	12.6	0.4	3.7	0.3	2.1	42.7	17.8	3.8	16.4	13.8
Neutralization No.	1.2	4.5	1.5	1.3	7.7	1.4	0.9	4.5	0.9	0.5	3.8	1.0	1.9	1.9	1.0
Viscosity increase	429	227	409	308	542	588	66	184	94	38	179	83	493	1095	430
Appearance	C	C+	B	A	C+	A-	A-	A-	A-	A	A-	A-	B	A	B+
Engine service characteristics	A heavy-duty oil having excellent oxidation resistance properties but limited in detergency			A heavy-duty oil having good detergency properties but limited in oxidation resistance			A heavy-duty oil possessing both detergency and resistance to oxidation			A heavy-duty oil satisfactory both as to detergency and stability under limited conditions but which may oxidize and/or corrode bearings under certain high temperature conditions					

^a Probably error, as there was no visible lacquer film.

oil of unknown performance. The above work has shown the test to be applicable for determining oil stability for B oils which represent a fairly divergent group. However, there are many types of oils and additives which may or may not respond as well. Table VI shows a group of oils known as the X oils for which the service characteristics have been determined but not yet released by the Corrosion Section of the Technical Committee B, Committee D-2 of the A.S.T.M. A Penn oil is also included. These are shown with the objective that service correlation may be available sometime.

SUMMARY

The service requirements of lubricating oils are so varied as to make their refining and testing extremely difficult. Indeed, the

“service performance” of an oil is a very vague term. In the present work by the application of reasonable chemistry a laboratory test procedure has been developed which gives substantial correlation, except for corrosion, with one type of “service” and for a certain few oils; but this development is by no means complete. By the application of certain “tolerance” tests a fundamental understanding of the mechanisms of various additives and of the decomposition of an oil is possible to a greater extent than with engine tests. Application of the principles developed may be of substantial aid to both routine testing and research work in the field of motor oils. However, completely satisfactory procedures must also give information upon bearing corrosion. A procedure for doing this in the proposed test is under investigation and will be reported later.

ACKNOWLEDGMENT

The authors are indebted to M. H. Campbell, C. W. Hiatt, III, H. P. Lankelma, J. M. Musselman, R. I. Potter, and M. L. Sunday for suggestions and much of the laboratory and engine work described herein.

LITERATURE CITED

- (1) Am. Soc. Testing Materials, Committee D-2, Proc. Am. Soc. Testing Materials, 42 (1942), appendix.
- (2) Anon., *Oil Gas J.*, 38, No. 30, 54 (1939).
- (3) Burk, R. E., Hughes, E. C., Scovill, W. E., and Bartleson, J. D., paper presented at the 102nd Meeting of AMERICAN CHEMICAL SOCIETY, September, 1941.
- (4) Davis, L. L., *Refiner*, 21, No. 4, 107 (1942).
- (5) Davis, L. L., Lincoln, B. H., Byrkit, G. D., and Jones, W. A., *IND. ENG. CHEM.*, 33, 339 (1941).
- (6) Dornte, R. W., and Ferguson, C. V., *Ibid.*, 28, 863 (1936).
- (7) Egerton, A. C., “Science of Petroleum”, Vol. IV, p. 2921, London, Oxford University Press, 1938.
- (8) Hanson, T. K., and Egerton, A. C., *Proc. Roy. Soc., London*, 163A, 90 (1937).
- (9) Lamb, G. G., Loane, C. M., and Gaynor, J. W., *IND. ENG. CHEM., ANAL. ED.*, 13, 317 (1941).
- (10) Larsen, R. G., and Armfield, F. A., *IND. ENG. CHEM.*, 35, 581-8 (1943).
- (11) Matthijsen, H. L., *J. Inst. Petroleum*, 26, 72 (1940).
- (12) Mougey, H. C., *Am. Soc. Testing Materials, Bull.* P34 (October, 1939).
- (13) Mougey, H. C., and Moller, J. A., *Am. Pet. Inst.*, meeting at San Francisco (Nov. 3, 1941).
- (14) Mougey, H. C., and Moller, J. A., S.A.E. meeting at Detroit (Jan. 16, 1942).
- (15) Pigott, R. J. S., S.A.E. Detroit meeting (Jan. 6, 1942).
- (16) Rugg, H. M., Pennsylvania Grade Crude Oil Assoc. (private communication).

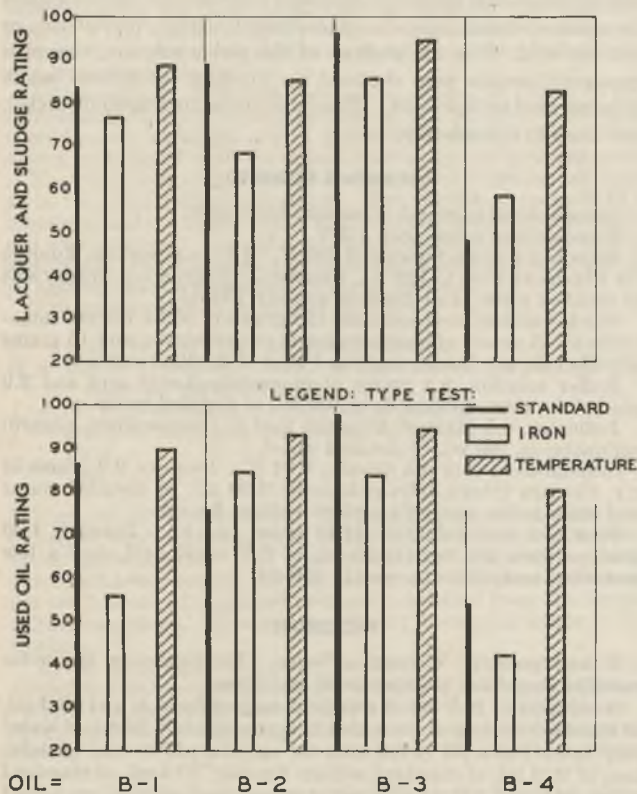


Figure 11. Tolerance Test Data on B Oils

PRESENTED before the Division of Petroleum Chemistry, Symposium on Bench Scale Techniques, at the 108th Meeting of the AMERICAN CHEMICAL SOCIETY, New York, N. Y.

Analysis of Hydrofluoric-Nitric Acid Stainless Steel Pickling Bath

WILLIAM E. MCKEE AND WILLIAM F. HAMILTON¹

Engineering Research Laboratory, Chemical Division, Lockheed Aircraft Corporation, Burbank, Calif.

The economical and efficient operation of the hydrofluoric-nitric acid stainless steel pickling bath requires control by chemical analysis. In this paper rapid quantitative analytical procedures are presented for the analysis of the bath. They include the determination of total acidity, iron, fluoride, and nitrate.

THE nitric-hydrofluoric acid pickle bath is used in cleaning the siliceous welding flux residue and scale from stainless steel parts after welding or annealing. The solution when originally made up contains approximately 1% anhydrous hydrofluoric acid and 12% anhydrous nitric acid by weight. These concentrations vary as the bath is replenished.

Since satisfactory analytical procedures were not available, control had consisted of adding hydrofluoric acid and nitric acid in the ratio of 1 to 10 parts by weight, respectively, to produce the desired pickling rate. The need for a rapid control analysis to determine both the factors influencing the efficiency of the bath and the concentrations of the components was obvious because of the erratic performance of the bath. Unnecessary additions and tank drainings can be eliminated if these factors are known. In the course of this investigation, it was found that proper control of the bath required the determination of total acid, as well as the iron, fluoride, and nitrate ions (4).

DISCUSSION

The separate quantitative determination of nitric and hydrofluoric acids by direct alkali titration is prevented by the accumulation of siliceous materials from the welding flux as well as iron, chromium, and nickel from the dissolved steel. In hydrofluoric acid, iron, chromium, and nickel form weak acids of the types H_2MF_6 and H_2FM_6 (5), where $M = Fe, Cr, \text{ or } Ni$. During the neutralization of these compounds, metallic hydroxides are precipitated. Ferric hydroxide starts to precipitate at about pH 4; chromium and nickel precipitate at slightly higher pH values. At pH 8, practically all of the iron and most of the chromium and nickel are precipitated. The nitric and hydrofluoric acids, as well as weak acids, are also completely neutralized at this pH value.

The total acidity can be arbitrarily considered as the sum of all acidic constituents which are titrated by an alkali to a pH of 8. The titration must be corrected for the amount consumed in precipitating the metallic ions as hydroxides. It is expressed as equivalents of acid per 100 ml. of sample. Since titration curves show that in hydrofluoric-nitric acid solutions of these metals the greatest inflection occurs at pH 8, it is possible to titrate to this pH, thus neutralizing all strong and weak acids, and to calculate their concentrations by applying a correction factor for the alkali used by the metals. This factor is obtained by separating the hydroxides and measuring the volume of the precipitate in graduated centrifuge cones under definite conditions.

When similar conditions of acidity and identical conditions of centrifuging are maintained, a satisfactorily constant relation is obtained between the volume of the precipitate and the amount of base required to produce the precipitate, even though the concentrations of the iron, chromium, and nickel ions vary over a wide range. In practice, the amount of dissolved iron is always several times greater than that of the chromium and nickel.

A number of quantitative procedures are available for the determination of fluorides. They include precipitation methods using calcium fluoride, lead chlorofluoride (8), or triphenyltin fluoride (2); the titration of evolved silicon tetrafluoride with alkali (1, 6); and various colorimetric methods. In general, they are not practical for the control analysis of the pickle bath, because large quantities of iron and other metals in solution result in interference.

A slightly modified form of the Rowley-Churchill determination was found to be rapid and satisfactory (7). Fluorides are separated from the interfering metals by distillation as fluosilicic acid and titrated in a buffered solution with thorium nitrate, using Alizarine Red S as an indicator. Nitric acid does not interfere.

The dissolved iron is present entirely in the ferric state. In the presence of chromium and nickel it may be determined by any one of several gravimetric procedures. In the following rapid method, the iron is estimated in graduated centrifuge cones by comparing the volume of ferric hydroxide precipitated from an aliquot of the pickle solution with that from known samples. The standard must be precipitated from a nitric acid solution containing fluorides, but the quantities present are not critical. An excess of sodium hydroxide and ammonia dissolves the bulky nickel and chromic hydroxides which coprecipitate with the ferric hydroxide. To obtain accurate results, the pickle solution and the standard must be precipitated and centrifuged in a similar manner.

The nitrate-ion concentration is conveniently determined by the ferrous sulfate method of Bowman and Scott (3), which applies to nitrate determination in concentrated arsenic, phosphoric, or sulfuric acid. For the analysis of the pickle solution, the most consistent results were obtained by titrating the nitrate ion in concentrated sulfuric acid. Fluorides, trivalent chromium nickel, and iron do not interfere.

REAGENTS REQUIRED

Standardized base, 0.5 *N* sodium hydroxide.

Standardized nitric acid, 1.5 *N*.

Standard sodium fluoride, 0.750 *N*. Dry c.p. sodium fluoride for 2 hours at 110° to 120° C., dissolve 3.150 grams of the dry salt in distilled water, and dilute to exactly 100 ml.

Stock stainless steel solution, 130 grams of ferric nitrate nonahydrate, 35 grams of chromic nitrate nonahydrate, and 16 grams of nickel nitrate hexahydrate in 1 liter of distilled water.

Buffer solution, 9.4 grams of monoacetic acid and 2.0 grams of sodium hydroxide in 100 ml. of distilled water.

Indicator, 0.5 gram of Alizarine Red S (monosodium alizarin sulfonate) in 100 ml. of distilled water.

Standardized thorium nitrate, 0.07 *N*. Dissolve 9.2 grams of c.p. thorium nitrate tetrahydrate in 1000 ml. of distilled water and standardize against standard sodium fluoride.

Standard iron solution, 0.010 gram per ml. Dissolve 1.00 gram of pure iron wire in 25 ml. of 6 *N* nitric acid, boil a few moments, and dilute to exactly 100 ml.

PROCEDURE

TOTAL ACIDITY. Correction Factor. The correction factor for metallic impurities is determined as follows:

A solution of 10.0 ml. of standard sodium fluoride and 10.0 ml. of standard nitric acid are added to approximately 20 ml. of water and titrated to a pH of 8.0 with the aid of a pH meter. A solution of 10.0 ml. of standard sodium fluoride, 10.0 ml. of standard nitric acid, and 5.0 ml. of stock stainless steel solution are added to approximately 15.0 ml. of water and the mixture is titrated to a

¹ Present address, Vaso Sulfa Laboratories, 1947 East Midwick Drive, Altadena, Calif.

pH of 8.0. The titration should be made slowly near the end point. If the final volume exceeds 100 ml., the precipitate is allowed to settle and some of the supernatant liquid is poured off. The precipitate is then stirred up into the remaining liquid and the suspension is distributed between two graduated 50-ml. centrifuge cones. The cones are filled to the 50-ml. mark, balanced by adding water, and centrifuged for at least 3 minutes. The time interval during centrifuging is accurately noted. The total volume of precipitate in the two cones is recorded.

The correction factor for metallic impurities is calculated as follows:

A = ml. of base to titrate 10.0 ml. of standard sodium fluoride, 10.0 ml. of standard nitric acid, and 5.0 ml. of stainless steel solution

B = ml. of base to titrate 10.0 ml. of standard sodium fluoride and 10.0 ml. of standard nitric acid

C = ml. of hydroxide precipitate

W = correction factor or ml. of base per ml. of precipitate

$$W = \frac{A - B}{C}$$

Total Acidity Determination. An aliquot of 5.0 ml. of pickling solution is added to approximately 35 ml. of water and titrated to a pH of 8.0. The amount of precipitate is determined as indicated above, using the same centrifuging time and speed. The total acidity is calculated as follows:

D = ml. of base required to titrate 5.0 ml. of sample

E = ml. of hydroxides precipitated from 5.0 ml. of sample

W = correction factor

N = normality of base

X = total acidity as equivalents of acid per 100 ml. of pickle solution

$$X = \frac{[D - EW]N}{50} = \text{total acidity}$$

IRON CONTENT. Any standard gravimetric method for the determination of iron in the presence of chromium and nickel may be used. However, the following rapid method is recommended.

Standardization. From 1.0 to 10.0 ml. of standard ferric iron solution are added to a solution of about 5.0 ml. of standard sodium fluoride and 5.0 ml. of standard nitric acid and diluted to about 40 ml. The solution is titrated to a pH of 8.0, 20 ml. of concentrated ammonia and 4 grams of sodium hydroxide are added, and the suspension is stirred until the sodium hydroxide has dissolved. The precipitate is centrifuged and measured under exactly the same conditions as used for the unknown sample. The volume-weight relation is found from the observed volume of the precipitated ferric hydroxide and the grams of iron required to produce it.

Determination. A 5.0-ml. portion of sample is added to approximately 35 ml. of water and titrated to a pH of 8.0; 20 ml. of concentrated ammonia and 4 grams of sodium hydroxide are added, and stirred until the sodium hydroxide has been dissolved.

The suspension of hydroxides is centrifuged in graduated cones as in the total acidity procedure. The volume of precipitate is measured and compared with a standard prepared from the standard iron solution. For most accurate results, equal amounts of precipitate should be used in comparing known amounts of iron, as against unknown amounts of pickle solution.

The iron content is calculated as follows:

G = grams of iron taken for standardization

H = ml. of precipitate obtained from known amount of iron taken for standardization

J = ml. of precipitate from 5.0 ml. of sample

Y = grams of ferric iron per 100 ml. of sample

$$Y = \frac{20GJ}{H}$$

NITRATE DETERMINATION. A 2.0-ml. portion of sample is delivered beneath the surface of 100 ml. of nitrate-free concentrated sulfuric acid. The concentrated sulfuric acid should be stirred while the sample is being delivered. The grams of nitrate ion per 100 ml. of pickle solution are calculated from the ferrous sulfate consumed. Bowman and Scotts' correction factor is also applied.

TOTAL FLUORIDE CONTENT. A 125-ml. distilling flask connected to a water-cooled condenser is fitted with a two-hole rubber stopper; a thermometer is extended down into the liquid and a dropping funnel arranged so that water can be added during the distillation. The distillate is conveniently collected in a 100-ml. volumetric flask.

A few glass beads and approximately 0.1 gram of sodium silicate are placed in the distilling flask, and 6 ml. of 70% perchloric acid

Table I. Determination of Total Acidity in Known Samples

Experiment No.	Total Acid Added, Equivalents per 100 ml.	Total Acid Found, Equivalents per 100 ml.	Difference, Equivalents per 100 ml.	Difference, %
1	0.154	0.149	-0.005	-3.2
2	0.154	0.150	-0.004	-2.6
3	0.215	0.219	+0.004	+1.9
4	0.215	0.216	+0.001	+0.46
5	0.215	0.205	-0.010	-4.7
6	0.277	0.268	-0.009	-3.2
7	0.277	0.283	+0.006	+2.2
8	0.307	0.314	+0.007	+2.3

Table II. Determination of Total Fluoride in Known Samples

Experiment No.	Total Fluoride Added, G./100 ml.	Total Fluoride Found, G./100 ml.	Difference	
			G./100 ml.	%
1	0.905	0.902	-0.003	-0.33
2	0.905	0.925	+0.02	+2.2
3	1.36	1.33	-0.03	-2.2
4	1.36	1.39	+0.03	+2.2
5	1.42	1.46	+0.04	+2.8
6	1.81	1.85	+0.04	+2.2
7	2.72	2.67	-0.05	-1.9
8	2.84	2.89	+0.05	+1.8

and 20 ml. of water are added. A 2.0-ml. sample is carefully pipetted into the flask. The distilling flask is heated, and the temperature of boiling solution is maintained at 115° to 125° C. by careful addition of water from the dropping funnel. The temperature should finally be allowed to reach 140° C. Approximately 60 to 75 ml. of distillate are collected in a 100-ml. flask and diluted to the mark with water. Once or twice during the distillation, the burner should be removed and the thermometer and stopper washed down with water. After the distillation is completed, any condensate is washed from the flask's arm and condenser into the volumetric flask and diluted to volume with distilled water.

A 25-ml. aliquot of the distillate is pipetted into a tall beaker and diluted to 100 ml. and 3 drops of Alizarine Red S indicator are added. Sodium hydroxide, 0.5 N , is added until the solution is permanently pink. The color is discharged by adding diluted hydrochloric acid (1 to 200) until the solution is just light yellow, then 2 ml. of the buffer solution are added. The solution is titrated over a white background with thorium nitrate until the appearance of a light pink color, which lasts for 3 to 4 minutes. The thorium nitrate is added slowly while the solution is stirred continuously. There is some pink color formed during the titration because of the absorption of the dye on the thorium fluoride precipitate. However, the sudden increase in pink color at the end point is easily discernible.

The normality of the thorium nitrate is determined in exactly the same manner by titrating against sodium fluoride, except that the distillation is omitted. Ten milliliters of the standard sodium fluoride solution are pipetted into a 100-ml. volumetric flask and diluted to the mark, and 10 ml. of this diluted solution are titrated as above. The weight of fluoride ion per 100 ml. of pickle solution is calculated as follows:

M = ml. of thorium nitrate required to titrate a 25-ml. aliquot of the distillate

P = normality of thorium nitrate solution

R = atomic weight of fluorine

Z = grams of fluoride ion per 100 ml. of pickle solution

$$Z = \frac{MPR}{5}$$

REMARKS

Analyses of a large number of pickling solutions has shown that for room-temperature operation of the bath the total acid and nitrate-ion concentrations are not critical if kept within the following approximate limits: total acid 0.15 to 0.35 equivalent, nitrate ion 7.5 to 20.0 grams per 100 ml. of sample (4). The absolute amounts of iron and fluoride present are not critical up to at least 3 grams of iron and 6 grams of fluoride per 100 ml. of sample, even though the ratio of their concentrations has an effect on the pickling rate. For the most rapid pickling action, the molar ratio of fluoride to iron should be kept about 6 to 1. If it falls below 3 to 1, pickling is generally very slow. The minimum ratio depends on the annealing conditions and the

Table III. Determination of Nitrate in Known Samples

Experiment No.	Nitrate Added	Nitrate Found	Difference	
	G./100 ml.	G./100 ml.	G./100 ml.	%
1	3.72	3.74	+0.02	+0.56
2	9.33	9.23	-0.10	-1.1
3	9.53	9.53	0.00	0.0
4	11.2	11.1	-0.1	-0.89
5	13.1	12.7	-0.4	-3.6
6	15.3	15.2	-0.1	-0.65
7	16.8	16.8	0.0	0.0
8	19.1	18.9	-0.2	-1.0

Table IV. Comparison of Iron Determinations by Gravimetric and Present Methods

Experiment No.	Gravimetric Method	Present Rapid Method	Difference	
	G./100 ml.	G./100 ml.	G./100 ml.	%
1	0.925	0.931	+0.006	+0.65
2	1.10	1.20	+0.10	+9.1
3	1.20	1.19	-0.01	-0.83
4	1.33	1.28	-0.05	-3.8
5	1.12	1.14	+0.02	+1.8
6	1.31	1.39	+0.08	+6.1
7	2.19	2.29	+0.10	+4.6
8	3.50	3.33	-0.17	-4.9

resulting oxide scale. The chromium and nickel content of the bath does not appreciably affect the pickling efficiency.

In some cases, the determination of sulfates may be desirable. Standard gravimetric methods such as those outlined by Treadwell and Hall (9) have been found satisfactory.

The accuracy obtained from the above outlined methods is more than sufficient in view of the wide ranges of concentration which are allowable. The procedures were designed for speed and practical convenience rather than for extreme accuracy.

Synthetic pickle solutions of known composition were analyzed by the outlined procedure. In each case the concentrations of iron, chromium, and nickel were varied. The data are shown in Tables I to IV. The results of each experiment represent an average of at least three determinations. Iron contents were determined by a gravimetric procedure in which the iron was separated from the other metallic ions, and finally weighed as ferric oxide. These gravimetric values compared favorably with those obtained by the present rapid method.

LITERATURE CITED

- (1) Adolph, W. H., *J. Am. Chem. Soc.*, **37**, 11, 2500 (1915).
- (2) Allen, N., and Furman, N. J., *Ibid.*, **54**, 4625 (1932).
- (3) Bowman, F. C., and Scott, W. W., *J. IND. ENG. CHEM.*, **7**, 766 (1915).
- (4) Hamilton, W. F., and McKee, W. F., Lockheed Aircraft Corp., *Report 4159* (1943).
- (5) Mellor, J. W., "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. II, pp. 138-9, New York, Longmans, Green and Co., 1922.
- (6) Offerman, H., *Z. anorg. Chem.*, **3**, 615 (1890).
- (7) Rowley, R. J., and Churchill, H. V., *IND. ENG. CHEM., ANAL. ED.*, **9**, 551-2 (1937).
- (8) Stark, G., *Z. anorg. allgem. Chem.*, **70**, 173 (1911).
- (9) Treadwell, F. P., and Hall, W. T., "Analytical Chemistry", 9th English ed., Vol. II, New York, John Wiley & Sons, 1942.

Determination of Water in Dry Food Materials Application of the Fischer Volumetric Method

C. M. JOHNSON

Western Regional Research Laboratory, Albany, Calif.

With the Fischer volumetric method it was possible to determine the moisture content of starches, sugars, pectin, and spray-dried egg powder fairly rapidly and to get results that agreed with those obtained by the standard vacuum-oven technique. The apparent moisture contents of a number of dehydrated vegetables and fruit powders when determined by electrometric titration were generally slightly higher than those obtained by the vacuum-oven method.

A RAPID and accurate method for the determination of water in many dried foods and food materials is necessary for the proper control of the finished product in manufacturing plants and inspection laboratories. At present the official vacuum-oven method for the determination of moisture in dried fruits (3) is used, with and without modifications, for the determination of moisture in dehydrated vegetables. The vacuum-oven method is slow and, as shown by Makower and Myers (9), does not give a satisfactory measure of the true moisture content of dehydrated vegetables. It apparently gives satisfactory results with such materials as starches, sugars, pectins, and egg powder, but it requires considerable time before the results are obtained.

The volumetric method developed by Fischer (5) is rapid and specific for water. The method involves the titration of a methanolic suspension or solution of the sample with a reagent composed of iodine and sulfur dioxide dissolved in pyridine and methyl alcohol. The chemistry of the Fischer reagent has been studied in considerable detail by Smith, Bryant, and Mitchell (15).

The end point, in uncolored solutions, can be observed fairly

accurately by the appearance of the brown iodine color. However, in colored solutions or in solutions containing considerable amounts of spent reagent, the visual detection of the end point becomes exceedingly difficult. Almy, Griffin, and Wilcox (1), Wernimont and Hopkinson (16), and McKinney and Hall (8) have described electrometric methods for the detection of the end point of this reaction, thus making it possible to determine the moisture content of colored liquids and suspensions.

The use of the Fischer volumetric method for the determination of moisture in organic liquids and technical products has been described in detail by many workers (1, 4, 5, 8, 10, 11, 15, 16). The volumetric determination of moisture in some foodstuffs, such as fats, marmalade, and cacao, has been described by Kaufmann and Funk (7) and Richter (14), but, to the author's knowledge, this method has not been used for the determination of moisture in the materials reported on here.

This paper presents the results of a study of the conditions necessary for the Fischer volumetric determination of moisture in starches, sugars, pectin, egg powder, and a number of dehydrated and spray-dried foods.

APPARATUS

The qualitative unit of the Senior model Fisher titrimeter was used for determination of the electrometric end point in these studies. Any of the other electrometric systems referred to above would doubtless have been equally satisfactory. It was found convenient to use a separate stirring and electrode system similar to that described by Wernimont and Hopkinson (16). The electrodes were connected to the brush posts of the titrimeter, thus making use of the amplifying and "magic eye" system of the titrimeter. The magic eye was set so that it was open about

Table I. Vacuum-Oven and Volumetric Moisture Values for Dehydrated Vegetables

(Vacuum-oven values after 38 hours at 70° C.; volumetric values after indicated times and temperatures of contact)

Material	Apparent Moisture, Vacuum-Oven Method	Apparent Moisture, Volumetric Method											
		Hours' Contact at 22° C.							Hours' Contact at 60° C.				
		0.5	2	16	48	64	88	96	0.5	2	4	6	24
%	%	%	%	%	%	%	%	%	%	%	%	%	
Carrots	6.62 ^a	6.33	7.01	7.12	7.14	7.05	7.30	7.31	7.32	7.34	7.29
White potato	6.84	2.81	3.90	5.50	6.16	6.47	4.98	6.09	6.63	6.85	7.26
Cabbage	3.63	3.12	3.15	4.00	3.76	3.91	4.00	4.17	4.65
Tomato powder	5.40 ^a	..	4.07	4.98	5.32	5.57	5.70	5.85	6.14

^a Interpolated from Figure 2.

Table II. Comparison of Vacuum-Oven and Volumetric Moisture Values of Dried Whole Egg Powder

Sample	Vacuum-Oven Method, 100° C., 5 Hours	0.5 hour at 22° C.	Volumetric Method, 0.5 hour at 60° C.	1 hour at 60° C.
	%	%	%	%
A	4.76	4.59	4.69	4.86
	4.72	4.57	4.71	4.87
B	2.65	2.64	2.67	2.83
	2.61	2.52	2.76	2.94
C	5.17	5.17	5.27	5.20
	5.20	5.15	5.20	5.26
D	4.38	4.34	4.24	4.37
	4.42	4.29	4.46	4.42
E	5.04	4.94	5.11	5.04
	5.10	5.01	4.98	5.07

0.6 cm. (0.25 inch) when the electrodes were in the solution containing an excess of the reagent. The eye closed completely at the end point when the excess reagent was titrated with standard water solution.

The reagents were stored in all-glass automatic buret systems and were protected from atmospheric moisture with Drierite tubes.

The samples were prepared and titrated in 250-ml. No. 27 glass-stoppered Erlenmeyer flasks.

REAGENTS

ABSOLUTE METHANOL. Most of the commercial absolute methanol tested in this study contained from 0.1 to 0.5% water. It was necessary, therefore, to dry the methanol before use. Drying the alcohol with magnesium as described by Gilman and Blatt (6) proved to be more satisfactory than distilling from either calcium oxide or Drierite. The alcohol so obtained contained from 0.01 to 0.03% of water.

FISCHER REAGENT. The Fischer reagent was prepared by dissolving 169 grams of resublimed iodine in 511 ml. of the dried methanol and 425 ml. of reagent-grade pyridine, and adding 128 grams of sulfur dioxide gas. The reagent did not heat appreciably when the sulfur dioxide was added at a rate of about 40 grams per hour. The molar ratios of iodine, sulfur dioxide, and pyridine in the reagent were 1 to 3 to 8. This solution deteriorated at the rate of about 1% per day when first prepared, becoming slightly more stable as it aged.

STANDARD WATER SOLUTION. The standard water solution was prepared by adding sufficient distilled water to dry methanol to give a solution containing approximately 5 mg. of water per ml.

The ratio, *R*, between the Fischer reagent and the water was determined daily in the manner described by Wernimont and Hopkinson (16).

The exact water value of the standard water solution was determined by titration of weighed amounts of distilled water and was checked at least weekly.

PROCEDURE

Sufficient material to contain 30 to 200 mg. of water was weighed into each dry glass-stoppered 250-ml. flask, and 25 ml. of dried methanol were added to each flask. In various experiments the samples were either allowed to stand tightly stoppered at room temperature or connected by means of ground joints to reflux condensers (protected from atmospheric moisture by Drierite) and maintained in a glycerol bath at 60° C. for the required length of time. Active refluxing of the alcohol was avoided because of occasional loss of sample and alcohol by

bumping. It was not necessary to wash the condenser, since vapors rarely ascended above the neck of the flask.

In later experiments the flasks were heated to 60° C. while connected to a condenser and then removed, quickly stoppered, and stored in an air oven at 59° ± 1° C. for the desired length of time.

The water content of the cooled sample was determined by adding Fischer reagent until the brown iodine color appeared and then back-titrating to the electrometric end point with the

standard water solution. The last few drops of standard water solution were added slowly, since a slight lag in the end point is characteristic of this reaction (1, 8). The direct titration with Fischer reagent was not satisfactory, as shown in the discussion of the electrometric behavior of this system by Almy, Griffin, and Wilcox (1).

The moisture content of the sample was then calculated after correction for the moisture content of the methanol used.

RESULTS

Fischer volumetric moisture determinations were made on samples of wheat starch, potato starch, sucrose, glucose, fructose, pectin, spray-dried whole eggs, and a number of dehydrated vegetables and fruit powders. The dehydrated and spray-dried products are referred to below only as carrots, tomato powder, eggs, etc.

Determinations of moisture on the starches, sugars, pectin, and spray-dried materials were made without further grinding. The dehydrated vegetables were ground in an intermediate Wiley mill fitted with a 40-mesh screen.

The apparent moisture content of some of the materials was determined after varying intervals of contact with the methanol at 22° and 60° C. Table I shows the relation between time and temperature of contact with methanol for four of the materials. The vacuum-oven values after 38 hours at 70° C. are included for comparison.

Dried whole egg powder was exceptional in its behavior, in that the moisture was liberated very rapidly (Table II). One-half hour of soaking in methanol at 22° C. yielded nearly the maxi-

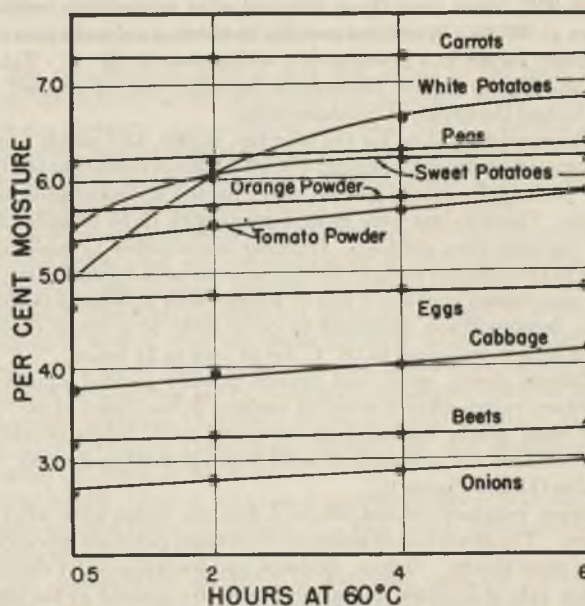


Figure 1. Fischer Volumetric Moisture Values of Dehydrated Foods as a Function of Time of Soaking in Methanol at 60° C.

Table III. Vacuum-Oven and Volumetric Moisture Values for Dry Foods

(Vacuum-oven values after indicated time at 70° C.; volumetric values after indicated times of contact at 60° C.)

Material	Vacuum-Oven Method		Volumetric Method		
	16 hours %	100 hours %	0.5 hour %	6 hours %	24 hours %
Potato starch	13.55	13.58	13.41	13.46	13.45
	13.60	13.65	13.43	13.42	13.51
Wheat starch	10.15	10.25	10.21	10.12	10.26
	10.15	10.32	10.08	10.22	10.22
Sucrose	8.37	8.37	8.31	8.30	8.31
	8.37	8.39	8.21	8.24	8.28
Glucose	3.52	3.58	3.46	3.44	3.41
	3.55	3.60	3.45	3.48	3.51
Fructose	1.91	2.20	1.51	1.54	1.58
	1.92	2.24	1.52	1.57	1.58
Pectin	9.86	10.03	10.00	10.08	10.03
	9.86	10.01	10.02	10.05	10.09
	38 hours				
Carrots	6.62 ^a		7.32	7.26	7.26
			7.30	7.28	7.33
Beets	3.06		3.18	3.29	3.49
	3.08		3.21	3.42	3.54
Peas	6.02		6.32	6.29	6.58
	5.99		6.04	6.41	6.48
Orange powder	5.71		5.71	5.76	5.81
	5.71		5.60	5.88	5.87
Sweet potato	5.41		5.60	6.21	6.40
	5.39		5.52	6.19	6.37
White potato	6.84		4.86	6.90	7.32
	6.85		5.10	6.81	7.20
Onion	2.81		2.70	2.96	3.28
	2.83		2.68	2.96	3.29
Cabbage	3.62		3.76	4.16	4.64
	3.64		3.77	4.18	4.66
Tomato powder	5.40 ^a		5.30	5.76	5.81
			5.35	5.88	5.87

^a Interpolated from Figure 2.

imum amount of water as compared with values obtained after 0.5, 2, 4, and 6 hours at 60° C. (Figure 1). These values are in agreement with those obtained by the official A.O.A.C. method (2).

Apparent moisture values were obtained for the other materials after contact with the methanol at 22° and 60° C. The values obtained after contact with the methanol at 22° C. were from 10 to 30% lower than those obtained after comparable contact times at 60° C. It was not possible to obtain constant apparent moisture values in a practicable working time at 22° C. Table III and Figure 1 show the relation between time of contact at 60° C. and the apparent moisture value.

The moisture values for the starches, sugars, and pectin were, for practical purposes, constant after 0.5 hour of contact at 60° C., and prolonged contact had no effect on the apparent moisture value. These values were in agreement with those obtained by the vacuum-oven method. Fructose decomposed to some extent in the vacuum oven at 70° C., as evidenced by darkening of the sample and continued loss of weight with prolonged drying. This decomposition appeared to occur only to a small extent when held in methanol at 60° C. for as long as 24 hours.

Carrots, beets, peas, and orange powder yielded apparent moisture values after 2 hours of soaking in methanol at 60° C. that were nearly constant, as compared with values obtained after soaking for as long as 6 or 24 hours in methanol at 60° C. (Table III and Figure 1).

Sweet potatoes did not attain a limiting value until after 4 hours. The liberation of moisture from white potatoes proceeded even more slowly. Onions, cabbage, and tomato powder showed a slow rate of increase in apparent moisture content as the time of soaking in methanol at 60° C. was prolonged.

The effect of thermal decomposition (in methanol at 60° C.) on the apparent moisture content of these materials is difficult

to evaluate. However, a consideration of the physical nature of dehydrated white potatoes, notably case-hardening and gelation effects (13), would lead one to suspect that the slowness in attaining constancy of apparent moisture content was largely due to slow diffusion of moisture from the particles.

On the other hand, the physical characteristics of onions, cabbage, and tomato powder did not appear to account for the slow, almost uniform rate of increase in the apparent moisture content of these materials. Rather it seemed more likely that thermal decomposition was making a considerable contribution to the increase in apparent moisture content after the first 0.5 to 2 hours in methanol at 60° C.

The moisture contents of the dried foods obtained by the Fischer volumetric method were compared with those obtained by the vacuum-oven method. Figure 2 illustrates the relation between percentage loss of weight and time of heating in vacuum at 70° C. It is apparent that a reasonably flat portion of the curve is attained only after prolonged drying. This continued loss in weight was due in part to actual loss of water from the interior of the cellular material and in part to thermal decomposition. It was, of course, impossible, from the vacuum-oven data alone, to determine the correct moisture value (9, 11). For purposes of this study, however, the 38-hour value was arbitrarily taken. A comparison of moisture values obtained in the 70° C. vacuum oven after 38 hours and the volumetric value after 0.5, 6, and 24 hours in methanol at 60° C. is given in Table III.

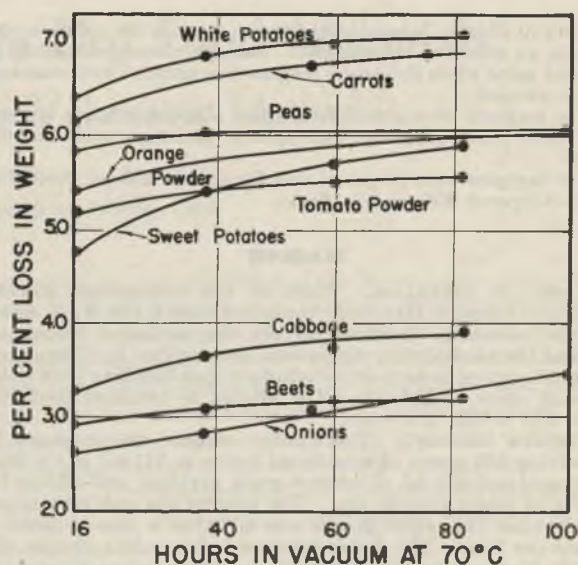


Figure 2. Loss of Weight of Dehydrated Foods as a Function of Drying Time

Determination of added water, was tested by addition of weighed amounts of distilled water to 1.000-gram samples of dried foods suspended in methanol. The samples were held at 60° C. for 2 hours and the water was determined in the usual manner. The results are presented in Table IV.

Soaking the samples in pyridine and pyridine-methyl alcohol mixtures did not increase the rate of removal of water from the materials and was not done in these studies.

Allowing the samples to stand in the presence of Fischer reagent at room temperature did not increase the rate of removal of water, and at 60° C. side reactions gave rise to erratic and inaccurate results. Prolonged contact of the Fischer reagent with the sample should be avoided because of two possible side reactions—oxida-

Table IV. Determination of Water Added to 1,000-Gram Samples of Dried Foods by Volumetric Method

Material	Water Originally Present in Sample ^a	Water Added	Total Water		Per Cent of Total Water Found
	Mg.		Mg.	Calculated	
Carrots	71.3	84.0	155.3	158.2	101.8
	71.3	130.9	202.2	201.0	99.4
Orange powder	53.9	80.3	134.2	131.5	97.9
	53.9	135.5	189.4	187.8	99.1
Onions	29.6	70.4	100.0	98.4	98.4
	29.6	117.5	147.1	146.3	99.5
Eggs	47.3	76.9	124.2	125.0	100.5
	47.3	115.5	162.8	162.0	99.6
None (water only)		86.6	86.6	86.4	99.6
		133.1	133.1	134.1	100.8

^a Average of replicate analyses by this method.

tion of organic matter by the iodine and the regeneration of iodine in the partly spent reagent (4).

EFFECT OF PARTICLE SIZE

The volumetric moisture method, in common with most other moisture methods, is dependent on a relatively slow rate of diffusion of water from the solid mass to the surrounding medium (atmosphere or solvent).

Particle size is known to be a very important factor in determining the apparent moisture value after any given time in the vacuum oven (9). Therefore, it seemed desirable to determine the effect of particle size on the rate of diffusion of water from the solid material suspended in methyl alcohol.

Samples of vegetables that had been stored in closed containers for at least 1 month, in order to attain a uniform distribution of moisture throughout the mass, were ground in a food chopper. A portion of the ground material as received from the food chopper was placed in a closed container at once; the remainder was rapidly separated into three groups of different average particle size by passage through U. S. Standard sieves of the fine series. Portions of each group, as well as of the original ground material, were reground in an intermediate Wiley mill fitted with a 40-mesh screen. Apparent moisture values were then run on each subsample.

The results given in Table V show that, of the four materials studied, white potato was the only one in which particle size was an important factor in the volumetric method. Makower and Myers (9) obtained large differences in apparent moisture content of carrots of various particle sizes by the vacuum-oven method. The data of Table V indicate that such differences are not obtained when the volumetric method is used for carrots.

A fairly finely divided sample is necessary to facilitate proper sampling and to permit rapid moisture determinations. On the other hand, the sample should not be too finely divided, since errors would be introduced by heating effects on grinding and by the increased hygroscopicity of the sample.

INTERFERENCES

Fischer (5), Kaufmann and Funk (7), Smith, Bryant, and Mitchell (15), and McKinney and Hall (8) have demonstrated that ethylenic bonds do not interfere in this determination.

Aldehydic and ketonic compounds yield high values by virtue of acetal and ketal formation in the methanol (15). Reactive carbonyl compounds are not likely to be present in dehydrated foods in sufficient quantity to cause serious interference.

A sample of *l*-ascorbic acid yielded an apparent moisture value of a little less than 10% when the vacuum-oven value was only 0.1%. This is in fair agreement with the calculated iodine consumption by reduced *l*-ascorbic acid. However, errors from this source are not likely to be serious—for example, few vegetables contain more than 10 mg. of ascorbic acid per gram of dry material. A maximum of 1.0 mg. of apparent water would then be present in the 1-gram sample (an apparent moisture value of 0.1%).

A determination of naturally occurring iodine-reducing substances was carried out by a modification of the method described by Prater, Johnson, Pool, and Mackinney (12). This modified method avoids interference by any sulfur dioxide that might be present in the material.

Two-gram samples of the dehydrated foods were soaked in 25 or 50 ml. of methanol for 2 hours at 60° C., and 400 ml. of water were added. After the addition of 40 ml. of acetone and sufficient sulfuric acid to bring the pH to 2 to 3, the samples were allowed to stand 10 minutes. The suspensions were then titrated to a starch end point with 0.1 *N* iodine solution. The results were calculated to the apparent water value that would result from an equal iodine reduction in the Fischer reagent. In no case was the iodine-reducing value, under these conditions, sufficient to account for more than 0.03% apparent moisture.

One cannot, logically, make a correction for these apparent water values, for they are probably more apparent than real. Except for cases where the ascorbic acid content is high, the correction would be minor.

Inorganic oxides and oxidizing-reducing agents interfere in the volumetric method (4). However, such substances are not ordinarily encountered in food products in significant amounts.

Table V. Effect of Particle Size on Apparent Moisture Value of Dehydrated Vegetables

Material	Particle-Size Distribution (According to U. S. Standard Sieves, Fine Series) ^a	Apparent Moisture	
		Material as described in Column 2	Material reground to pass 40-mesh sieve
		%	%
Potatoes (white)	As received from food chopper	4.97	6.74
	4-10 mesh	3.42	6.82
	10-18 mesh	4.85	6.86
	18-35 mesh	6.32	7.00
Carrots	As received from food chopper	7.05	7.20
	4-10 mesh	7.18	7.30
	10-18 mesh	7.05	7.17
	18-35 mesh	7.07	7.06
Cabbage	As received from food chopper	6.47	6.54
	4-10 mesh	6.48	6.53
	10-18 mesh	6.53	6.49
	18-35 mesh	6.61	6.60
Onions	As received from food chopper	3.84	3.87
	4-10 mesh	3.75	3.71
	10-18 mesh	3.70	3.73
	18-35 mesh	3.72	3.77

^a For example, passing No. 4 but retained on No. 10.

APPLICABILITY AND RECOMMENDED PROCEDURE

The volumetric method is very well suited to the rapid and accurate determination of moisture in starches, sugars, pectin, and egg powders. Inspection of Tables II and III reveals that 0.5 hour's contact with methanol at 60° C., followed by cooling and titration as described above under Procedure, yields maximum and constant moisture values for these materials.

The volumetric method is also satisfactory for such materials as carrots, beets, peas, and orange powder, provided the results are calibrated against those obtained by some acceptable reference method. However, for practical purposes no method is known that gives a true moisture value for such materials. Contact times of 0.5 to 24 hours with methanol, followed by cooling and titration as described above, yield fairly constant results for these materials, although in general these apparent moisture values are slightly higher than those obtained by the vacuum-oven method (38 hours at 70° C.).

The results obtained with sweet potatoes indicate that slightly longer contact times are necessary (4 to 6 hours) before constant results are obtained.

The considerable variation of apparent moisture values of white potatoes, onions, cabbage, and tomato powder with different contact times probably results from slow diffusion of moisture to the methanol and slow thermal decomposition. It may

be possible, however, to standardize the time and temperature of contact, so that results agreeing with those obtained by a reference method can be duplicated.

LITERATURE CITED

- (1) Almy, E. G., Griffin, W. C., and Wilcox, C. S., *IND. ENG. CHEM., ANAL. ED.*, **12**, 392-6 (1940).
- (2) Assoc. Official Agr. Chem., *Official and Tentative Methods of Analysis*, 5th ed., p. 308 (1940).
- (3) *Ibid.*, p. 335.
- (4) Bryant, W. M. D., Smith, D. M., Mitchell, J., Jr., and Ashby, E. C., *J. Am. Chem. Soc.*, **63**, 2924-26 (1941).
- (5) Fischer, K., *Angew. Chem.*, **48**, 394-6 (1935).
- (6) Gilman and Blatt, "Organic Syntheses", Collective Volume I, 2nd ed., pp. 219-49, New York, John Wiley and Sons, 1941.
- (7) Kaufmann, H. P., and Funk, S., *Fette u. Seifen*, **44**, 345 (1937).
- (8) McKinney, D. C., Jr., and Hall, R. T., *IND. ENG. CHEM., ANAL. ED.*, **15**, 460-2 (1943).
- (9) Makower, B., and Myers, S., *Proc. Inst. Food Tech.* **1943**, 156-64.
- (10) Mitchell, J., Jr., *IND. ENG. CHEM., ANAL. ED.*, **12**, 390-1 (1940).
- (11) Porter, W. L., and Willets, C. O., *J. Assoc. Official Agr. Chem.*, **27**, 179-194 (1944).
- (12) Prater, A. N., Johnson, C. M., Pool, M. F., and Mackinney, G., *IND. ENG. CHEM., ANAL. ED.*, **16**, 153-7 (1944).
- (13) Reeve, R. M., *Food Research*, **8**, 128-36 (1943).
- (14) Richter, *Angew. Chem.*, **48**, 776 (1935).
- (15) Smith, D. M., Bryant, W. M. D., and Mitchell, J., Jr., *J. Am. Chem. Soc.*, **61**, 2407-12 (1939).
- (16) Wernimont, G., and Hopkinson, F. J., *IND. ENG. CHEM., ANAL. ED.*, **15**, 272-4 (1943).

Determination of Water in Liquid Petroleum Fractions

O. T. AEPLI¹ AND W. S. W. McCARTER

Porocel Corporation, 260 South Broad St., Philadelphia, Pa.

Small amounts of water (0 to 60 p.p.m.) in unleaded gasoline, naphtha, and electrical insulating oils can be determined by the Karl Fischer reagent through the use of a specially designed apparatus which effects the total exclusion of atmospheric moisture during the sampling and titration.

RECENT work (4) on the desiccant properties of Driocel (activated bauxite) required the accurate determination of very small amounts of water in liquid hydrocarbons. Preliminary investigation of the available methods indicated that the Karl Fischer reaction could be most satisfactorily adapted to the needs. This reagent (2, 5) is quantitatively specific for water and its use for the determination of water in alcohols, carboxylic acids, saturated, ethylenic, and aromatic hydrocarbons (5), and petroleum fractions (1) has been reported. Early in the authors' study it became evident that for the small amounts of water involved in their work (0 to 60 parts per million) reproducibility could be obtained only through the use of a sampling and analytical technique which would effect the complete exclusion of atmospheric moisture. Publication of the apparatus and method used in this laboratory is prompted by the increasing significance of moisture content in many processes of the chemical and petroleum industries.

REAGENTS

Directions for the preparation of the Karl Fischer reagent appear in the literature (2, 5). Since the concentration of the reagent generally decreases rapidly over several days immediately following its preparation (Figure 1), it is advisable to make the solution at least 24 hours prior to use and to standardize it frequently thereafter until the concentration has become stable. The need for frequent standardization of the reagent is further emphasized by the three curves which show that the rate of decrease in concentration is not predictable. The reagent was standardized against a solution of water in methanol containing 1 mg. of water per milliliter.

APPARATUS

The sampling bulb shown in Figure 2 was designed to secure 150-ml. portions of the liquid to be analyzed, either from stream or from bulk, without exposure to the atmosphere. Stream samples, as from a drying tower, may be secured by attaching the bulb to the effluent tube of the tower by means of the ground-glass connection, f_1 . With h_3 closed, stopcocks h_1 and h_2 are opened to allow the bulb to fill. Samples from bulk may be obtained by attaching at f_2 an extension tube long enough to dip well into the body of liquid. With h_1 closed, h_2 and h_3 are opened and the bulb is filled by applying slight vacuum at h_2 . Before

taking a sample for analysis, the dried bulb should be rinsed with the liquid to adjust the adsorbed water concentration on the walls of the vessel.

Titration was carried out in the totally enclosed apparatus shown in Figure 2. A motor-driven glass stirrer, a , enters the 500-ml. flask through a mercury seal, b , attached by means of a 34/45 ST ground-glass joint. The flask is provided with three side necks: c , a 10/30 ST joint through which enters the tip of a 50-ml. Schilling buret for standard water-in-methanol solution; d , a 14/35 ST joint to hold a platinum electrode assembly; and e , a 10/30 ST joint to accommodate in turn joint f_2 of the sample bulb, the tip of a 10-ml. Schilling buret (not shown) for Karl Fischer reagent, and a desiccant tube, g .

The "dead stop" end-point method (3, 6) was adopted in preference to the more difficultly detectable and less precise visual end point. The electrodes and wiring diagram required by this method are shown in Figure 2. By means of a battery and variable resistance an e.m.f. of 0.5 to 1.0 millivolt is imposed across the platinum electrodes which dip into the Karl Fischer reagent. The lower e.m.f. requirement as compared to Wernimont's value is probably related to the immiscibility of the reagent in petroleum fractions. When the end point is reached one of the electrodes becomes polarized and current ceases to flow. This condition is indicated by the gradual return of the galvanometer spot to the zero position. A Leeds & Northrup enclosed lamp and scale galvanometer, catalog No. 2420-B (sensitivity, 25 microvolts per millimeter; period, 3 seconds; coil resistance, 23 ohms), is a suitable instrument.

METHOD

For gasoline and naphthas, which are normally lighter than Karl Fischer reagent, the electrodes extend to the bottom of the flask. With heavier immiscible liquids, such as electrical insulating oils, the electrodes are constructed to contact the upper

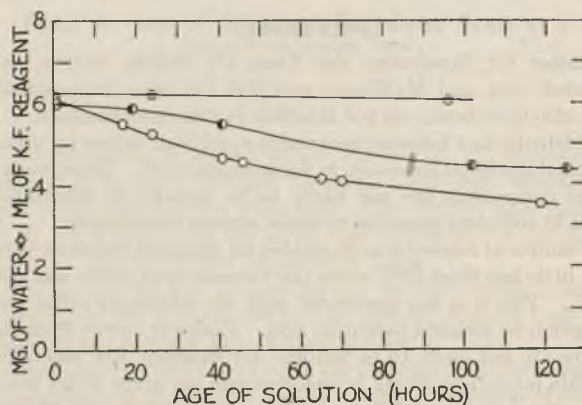


Figure 1. Decomposition of Representative Solutions of Karl Fischer Reagent

¹ Present address, Pennsylvania Salt Manufacturing Co., Philadelphia, Pa.

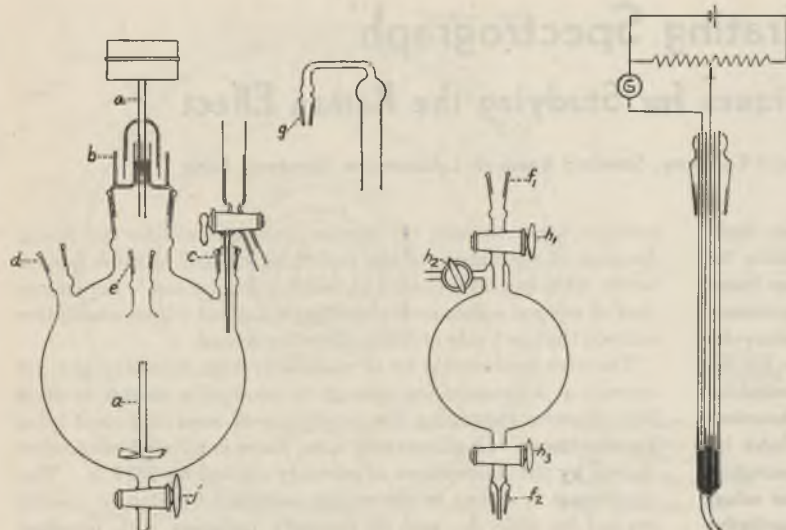


Figure 2. Titration Flask, Sampling Bulb, and Electrode Assembly

Table I. Standardization of Karl Fischer Reagent

Solution No.	(Mg. of H ₂ O ~ 1.00 ml. of KF reagent)		
	First Titration	Second Titration	Third Titration
1	5.00	5.43	5.44
2	3.21	3.77	3.77
3	2.71	3.59	3.60
4	2.38	2.61	2.61
5	2.19	2.54	2.54
6	1.14	1.81	1.80

Table II. Effect of Stirring Time

Stirring Time, Min.	(Parts per million of water)					
	Unleaded Gasoline		Naphtha	Insulating Oil		
	1	2		1	2	
0	26.2	27.8	..	20.3	..	
15	34.9	34.3	16.2	20.6	20.8	
30	37.2	
60	36.5	..	16.8	20.9	20.9	
120	36.2	

Table III. Reproducibility of Method

(Parts per million of water)					
Unleaded Gasoline		Naphtha		Insulating Oil	
1	2	1	2	1	2
1.82	1.08	0.53	0.40	5.2	5.6
19.9	18.6	9.1	8.5	8.0	7.4
26.2	27.8	26.2	25.0	9.0	9.7
34.9	34.3	35.2	34.0	28.2	27.3
63.5	62.4	61.2	61.5	31.1	30.2

liquid layer. In the latter case, for obvious reasons, approximately the same volume of liquid hydrocarbon should always be taken for analysis.

For standardization, 6 to 7 ml. of the Karl Fischer reagent are drained from the buret into the titration flask at *e*. The buret is removed and immediately replaced by the drying tube, *g*, before titrating with the standard water-in-methanol solution.

As shown in Table I, the first titration of the day gives a lower value than subsequent titrations. The agreement between the second and third titers indicates that adequate protection is afforded by the apparatus.

Following the standardization, the reaction mixture is drained from the flask through the capillary stopcock, *j*, with the drying tube still in place at *e*. The apparatus is then ready for actual analysis.

A sample to be analyzed for water is collected in the sample bulb and weighed. Drying tube *g* is removed from the titration flask at *e* and quickly replaced by the sample bulb. The drying tube is then attached to the sample bulb at *f*₁. By opening stop-

cocks *h*₁ and *h*₃ the sample is drained into the titration flask. The sample holder is then quickly replaced by the buret for Karl Fischer reagent, and from 7 to 9 ml. of reagent are added to the flask. As this buret is removed the drying tube is quickly slipped into place at *e*. The emptied sample holder is reweighed to determine the amount of liquid transferred to the flask. The addition of 5 to 6 ml. of standard water-in-methanol solution at *c* helps to prevent adherence of the reagent to the walls of the flask after subsequent agitation. After mechanical stirring the excess Karl Fischer reagent is titrated with standard water-in-methanol solution. In this back-titration each addition of water-in-methanol solution is followed by a brief period of stirring, after which the mixture is allowed to separate into layers. At the completion of the titration the sample is drawn off at *j* and the titration flask, without further preparation, is ready for the next analysis.

The effect of time of stirring following the addition of the Karl Fischer reagent to the hydrocarbon is shown in Table II. It appears that 15 minutes is adequate to bring about substantially complete reaction.

REPRODUCIBILITY

The results of duplicate determinations of the water content of unleaded gasoline, naphtha, and insulating oil samples are given in Table III. The time of stirring in each determination was 15 minutes.

The agreement between the two determinations on each sample is within 2 p.p.m. and in some cases, especially in the lower concentrations of water, the deviation is within 1 p.p.m.

ACCURACY

Because of the difficulties and uncertainties involved in preparing water-in-hydrocarbon solutions of known concentration in the range under consideration, an evaluation of the "absolute" accuracy of the method would be questionable. As an alternative, the accuracy was estimated by an indirect method with solutions prepared through the medium of a third component. These solutions were prepared by mixing small weighed quantities of a water-in-pyridine solution of known concentration (determined by titration) with weighed quantities of exhaustively dried naphtha. The results show no interference by the hydrocarbon:

Parts per million of water	
Present	Found (Av.)
9.3	8.8
20.8	20.5
30.7	30.2
33.6	33.3
60.7	60.4
104.9	104.4

The method is not applicable to gasoline containing tetraethyllead. A sample of gasoline known to have a water content of 19.3 p.p.m. showed an apparent water content of 243 to 247 p.p.m. after the addition of 4 ml. of Ethyl Fluid per gallon. Obviously the reagent is consumed by the Ethyl Fluid, giving erroneously high values.

LITERATURE CITED

- (1) Capell, R. G., Amero, R. C., and Moore, J. W., *Chem. & Met. Eng.*, 50, 107 (1943).
- (2) Fischer, K., *Angew. chem.*, 48, 394 (1935).
- (3) Foulk, C. W., and Bawden, A. T., *J. Am. Chem. Soc.*, 48, 2045 (1926).
- (4) La Lande, W. A., McCarter, W. S. W., and Sanborn, J. B., *IND. ENG. CHEM.*, 36, 99 (1944).
- (5) Smith, D. M., Bryant, W. M. D., and Mitchell, J. J., *J. Am. Chem. Soc.*, 61, 2407 (1939).
- (6) Wernimont, G., and Hopkinson, S. J., *IND. ENG. CHEM., ANAL. ED.*, 15, 272 (1943).

A Fast Grating Spectrograph¹

Accessories and Techniques for Studying the Raman Effect

ROBERT F. STAMM, American Cyanamid Company, Stamford Research Laboratories, Stamford, Conn.

This paper outlines the design and construction of a fast, high-resolution, moderate-dispersion grating spectrograph suitable for use in an industrial laboratory. The experimental techniques found satisfactory for the obtaining of Raman spectra in a routine manner are described along with the special appurtenances necessary for such work. Many structural problems which are soluble by the special methods of Raman spectroscopy arise in the chemical industry. For those not acquainted with the method, an elementary discussion on the elucidation of molecular structure has been included. This has necessitated the inclusion of a short description of an experimental method used in obtaining depolarization values of Raman lines. Finally, the subjects of qualitative and quantitative analysis by Raman effect are discussed and practical examples are given to show results obtainable.

SINCE its discovery in 1928, the phenomenon known as the Raman effect has proved of prime importance as a method for the elucidation of molecular structures and for locating various functional groups or chemical bonds in molecules. Since the Raman spectrum of a solution of several components is a superposition of the spectra of the individuals comprising the solution, the method is useful for qualitative analyses. The intensities of the Raman lines of each substance in a solution are indicative of the amount of that substance present in the solution giving rise to the spectrum. This extends the use of the method to quantitative molecular analysis and has, along with the other capabilities, made the method potentially popular in industrial laboratories.

This popularity, however, has been hindered by a dearth of very fast, moderate-dispersion spectrographs on the market. Presented here are the results of the author's efforts to counteract this situation by buying high-quality optical parts and building his own instrument. The essential appurtenances are also described, since they too are vital.

In obtaining a Raman spectrum, monochromatic light originates in a suitable source, passes (usually) through filters into the sample in a suitable container, and is scattered by the substance, the scattered light being then dispersed by a spectrograph and the spectrum recorded. The frequency shifts of the Raman lines are then determined, and they are the Raman active vibrational frequencies of the molecule scattering the light. The essential parts are discussed in the above order.

Light Source for Excitation

The intensity of the scattered light is proportional to the fourth power of the frequency of the exciting line. Thus it is advantageous to use as high a frequency line as possible. Table I gives the wave lengths of the lines in the mercury arc that have been used the most for the excitation of Raman spectra. The fourth to seventh columns of the table are devoted to a comparison of the efficacies of the various lines in exciting Raman spectra. These figures are only approximate because the lines are not equally intense.

The frequency of the exciting line must have less energy than the minimum energy required to put the molecule being irradiated into the lowest lying, observable, excited electronic state; otherwise, absorption followed by fluorescence or photodecom-

position (or both) and no Raman spectrum will be the result. Because of the nature of the molecules studied in these laboratories, 4358 has been chosen as best for general use. For excitation of colored substances absorbing 4358 but whose absorption ends on the low λ side of 5461, the latter is used.

The arcs used should be of reasonably high intensity and yet operate at a pressure low enough to produce a narrow exciting line (thereby enhancing the possibility of resolving close lying Raman lines). In all mercury arcs, there is a broad continuum caused by the fluorescence of mercury excited by 2537 Å. This continuum is strong in the region occupied by Raman spectra excited by 4358 Å., and its intensity increases with pressure. A double-jacketed mercury arc will operate with rather constant intensity, but the pressure will be considerably higher than that existing in a single-jacketed arc containing a limited amount of mercury to control the pressure. Thus the single-jacketed arc will usually possess sharper lines and have a more favorable (line intensity)/(continuum intensity) ratio than a double-jacketed arc. On the other hand, the former is much more susceptible to intensity alterations caused by variation in the ambient temperature. The single-jacketed source should be used in a constant-temperature room if it is necessary to maintain constant intensity.

The light source used consists of twelve single-jacketed General Electric Type AH-2 (250-watt) mercury arcs, each provided with an individual auto transformer (G. E. Catalog No. 58G42, 115 volts primary, 150 volts secondary, 300 watts, 60 c.p.s.). These transformers are divided into two banks of six, each bank being furnished constant voltage by one of two Sola stabilizers (Catalog No. 3061, primary volts 95-125, secondary volts 115, 2000 volts \times ampere. These stabilizers are not necessary for doing only photographic work.)

With these arcs running hot (a single fan blows downward on them) the 4358 line is relatively sharp. (The resolution obtainable is discussed below.) Their useful lifetime will be approximately 9 months operating 8 hours a day for a 6-day week (1700 hours). The arc assembly is surrounded by a cylindrical reflector of aluminized glass, cut from a 5-gallon carboy (two such cylinders are kept on hand).

The writer learned this simple method of cracking large glass cylinders from L. Pinney at Iowa State College. The method does not seem to be very well known and is worthy of description. Paper toweling is cut and folded to form double-thickness strips. The folded edge should be nearly straight. The tubing should be nicked with a deep file mark about 0.3 to 0.6 cm. (0.125 to 0.25 inch) long perpendicular to an element. The wet toweling strips are then wrapped in two bands around the body of the cylinder with the folded edges facing one another. The scratch is in between them. The total separation of the strips should be ca. 1 cm. for small tubing, 2 cm. for large tubing. An air-gas blast lamp is made to produce a moderately hot flame about 2.5 cm. (1 inch) long. The cylinder is then rotated for 8 to 12 revolutions with the flame directed at the area in between the strips; then it is removed from the flame. If it is soft glass, it will crack of its own accord; if Pyrex, a drop of water on the

Table I. Relative Power of Mercury Lines in Light Scattering

λ (Air), Å.	Color	ν (Vacuum), Cm. ⁻¹	ν^4/ν^4 5791	ν^4/ν^4 5461	ν^4/ν^4 4358	ν^4/ν^4 4047
2537	Ultraviolet	39,412	27.2	21.6	8.7	6.4
4047	Violet	24,705	4.2	3.3	1.4	1
4078	Violet	24,516	4.1	3.2	1.3	...
4358	Indigo	22,938	3.1	2.5	1	...
5461	Green	18,308	1.3	1
5770	Yellow	17,328
5791	Yellow	17,265	1

¹ Other papers presented at the New York Meeting, sponsored by the North Jersey Section, in the Symposium on Spectrochemical Methods of Analysis, were printed in the February issue, pages 65 to 88.

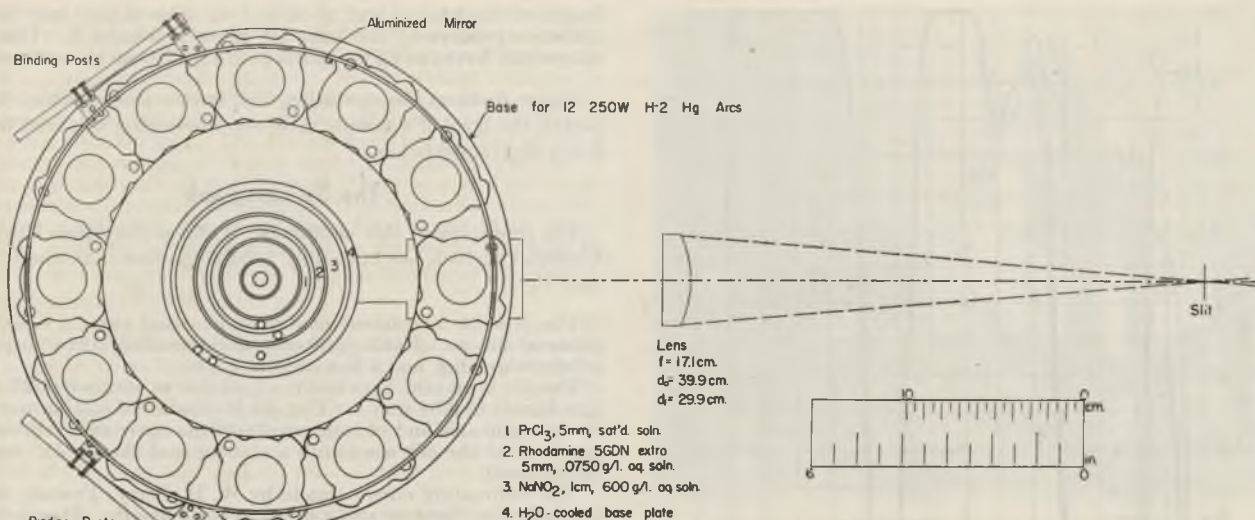


Figure 1. Raman Excitation Unit

scratch will produce a clean break. Cylinders may be cracked along an element by the same method provided strips are put on both the outside and inside surfaces.

It is necessary to realuminize the surface about every 2 months because of dust and fumes. These are much better reflectors than polished aluminum or chromium, and are therefore worth the extra trouble. The excitation unit is shown diagrammatically in Figure 1.

Filters and Sample Tubes

Filters are usually interposed between the source and the sample in order to remove high energy light which might cause fluorescence of photodecomposition, isolate a single exciting line, and remove the continuous spectrum in the region occupied by the Raman lines. Three filters are usually necessary for 4358 and 5461 excitation.

There is a paucity of transmission data on these filters in the literature, even though a number of people have used them. The writer feels that these data will be of service to a number of people who work with Raman spectra.

For 4358 excitation a saturated solution of sodium nitrite is used to remove ultraviolet and violet light; praseodymium chloride is used to remove the continuum to the high λ side out to 4850 Å.; Rhodamine 5GDN Extra is used to clean up the blue-green and green regions. The nitrite and dye are circulated through the filter jacket by means of midget centrifugal pumps (from Eastern Engineering Co., New Haven, Conn. Stainless steel type). The nitrite passes through a water-cooled condenser. The praseodymium is stagnant. The transmission curves for these filters are given in Figures 2 and 3.

Praseodymium is purchased from the Maywood Chemical Co., Maywood, N. J., as the oxalate, $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$, and contains a small amount of neodymium and 10 to 15% lanthanum. The lanthanum is easily removed by conversion to the chloride (via the oxide) followed by precipitation of the oxalate from a strongly acid solution. The praseodymium oxalate is insoluble, the lanthanum oxalate soluble. Three such treatments will lower the lanthanum concentration to the point where it is not objectionable.

Rhodamine is obtained from E. I. du Pont de Nemours & Co. This material is used in water solution and is protected from the direct light of the arcs by the sodium nitrite. It fluoresces less strongly in water than in alcohol.

The concentration of the praseodymium chloride is not given because the purity is not known. It is approximately an 80% solution of $\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$.

When working with solutions containing colloidal material which cannot be removed, very dilute solutions, or crystal powders, it is desirable (and sometimes absolutely essential) to keep 4358 from getting into the spectrograph. For this purpose,

a solution of potassium ferricyanide in a 1-cm. layer in front of the slit is useful. (Mercury atoms in the $6p, ^3P_1$ state would perform this function very nicely. The writer has assembled the parts for such a filter but has not had the opportunity of trying it.) The ferricyanide is better for this purpose than any other filter supposed to perform the same task.

For 5461 excitation an outer layer of sodium chromate, 1 cm. thick, pH 8.7, is used. This is circulated and cooled; next comes a 5-mm. layer of 2 molar cupric nitrate (stagnant), and finally a 5-mm. layer of saturated neodymium chloride (stagnant). This

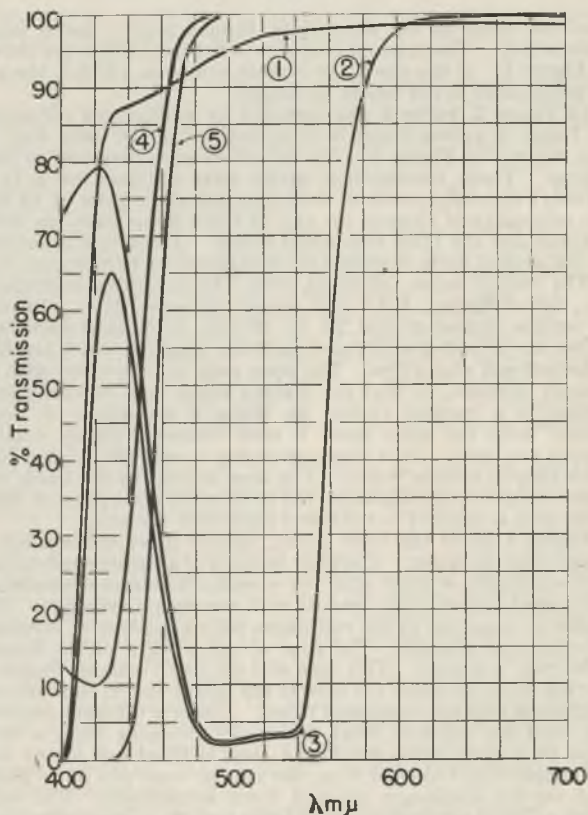


Figure 2. Transmission Curves

1. NaNO_2 , 600 grams per liter, 1 cm.
2. Rhodamine 5 GDN Extra, 0.075 gram per liter (aq.), 5 mm.
3. 1 plus 2, 61.5% 4358
4. $\text{K}_3\text{Fe}(\text{CN})_6$, 0.001 molar, 1 cm., 22% 4358
5. $\text{K}_3\text{Fe}(\text{CN})_6$, 0.003 molar, 1 cm., 1% 4358

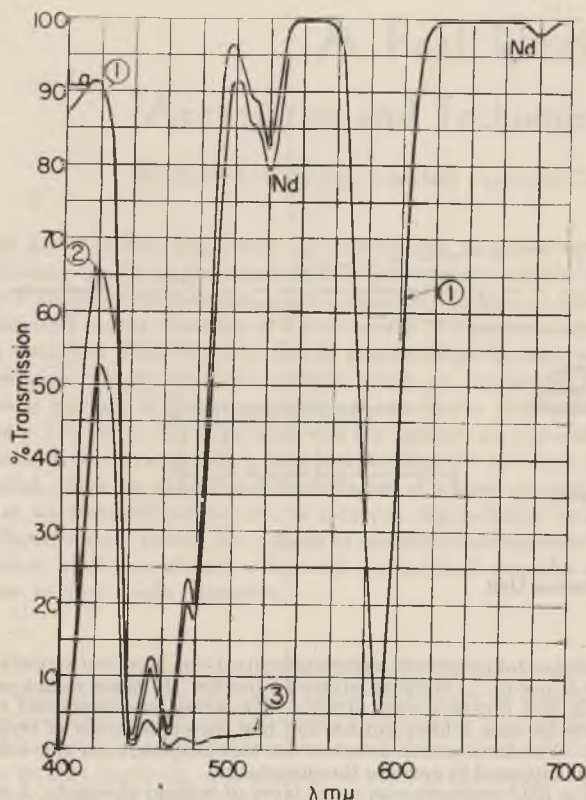


Figure 3. Transmission Curves

1. Saturated PrCl_3 , 5 mm., 19.7% 4358
2. 1 plus NaNO_2 , 600 grams per liter, 1 cm., 17.2% 4358
3. 2 plus Rhodamine 5 GDN Extra, 0.075 gram per liter, 5 mm., 12% 4358

does not clean up the entire 5461 Raman region, but is fairly satisfactory. The transmission curves for these filters are shown in Figure 4. If the chromate is more acid than pH 8.7, the absorption curve is not nearly so sharp.

In Figure 2, curve 3 was obtained by multiplying ordinates. In Figure 3, curves 2 and 3 were obtained in the same way, as was curve 5 in Figure 4. All the others were observed as they appear. These transmission curves were obtained on a G.E. (Hardy) spectrophotometer with spectral slit widths of 10 $\text{m}\mu$. No originality is claimed for any of these filters save the ferricyanide and the filter mentioned above. (Literature references to the original users of certain of these filters are to be found, 2.)

The sample tubes (obtained from The American Instrument Co., Silver Spring, Md.) used are of two sizes, 23 cm. (15 mm. in outside diameter) and 2.5 cc. (6 mm. in outside diameter). These are provided with fused-on Pyrex windows which are flat, polished, and strain-free. The open ends are provided with $\frac{1}{8}$ ground stoppers, so that the Raman tubes may be easily connected to a vacuum system for filling if necessary. A "cold finger" with the same taper is used whenever highly volatile liquids are used. (It is time-consuming to seal the Raman tube each time in routine work.) The horn is painted flat black and then wrapped with aluminum foil to decrease absorption of light. (The horn is exposed to the direct light from the arcs.)

Figure 5 shows the filter jacket, sample tube, and method of supporting the latter. The filter jacket is of all-glass construction and was finally evolved after the constant irritation concomitant with using gaskets and cements with concentric cylinders. The jacket is cemented to the end plates with a mixture of shredded asbestos and Glyptal. The edge of the window of the Raman tube rests in a cone. This cone and the two V-shaped fingers at the top serve to center the tube in the jacket and to eliminate realignment between changes of tubes. Cones of different aperture are used for different sized tubes. In changing from a large tube to a small tube, the bigger cone is lifted out of the well by means of a T-shaped wire, the smaller cone put in its place, and the iris diaphragm stopped down accordingly. The cones have polished windows on their lower ends to prevent dust from falling down onto the right-angle prism. Wherever feasible, the glass surfaces should be made nonreflecting. This has not been done but would conserve light.

A lens especially chosen for the job is used to focus the center of the illuminated portion of the tube onto the slit. The focal

length of the lens as well as d_0 and d_1 (the object and image distances relative to the lens) are given in Figure 1. This arrangement serves to fill the grating with light from the collimator.

Figure 6 shows the excitation unit (minus the reflector), filter jacket, the horn of a sample tube, the condensing lens, and other items mentioned below.

The Spectrograph

The prototype of this instrument is one at the Johns Hopkins University which has been only briefly mentioned in the literature (4).

The present instrument has as its essential parts a Gaertner bilateral slit, an off-axis paraboloidal collimating mirror, a plane echelette grating, and a fast objective lens.

The slit is 18 mm. high and is adjustable to within 0.0025 mm. (graduated in 0.01 mm.). The slit is capable of motion parallel to the optic axis and of rotation about the optic axis. Proceeding on past the slit are found a shutter and then a 45° mirror (aluminized).

The collimating mirror (made by W. H. Perry, Towson, Md.) is 6 inches in diameter and 1 meter in focal length. It was made 6° off axis and is so used. The mirror is capable of motion towards and away from the grating as well as tilt about a horizontal axis. The surface is aluminized.

The grating was ruled by W. H. Perry under the supervision of R. W. Wood at Johns Hopkins. It is a 1-inch thick Pyrex disk, 8 inches in diameter, which has had one face ground and polished flat, then aluminized and ruled. The ruled area is ca. 6.25 × 4.25 inches with 15,000 lines per inch and a total of ca. 90,000 lines. It is an echelette-type grating and concentrates the diffracted light in the blue and blue green region of the spectrum in one of the first orders. The grating is capable of rotation about a vertical axis which lies in the plane of the face and of tilt about a horizontal axis. For convenience in getting the lines of the grating parallel to the slit, the grating should also be capable of rotation about an axis normal to the face. Lacking this adjustment, satisfactory results were obtained by trial and error. First the slit was fixed at the principal focus of the collimator by using a plane mirror in front of the grating, thus send-

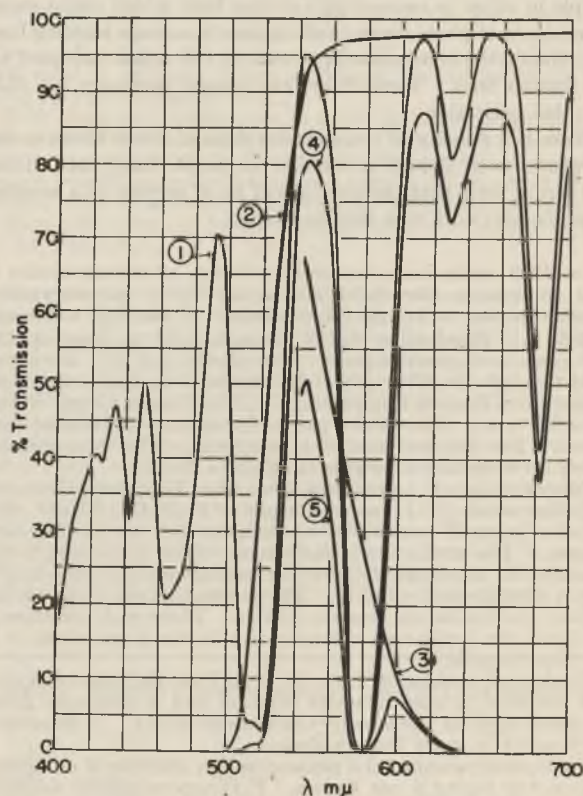


Figure 4. Transmission Curves

1. Saturated NdCl_3 , 5 mm.
2. Saturated Na_2CrO_4 , pH 8.7, 1 cm.
3. 2 molar $\text{Cu}(\text{NO}_3)_2$, 5 mm.
4. 1 plus 2, 80% 5461
5. 1 plus 2 plus 3, 50.5% 5461

ing parallel light back to the collimator and focusing the image of the slit in the plane of the slit when the slit to collimator distance was correct. Next the slit was set in a vertical direction by the use of a plumb line and a telescope. Finally a short focal length lens was used to throw an enlarged image of the green mercury line issuing from the camera onto a suitable screen in juxtaposition with a plumb line. The grating was then rotated about a horizontal axis normal to its face until the image was vertical.

The objective is a high quality Petzval type lens, designed especially for this instrument, and obtained from the Perkin-Elmer Corporation, Glenbrook, Conn. It has a focal length of 18 inches (F:3.6), produces a flat focus normal to the beam from 4300 to 5200 Å., and does not impair the linear dispersion of the grating. The dispersion⁻¹ is 36.97 Å. per mm.

Raman spectra excited by 4358 extend to, ca. 5200 Å. The middle of the 4358 Raman region is ca. λ 4780 Å. For this reason, the angle between the incident beam and the optic axis of the lens has been fixed at ca. 16.5°, so that λ 4780 has a diffraction angle of 0°. Thus λ 4780 falls on the middle of the plate and passes parallel to the optic axis of the lens. The dispersion is therefore a minimum and linear in the immediate vicinity of the middle of the plate and departs very slightly from linearity on either side.

The cassette ways are vertical and allow twenty-six spectra to be taken on a plate with the centers 2 mm. apart. The mounting for these ways is connected to the lens by means of a bellows (made to order by Willoughby's in New York) and is capable of motion parallel to the optic axis by means of a No. 32 screw as well as rotation about a vertical axis lying in the middle of the plane of the plate. Coarse and fine indexes are provided for these adjustments. The plates used are 4.25 × 3.25 inches with the former dimension horizontal.

Because of the high intensity of the exciting line, a mask has been built into the camera, so that the exciting line may be blocked off mechanically. This mask can be flipped up and down rapidly without disturbing anything else. It covers the portion of the plate where the exciting line hits and in this position is about 1 mm. in front of the emulsion. It can be moved parallel to λ to allow accurate adjustment. The external arm actuating the mask is shown in Figure 7.

By rotating the grating to bring the 5461 region into the center of the plate it is possible to get a flat focus for this region by rotating the plate through an angle of ca. 54', the red side being farther from the lens.

Figure 8 is a schematic scale drawing of the instrument. The optic axis is 9 inches above the table top. The base is a piece of annealed, aged, ribbed channel 5 × 1 foot × 3 × 0.375 inches. The case is made of 1/32 inch black iron and extends 12 inches above the top of the channel. It is provided with an easily removable, light-tight lid. The portion of the case admitting the front 1.5 inches of the lens is a panel perpendicular to the optic axis.

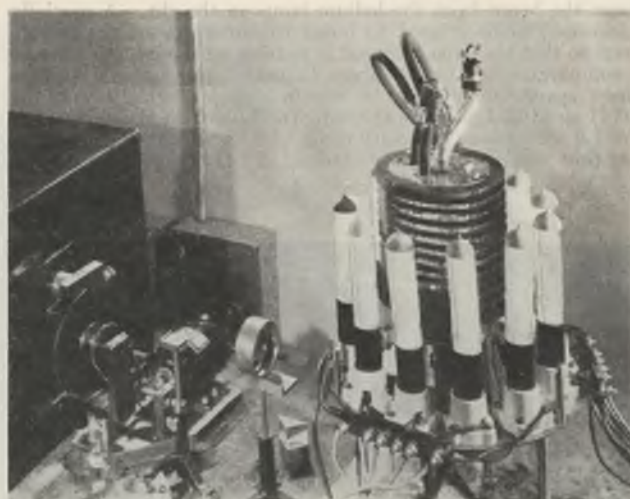


Figure 6. Excitation Unit

The spectrograph rests on a 6 × 4 foot × 2 inch Alberene-top table with nine steel legs. The table is 31 inches above the floor thus making the top of the spectrograph only 46 inches above the floor. The process of standing on a stool or kneeling on a table in order to look into the spectrograph while lining it up is thus avoided. An extension on one corner of the table supports the excitation unit.

Figures 9 and 10 show various details of the instrument.

Accessories

This category includes plates, darkroom equipment, microphotometer, means of plate calibration, means of wave-length measurement, contrivances for depolarization measurements, and apparatus for purifying samples.

For 4358 excitation 103-H or 103-J Eastman spectroscopic plates are used, ordered with antihalation backing. The H is usually faster than the J in the gross or half-gross batches which the author has ordered. The 103a emulsion is too grainy and fogs too easily for this work. For anyone not caring about color sensitization—i.e., no shifts above 1800 cm.⁻¹—the writer would recommend the 103-O emulsion.

For 5461 excitation the writer uses the Eastman 103-B or 103-F for an over-all survey. The F sensitization extends to longer λ and is more uniform than the B. However, the B sensitization is faster and therefore used more unless shifts belonging to O—H or N—H stretching frequencies are being studied. In this event, the F is used, but the study of these frequencies is a long process by 5461 excitation. There are available a variety of sensitizations which will be much faster in certain portions of the 5461 Raman region (5461—6700 Å.)—for example, for shifts below 700 cm.⁻¹ the writer uses the 103-G; for shifts from 700—1600 cm.⁻¹, the 103-D.

Because of oxidation of the developer in open tray development and the chance of scratching the emulsion with brush development, a stainless steel tank is used (Figure 11). This tank is provided with two vertical grooves, one for the plate, the other for a manually operated plunger. The horizontal blade of the plunger has one edge 1/32 inch from the emulsion, thus producing considerable turbulence in the solution and enhancing the possibility of obtaining uniform development. The plates are developed in Eastman D-19 for 4 minutes at 18° ± 0.5° C., rinsed for 20 to 30 seconds, and fixed for 15 minutes in Eastman F5, all at 18° C. (These fast plates take about twice as long to clear as the Eastman No. III emulsion.) The water is heated in the winter by a water-jacketed rheostat (Cenco 20.5 ohms) and cooled in the summer by a drinking fountain cooling unit. Fenwall (Fenwall, Inc., Ashland, Mass.) thermostats are used for temperature control.

For plate calibration, a helium discharge tube (4-mm. bore, 3000 volts, 30 ma., 10× enlargement on slit) is used in conjunction with a 1 to 1.9, two-series six-step sector rotating at ca. 1300 r.p.m. The sector is left in the open position when not in use and is thus always in readiness. A 45° prism is used on a pedestal between the slit and the condensing lens for Raman light to

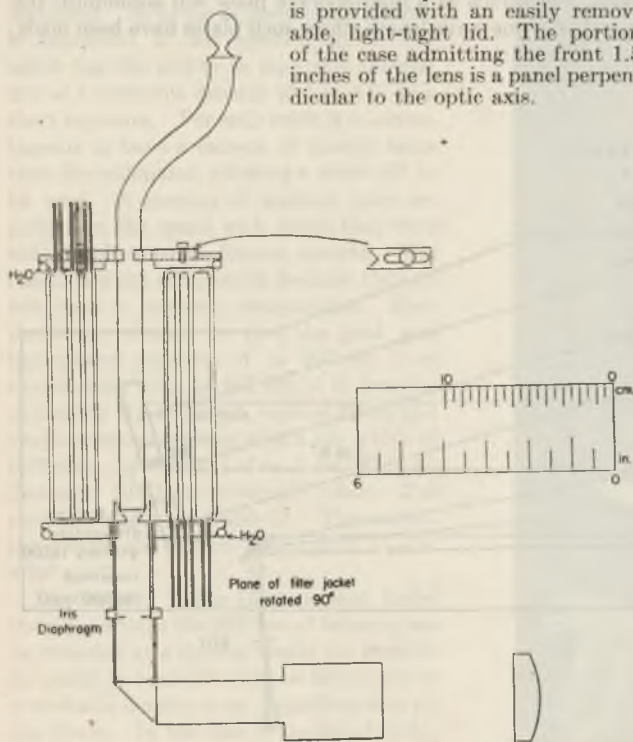


Figure 5. Sample Tube and Filter Jacket Assembly

throw the beam from the helium lamp on the slit. A partially aluminized plate is used to lower the intensity of the helium lamp, so that the time involved in putting on the intensity marks is comparable to that involved in taking the Raman spectra. These accoutrements may be seen in Figures 6 and 10. On the 103-H and 103-J plates in the indigo and blue, the six steps of the 1 to 1.9 sector span a density range of 0.03 to 2.00 when the correct time and slit width are chosen. The highest density read-

able on the microphotometer is 2.4, and this is the reason for the choice of the 1 to 1.9 ratio. The estimated accuracy in cutting the sector angles is ± 6 seconds (an accuracy of ± 1 minute would be adequate).

The microphotometer used is by Leeds & Northrup. It is equipped with a Speedomax pen recorder and gives densities directly. The paper moves at a speed of 52.5 mm. per minute; the plate can be scanned at speeds of 0.1, 0.2, and 0.5 ($\times 1$, $\times 10$, $\times 100$) mm. per minute. When used at maximum resolution, two lines 0.01 mm. apart are resolvable by the microphotometer.

The linear dispersion⁻¹ (36.97 Å. per mm.) simplifies the measurement of wave length. The light from a helium Geissler tube is focused on the slit by means of a 45° prism used in conjunction with the condensing lens. The reference spectrum is superimposed on the Raman spectrum. Five helium lines suffice to measure all the Raman lines with an accuracy of ± 2 cm.⁻¹ The microphotometer trace contains the helium lines along with the Raman lines, the latter being measured by interpolation between the former. The plate is scanned at a speed of 0.5 mm. per minute with a resultant enlargement of 105 \times . The measurements of λ (Å. in air) are converted to ν (cm.⁻¹ in vacuo) by means of Kayser's "Tabelle der Schwingungszahlen" and the $\Delta\nu$'s then determined.

A totally symmetrical vibrational frequency will be Raman-active and polarized ($\rho < \frac{6}{7}$). A vibrational frequency which is antisymmetrical or degenerate to one or more symmetry elements will be depolarized ($\rho = \frac{6}{7}$) if observable or else will be inactive. Thus the important thing is to be able to distinguish $\rho = \frac{6}{7}$ from $\rho < \frac{6}{7}$. For depolarization measurements the writer uses a calcite Wollaston prism between the lens and the slit at such a distance that the two images are just separated on the slit. In traversing a prism instrument, the vertically polarized component is weakened more than the horizontally polarized component because of preferential reflection from the prism faces. In a grating instrument, on the other hand, the horizontal component is weakened the more of the two. However, in the latter case, this weakening does not occur to so great an extent as does the inverse effect in the prism instrument. Because of this, there is interposed between the Wollaston and the slit a quarter-wave plate of mica with its principal directions at 45° to the vertical. This converts the two linearly polarized components into circularly polarized light, so that no preferential weakening of either beam will occur in traversing the spectrograph. Inasmuch as a quarter-wave plate will accomplish this feat at only one wave length, three such plates have been made;

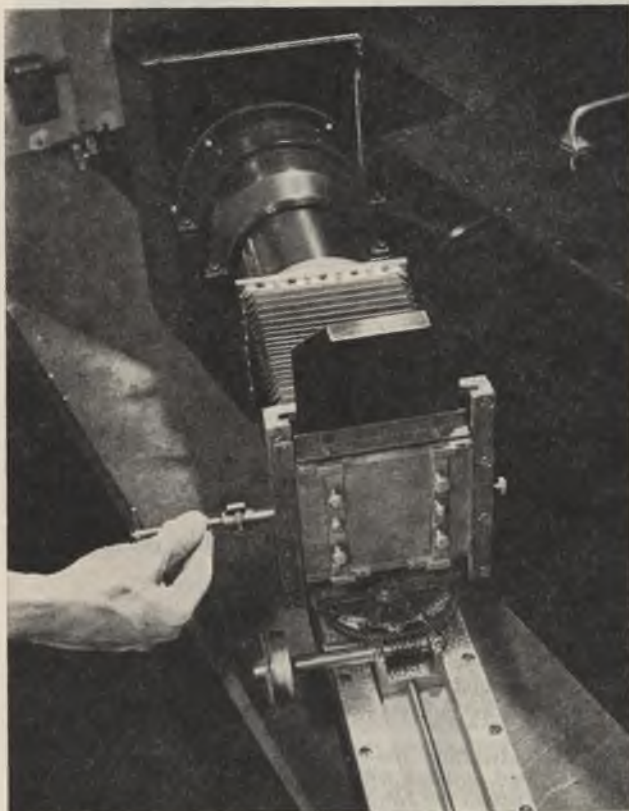


Figure 7. Camera

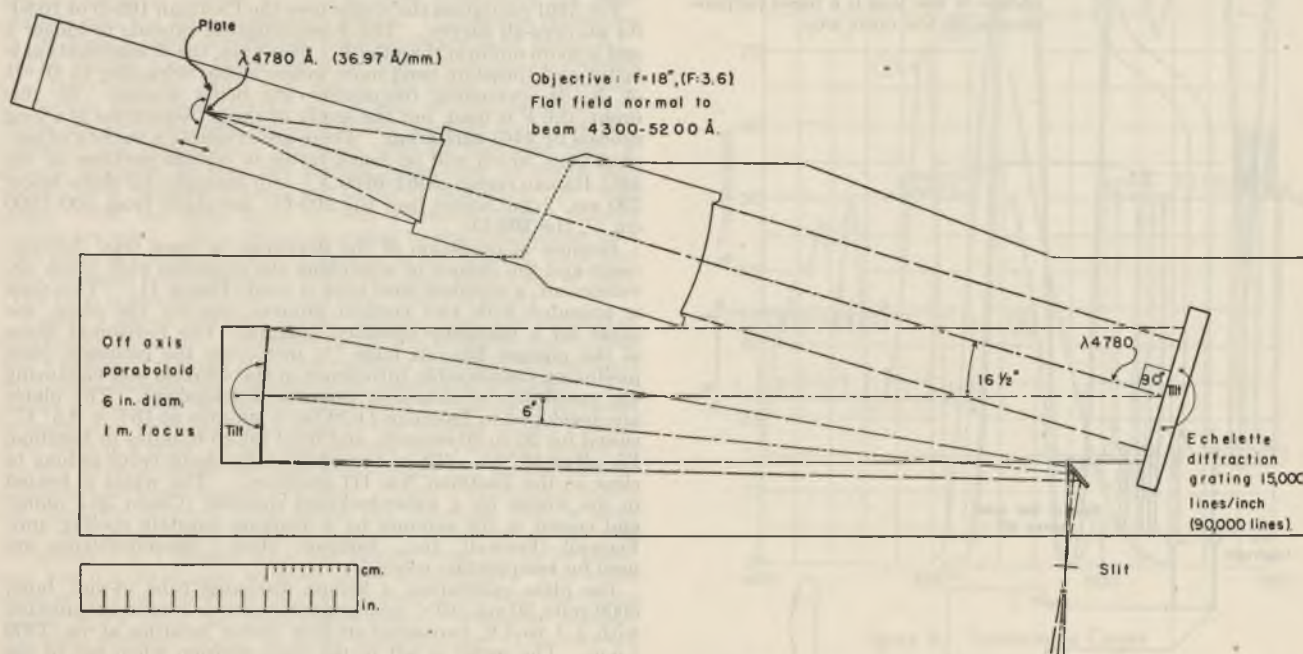


Figure 8. Raman Spectrograph

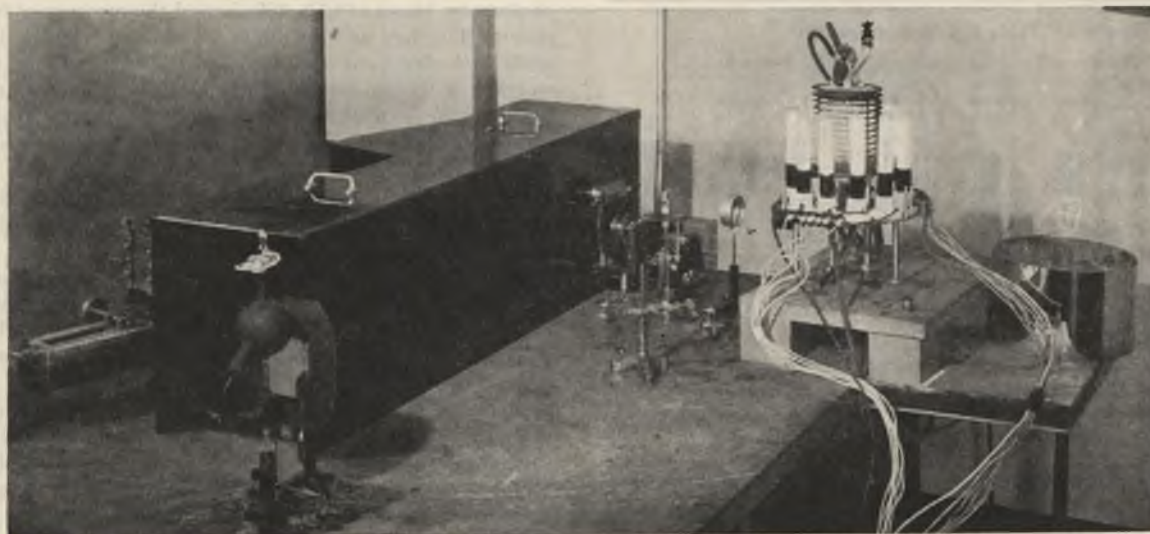


Figure 9. General View of Spectrograph and Accessories

these produce quarter-wave retardations at $\lambda\lambda$ 4358, 4725, and 4975 Å. For general work the second one is used. If only low or high frequencies are to be examined, the first or third ones are used accordingly. A thin calcite wedge would serve as a depolarizer in place of the mica (1, 10).

In many instances the writer is confronted with the necessity of purifying relatively small quantities of materials, often by distillation of 99.9% of a sample away from 0.1% of a fluorescent impurity. All the distillate must be recovered and in many cases no heat can be applied during the distillation. The simple still shown in Figure 12 accomplishes this nicely. Liquid air is used as a refrigerant.

Performance

In this section, speed, resolution, etc., are discussed. In so far as photographic work is concerned, a fast spectrograph is one which has the ability to register a spectral line at a workable density (0.4 to 2.0) in a short exposure. For such work, it is advantageous to have a camera of shorter focus than the collimator, allowing a wider slit to be used. A number of workers have reported on the speed with which they were able to photograph Raman spectra. The results are not comparable because they do not have a common denominator. Here the writer chooses to give the peak and background densities of $\Delta\nu$ 801 cm^{-1} of cyclohexane and $\Delta\nu$ 992 cm^{-1} of benzene excited by Hg 4358 with various filters and various exposure times with a slit width of 0.06 mm. (spectral slit of ca. 5 cm^{-1}) on an Eastman 103-J spectroscopic plate. The results are shown in Table II. The scattering volume was 17.9 cc. ($12.5 \text{ cm.} \times \frac{1}{4}\pi \times 1.35^2 \text{ cm.}^2$).

The data in Table II show that under these conditions the 992 line of benzene can be recorded at a density nearly too great to be usable in 1 minute with no filters and at a workable density in ca. 2 minutes with all the filters. In the case of $\Delta\nu$ 801 of cyclohexane, 1 minute is sufficient to record the line with no filters and ca. 10 minutes are

required with all the filters. The use of the baffles is discussed below.

In discussing resolving power, such items as the resolution of the grating, camera lens, and photographic plates must be considered as well as the limitations imposed by the width of the exciting line and temperature and pressure fluctuations.

In order to test the resolution, an air-filled Geissler tube was used (3000 volts, 30 ma., 1-mm. bore) with a slit of 0.02 mm. (1.75 cm.^{-1}). The new Eastman 548 emulsion was used (capable of resolving 500 lines per mm.). The plates are very slow, and a 3-hour exposure was necessary. One hundred lines per mm. were resolvable in the blue. (This limit is set by the slit width.) The

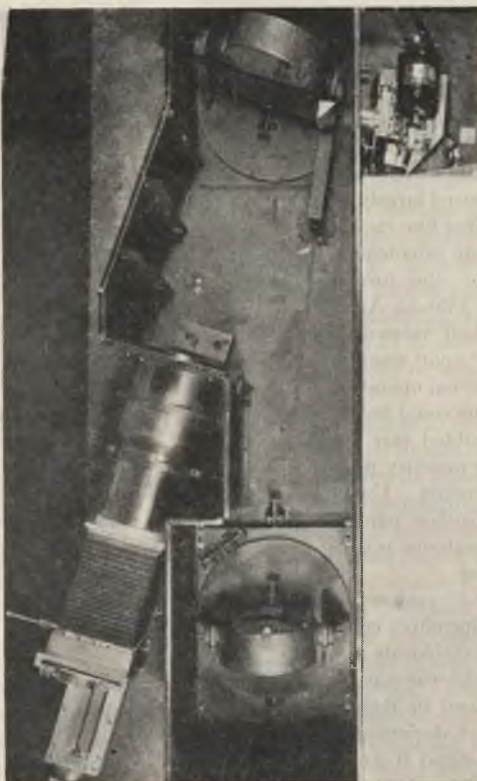


Figure 10. View of Spectrograph, Lid Removed

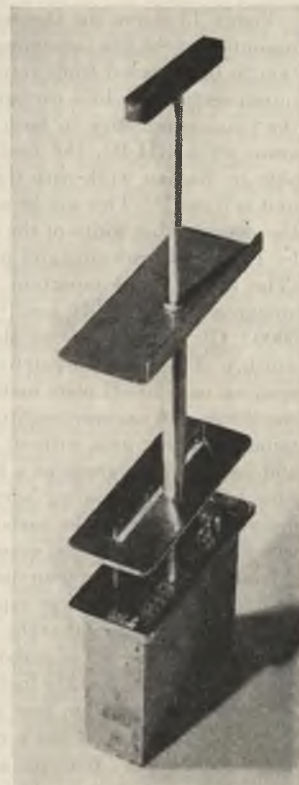


Figure 11. Developing Tank

Table II. Test of Speed

(Twelve 250-watt arcs, mirror in use for 2 months)

Test	Peak Density	Back-ground Density	Corrected Line Intensity	Int. X/ Int. A	Int. X'/ Int. A'	Int. X''/ Int. A''
I, A, 1	2.26	0.107	29.60	1.000
I, A', 1	1.365	0.041	11.75	...	1.000	0.398
I, B, 1	1.91	0.041	21.02	0.710
I, B', 1	1.203	0.029	10.21	...	0.869	0.486
I, C, 1	1.500	0.012	14.12	0.476
I, C', 1	0.840	0.002	7.57	...	0.644	0.536
I, D, 1	0.426	0	4.75	0.160
I, E, 1	0.287	0.002	3.66	0.123
I, E, 4	1.281	0	12.31
II, A, 1	0.630	0.031	5.39	1.000
II, A', 1	0.232	0.023	2.56	...	1.000	0.475
II, B, 1	0.436	0.011	4.40	0.816
II, B', 1	0.186	0.024	2.16	...	0.844	0.491
II, C, 1	0.241	0.009	2.95	0.546
II, C', 1	0.080	0.003	1.50	...	0.586	0.508
II, D, 1	0.030	0	0.70	0.128
II, E, 1	0.015	0	0.36	0.067
II, A, 4	1.93	0.195	19.6	1.000
II, A', 4	1.155	0.069	9.07	...	1.000	0.463
II, B, 4	1.611	0.040	15.27	0.778
II, B', 4	0.902	0.032	7.45	...	0.821	0.488
II, C, 4	1.121	0.012	9.77	0.498
II, C', 4	0.561	0	5.55	...	0.611	0.567
II, D, 4	0.251	0	3.24	0.165
II, E, 4	0.153	0	2.39	0.122
II, D, 16	1.143	0.012	9.96
II, E, 16	0.800	0	7.32

I. C_2H_4 , $\Delta\nu$ 992 cm^{-1} II. C_2H_2 , $\Delta\nu$ 801 cm^{-1}

A. No filters.

B. $NaNO_2$.C. $NaNO_2$ + rhodamine 5GDN Extra.D. $NaNO_2$ + $PrCl_3$.E. $NaNO_2$ + rhodamine 5GDN Extra + $PrCl_3$.

1. 1 minute.

4. 4 minutes.

16. 16 minutes.

Primes on letters indicate that baffles were used between arcs and filter jacket.

lens is supposedly capable of resolving 160 lines per mm. To achieve this would require a narrower slit and a more intense source as well as constant temperature and pressure conditions which are not available at present.

Figure 13 shows the theoretical resolution of the grating, the resolution of the lens (assuming 100 lines per mm.), and the resolution to be expected from various plates. Each curve is divided into a section for 4358 excitation and one for 5461 excitation if the plate is sensitive to both regions. Even with a fairly fine-grain plate (III-H), the best resolution obtainable in Raman work with the present excitation unit is 6 cm^{-1} . This can be attributed largely to the considerable width of the exciting line caused by Doppler broadening and pressure broadening. (The latter is all-important here; the former amounts to only 0.076 cm^{-1} for 4358.35 Å. at 5000° C. This value is the "half intensity" width.) This same line pair 6 cm^{-1} apart was also resolved on a 103-H plate under normal operating conditions. A narrower exciting line could be obtained by using arcs without an added rare gas and by operating them at a lower mercury pressure by suitable cooling arrangements. Under ordinary conditions, the carbon bisulfide pair at 648-656 is easily resolved even though one is considerably more intense than the other.

Since the instrument is capable of performing the task, it was hoped that the isotope effect could be resolved in $\Delta\nu$ 459 of carbon tetrachloride and thus show clearly that the instrument was capable of the utmost resolution ever attained in Raman spectra even though it has a modest dispersion⁻¹ of 37 Å. per mm. With the argon-filled H-2 arcs running hot or running cold (cooled by air blasts) and using 4358, 5461, and 5769 excitation, the micro-

photometer traces of CCl_4 459 showed the presence of four components, but they were definitely not resolved. This will be tried again with direct current arcs when the room housing the spectrograph is thermostated. Thus the present light source limits the resolution to 6 cm^{-1} . The writer is satisfied with this resolution, especially in view of the fact that it is accompanied by considerable speed.

In the close-up of the excitation unit (Figure 6), the reader will note a set of baffles surrounding the filter jacket. These baffles are not used in routine work along with filters. For very poor scatterers, however, they ensure essentially right-angle scattering with a much higher secondary/primary intensity ratio in the light leaving the window of the Raman tube. This allows the taking of longer exposures without filters with a resultant background of moderate density. They also are used whenever a small-diameter sample tube is employed, especially if a liquid of very low refractive index is being studied. A reasonable substitute for these baffles consists of a set of thin washers used as fins directly on the sample tube. Over a 4.5-inch length of tube, about eight washers 1 to 1.5 inches in diameter will suffice. An inspection of the data in the last column of Table II will show that the intensity of excitation is more than halved by these baffles.

In discussing the light source for excitation it was mentioned that the center of the illuminated portion of the tube was imaged on the slit. Under these conditions the image consists of a relatively dark circle with a brighter ring surrounding it. (The bright ring can be eliminated by using smaller aperture baffles between the tube and condensing lens, thereby lowering the intensity.) A diaphragm on the slit allows the center portion of this image to pass through the slit. Under these conditions, the primary light intensity will be lowered but the lines will be fatter in the center, a very undesirable feature when comparing densities of lines in two different spectra. Therefore, under these conditions of illumination, it is best whenever feasible to superimpose the spectra containing the lines whose densities are to be compared.

With the Wollaston prism being used with its refracting edge horizontal for depolarization measurements, the spectra cannot be superimposed, and it is better to focus the window of the sample tube on the slit. Under these latter conditions, the image will be of nearly uniform intensity and thus make spectral lines of uniform density throughout their length, but more primary light

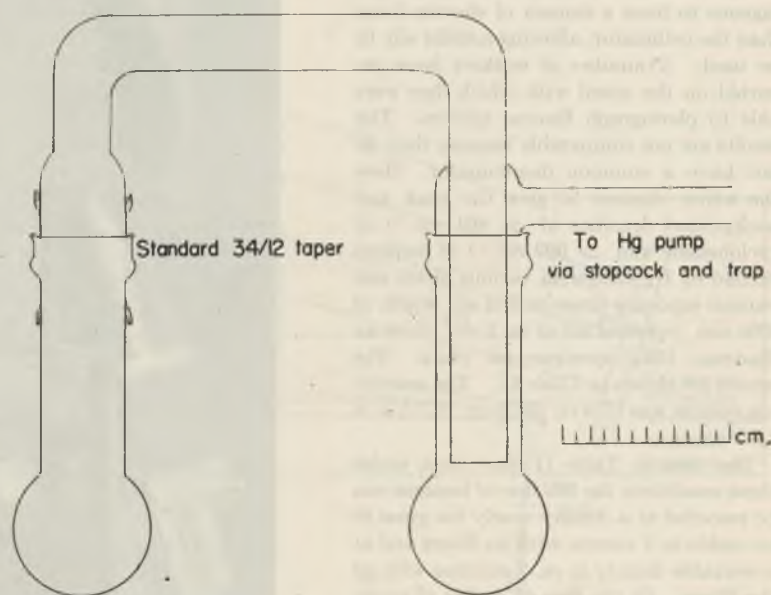


Figure 12. Low-Pressure Distillation Unit

will get into the spectrograph. To cut down the amount of primary light, baffles are used between the source and the tube. These allow illumination from two opposite sides by only two arcs, ensure essentially right-angle scattering, and permit the elimination of filters as mentioned above. In this work also, the two unilluminated quarter sections of the sample tube are painted black along the entire length of the tube.

If a number of spectra are to be taken on one plate, so as to conserve plates and minimize plate storage problems, it is essential that an unexposed area intended for occupancy by a spectrum later on in the course of work be fogged during the process of taking a spectrum on a closely adjacent area. For this purpose the modern prism spectrographs include a mask directly in front of the plate, so as to nullify fogging. In this spectrograph, the slot that permits the spectra to pass through to the plate is high enough to allow three such spectra to pass. Even so, the clear-plate density between adjacent spectra is the same as that of the unexposed portion of the plate that is covered during all the exposures. The scattered light is thus much less than in a prism instrument. Since, in taking Raman spectra, the light belonging to the Rayleigh line (or lines) is much more intense than that belonging to the Raman lines, and since a prism is a finite volume of a material substance and therefore has the ability to scatter light in all directions when illuminated originally in only one direction, this amount of scattered light is fairly objectionable when taking the relatively long exposures usually necessary in Raman work.

At present, work is under way to convert this instrument to automatic recording (7, 8). The detector will probably be an R.C.A. 931-A electron multiplier tube. Instead of rotating the grating, the spectrum will be scanned by a vertical slit which will sweep across the focal plane.

ACKNOWLEDGMENT. It is a pleasure to acknowledge many kindnesses of R. C. Lord, Jr., of the Johns Hopkins University. The excellence of the grating is attributable to R. W. Wood and W. H. Perry. The high quality of the lens is indicative of the pains taken in the calculation of its elements by E. L. McCarthy of the Perkin Elmer Co., as well as in the actual figuring by the staff of the same Company. Thanks are also due to the staffs of the Physics Division and the machine shop of these laboratories.

Raman Effect and the Elucidation of Molecular Structure

THE VIBRATING MOLECULE

THE MECHANICAL MODEL. Molecules may be imagined to be made up of a system of point masses (the atoms) bound together by springs (the valence bonds). These atoms are constantly in motion about positions of equilibrium. In general the motion is of a very haphazard nature and probably is extremely complicated; however, any motion which the atoms undergo can be obtained by a superpositioning of certain so-

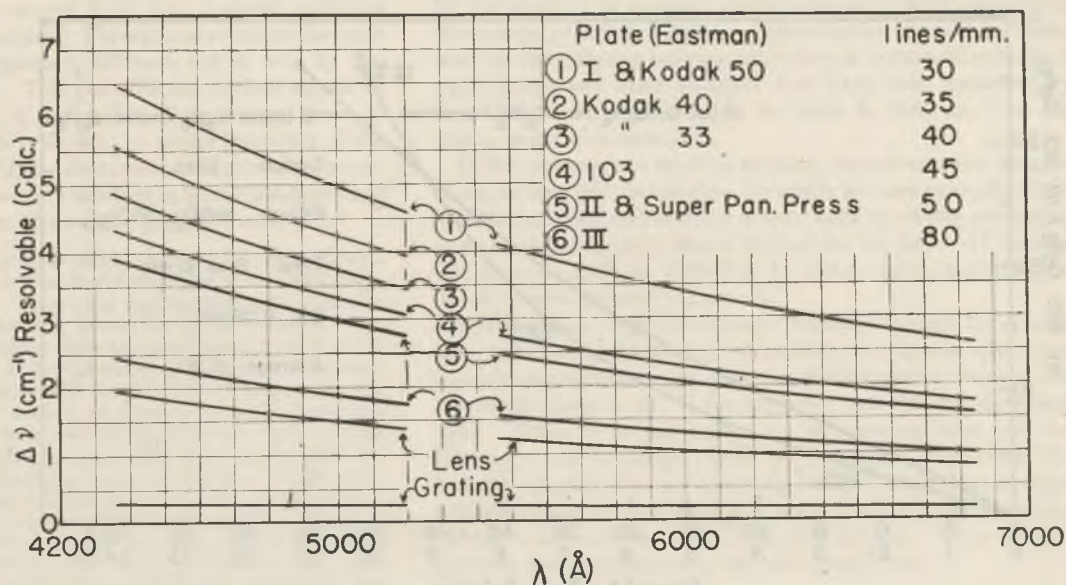


Figure 13. Factors Affecting Resolution

called normal vibrations. The normal vibrations are defined in a narrow sense as being those vibrations in which all the atoms of a given molecule pass through their equilibrium positions simultaneously and likewise through their extreme positions simultaneously. (They move in straight lines and move in phase.) In a wider sense, a normal vibration is defined as one in which all degrees of freedom (see below) undergo harmonic motions of equal frequency.

If each atom is referred to a set of rectangular axes, it is seen that three coordinates are required to specify the position of each atom at any instant. Dynamical systems are designated as holonomic (or nonholonomic) according as arbitrary infinitesimal increments of the coordinates define (or do not define) a possible displacement of the system. Holonomic systems possess the same number of degrees of freedom as there are independent coordinates required to specify the configuration of the system. The systems dealt with here are holonomic. Thus for a molecule with N atoms, $3N$ coordinates are required to specify the positions of the atoms; also, there are $3N$ degrees of freedom. Of these, 6 (only 5 in the case of linear molecules) are required to describe the outer motions of the system—namely, 3 for the motion of the center of gravity (translation of the molecule as a unit) and 3 (or 2 in the case of a linear molecule) for the rotation around the 3 (or 2) mutually perpendicular axes. These outer motions have no accompanying restoring forces as do the remaining $3N-6$ (or $3N-5$) inner degrees of freedom and may be regarded as vibrations of zero frequency having an infinitely long period.

These $3N-6$ (or $3N-5$) inner degrees of freedom are also known as the fundamental modes of vibration of the molecule in question. The problem at hand is that of finding the number and nature of these fundamental modes as well as their exact frequencies by spectroscopic means. The frequencies are governed by the masses of the atoms, the geometrical characteristics of the molecule, and the Hooke's law force constants of the valence bonds and angles. (Hooke's law states that the restoring force is proportional to the displacement and opposite in sign. In the present instance it seems appropriate to say that a valence bond tends to maintain a fixed length and that two valence bonds tend to keep a constant angle between them. The former tendency is stronger than the latter.) Once the frequencies have been found, the ultimate goal is that of postulating several models, deriving a set of equations for each model relating the frequencies to the structural factors and force constants, and

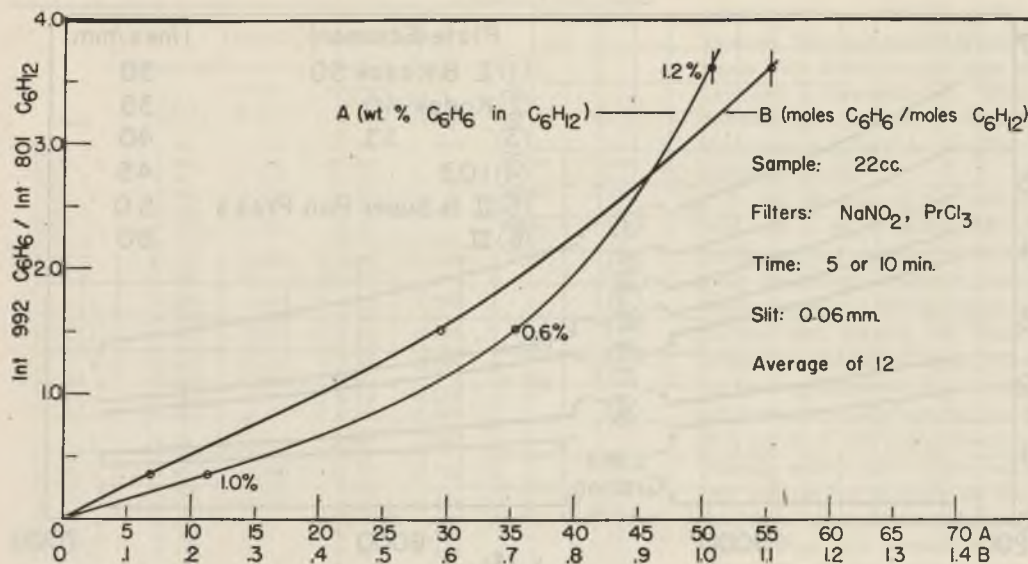


Figure 14. Binary Solutions

then finding a set of force constants that permits the calculation of a set of vibrational frequencies (from one given set of equations) in agreement with those found experimentally. The model giving such a set of equations is taken to be the correct model out of the several postulated. Because of mathematical difficulties this goal is reached only in the case of relatively simple molecules.

MOLECULES WITH SYMMETRY ELEMENTS. A molecule is spoken of as possessing a plane, a center, a p -fold rotation axis, or a p -fold rotation-reflection axis of symmetry according as reflection across the plane, inversion through the center, rotation around the axis by $\frac{2\pi}{p}$ radians, or rotation by $\frac{2\pi}{p}$ followed by reflection across a plane perpendicular to the axis gives rise to a molecule identical with the molecule before the symmetry operation was applied. The molecules are assigned these symmetry properties with the nuclei in their equilibrium positions.

The various vibrational modes are classified as being symmetrical, antisymmetrical, or degenerate to these symmetrical elements. [Degenerate frequencies occur only when the molecule has a 3-fold (or higher) rotational or rotation-reflection axis of symmetry. A frequency is said to be doubly, triply, etc., degenerate when there are two, three, etc., modes all having the same frequency.] If, in a given mode, the molecule is examined with the nuclei at their extreme positions, it can be seen whether or not the mode is symmetrical or antisymmetrical to the various symmetry elements possessed by the molecule at rest. To differentiate between a degenerate mode and an antisymmetrical mode it is necessary to compare the atoms in the displaced position after applying the symmetry operation with the atoms one-half period later at the other extreme position without applying the symmetry operation. If the two are the same, the mode is not degenerate to that symmetry element; it is only antisymmetrical. If the two are different, the mode is either degenerate or symmetrical to that symmetry element, and the latter is redundant.

By turning to the mathematical formalism of group theory, Wigner (13), Tisza (12), Wilson (14, 15), Placzek (6), and Rosenthal and Murphy (11) have developed tables for the different crystallographic point groups (and for additional groups too) characteristic of each possible type of molecular symmetry. These show the number of vibrational frequencies appearing in infrared absorption, in Raman effect, in both, in neither, and the polarization properties of the frequencies if they are Raman-active. A very convenient summarization of these data is

given by Kohlrausch (2, 1931-1937 Supplement). The investigation of the number and symmetry properties of the normal modes of oscillation of a given molecular model is now a matter of routine.

From Kohlrausch (2, pp. 34-5) the writer cites the following general rules:

1. As a general rule, the intense Raman lines belong to totally symmetrical vibrations. Overtones and combination frequencies occur only weakly if at all.
2. Totally symmetrical vibrations are polarized in the Raman effect—i.e., the depolarization ratio is small or zero.
3. Frequencies that are antisymmetrical or degenerate to one or more elements of symmetry are either Raman-active and depolarized or else forbidden.
4. In molecules having a center of symmetry those vibrations antisymmetrical to the center of symmetry are forbidden. (This case is interesting, inasmuch as Raman active vibrations for such a molecule are inactive in infrared absorption and vice versa.)

To these rules should also be added the statement that the appearance of a vibrational frequency in infrared absorption depends on that frequency's causing a change in the dipole moment of the molecule. On the other hand, a vibration must be accompanied by a change in the polarizability of the molecule if that frequency is to be Raman-active.

THE EMPIRICAL SIDE OF THE QUESTION. *Characteristic Vibrations.* A vast amount of work on the Raman and infrared absorption spectra of a multitude of compounds has shown that, to a very marked degree, like linkages exhibit like frequencies even when these linkages occur in rather radically different molecules. Thus it has become customary to speak of a C—H aromatic frequency or a C—H aliphatic frequency; of a C=O ester, acid, aldehyde, ketone, or acid anhydride frequency; of C≡C, C≡N, C=C, C=N, N=O, N $\begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$, Se—H, S—H, O—H, N—H, C $\begin{smallmatrix} H \\ \diagdown \\ H \end{smallmatrix}$, C—(OH), C—(NH₂), C—(C≡N), C—Cl, C—Br, C—I frequencies, and also of ring frequencies of various types as well as frequencies characteristic of methyl and ethyl groups, etc. These characteristic frequencies are often very helpful to the chemist as long as he does not believe that the structure of any complicated molecule is always going to be solved merely by finding its vibrational frequencies. The writer is a bit more prone to take a slightly pessimistic attitude rather than the viewpoint that the method will always work.

Limitations. The biggest nuisance in Raman spectroscopy is that a slight amount of fluorescent impurity in the sample can give rise to a continuous background which oftentimes completely masks the Raman lines. In the case of a pure liquid a simple distillation will usually remove the offending substance. Treatment with activated charcoal and activated alumina can also be used to great advantage (this must not be resorted to in the case of solutions because of preferential adsorption). In the case of a solid, dissolution followed by clarification and recrystallization will help. For organic liquids, adding a small quantity of nitrobenzene will often quench the fluorescence to a high degree. (This is brought about by deactivation of the fluorescing mole-

cules by collisions of the second kind—i.e., inelastic collisions with the nitrobenzene molecules.) For aqueous solutions the same result can often be accomplished, although not so well, by employing potassium iodide. This deactivating method should be used only as a last resort, in the opinion of the writer.

Attention was called above to relation of the frequency of the exciting line to the lowest lying electronic absorption frequency. To the reader not accustomed to thinking in terms of energy-level diagrams, this statement might well be explained more fully.

If a substance is a pale yellow color, an investigation of its absorption spectrum will show that it absorbs light in the near ultraviolet and violet regions. To get the Raman spectrum of such a substance it would be necessary to use an exciting line of lower frequency (higher wave length) than the low-frequency side of the absorption band (the 4358 Å. line of mercury can be used for such substances). If the substance is bright yellow or orange, the absorption band has now moved, or spread, to lower frequency (longer wave length) and so a lower frequency line must be used to excite the Raman spectrum successfully (the green, 5461 Å., line of mercury could be used for such substances). If the substance is red, the absorption band will be in the green, and it would be necessary to use, say, a yellow line to excite the Raman spectrum. If the absorption band is in the yellow, it would be necessary to use a red exciting line. The exciting line must have a frequency less than the lowest lying electronic absorption frequency. Obviously then, the investigation of the Raman spectra of colored substances is a nuisance and is beset with difficulties.

Advantages. In obtaining a Raman spectrum, the entire range of frequencies occupied by the fundamentals is covered

by one exposure (if recorded photographically) or by one tracing (if recorded photoelectrically). These Raman lines can be measured by interpolating between secondary or tertiary standards of wave length and these standard lines have been measured by three different investigators to ca. 0.002 Å. (0.01 cm^{-1} in the region under consideration).

If it is necessary to study a solution, the solvent may be anything, so long as it is colorless (or nearly so) and optically clear. The Raman spectrum of water is very weak by visible excitation, and the only frequency region blotted out by the O—H band of the water is 3200 to 3700 cm^{-1} (This region also includes N—H stretch and $\equiv\text{C—H}$ stretch.)

In following a given vibrational frequency through the spectra of a series of closely related compounds, the Raman effect permits three quantities to be found for the frequency—namely, the numerical value in cm^{-1} , the intensity, and the depolarization ratio. These three parameters are of more use than just the frequency and intensity would be. Although only these two last-named quantities are found by infrared absorption spectra, both spectra must be obtained in attempting to prove the structure of a molecule by vibrational spectroscopy. Thus the two methods are complementary and not competitive.

Analytical Applications

QUALITATIVE ANALYSIS

A FUNDAMENTAL HYPOTHESIS. If several molecular species are present in a solution, the Raman spectrum of the solution should be a superposition of the spectra of the several components comprising the solution. Departures from this in the way of actual frequency shifts (the error of these measurements usually being equal to ± 1 or 2 cm^{-1}) will not be observed as a general rule. However, for polar molecules this is often not true, inasmuch as the strong interaction forces of species A on species B and vice versa can change the spectra of either or both relative to those of the pure compounds. For hydrocarbons, even in the liquid state, the initial hypothesis is valid. It is true that slight intensity alterations may occur, but they will be so small as to be of importance only for quantitative analysis. This whole question of molecular interaction and its influence on vibrational frequencies is characterized by the ease with which vague wordy descriptions can be made to describe what is going on and by the difficulty involved in making quantitative calculations or predictions about these interactions.

MAIN USES AND LIMITATIONS. Because of the fact that very few overtone and combination frequencies are observed in the Raman effect (the nonappearance of overtone and/or combination frequencies provides a simpler spectrum; a particular advantage in a mixture), the method is of a great deal of use in following the course of a distillation, especially if the distillation is a first attempt to fractionate the products of a new reaction. It often happens that unsuspected azeotropes are discovered during this first distillation. Much time may be saved if it is possible to identify the components of such azeotropes spectroscopically. If the interest is directed only toward the main products, the Raman method will generally be of more use than methods involving absorption spectra. This is attributable to the fact that the Raman spectra of the minor components will be so weak that the spectra of the major components will stand out above all else.

This failure of Raman spectra to show the lines of minor constituents is an advantage in one way. On the other hand, it offers severe limitations to the method, in that the spectra of substances present in low concentration are usually not detectable. No definite figures can be set forth on this subject; only approximate ones. Using 4358 excitation, many substances possessing strong absorption bands in the violet or near ultraviolet—e.g., aromatics, conjugated olefins, nitriles, etc.—can be detected

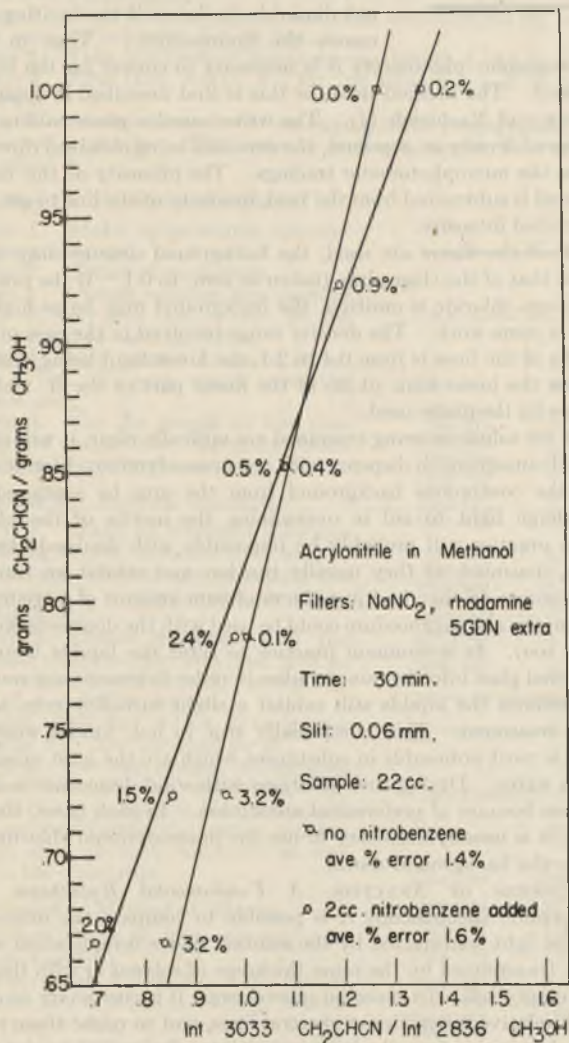


Figure 15. Binary Solutions

Table III. Binary Solutions

		C ₆ H ₆ —C ₆ H ₁₂													
		Int. 992 C ₆ H ₆		Av. % Dev.		Max. % Dev.		% C ₆ H ₆ ,		% Error,		% C ₆ H ₆ ,		% Error,	
		Int. 801 C ₆ H ₁₂		in Intensity		in Intensity		Method A		Method A		Method B		Method B	
Actual	Actual	10	5	10	5	10	5	10	5	10	5	10	5	10	5
% C ₆ H ₆	Mole Ratio C ₆ H ₆ /C ₆ H ₁₂	min.	min.	min.	min.	min.	min.	min.	min.	min.	min.	min.	min.	min.	min.
50.68	1.1069	3.625	3.622	12.1	7.5	22.2	13.4	45.6	45.6	10	10				
35.43	0.5911	1.522	1.501	2.4	4.9	4.5	9.5	26.0	25.7	27	27	30.1	29.9	15	15.5
11.30	0.1373	0.364	0.415	3.8	12.9	8.5	29.4	7.8	8.7	31	23	9.3	10.5	17	7

Method A. 19 pairs of superimposed spectra of C₆H₆ and C₆H₁₂ used. Exposure time for each, 3 minutes. Average intensity ratio 992/801 = 4.938. Average deviation = 6.8% from mean. 992/801 = 4.011 for a 1:1 mole ratio.

Method B. Twelve 10-minute and twelve 5-minute exposures of each solution (four different plates, intensity marks on each plate). 992/801 = 3.275 for a 1:1 mole ratio as obtained from the data for the solution with mole ratio of 1.1069 × (3.275 = 3.625 / 1.1069).

Table IV. Binary Solutions

[(A) C ₆ H ₆ , (B) CCl ₄ . Filter, NaNO ₂ . Slit, 0.10 mm. (8.8 cm. ⁻¹). Exp. time, 4 or 8 minutes]													
		90.01% A, A/B = 17.745				65.08% A, A/B = 3.671				33.63% A, A/B = 1:1			
		Av. %		% A		Av. %		% A		Av. %		% A	
Line Pair	Int. ratio	dev. int. ratio	% A	% Error	Int. ratio	dev. int. ratio	% A	% Error	Int. ratio	dev. int. ratio	% A	% Error	
604/314	2.886	6.3	88.7	-1.4	0.675	2.2	64.8	-0.5	0.186	3.2			
1178/314	2.718	6.3	88.8	-1.3	0.656	3.2	65.6	+0.8	0.174	8.1			
1584/314	2.048	6.4	88.5	-1.7	0.511	1.4	65.8	+1.1	0.135	5.2			
1603/314	1.480	7.1	88.6	-1.6	0.356	2.5	65.0	-0.2	0.097	16.5			
604/459	3.249	4.4	89.5	-0.6	0.678	1.6	64.0	+1.7	0.193	4.2			
1178/459	3.100	2.7	89.6	-0.4	0.661	2.3	64.6	+0.8	0.184	8.2			
1584/459	2.340	5.6	89.6	-0.4	0.515	0.8	65.3	+0.3	0.139	7.9			
1603/459	1.691	7.2	89.4	-0.7	0.359	2.2	64.2	+1.4	0.102	17.7			
Av. of 40—5 spectra			89.1				64.9						

at concentrations as low as 0.2 to 1.0% by their Raman spectra. However, only one or two of the very strongest lines will appear and one or two lines can only serve to suggest the possibility of the presence of a given molecule; they cannot prove its presence. Such substances, of course, would be easily detected by ultraviolet absorption methods, especially if they were minor constituents accompanying a major component that was a weak absorber. If, on the other hand, both major and minor components were strong absorbers, Raman spectra might serve to detect the minor component (at least one or two of its strongest lines) with greater facility. The intensity of a Raman line is inversely proportional to $(\nu^2_e - \nu^2_{ex})^2$ (the former is the frequency of the lowest lying electronic absorption frequency, and the latter is the frequency of the exciting line), and directly proportional to the squares of the changes in average polarizability and/or optical anisotropy brought about by the vibration belonging to the Raman line in question. There are additional compounds which do not have absorption bands in the near ultraviolet but still give rise to some strong Raman lines because they have certain vibrations involving large polarizability changes, and certain highly symmetrical molecules possess multiple degenerate frequencies which often lead to strong lines. Such compounds are also detectable in relatively low concentrations by the Raman effect, even though they may not be strong ultraviolet absorbers. Finally, a molecule possessing a preponderance of a certain specific structural unit—C—H, for example—will yield intense lines attributable to these linkages.

QUANTITATIVE ANALYSIS

In the spectrum of a solution containing several molecular species, the intensities of the spectral lines attributable to each of the species will be indicative of their respective concentrations in the solution. Thus, in order to perform quantitative analyses, a method of obtaining intensities of spectral lines is a prerequisite. If the spectra are recorded by photoelectric means, the photoelectric intensities are obtained directly. If, on the other hand, photographic plates are used, recourse must be had to photographic photometry.

The results discussed here were obtained by the latter method,

and they involve photographic photometry at its worst. Because of the weakness of the light being photographed it is customary (and usually necessary) to use very fast plates. These are grainy and are easily fogged, and usually have low contrast. This is a disadvantage in that the density change produced by a given alteration in exposure is not so great as that produced in the case of a higher contrast plate.

On the other hand, the wider latitude is favorable because it allows a coverage of a greater intensity range with a given exposure time than does a high contrast plate.

Finally, unless very concentrated filter solutions are used, there will be a continuous background in addition to the discrete Raman lines. This background is caused by Rayleigh scattering of the continuum in the arcs and by fluorescent impurities in the sample (the filter will not diminish the latter if the exciting line causes the fluorescence). Thus in the

photographic photometry it is necessary to correct for the background. The method used for this is that described in detail by Pierce and Nachtrieb (5). The writer uses a plate calibration curve of density vs. exposure, the densities being obtained directly from the microphotometer tracings. The intensity of the background is subtracted from the peak intensity of the line to get the corrected intensity.

If all the filters are used, the background density may vary from that of the clear plate (taken as zero) to 0.1. If the praseodymium chloride is omitted, the background may be as high as 0.6 in some work. The density range involved in the case of the peaks of the lines is from 0.4 to 2.1, the lower limit being slightly below the lower limit (0.55) of the linear part of the H. and D. curve for the plates used.

If the solutions being examined are optically clear, it will often be advantageous to dispense with the praseodymium chloride and let the continuous background from the arcs be scattered as Rayleigh light to aid in overcoming the inertia of the plate. This practice will probably be impossible with double-jacketed arcs, inasmuch as they usually run hot and exhibit an intense continuum (if they had just the minimum amount of mercury in them, the above procedure could be used with the double-jacketed arcs too). It is common practice to filter the liquids through sintered glass into the sample tubes in order to remove any notes. Sometimes the liquids still exhibit a slight turbidity even after this treatment. This is especially true in hot, humid weather and is most noticeable in substances which are the least miscible with water. Drying such solutions with solid desiccants is dangerous because of preferential adsorption. In such cases, therefore, it is usually necessary to use the praseodymium chloride to keep the background down.

SCHEMES OF ANALYSIS. A Fundamental Hypothesis. In absorption spectroscopy it is possible to compare the intensity of the light transmitted by the solution under investigation with that transmitted by the same thickness of solvent or with that of the empty cell. In emission spectroscopy it is customary to deal with relative intensities of spectral lines, and to relate these relative intensities (usually in terms of intensity ratios) to concentrations or to concentration ratios. Here our fundamental hy-

pothesis will be that the intensity of the scattered light is directly proportional to the number of molecules in the scattering medium. Several analytical schemes are described below incorporating this hypothesis and examples are given. It is shown that this hypothesis is not always valid and that other schemes must then be used.

Method A. Intensity \propto number of molecules (no standards involved).

Step 1. Superimpose the Raman spectra of *A* and *B* taken under identical volume conditions.

Step 2. Pick a line of *A* and a line of *B* uninfluenced by any other lines. Find the ratio, $\text{Int. } A/\text{Int. } B$ in the superposed spectra.

Step 3. Take spectrum of unknown containing *A* and *B*.

Step 4. Find $(\text{Int. } A/\text{Int. } B)_x$ for the same line pair in this spectrum.

Step 5. Assume intensity of scattering to be proportional to number of molecules. Correct intensity ratio in step 2 by incorporating the ratios of the molecular weights and densities of *A* and *B* in the correct manner to get the intensity ratio for a 1 to 1 mole ratio.

Step 6. $\text{Int. } A = K_A \text{ moles } A.$

$\text{Int. } B = K_B \text{ moles } B.$

$(\text{Int. } A/\text{Int. } B)_x = K (\text{moles } A/\text{moles } B)_x.$ But

$(\text{Int. } A/\text{Int. } B)_{1:1} = K$ for a 1 to 1 mole ratio, and so

$$(\text{moles } A/\text{moles } B)_x = \frac{(\text{Int. } A/\text{Int. } B)_x}{(\text{Int. } A/\text{Int. } B)_{1:1}}$$

Method B. Intensity \propto number of moles (one standard solution involved).

Step 1. Take Raman spectrum of a solution containing *A* and *B* in a 1 to 1 mole ratio.

Step 2. Pick a line of *A* and one of *B* uninfluenced by any other lines. Find ratio $(\text{Int. } A/\text{Int. } B)_{1:1}.$

Step 3. Take spectrum of unknown containing *A* and *B*.

Step 4. Find $(\text{Int. } A/\text{Int. } B)_x$ for the same line pair in this spectrum.

Step 5. Assume intensity of scattering to be proportional to number of molecules. This leads to final relationship in step 6 of Method A.

Method C. Synthetic standards.

Step 1. Make up solutions containing known amounts of *A* and *B*.

Step 2. Obtain their spectra.

Step 3. Choose suitable line pairs of *A* and *B*, and find $(\text{Int. } A/\text{Int. } B)$ for each line pair in each spectrum.

Step 4. Plot (grams *A*/grams *B*) vs. $(\text{Int. } A/\text{Int. } B)$, each graph involving one line pair.

Step 5. Use the graphs to find concentration ratios from intensity ratios in spectra of unknowns.

Method D. Internal standard.

Step 1. Make up standard solutions containing known amounts of *A* and *B*. Add to each solution approximately the same weight % of substance *S*, the internal standard.

Step 2. Obtain the spectra of the standard solutions, and find $(\text{Int. } A/\text{Int. } S)$ as well as $(\text{Int. } B/\text{Int. } S)$ for as many lines of *A* and *B* as desired.

Step 3. Plot $(\text{Int. } A/\text{Int. } S)$ vs. (grams *A*/grams *S*). Do the same for *B*.

Step 4. Use the graphs as working curves for analyzing unknowns, the spectra of the unknowns being obtained with approximately the same concentration of *S* in each unknown as was used in the standards.

Method E. Method of dilution.

To find: % *A* in *I* (a solution containing *A* and *B*)

Given: $(\text{Int. } A/\text{Int. } B)_I = K'$ (moles *A*/moles *B*)_{*I*} = $K[X/(1-X)]_I$ where *X* = grams *A*/gram of solution in *I*.

Add: *Y* grams of *A* to 1 gram of *I*; get $(X+Y)$ grams *A*, $(1-X)$ grams *B* in solution *II*.

Since: $\frac{(\text{Int. } A/\text{Int. } B)_I}{(\text{Int. } A/\text{Int. } B)_{II}} = R_I/R_{II} = \frac{X}{X+Y}$

Thus: $X = Y[R_I/(R_{II} - R_I)]$ = grams *A*/gram of original solution.

Discussion. Method A would be used only in the event that it was impossible to use one of the other methods. It takes no account of molecular interaction.

The ideas incorporated in Methods A and B can be extended to solutions of more than two components. The ratios of the molecular weights can be incorporated in the constant, to obtain an expression involving grams. If the total percentage of all the components is known, expressions for direct percentages of the various components can be obtained by simple algebraic manipulations.

Method C is used when B will not work—i.e., when the molecular interaction is so great or changes so markedly with concentration as to invalidate the fundamental hypothesis.

Method D would be most usefully employed as an extension of B. This would involve adding a fixed weight per cent of the standard to each of the components involved and the same per cent to the unknowns. The "scattering coefficients" (9) of each component could then be used to find the composition of the unknown. With regard to the work in (9), the writer is not in sympathy with the method of using volume per cent, nor with using activated alumina for removing fluorescent impurities (because of preferential adsorption). He also feels that it would be better to put a fixed per cent of internal standard in a solution containing equal quantities of all the components present in the unknown which is to be analyzed by the method of scattering coefficients, and to use the scattering coefficients obtained with this solution rather than those obtained from the binary solutions involving each of the various components along with the internal standard. The internal standard should be a molecule with as few atoms as possible and with a high degree of symmetry, in order to contribute the least possible number of vibrational fre-

Table V. Binary Solutions

[(A) C₆H₅CH₃, (B) CCl₄. Filter, NaNO₂. Slit, 0.10 mm. (8.8 cm.⁻¹). Exp. time, 4 or 8 minutes]

Line Pair	90.02% A, A/B = 15.062				65.14% A, A/B = 3.120				37.51% A, A/B = 1:1	
	Int. ratio	Av. % int. ratio	% A	% Error	Int. ratio	Av. % int. ratio	% A	% Error	Int. ratio	Av. % int. ratio
520/314	3.048	5.7	86.8	-3.5	0.767	6.1	62.3	-4.3	0.278	9.4
788/314	7.778	4.8	84.5	-6.1	2.108	8.8	59.7	-8.3	0.854	9.5
1003/314	14.548	5.2	86.8	-3.5	4.024	11.7	64.5	-0.9	1.327	11.9
1028/314	3.815	8.8	87.3	-3.0	0.978	6.5	63.6	-2.3	0.334	8.7
1205/314	3.482	8.4	87.4	-2.9	0.903	7.2	64.2	-1.4	0.302	5.0
1375/314	1.248	15.1	85.2	-5.3	0.329	6.7	59.5	-8.6	0.130	12.3
1580/314	1.142	9.3	87.4	-2.9	0.293	4.1	63.9	-1.8	0.099	16.2
1603/314	2.250	7.6	86.6	-3.8	0.626	5.9	64.3	-1.2	0.208	6.7
520/459	2.622	5.3	85.4	-5.1	0.719	6.5	61.2	-6.0	0.274	8.0
788/459	6.698	4.7	82.8	-8.0	1.973	8.2	58.5	-10.0	0.836	11.1
1003/459	12.925	7.5	85.6	-4.9	3.773	10.0	63.5	-2.5	1.297	11.4
1028/459	3.272	4.6	85.7	-4.8	0.920	9.7	62.8	-3.5	0.327	10.7
1205/459	2.988	6.0	85.8	-4.7	0.846	6.6	63.1	-3.1	0.297	8.1
1375/459	1.062	9.1	83.4	-7.3	0.308	8.4	59.2	-9.1	0.127	15.0
1580/459	0.980	4.5	85.7	-4.8	0.273	6.2	62.6	-3.8	0.098	14.3
1603/459	1.932	7.0	85.0	-5.6	0.585	5.1	63.4	-2.6	0.204	9.8
Average of 80-5 spectra			85.7				62.3			

Table VI. Binary Solutions

[(A) C₆H₁₂, (B) CCl₄. Filter NaNO₂. Slit, 0.10 mm. (8.8 cm.⁻¹). Exp. time, 8, 16, or 22.5 minutes]

Line Pair	88.12% A, A/B = 13.697				64.11% A, A/B = 3.274				35.38% A, A/B = 1:1	
	Int. ratio	Av. % dev. int. ratio	% A	% Error	Int. ratio	Av. % dev. int. ratio	% A	% Error	Int. ratio	Av. % dev. int. ratio
801/314	11.919	11.5	88.1	0.0	2.714	3.4	63.8	-0.5	0.884	1.9
1026/314	4.743	9.1	87.7	-0.5	1.183	2.6	63.9	-0.3	0.366	3.0
1264/314	3.937	8.0	87.9	-0.2	0.956	3.1	63.8	-0.5	0.297	2.0
1442/314	3.796	9.3	88.4	+0.3	0.919	2.6	64.7	+0.9	0.274	5.1
801/459	12.634	5.6	88.4	+0.3	2.716	2.1	62.1	-3.1	0.909	3.2
1026/459	5.038	2.7	88.3	+0.2	1.185	4.0	63.9	-0.3	0.367	1.4
1264/459	4.188	1.3	88.5	+0.7	0.959	5.5	63.7	-0.6	0.299	3.7
1442/459	4.031	2.4	88.9	+0.9	0.921	3.5	64.6	+0.8	0.276	5.1
Average of 40-5 spectra			88.3				63.8			

Table VII. Binary Solutions

[(A) $C_6H_5CH_3$, (B) C_6H_{12} . Filter, $NaNO_2$. Slit, 0.06 mm. (5.3 cm^{-1}). Exp. time, 14 or 28 minutes]

Line Pair	10.13% A, A/B = 0.1030				36.87% A, A/B = 0.5335				52.29% A, A/B = 1:1	
	Int. ratio	Av. % dev. int. ratio	% A	% Error	Int. ratio	Av. % dev. int. ratio	% A	% Error	Int. ratio	Av. % dev. int. ratio
520/801	0.034	5.9	9.1	-9.9	0.192	3.1	36.3	-1.6	0.369	3.3
788/801	0.103	11.7	11.8	+16.8	0.475	1.5	38.0	+2.8	0.845	0.4
1003/801	0.177	2.3	10.4	+2.6	0.884	1.2	36.6	-0.8	1.674	8.3
1205/801	0.050	10.0	12.5	+23.7	0.209	5.3	37.4	+1.4	0.383	3.7
Av. of 16-4 spectra			11.0				37.3			

quencies to clutter up the spectrum. The writer prefers carbon bisulfide to carbon tetrachloride although full arc excitation cannot be used with the former because even 3650 Å. radiation will destroy it. A strong objection to the use of the internal standard is that fairly large quantities of pure materials are contaminated by its use.

Method E is sometimes handy for analyzing a single unknown when a great deal of work is unwarranted.

BINARY SOLUTIONS. In order to see whether the aforementioned fundamental hypothesis were tenable, five binary solutions (three solutions for each binary pair, one out of each three having a 1 to 1 mole ratio) were examined according to Method B. One pair, $C_6H_6 + C_6H_{12}$, was also examined by Method A. In this last case, the spectra were superimposed in 19 different spectra, the pictures being taken by using two Raman tubes as nearly alike as possible and including spectra obtained with all possible combinations of tubes and liquids.

The results are shown in Tables III to VII, inclusive. The 1 to 1 mole ratio solution included in each series was used as a single standard solution to obtain the results on the other solutions which were treated as unknowns. For these five binary pairs, three yielded satisfactory results and two did not. The latter two consist of the pairs $C_6H_6 - C_6H_{12}$ and $C_6H_5CH_3 - CCl_4$. This work should be repeated, but it cannot be done now because of more pressing matters. The failure of Method B to work

necessitates making up standard solutions to obtain an analytical curve. The data from Table III were employed in making Figure 14, which would yield errors in analysis shown beside each of the points.

Figure 15 shows several working curves for acrylonitrile ($CH_2=CHC\equiv N$) plus methanol. The exposure time (30 minutes) listed is that when using a Zeiss Tessar at F:8. The time with the Petzval lens would be shorter by a factor of $1/5$. One curve is from a set of standards containing nitrobenzene, which was examined to determine the effect of nitrobenzene on the curve. The nitrobenzene was intended to be added to fluorescent unknowns, thereby doing away with the time necessary to redistill such samples. The working curve obtained with standards not containing nitrobenzene is reproducible; that obtained with standards containing nitrobenzene is not. This last statement is made on the basis of considerable experience. In the case of the standards with nitrobenzene, experiments were conducted with two sets of standards, with the nitrobenzene being added directly before starting the exposures. The lines used were the pair shown in Figure 15 as well as $\Delta\nu$ 1342 of nitrobenzene in combination with the $C=C$ line and the $C=N$ line of the acrylonitrile. The results were unsatisfactory and cannot be explained by the writer. It was thought that enough 4047 or 4078 radiation might be getting through the sodium nitrite filter to excite the nitrobenzene electronically, which in turn might enhance the velocity of polymerization of the acrylonitrile.

Table VIII. Analysis of *o*-, *m*-, *p*-Xylenes

[Filter, $NaNO_2$. Slit, 0.06 mm. (5.25 cm^{-1}). Exp. time, 5 or 10 minutes. One standard solution used—33.2% *o*, 33.8% *m*, 33% *p*. Two 5-minute exposures and two 10-minute exposures]

Lines Used	True value:			<i>o</i> -Xylene 20.1	<i>m</i> -Xylene 55.1	<i>p</i> -Xylene 24.8
	<i>o</i>	<i>m</i>	<i>p</i>			
1226	1248	1203	20.2	56.5	23.6	
1056	1002	1203	20.5	55.5	24.0	
582	534	642	21.7	53.0	25.3	
1056	1002	827	20.8	56.3	22.9	
582	534	457	20.7	51.9	27.5	
	Av.		20.7	54.7	24.7	
	% Error		+3.0	-0.7	-0.4	

Four more sets of standards were then made up with nitrobenzene added to two and hydroquinone (to inhibit polymerization) plus nitrobenzene to the other two. Each solution was used to give three spectra taken one after the other and of equal duration to find an explanation. The results obtained did not permit any explanation. All this is to show that it is sometimes dangerous to add nitrobenzene to highly reactive materials.

Figure 16 is a working curve for the analysis of butyl acrylate. The standards contained butyl acrylate plus butyl alcohol. To each standard was added 5% by weight of carbon bisulfide. The $C=C$ line of the ester produces a nice analytical curve but the acrylate concentration can be found more easily by other methods. In some spectra, several butanol lines were related to the carbon bisulfide line but no satisfactory working curves resulted. There is evidently strong interaction between the alcohol and the $C=O$ group of the ester in this case. This is demonstrated by the doubling of the carbonyl line in the ester when the alcohol is added. In liquid butyl acrylate this line is at 1727 cm^{-1} , when butanol is added (1 to 1) two lines appear at 1709 and 1727. This is an example of what may arise to plague the vibrational

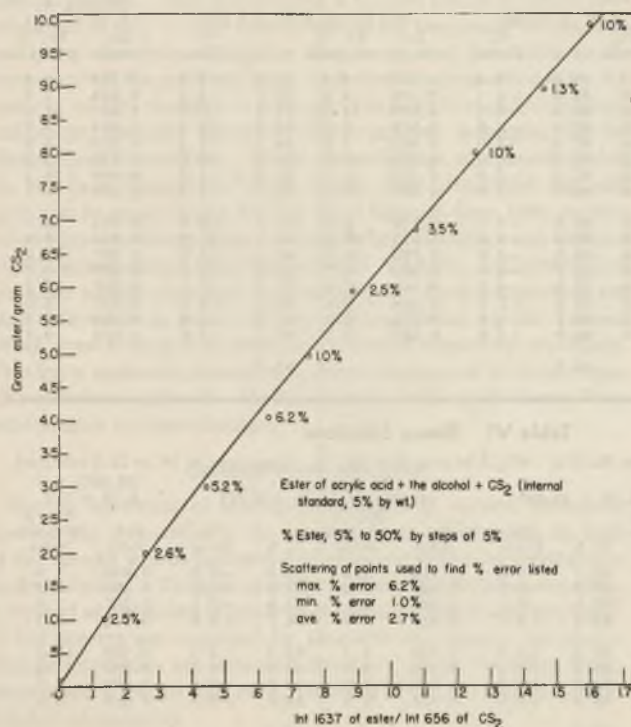


Figure 16. Working Curve for Analysis of Butyl Acrylate

Table IX. Analysis of *o*-, *m*-, *p*-Xylenes Plus Styrene

[Filter, NaNO₂. Slit, 0.06 mm. (5.25 cm.⁻¹). Exp. time, 5 or 10 minutes. One standard solution used: 28.2% *o*, 28.7% *m*, 28.0% *p*, 15.1% styrene. Two 5- and two 10-minute exposures of each solution]

<i>o</i>	Lines Used				<i>o</i> -Xylene				<i>m</i> -Xylene				<i>p</i> -Xylene				Styrene			
	<i>m</i>	<i>p</i>	<i>s</i>	True %	% Found	Δ	% Δ	True %	% Found	Δ	% Δ	True %	% Found	Δ	% Δ	True %	% Found	Δ	% Δ	
1226	1248	1203	1628	15.0	15.0	0.0	0.0	40.0	38.0	-2.0	-5.0	35.0	36.4	+1.4	+4.0	10.0	9.4	-0.6	-6.0	
1056	1002	827	1628	15.0	15.7	+0.7	+4.7	40.0	37.6	-2.4	-6.0	35.0	34.2	-0.8	-2.3	10.0	9.8	-0.2	-2.0	
582	534	642	1628	15.0	15.6	+0.6	+4.0	40.0	40.5	+0.5	+1.2	35.0	34.0	-1.0	-2.9	10.0	10.0	0.0	0.0	
582	534	457	1628	15.0	15.5	+0.5	+3.3	40.0	41.4	+1.4	+3.5	35.0	33.2	-1.8	-5.1	10.0	9.9	-0.1	-1.0	
Av.					15.5	0.5	3.0		39.4	1.6	3.9		34.5	1.3	3.6		9.8	0.3	2.3	
1226	1248	1203	1628	19.1	19.5	+0.4	+2.1	52.4	52.2	-0.2	-0.4	23.5	23.3	-0.2	-0.8	5.0	4.7	-0.3	-6.0	
1056	1002	827	1628	19.1	20.9	+1.8	+9.4	52.4	51.5	-0.9	-1.7	23.5	22.6	-0.9	-3.8	5.0	5.0	0.0	0.0	
582	534	642	1628	19.1	18.0	-1.1	-5.8	52.4	52.6	+0.2	+0.4	23.5	24.9	+1.4	+6.0	5.0	4.5	-0.5	-10.0	
582	534	457	1628	19.1	19.4	+0.3	+1.6	52.4	54.6	+2.2	+4.2	23.5	21.2	-2.3	-9.8	5.0	4.9	-0.1	-2.0	
Av.					19.5	0.9	4.8		52.7	0.9	1.6		23.0	1.2	5.1		4.8	0.3	4.5	

spectroscopist when working in the liquid state with substances other than hydrocarbons.

MULTICOMPONENT SOLUTIONS. In the case of solutions of more than two components it is an advantage to be able to use Method B or an extension of this method in conjunction with an internal standard because of the time and materials involved in making up synthetic standards bracketing the concentration range of the unknowns to be analyzed.

5GDN extra filters. The exposures varied from 30 to 90 minutes (these exposure times would now be 6 to 18 minutes).

CHIEF USES AND LIMITATIONS. For quantitative work Raman spectroscopy should not be used below ca. 5% for substances which scatter light strongly nor below ca. 10% for substances which are poor scatterers. Thus the Raman method is best for that region where absorption spectral methods are poorest—i.e., at high concentrations.

The biggest objections to its use in industry are the scarcity of suitable spectrographs, and the time involved in obtaining spectra by the photographic method and the resultant photographic photometry.

The writer maintains that it is possible to use a "home-made" spectrograph. As to the latter, it is certain that additional developments in the field of automatic recording Raman spectrographs will extend the use of this method to problems in laboratories which would not consider adopting it at present.

ACKNOWLEDGMENT. The writer wishes to acknowledge the contributions of his associates, John W. Berry and John J. Whalen.

ADDENDUM

A new book on Ramanspektren (3) may soon be lithographed by Edwards Brothers, Ann Arbor, Mich., under the auspices of the office of the Alien Property Custodian.

LITERATURE CITED

- (1) Hanle, W., *Z. Instrumentenk.*, **51**, 488 (1931).
- (2) Kohlrausch, K. W. F., "Der Smekal-Raman Effekt", *Ergänzungsband 1931-1937*, pp. 77-9, Berlin, J. Springer, 1938.
- (3) Kohlrausch, K. W. F., "Ramanspektren", Leipzig, Akademische Verlagsgesellschaft, 1943; Eucken Arnold, "Hand- und Jahrbuch der chemischen Physik", Bd. 9.
- (4) Lord, R. C., Jr., and Miller, F. A., *J. Chem. Phys.*, **10**, 328-41 (1942).
- (5) Pierce, W. C., and Nachtrieb, N. H., *IND. ENG. CHEM., ANAL. ED.*, **13**, 774-81 (1941).
- (6) Placzek, G., "Handbuch der Radiologie", Vol. 6, Part 2, 2nd ed., p. 205, Leipzig, Akademische Verlagsgesellschaft, 1934.
- (7) Rank, D. H., Pfister, R. J., and Coleman, P. D., *J. Optical Soc. Am.*, **32**, 390-96 (1942).
- (8) Rank, D. H., Pfister, R. J., and Grimm, H. H., *Ibid.*, **33**, 31-5 (1943).
- (9) Rank, D. H., Scott, R. W., and Fenske, M. R., *IND. ENG. CHEM., ANAL. ED.*, **14**, 816-19 (1942).
- (10) Reitz, A. W., *Z. physik. Chem.*, **B33**, 368 (1936).
- (11) Rosenthal, J. E., and Murphy, G. M., *Rev. Mod. Phys.*, **8**, 317 (1936).
- (12) Tisza, L., *Z. Physik*, **82**, 48 (1933).
- (13) Wigner, E., *Göttinger Nachrichten*, 133 (1930).
- (14) Wilson, E. B., Jr., *J. Chem. Phys.*, **2**, 432 (1934).
- (15) Wilson, E. B., Jr., *Phys. Rev.*, **45**, 706 (1934).

PRESENTED before the Divisions of Analytical and Micro Chemistry and Physical and Inorganic Chemistry, Symposium on Spectrochemical Methods of Analysis, at the 108th Meeting of the AMERICAN CHEMICAL SOCIETY, New York, N. Y.

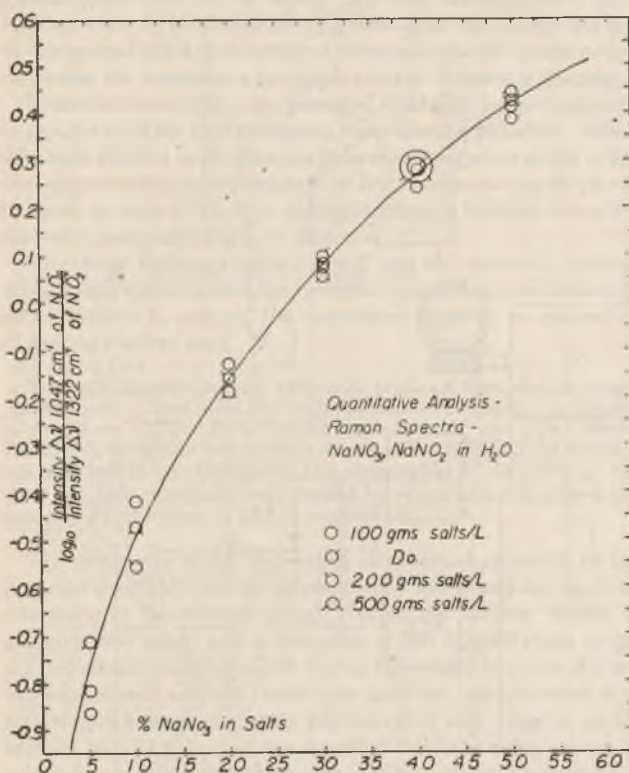


Figure 17. Analysis of Inorganic Salts in Water Solutions

Tables VIII and IX show results obtained on two practical problems by method B. Only one standard solution is involved. Some of the weaker lines are too faint to give accurate results. Obviously, in routine work the set of lines giving the best results would be employed and the others disregarded.

Figure 17 is an example of analysis of inorganic salts in water solutions. The plot of intensity ratios vs. concentration ratios produces a greater curvature than the plot shown. The working curve does not change markedly with total salt concentration. This work was done at F:8 with sodium nitrite and rhodamine

Automatic Apparatus for Electrolysis at Controlled Potential

JAMES J. LINGANE, Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Mass.

CONTINUING experiments on separations of metals by electrolysis with a mercury cathode at a controlled potential (3) created the need for an apparatus that would automatically maintain the potential of an electrode at a constant value during the course of electrolysis, and thus relieve the experimenter of the tedious task of manually controlling the potential. Ingenious circuits for performing this function have been described recently by Hickling (2) and by Caldwell, Parker, and Diehl (1), but both of these leave something to be desired from the standpoint of simplicity and versatility.

Hickling's circuit has the advantage of being completely electronic without moving mechanical parts, but it is practical only for electrolysis currents of a few tenths of an ampere, and it controls in only one direction. The circuit of Caldwell, Parker, and Diehl can handle large currents, but it is limited to the use of a total applied e.m.f. of 10 volts, and it also controls in only one direction—i.e., it prevents the cathode potential from becoming more negative than a given value during the course of electrolysis, but it does not correct a positive drift. Both circuits require preliminary calibration before use. The apparatus described herein controls in both directions, it is applicable with applied voltages and currents of any magnitude, its component parts are commercially available and relatively easy to assemble, and it does not require preliminary calibration.

The essential features of the circuit are shown schematically in Figure 1.

The total voltage applied to the electrolysis cell is adjusted by a 100-watt, 30-ohm radio potentiometer rheostat, R_1 , and indicated by the voltmeter V_1 (0 to 15-volt scale). Rheostat R_1 (General Radio Co., Type 333-A) is powered from the direct current house main, or with lead storage batteries, and a 50- or 100-ohm variable resistance, R_2 , is provided for convenience in adjusting the voltage across R_1 to the optimum value for a particular experiment. For most purposes 10 to 15 volts across R_1 are convenient, but a smaller or larger value may be used in special cases. For some purposes it may be desirable to connect R_1 into the electrolysis circuit as a series resistance, rather than as a potential divider, but for the usual type of electrolysis experiment the arrangement shown is most suitable.

The electrolyzing current is read on the multiple range ammeter, A . The range of the ammeter may be varied to suit the particular electrolysis conditions; for work with the mercury cathode under the conditions previously described (3, 4) two ranges from 0 to 0.1 and 0 to 1 ampere are most useful.

The e.m.f. between the working electrode and the reference electrode (usually a saturated calomel electrode, *S.C.E.*) is opposed by an e.m.f. from a 100-ohm radio-type potentiometer rheostat, R_3 , which may be powered by a single No. 6 dry cell or a 2-volt lead storage cell. Obviously, R_3 cannot be powered from the same source as R_1 , because this would create a short circuit between the electrolyzing and control circuits. The opposing e.m.f. ("cathode potential") is read on voltmeter V_2 (0 to 1.5 volts), which should be calibrated and capable of being read to 0.01 volt.

A galvanometer relay, G , sensitive to ± 0.02 volt (Weston Electric Instrument Co., Model 30), is placed in series in the control circuit as shown. Off-balance between the cathode-reference electrode e.m.f. and the opposing e.m.f. set on R_3 causes the galvanometer relay to make contact either right or left and operate one or the other of the two electronic relays, R_y (E. Greiner and Co., Catalog No. E-1804), which control the direction of rotation of the reversible synchronous motor, M . In turn, the motor rotates rheostat R_1 until the total e.m.f. applied to the cell is decreased or increased by such an amount that the cathode potential returns to the value set on R_3 , and thus balance in the control circuit is restored. The motor operates only when the control circuit is unbalanced.

The small motor used required only 9 watts at 110 volts

alternating current, and it is provided with a built-in gear train which provides a shaft speed of 60 r.p.m. and a torque of 5 oz. in. (Holtzer-Cabot Electrical Co., Boston, Mass., Type RWC 2505). A worm-gear combination as shown is used to decrease the speed further to 0.60 r.p.m. Mechanical connection to R_1 is made by a belt drive with wooden pulleys, whose ratio is 2.7, so that R_1 rotates at only 0.22 r.p.m. In addition to its simplicity the belt drive has the advantage of serving as a simple friction clutch, so that R_1 can be moved manually without having to bother with locking devices.

The rate of rotation of R_1 should be small to prevent overshooting and hunting, and yet great enough so that off-balance in the control circuit is corrected without delay. With one revolution in about 5 minutes hunting is avoided, and the time required to restore balance in the control circuit is seldom greater than about 10 seconds and usually is considerably less.

The time of response between the instant when the galvanom-

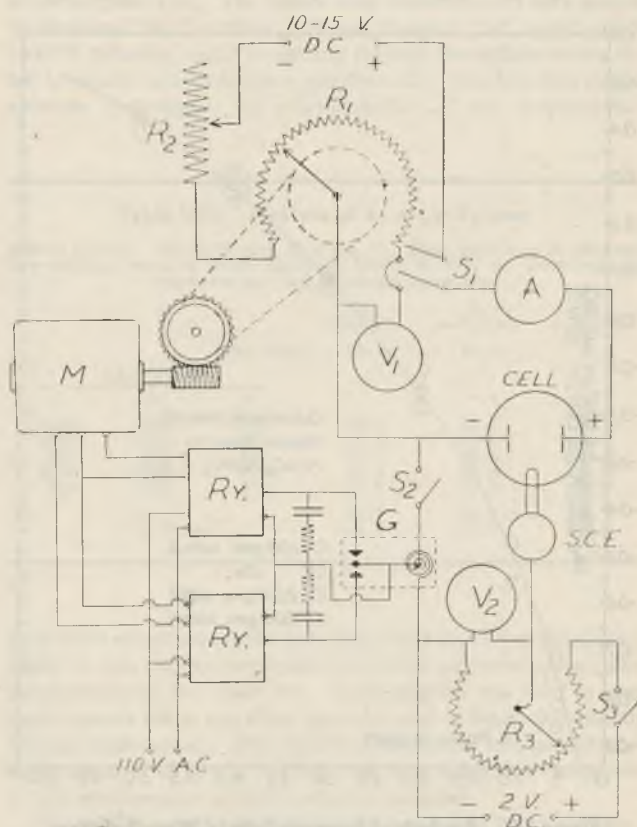


Figure 1. Schematic Circuit Diagram of Apparatus for Electrolysis at Controlled Potential

- R_1 . 100-watt, 30-ohm radio potentiometer (General Radio Co., Type 333-A)
- R_2 . 50- or 100-ohm regulating resistance
- R_3 . 100-ohm radio potentiometer (General Radio Co., Type 301)
- A . Multiple range ammeter (0- to 0.1- and 0- to 1-ampere scales)
- V_1 . Voltmeter (0- to 15-volt scale)
- V_2 . Calibrated voltmeter with scale from 0 to 1.5 volts, capable of being read to 0.01 volt
- G . Galvanometer relay sensitive to ± 0.02 volt (Weston Electric Instrument Co., Model 30)
- R_y . Electronic relays set for normally open (E. Greiner and Co., Catalog No. E-1804)
- M . Reversible, synchronous electric motor with shaft speed of 60 r.p.m. or less (Holtzer-Cabot Electrical Co., Boston, Mass., Type RWC 2505)
- S.C.E.*. Saturated calomel reference electrode
- Cell*. Electrolysis cell

eter relay makes or breaks contact and the instant that R_1 begins to move or stops is only a few tenths of a second.

When the electrolysis current is large, a relatively large change in the total applied e.m.f. is required to produce a given change in the potential of the working electrode, because the major fraction of the total e.m.f. is dissipated as iR drop through the cell, but near the end of an electrolysis when the current becomes very small the potential of the working electrode changes virtually directly with the total applied e.m.f. Hence there is a greater tendency for the instrument to hunt its balance point near the end of an electrolysis when the current is small. For this reason the total voltage applied to R_1 should not be larger than necessary, so that R_1 is nearly fully open at the beginning of an experiment—i.e., so the increment of applied e.m.f. caused by momentary operation of the motor will be relatively small. Hunting can also be eliminated by increasing R_2 to decrease the voltage across R_1 after the current has dropped to a small value, but this usually is not necessary. With these precautions hunting was not a problem.

Considerable difficulty was experienced at first with sticking of the contacts of the galvanometer relay, even though the alternating control current of the electronic relays amounts to only about 2 microamperes and there was no visible sparking. This difficulty was eliminated completely by placing two 0.25-microfarad paper condensers, each of which is in series with a 100-ohm resistance to the common center contact, across the galvanometer contacts as shown. By trial the condensers must be connected so that their ground sides bear the proper relation to the ground sides of the control circuits of the electronic relays, otherwise the condensers may leak current to operate the relays.

If the electronic relays are provided with pilot lamps connected in parallel with the load terminals, these must be removed; otherwise both circuits in the motor will be energized when either of the two relays operates. Pilot lamps of low resistance may be placed in series in each of the two motor circuits to indicate when the controller is operating and its direction.

Since both the total applied e.m.f. and the potential between the working electrode and the reference electrode are read directly on voltmeters V_1 and V_2 , the instrument requires no calibration of any sort before use.

To begin an experiment, switch S_3 is closed first, and R_3 is adjusted until V_2 indicates the cathode potential which it is desired to maintain. Then R_1 is turned back to zero, and S_1 is closed. Finally S_2 is closed to activate the control circuit, and the apparatus is left to itself until the electrolysis is completed. At the end of an experiment S_2 should be opened to disconnect the control circuit before S_1 and S_3 are opened.

The sensitivity of the instrument is governed primarily by the intrinsic sensitivity of the galvanometer relay, and by the total resistance in the control circuit. With the Weston Model 30 galvanometer relay, and a resistance of 700 to 1000 ohms in the control circuit, most of which was in the bridge between the reference electrode and the electrolysis solution, the apparatus controlled over a range of slightly less than 0.04 volt—that is, an off-balance of 0.02 volt in either direction from the value set on V_2 was sufficient to actuate the motor. This sensitivity is more than ample for the great majority of electrolysis experiments. For some purposes it may be desirable to work at a lower sensitivity, and this can be obtained by increasing the spacing between the contacts of the galvanometer relay, and/or shunting the relay with suitable resistances.

The apparatus has been in use for several months for electrolytic separations of metals with the mercury cathode under the conditions previously described (3), and has given very satisfactory service. In a number of instances quantitative separations of metals whose standard potentials differ by only 0.20 volt have been achieved. These experiments will be described later.

In addition to purely analytical applications, the apparatus has proved very useful for the electrolytic preparation of organic com-

pounds by controlled potential electrolysis according to the "polarographic synthesis" technique described by Lingane, Swain, and Fields (4).

Although the instrument was designed primarily for use with the mercury cathode, it is, of course, equally suitable for use with platinum electrodes according to the procedures developed by Sand and his collaborators (5), with any combination of working electrode and reference electrode, and for controlling the potential of an anode. By connecting the control circuit across the cathode and anode of an electrolysis cell the instrument can be used to control the total applied e.m.f., if desired.

SUMMARY

An apparatus is described which automatically maintains the potential of an electrode constant during electrolytic determinations and separations. The instrument is sensitive to ± 0.02 volt, it is applicable with currents and applied voltages of any magnitude, its component parts are commercially available and relatively easy to assemble, and it does not require preliminary calibration. Although the instrument was designed particularly for controlling the potential of a mercury cathode, it is equally suitable for use with platinum or other metal electrodes, and it can be employed with any combination of working and reference electrodes.

LITERATURE CITED

- (1) Caldwell, C. W., Parker, R. C., and Diehl, H., *IND. ENG. CHEM., ANAL. ED.*, **16**, 532 (1944).
- (2) Hickling, A., *Trans. Faraday Soc.*, **38**, 27 (1942).
- (3) Lingane, J. J., *IND. ENG. CHEM., ANAL. ED.*, **16**, 147 (1944).
- (4) Lingane, J. J., Swain, C. G., and Fields, M., *J. Am. Chem. Soc.*, **65**, 1348 (1943).
- (5) Sand, H. J. S., "Electrochemistry and Electrochemical Analysis. Vol. II, Gravimetric Electrolytic Analysis", London and Glasgow, Blackie and Son, 1940.

BOOK REVIEW

A.S.T.M. Standards, 1944. Part I, 2047 pages, Part II, 1649 pages, Part III, 2240 pages. American Society for Testing Materials, 260 Broad St., Philadelphia 2, Pa. Price, \$10 for each part; supplement, \$4 for each part.

The 1944 Book of A.S.T.M. Standards, issued in three parts, contains in their latest approved form all the society's widely used specifications and tests for materials: 1235 specifications and standard methods. All specifications, whether formal standards or tentative, are given.

Part I, Metals, deals with ferrous and nonferrous metals (all A and B and some E serial designations) except methods of chemical analysis and with general testing methods (E serial designations).

Part II, Nonmetallic Materials, covers constructional cementitious materials, concrete and aggregates, masonry building units, ceramic, pipe and tile, thermal insulating materials (all C serial designations); wood and wood preservatives, paints, varnishes, and lacquers, road materials, waterproofing and roofing materials, soils (certain D serial designations); general testing methods, thermometers (E serial designations).

Part III, Nonmetallic Materials, General, includes fuels, petroleum products, electrical insulating materials, rubber, textiles, soaps and detergents, paper, plastics, water (remainder of D serial designations); general testing methods, thermometers (E serial designations).

An innovation is the inclusion of all emergency standards and emergency alternate provisions which have been widely used to expedite production and procurement of important materials. Each part has a complete subject index (from 36 to 44 pages).

To keep the books up to date, a supplement will be issued to each part late in 1945. A complete 200-page Index to Standards is furnished without additional charge and a copy accompanies the purchase of each part or complete set.

Microdetermination of Acetyl Groups in Acetates of Sugars and Glycosides

RAY CLARKE AND BERT E. CHRISTENSEN

Department of Chemistry, Oregon State College, Corvallis, Ore.

IN CONNECTION with the studies of a fructosan in *Yucca mohavensis* it was necessary to devise micromethods for the determination of the acetyl groups in sugar derivatives.

The fact that the acetyl esters of sugars are easily hydrolyzed with dilute alkali at room temperature has been known for some time. In 1902 (14) and 1904 (1), the rate of the hydrolysis of acetylated monoses and bioses was studied. The hydrolysis was carried out in an alcohol-water solution with 0.04 *N* sodium hydroxide solution. It was generally concluded for most of the sugars used that *K* (velocity coefficient) was not constant, but decreased as the change proceeded, indicating that the acetyl groups were not separated at the same rate. Armstrong and Arup (1), in order to obtain further evidence as to the manner in which the acetyl groups were removed extended the study to acetates of methyl glycosides of α - and β -glucose and α - and β -galactose. They found that these glycoside acetates were hydrolyzed at about the same rate and that *K* remained fairly constant for about three fourths of the hydrolysis. Near the end the hydrolysis proceeded far less rapidly.

The action of alkali on sugars has been studied extensively. de Bruyn and van Ekenstein (3) postulated a series of transformations for *D*-glucose and *D*-galactose in an alkaline solution.

Nef (18, 19) and his co-workers postulated for these hexoses the existence of a series of enediols in an alkaline solution.

Evans (4-11) and co-workers have studied the influence of temperature and alkali concentrations on certain mono- and disaccharides by characterizing the volatile acids and residues which result from the splitting of any possible enols.

The problem of devising an analytical method based on alkaline hydrolysis centers principally on behavior of the reducing sugars.

For the purpose of this paper, the conclusion can be drawn from the above work that oxidation of reducing sugars takes place much less readily with dilute alkaline solutions at temperatures below 25° C. Nef (18, 19) stated that the enediols do not exist in solutions of an alkalinity less than 0.033 *N* and that they begin to decompose in systems of alkalinity above 0.05 *N*. It thus becomes obvious that the alkaline hydrolysis micromethod of Kuhn and Roth (15) would not give satisfactory results for reducing sugars.

Since the fructosan studied in this laboratory was nonreducing, it was possible to obtain very satisfactory results by dissolving the sample in 95% ethanol and then hydrolyzing with an aqueous 0.1 *N* sodium hydroxide solution at room temperature for 4 to 15 hours and back-titrating the excess alkali with standard sulfuric acid. A similar macromethod has been described by Kunz and Hudson (16). This method has been used successfully for fructose pentaacetate hydrolyzing at 0° C. with 0.1 *N* sodium hydroxide for 3.5 hours (13). It has also apparently been used on *D*, α -phenyl xylose triacetate (17).

In view of the above, a micromethod for the determination of acetates of sugars and sugar derivatives was investigated.

EXPERIMENTAL

The sugar and glycoside acetates used in this investigation were prepared from pyridine-acetic anhydride mixtures using essentially the procedure of Haworth and Percival (12).

To 3.0 grams of sugar (or glycoside) were added 35 ml. of anhydrous pyridine. The solution was agitated intermittently until all the sugar had dissolved. Then 30 ml. of acetic anhydride were slowly added with stirring and the solution was

allowed to stand for approximately 24 hours at room temperature. This mixture was then poured with vigorous stirring onto 500 grams of ice. The white solid, which usually formed immediately, was removed by filtration, washed with cold water, and dried. Further purification by recrystallization from alcohol could be accomplished when necessary.

When the above procedure was used with galactose, an oil was formed when the reaction mixture was poured upon ice. This oil was dissolved in hot alcohol and crystallized upon cooling.

Several of the β -glucoside tetraacetates used were prepared by the method of Bemby and Powell (2).

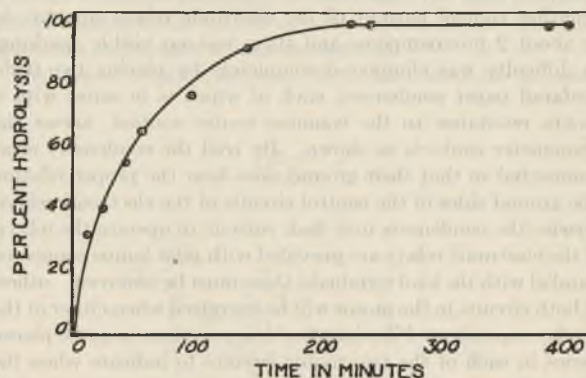


Figure 1. Rate of Hydrolysis of Sucrose Octaacetate

In order to establish the optimum conditions for the quantitative hydrolysis of these acetates a number of initial studies were made.

RATE OF HYDROLYSIS. Studies with sucrose octaacetate indicated that deacetylation of this compound with 0.045 *N* sodium hydroxide at 20° C. was complete in 3.5 hours (see Figure 1).

Similar tests with acetates of glucose and maltose indicated complete deacetylation in 3.5 hours in the case of the disaccharides, while glucose gave results higher than theoretical. On continued hydrolysis maltose (21 hours), lactose (19 hours), as well as galactose (14 hours) gave high and erratic results.

Since this excess was best accounted for on the basis of enolization, splitting, and oxidation of the breakdown products of the sugar, test runs were made using a layer of a hydrocarbon to shield the acetates from the air.

The results of these experiments are given in Table I.

CONCENTRATION OF THE ALKALI. Because of the critical nature of the concentration factor (4-11), several experiments were conducted to establish optimum condition. According to Nef (19), enolization and breakdown of reducing sugars do not occur

Table I. Rate of Hydrolysis

Acetate	Temperature ° C.	Time Hours	Concentration of Base <i>N</i>	Hydrolysis %
Glucose (with a layer of a hydrocarbon)	20	6	0.045	98.6
	20	26	0.045	102
	20	72	0.045	116

in solutions of less than 0.033 *N* base. The results of a series of experiments in which this factor was tested are tabulated in Table II.

PROCEDURE OF ANALYSIS. On the basis of these studies the following procedure was adopted:

A 5- to 10-mg. sample of the acetate is weighed out in a small glass boat and placed in a 25-cc. Erlenmeyer flask. The sample is then dissolved in 95% ethanol, 2 to 5 cc. depending upon the solubility of the acetate, being warmed if necessary to obtain solution. Four milliliters of 0.045 *N* sodium hydroxide (carbonate-free) are added from a microburet. The flasks are stoppered and shaken mechanically or intermittently by hand for 4 to 24 hours at 20° C. The excess alkali is neutralized with dilute sulfuric acid (0.05 *N*) using phenolphthalein indicator. The per cent acetate is calculated as follows:

$$\% \text{CH}_3\text{COO} = \frac{[\text{ml. of base} - (\text{ml. of acid} \times T)] \times N_b \times 5900}{\text{mg. of sample}}$$

T = normality ratio of acid to base
N_b = normality of base

Using this procedure the data in Table III were obtained.

DISCUSSION

As indicated by the results in Table III, the determination of the acetate with 0.045 *N* sodium hydroxide at 20° C. is complete in from 4 to 24 hours. These conditions appear to be satisfactory in all tests except those applied to the reducing monosaccharides.

In the case of these reducing sugars, the minimum concentrations necessary for enolization and splitting as reported by Nef were confirmed. Lower concentrations of alkali were not satisfactory for analytical purposes in all cases.

Since deacetylation of glucose pentaacetate even with 0.015 *N* sodium hydroxide at 20° C. gave high results, oxidation is evidently taking place. At 0° C. more normal results are obtained, owing to slow rate of hydrolysis and probable absence of oxidation.

From the data in Table I it appears probable that increased acidity results from a self-oxidation. In the case of glucose, high values under certain conditions may be due to lactic acid formation, owing to the rearrangement of glyceric aldehyde resulting from the fragmentation of the original molecule (8).

Evans (4) has pointed out that sucrose octaacetate should not give values in excess of theory in the absence of oxygen since the

sucrose formed cannot undergo transformations to form double bonds as in enediols. This viewpoint is supported by the data in Tables II and III.

According to the information in Table III, this procedure gives fairly consistent results with an average deviation of approximately 0.7%, which is satisfactory for a microdetermination of this type.

Table III. Determination of Acetyl Groups

Acetate	No. of Determinations	Time Hours	$\text{CH}_3\text{C}(=\text{O})\text{O}$	$\text{CH}_3\text{C}(=\text{O})\text{O}$	Average Deviation P.p.1000
			Theory %	Found (Average) %	
Glucose	7	6	75.6	77.1	5.9
Galactose	4	14	75.6	77.0	9.0
Sucrose	14	4	69.6	69.7	6.0
Lactose	7	16	69.6	69.7	3.7
Maltose	7	4	69.6	69.7	3.0
Raffinose	6	14	67.2	67.0	2.0
Inulin	5	10	..	61.7	6.8
Glycogen	7	24	..	61.4	10.0
Fructosan	5	15	..	61.8	3.2
Salicin	10	8	59.5	59.6	7.7
Amygdalin	6	10	55.0	55.6	7.5
Digitalin	5	6	..	46.6	2.6
Phloridzin	4	9	56.6	55.0	3.6
Arbutin	4	11	61.0	60.8	2.5
Aesculin	3	11	53.4	54.6	6.8
Eugenol-β-d-glucoside	7	8	47.8	48.5	6.2
Phenyl-β-d-glucoside	4	6	55.8	55.2	6.8
Guaiacol-β-d-glucoside	6	5	52.1	52.0	7.7

LITERATURE CITED

- (1) Armstrong, E. F., and Arup, P. S., *J. Chem. Soc.*, 85, 1043 (1904).
- (2) Bembry, T. H., and Powell, G., *J. Am. Chem. Soc.*, 64, 2419 (1942).
- (3) Bruyn, Lobry de, and Ekenstein, Alberda van, *Rec. trav. chim.*, 14, 156, 203 (1895).
- (4) Evans, W. L., *Chem. Revs.*, 31, 537 (1942).
- (5) Evans, W. L., and Benoy, M. P., *J. Am. Chem. Soc.*, 52, 294 (1930).
- (6) Evans, W. L., Buehler, C. A., Looker, C. D., Crawford, R. A., and Holl, C. W., *Ibid.*, 47, 3085 (1925).
- (7) Evans, W. L., and Conaway, R. F., *Ibid.*, 52, 3680 (1930).
- (8) Evans, W. L., Edgar, R. H., and Hoff, G. P., *Ibid.*, 48, 2665 (1926).
- (9) Evans, W. L., and Hutchman, J. E., *Ibid.*, 50, 1496 (1928).
- (10) Evans, W. L., Nicoll, W. D., Strouse, G. C., and Waring, C. E., *Ibid.*, 50, 2267 (1928).
- (11) Evans, W. L., and O'Donnell, D. C., *Ibid.*, 50, 2543 (1928).
- (12) Haworth, W. N., and Percival, E. G. V., *J. Chem. Soc.*, 1932, 2277.
- (13) Hudson, C. S., and Brauns, D. H., *J. Am. Chem. Soc.*, 37, 1283, 2736 (1915).
- (14) Kremen, R., *J. Chem. Soc.*, 82, 712 (1902).
- (15) Kuhn, R., and Roth, H., *Ber.*, 66, 1274 (1933).
- (16) Kunz and Hudson, *J. Am. Chem. Soc.*, 48, 1978 (1926).
- (17) Montgomery, E. M., Richtmeyer, N. K., and Hudson, C. S., *Ibid.*, 64, 690 (1942).
- (18) Nef, J. U., *Ann.*, 403, 205 (1914).
- (19) *Ibid.*, 403, 224 (1914).

PUBLISHED with the approval of the Monographs Publications Committee, Oregon State College as Research Paper No. 88, School of Science, Department of Chemistry.

Table II. Rate of Hydrolysis

Acetate	Temperature ° C.	Time Hours	Concentration of Base <i>N</i>	Hydrolysis %
Glucose	20	10	0.09	105
	20	34	0.09	114
	20	60	0.09	126
	20	6	0.045	102
	20	24	0.045	106
	20	60	0.045	113
	0	4	0.045	101
	0	26	0.045	103
	20	4	0.015	101
	20	7	0.015	103.6
	20	19	0.015	103.8
	0	12	0.015	96.6
	0	24	0.015	100.6
	0	41	0.015	100.5
	0	68	0.015	100.6
	Maltose	20	11	0.015
20		24	0.015	103
0		45	0.015	98.2
0		69	0.015	98.8
Lactose	20	8	0.015	98.5
	20	18	0.015	99.6
Sucrose	20	11	0.015	99.3
	0	45	0.015	95.3
	0	68	0.015	97.3



Report of the Committee on Analysis of Commercial Fats and Oils

E. W. BLANK, E. W. COLT, F. G. DOLLEAR, J. L. LAING, J. FITELSON, C. P. LONG, J. E. MARONEY, R. T. MILNER, L. B. PARSONS, H. A. SCHUETTE, S. O. SORENSEN, L. M. TOLMAN, F. C. WOEKEL, V. C. MEHLENBACHER, *Chairman*

THIOCYANOGEN VALUES

LAST year this committee attempted to determine whether thiocyanogen constants, stoichiometrically calculated from fatty acids to glycerides, could be used with satisfactory accuracy. In that program the committee was unable to obtain agreeing results in the several laboratories. This year it undertook to find out why. Accordingly, samples were sent out and reagents were supplied from two sources, so that all collaborators used identical materials. The thiocyanogen values were run using these reagents and the reagents regularly used by each member. The results are shown in the following tabulation:

Laboratory	Cottonseed Oil		Peanut Oil		Soybean Oil	
	Regular	Special	Regular	Special	Regular	Special
1	68.2	67.5	72.0	71.8	86.0	86.0
2	66.9	67.3	71.5	71.8	85.9	86.1
3	65.2		69.9		83.1	
4	66.8	67.0	71.1	71.4	84.9	85.4
5	66.4		70.8		83.9	
6	68.7	67.6	73.1	71.8	86.0	86.4
7	67.0	67.0	72.0	71.7	85.2	85.6
Av.	67.5	67.3	72.0	71.7	85.6	85.9
Av. deviation	0.7	0.3	0.5	0.1	0.4	0.4

Laboratories 3 and 5 not included in averages.

In all of these determinations 200% excess reagent and 1.66 grams of powdered potassium iodide were used.

For the most part these results are in much better agreement than previous figures.

Some samples, especially the higher melting point fats, are not completely soluble in the reagent. Their solubility is improved by the addition of carbon tetrachloride. Therefore, a comparison has been made of thiocyanogen results with and without the addition of carbon tetrachloride. The carbon tetrachloride was purified by a method supplied by one of the committee members.

PURIFICATION OF CARBON TETRACHLORIDE. *Removing Reducing Substances.* The carbon tetrachloride is shaken in a separatory funnel with about 50 ml. of concentrated sulfuric acid (A.C.S. grade) per liter of carbon tetrachloride and allowed to stand for 2 hours. This acid treatment is repeated with fresh charges of acid until a color no darker than a light straw develops in the acid layer on standing for 2 hours. After the acid layer is separated, the larger portion of the acid remaining in the carbon tetrachloride is washed out with water. The last traces of acid are removed by two consecutive washings with 50% aqueous potassium hydroxide (50 ml. per liter of carbon tetrachloride). The carbon tetrachloride is then partially dried by allowing it to stand several hours over pellets of potassium hydroxide. It is then decanted into a distilling flask and distilled. At this stage the carbon tetrachloride is suitable for use in iodine number determinations but must be freed of the last trace of moisture before use in the thiocyanogen reagent.

Drying. To remove the last traces of moisture, the carbon tetrachloride is placed in a flask with phosphoric anhydride (50 grams per liter of carbon tetrachloride), and allowed to stand several hours with occasional shaking. The phosphoric anhydride is then filtered off, the filtrate collected in a distilling flask with another charge of phosphoric anhydride (10 grams per liter of carbon tetrachloride), and the dry carbon tetrachloride distilled off. All equipment used in distilling the carbon tetrachloride must be dried for at least 1 hour at 120° C., and all connections in the distillation apparatus should preferably be made with ground-glass joints. The use of a two- or three-necked receiving flask to collect the distillate is recommended. One outlet should be fitted with a drying tube. See Table I.

A summary of results obtained to date indicates that the use of carbon tetrachloride is undesirable except possibly in the case of high melting point fats which are difficultly soluble in the regular reagent. More work is contemplated.

In a previous report this committee recommended that the amount of reagent be increased from an excess of 100–150% to 150–200%. It is now recommended that the quantity of potassium iodide be increased from 1 to 1.66 grams.

FAT STABILITY TEST

Additional work has been done on the fat stability test. This work has been concentrated on further standardization of the details of the method.

Samples were distributed among committee members, who reported the following results:

Laboratory	Sample			
	2	3	4	5
8	30	45	34	35
2	22–20–26–21	46	31	28
7	29	45	33	30
9	28	45	35	30
12	35	48	40	34
6	31	52	35	33
4	28	47.5	31	31
5	26		31	33
11	25	42	29.5	25.5
10	24	47.5	32	21
Av.	26	46	33	30
Av. deviation	3.5	1.9	2.3	2.2

While there are some large individual differences, the average deviations are much improved over previous results. More work is contemplated on this method.

Table I. Effect of Carbon Tetrachloride

Laboratory	Sample	Regular	Carbon Tetrachloride Added		
			25%	40%	10 ml. 5 ml.
1	Cottonseed oil	67.5	66.3		
1	Peanut oil	71.8	70.7		
1	Soybean oil	86.0	85.3		
4	Cottonseed oil	67.0	66.9		
4	Peanut oil	71.4	71.1		
4	Soybean oil	85.4	85.2		
2	Not designated	24.2	25.5	24.1	23.7
2	Not designated	44.5	45.5	46.1	45.0
1	Not designated	55.9	57.7	59.3	56.2
2	Soybean oil	85.2	85.7		
1	Peanut oil	70.9	71.2		
4	Glycerides	87.0 ^a	85.5 ^a	89.4 ^a	83.5 ^b
4	Glycerides	84.5	84.2	86.8	83.5
4	Fatty acids	91.3	89.3	90.0	86.6
4	Fatty acids	24.2	23.4	22.7	22.9
7	Cottonseed oil	66.7	66.3 ^c		
7	Peanut oil	71.7	69.7		
7	Soybean oil	85.5	82.5		
7	Tallow 1	47.3	47.0		
7	Tallow 2	42.4	42.5		
7	Tallow 3	47.0	46.2		
7	Fatty acids, tallow 1	48.2	45.9		
7	Fatty acids, tallow 2	44.2	43.1		
7	Fatty acids, tallow 3	47.2	46.7		
5	Not designated	70.9			69.3
5	Not designated	61.3			60.2
5	Not designated	62.2			61.0
5	Not designated	56.2			56.8
5	Not designated	69.1			68.4
5	Not designated	73.2			70.7

^a Effective normality of thiocyanogen reagent 0.194 to 0.206.

^b Effective normality of thiocyanogen reagent 0.140.

^c Effective normality of thiocyanogen reagent 0.200.

The Army Quartermaster Corps requested that the committee supply them with a method for the fat stability test incorporating the best technique known at this time. Therefore, a procedure has been written and approved by the committee and submitted to the Quartermaster Corps. While this procedure has not yet been accepted as final by the Committee and may require modification, it is agreed that it represents an acceptable method.

APPARATUS. (The entire apparatus, including calibrated capillary tubes, may be obtained from E. H. Sargent & Co., 155 East Superior St., Chicago, Ill.)

The apparatus consists of an aerating train, which is designed to supply washed air to the samples and a bath to keep the samples at constant temperature. The entire unit is calibrated in such a way that a constant volume of air (2.33 cc. per second) passes through each sample. The apparatus and procedure of standardization of the air flow are illustrated and described in the original paper (2).

The bath consists of a water jacket in which water is kept at the boiling point, using a reflux condenser to keep the volume constant. This water jacket encloses a mineral oil bath in which is contained a rack accommodating 25 by 200 mm. test tubes. The bath is maintained at such a temperature that the samples within the tubes will remain at $208^{\circ} \pm 0.5^{\circ} \text{ F.}$ (97.7° C.). The temperature of the outer bath may be regulated by the addition of alcohol to lower or glycerol to raise the boiling point. The bath is preferably insulated with about 1.5 inches of asbestos. This facilitates the maintenance of a uniform temperature. The bath may be heated with either gas or electricity. The heating must be arranged so as to give uniform heating throughout the length of the bath. It is important to be sure the temperature is the same over-all.

The only modification to the original design of the aerating train is that a reflux condenser is inserted in bottle *E* which contains the air-washing liquid (Figure 1). The air passes from bottle *E* through the condenser to remove as much water as possible. From the condenser the air passes to the regular manifold distributing bottles, *G* and *F*. A satisfactory arrangement is described by Riemenschneider, Turer, and Speck (4). Bottle *B* and cylinders *C* and *D* contain water. Bottle *E* contains a solution of 2% potassium dichromate in 1% sulfuric acid.

All-glass aeration tubes as described by Riemenschneider, Turer, and Speck are permissible but not required (4).

SOLUTIONS. 1. Sodium Thiosulfate, 0.1 *N* accurately standardized.

2. Sodium Thiosulfate, 0.01 *N*, accurately standardized.

Use reagent grade thiosulfate, freshly distilled water, and

store in brown glass bottles. Add 10 ml. of isoamyl alcohol and 0.1 gram of sodium carbonate per liter to stabilize the solution. Prepare a solution approximately 0.1 *N* and standardize as follows:

Prepare 0.1 *N* potassium dichromate by dissolving 2.452 grams of finely powdered and dried reagent grade potassium dichromate in distilled water and make up to 500 ml. Pipet 25 ml. of this solution into a glass-stoppered Erlenmeyer flask, add 5 ml. of concentrated hydrochloric acid, 5 ml. of potassium iodide solution (150 grams per liter), and 50 ml. of distilled water. Add the thiosulfate slowly with continuous and vigorous swirling until the yellow color has almost disappeared. Add about 1 ml. of starch indicator and continue the titration, shaking as before, until the blue color just disappears. Adjust the thiosulfate solution to exactly 0.1 *N*.

Dilute thiosulfate solution (0.01 *N*) may be prepared by accurately pipetting 100 ml. of 0.1 *N* thiosulfate solution into a 1000-ml. volumetric flask and diluting to volume with boiled and cooled distilled water.

3. Starch Indicator Solution. Make a homogeneous paste of 10 grams of soluble starch (Lintner) in cold distilled water. Add to this 1 liter of boiling distilled water, stir rapidly, and cool. Salicylic acid (1.25 grams per liter) may be added to preserve the indicator solution. If long storage is required, the solution should be kept in a refrigerator.

4. Air Washing Solution. An aqueous solution containing 2% potassium dichromate and 1% sulfuric acid. This solution must be changed at least weekly.

5. Potassium Iodide Solution. Saturate distilled water with reagent grade potassium iodide. Be sure solution remains completely saturated. This is best indicated by the presence of crystals of undissolved salt in the solution bottle. Store in the dark. This solution turns a light brown on standing and may become faulty with age.

6. Acetic Acid-Chloroform Solvent. Mix 60% reagent grade glacial acetic acid and 40% U.S.P. chloroform by volume.

7. Cleaning Solution. Place 5 to 10 grams of technical potassium dichromate in a 1-liter Erlenmeyer flask with about 50 ml. of water. Warm the flask under the hot water tap to dissolve as much dichromate as possible. Add concentrated sulfuric acid slowly and carefully until the volume is about 200 ml. Allow the hot solution to stand for about 5 minutes, then dilute to 1 liter with concentrated sulfuric acid.

The life of the cleaning solution depends upon the thoroughness of removal of the fat from tubes, beakers, etc. The solution is discarded when the distinctly red chromic acid color has changed to brown. If the fat has been well washed away, the solution can be used for 3 or 4 weeks. Its life may be still longer if not in daily use.

SAMPLING. All equipment and containers must be scrupu-

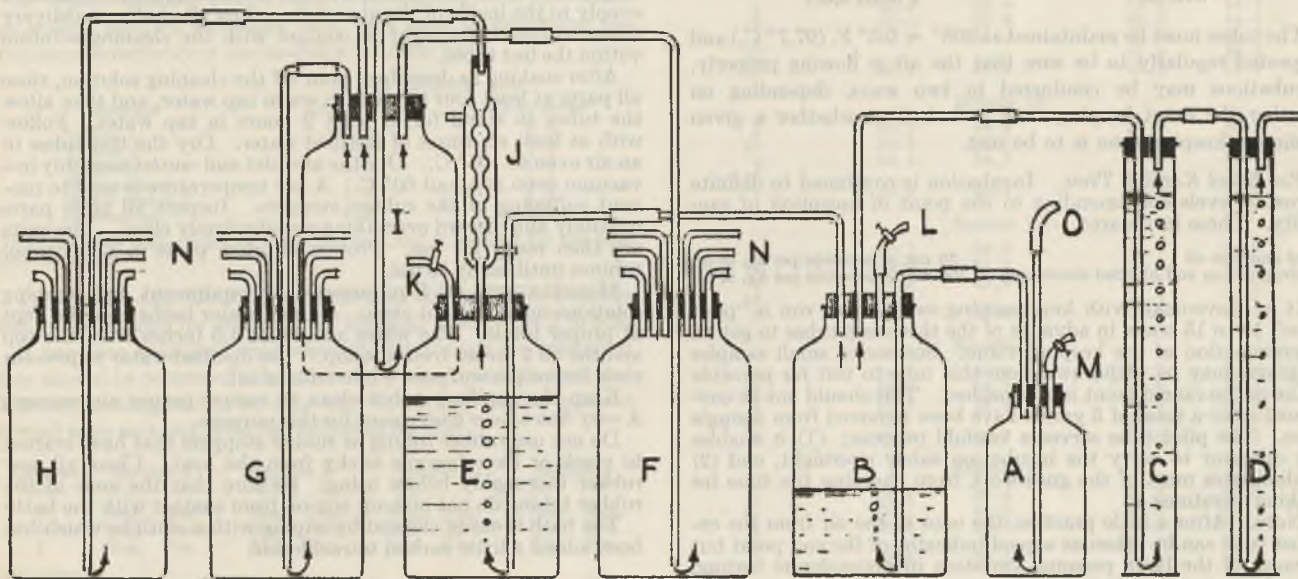


Figure 1. Diagram of Air-Distributing System

- A. Device to control pressure of incoming air
- B. Bottle containing water for washing air
- C, D. Water columns. Air in space above water in B is kept under constant pressure sufficient to by-pass air through C and D at a steady rate
- E. Bottle containing acid dichromate solution. Air from E passes through condenser. J into bottle I, thence into bottles F, G, and H, which distribute air to tubes N, which lead to the aeration tubes
- K, L. Pinchcocks to release pressure when shutting off apparatus
- M. Screw clamp to regulate flow of air
- O. Connection to source of air pressure

lously clean. The containers may be new (unused) tinned cans or glass jars. Metals such as copper, bronze, and brass must, under no circumstances, be allowed to come in contact with samples. Glass containers are cleaned with cleaning solution, thoroughly rinsed with distilled water, and dried by heat. Mason fruit jars with rubber gaskets are satisfactory, but all parts must be cleaned as described above. Jars with plastic or enameled tops, or covers containing paper liners, are not recommended.

Samples are removed from tierces or similar packages with a stainless steel trier (butter type, 18 to 36 inches long) which has previously been well cleaned with soap and water, thoroughly rinsed with distilled water, and completely dried by heat or with new paper towel. Samples must be so taken that none of the shortening will be taken less than 2 inches from the wall of the container or from the surface.

Samples must be packed and transported to the destination laboratory in such a way that they will arrive in a solid state. Samples that have been melted or partially melted at any time are not to be used.

Porcelain or stainless steel spatulas are used in the laboratory for removing the test portion from the container. Clean the spatula between samples in a stream of hot water and wipe with paper towel. Select a portion of the test, after removing the top surface and discarding, in such a way as to avoid taking any fat which has been in contact with the sample container. Place in a beaker which has been cleaned with cleaning solution, thoroughly rinsed with distilled water, and dried with heat. Completely melt the contents of the beaker but do not allow the temperature to rise more than a few degrees above the melting point of the sample.

AERATION OF SAMPLE. Caution. The control of temperature, maintenance of absolute cleanliness, and elimination of any chance of contamination cannot be overemphasized. If these factors are not well guarded, the results are likely to be incorrect.

Pour 20 ml. of liquefied sample into each of three 200-mm. test tubes, which for convenience should be calibrated at the 20-ml. level. Place one of the tubes in the oil bath, which has previously been brought to the desired temperature, and make necessary connections to start the air flow. Record time of starting. Stopper the second and third portions and hold at a cool temperature until the time arrives for their incubation. At the desired time after starting the first portion, start the second portion of the sample and similarly the third portion.

The time spacing of tubes is conveniently regulated as follows:

Keeping Time, Hours	Space Tubes
0-16	1 hour apart
16-32	2 hours apart
32-50	3 hours apart
Over 50	4 hours apart

The tubes must be maintained at $208^{\circ} = 0.5^{\circ} \text{ F. (} 97.7^{\circ} \text{ C.)}$ and inspected regularly to be sure that the air is flowing properly. Incubations may be conducted in two ways, depending on whether the exact keeping time is desired or whether a given minimum keeping time is to be met.

For Exact Keeping Time. Incubation is continued to definite peroxide levels corresponding to the point of inception of rancidity. These levels are:

Lard and oleo oil	20 me. of peroxide per kg. of fat
Hydrogenation and blended shortening	100 me. of peroxide per kg. of fat

It is convenient, with long keeping samples, to run a "pilot tube" 12 to 15 hours in advance of the three test tubes to get an approximation of the keeping value. Successive small samples (1 gram) may be withdrawn from this tube to test for peroxide value as the rancid point is approached. This should not be continued after a total of 5 grams have been removed from a single tube. The pilot tube serves a twofold purpose; (1) it enables the operator to carry the incubation safely overnight, and (2) it eliminates most of the guesswork from choosing the time for making titrations.

Note. After a little practice, the odor of the air from the exhaust tube can be taken as a good indicator of the end point but because of the large personal variation in organoleptic testing, the odor is not accepted as final.

It is desirable to incubate samples continuously until they have reached a stage at which, if continued throughout the night, rancidity will have developed before morning. When this stage has been reached, the tubes are removed from the bath and immediately chilled. They must be held in the chilled condition until incubation under constant supervision can be resumed.

All tubes are titrated when the end point has been reached. Results are reported in terms of hours to the nearest hour at which the peroxide value just fails to exceed 20 or 100 me. as the case may be.

Example. Hydrogenated or Blended Shortening

Tube No.	Hours	Me. of Peroxide per Kg.
1	120	110
2	116	90
3	112	80

It will be seen from a simple graph of the results that at the end of 118 hours the peroxide value just reaches 100 me. of peroxide per kg. Report 118 hours.

For Minimum Keeping Time. To determine whether a sample meets a specified keeping time requirement it is necessary to conduct the incubation of the three tubes as outlined above for exact keeping time, except that the incubation may be interrupted when the specified time has elapsed. The pilot tube is not needed if the operator arranges his work so as to be able to stop the incubation at the proper time.

DETERMINATION OF PEROXIDES. Weigh 5 grams (± 0.05) of sample into a 200 to 300-cc. Erlenmeyer flask and dissolve in 30 ml. of the acetic acid-chloroform. Add 0.5 ml. of saturated potassium iodide solution and shake until the solution becomes clear. After 2 minutes, add 30 ml. of distilled water and titrate with standard sodium thiosulfate. Add starch indicator when near the end point. The flask should be shaken vigorously near the end of the titration to liberate all the iodine from the chloroform layer. The number of milliequivalents of peroxide present per 1000 grams of sample is calculated from the amount of sodium thiosulfate solution required to titrate the liberated iodine.

Milliequivalents of peroxide per 1000 grams of sample equal:

$$\frac{\text{Titration (ml.)} \times \text{normality} \times 1000}{\text{wt. of sample (5 grams)}}$$

A blank titration should be made daily on all reagents and should never exceed 0.1 ml. of sodium thiosulfate.

CLEANING PROCEDURE. Wash the used tubes from the stability determinations with soap and water and rinse with tap water. Place on a test-tube rack and nearly fill with cleaning solution. Wash off the air-inlet and -outlet assembly, including the rubber stopper, with ethyl ether or light gasoline before washing with soap and water. This solvent wash is necessary on the inside of the glass tubes; since the small diameter makes it impossible to scour the inside with a brush. After the soap and water wash and several rinses, place the inlet and outlet assembly in the test tubes containing cleaning solution. By means of a rubber tube and a vacuum line draw some of the cleaning solution up into the air-inlet and air-outlet tubes and allow to drain back. Repeat this several times until a film of cleaning solution adheres evenly to the inside of the glass tubes, then allow the air delivery tubes to stand overnight in contact with the cleaning solution within the test tubes.

After soaking as described, pour off the cleaning solution, rinse all parts at least four times with warm tap water, and then allow the tubes to stand for at least 2 hours in tap water. Follow with at least six rinses of distilled water. Dry the test tubes in an air oven at 105° C. Dry the air-inlet and -outlet assembly in a vacuum oven at about 60° C. A low temperature is used to prevent softening of the rubber stoppers. Inspect all glass parts minutely and discard everything not absolutely clean. The units are then ready for use. Protect all glass parts in a dustproof cabinet until ready to use.

MAINTENANCE OF EQUIPMENT. All equipment and washing solutions must be kept clean. Oil and water baths must be kept at proper levels. The water should be 1.5 inches from the top and the oil 2 inches from the top. Use distilled water to prevent scale formation and pure white mineral oil.

Keep the capillary tubes clean to ensure proper air passage. A very fine wire is convenient for this purpose.

Do not use rubber tubing or rubber stoppers that have started to crack or have become sticky from the heat. Clean all new rubber thoroughly before using. Be sure that the ends of the rubber tubing do not pick up any oil from contact with the bath.

The bath is easily cleaned by wiping with a cloth to which has been added a little carbon tetrachloride.

INSOLUBLE BROMIDES (HEXABROMIDE TEST)

The insoluble bromide test has stimulated considerable interest this year because of its application to the evaluation of soaps intended for use in the production of synthetic rubber. Some time ago this committee did some work in an attempt to make this

test quantitative. While those data were not published, they can be summarized by the statement that the results had no quantitative significance. Several of the members, especially the Southern Regional Research Laboratory, made a very thorough investigation and concluded that the method and several modifications of this method were unreliable.

This time interest has been in the qualitative aspects of the hexabromide test. The method generally used is as follows:

PROCEDURE. Add approximately 1 gram (if solid) or 1 ml. (if liquid) fatty acids to 25 ml. of acetic acid-ether solvent (4 parts by volume of ethyl ether to 1 part of glacial acetic acid) in a Soxhlet flask. Cool to 0° to 5° C. and hold at this temperature for 2 hours. If a precipitate forms, filter the solution cool through a small filter paper into another cool Soxhlet flask which has been rinsed with acetic acid-ether solvent. If there is no precipitate, proceed immediately to the next step.

Add bromine to the contents of the flask from a dropping bottle until a deep red color is imparted to the mixture. Do this under a hood. Cool the mixture again to 0° to 5° C. and hold it in this range for an additional 4 hours. Examine the contents of the flask again. If a heavy precipitate has formed, report as "Positive". If the solution is clear and brilliant, report as "Negative".

Investigation of the details of this procedure has brought out some of the following facts.

a. The quantity of bromine used is of some significance in determining whether a precipitate will form:

Sample	Color of Solution after Adding Bromine	Precipitate
Tallow a	Orange	Positive
Tallow b	Orange	Negative
White grease a	Orange	Positive
White grease b	Orange	Positive
Tallow a	Deep red	Negative
Tallow b	Deep red	Negative
White grease a	Deep red	Negative
White grease b	Deep red	Negative

The melting points of the precipitates obtained from several samples of known purity were:

Tallow glycerides	60- 65° C.
Tallow fatty acids	60° C.
White grease glycerides	65- 70° C.
Soybean glycerides	135-140° C.
Soybean fatty acids	176-180° C.

The melting point data suggest that the precipitates obtained from tallows and greases are not hexabromides.

b. Spectrographic determinations of linolenic acid were made on several samples and these data were used to determine the minimum sensitivity of the insoluble bromide test:

Sample	% Linolenic Acid	
	Triglycerides	Fatty acids ^a
Tallow 1	0.6	0.9
Tallow 2	0.8	1.1
Tallow 3	1.2	1.1
White grease 1	1.7	1.6
White grease 2	1.7	1.9
Soybean oil	6.4	7.2

^a Fatty acids were separated according to A.O.C.S. method for the titer determination.

These data and Table II indicate that the insoluble bromide test is not reliable for quantities of linolenic acid below 2 to 3%.

It has been suggested that when the fatty acids are separated they should be protected at all times by a blanket of nitrogen and that any heating should be done only in vacuo. A few samples of soap were sent out, with the following results:

Laboratory	Sample 1 NP P	Sample 2 NP P	Sample 3 NP P	Sample 4 NP P
7	Neg. Neg.	Neg. Neg.	Neg. Neg.	Neg. Neg.
2	Neg. Trace	Neg. Pos.	Neg. Trace	Neg. Pos.
1	Neg. Pos.	Neg. Pos.	Neg. Pos.	Neg. Pos.

Collaborator .. Pos. .. Pos. .. Pos. .. Pos.

NP. Not protected. P. Protected.

In no case were the positive results confirmed by a melting point. The literature indicates that the melting point of the hexabromide derivative of linolenic acid is approximately 180° C.

The indications are that a positive test should always be confirmed by a melting point of the precipitate.

There is some evidence that in the separation of fatty acids from soap, the procedure of splitting the fatty acids may have some significance. Spectrographic determinations were made of linolenic and linoleic acids on several samples of pure soap, and fatty acids separated from these soaps. The fatty acids were separated according to the A.O.C.S. method:

Sample	Linolenic Acid		Linoleic Acid		Total	
	Soap	Fatty acid	Soap	Fatty acid	Soap	Fatty acid
1	0.87	0.50	2.20	2.56	3.07	3.06
2	0.52	0.29	2.68	2.97	3.20	3.26
3	0.51	0.51	2.14	2.47	2.65	2.98

All results calculated to the same basis for comparison.

While these differences are significant from the viewpoint of

Table II. Mixture of Palmitic and Soybean Oil Acids

% Linolenic Acid	Precipitate Formed with Insoluble Bromide Test
1.1	Negative
1.8	Negative
3.0	Positive
4.0	Positive

Table III. Congeal Point

Laboratory	A.O.C.S. Method Cloud Congeal	Proposed Method Cloud Congeal
Sample 1		
2	31.4	32.0
12
4	30.2	30.7
13
7	29.6	30.4
Sample 2		
2	30.9	31.3
12
4
13
7	28.8	29.6
Sample 3		
2	32.1	32.2
12
4
13
7	28.0	28.6
Sample 10		
2	33.2	33.6
12	32.0	32.8
4	30.7	31.2
13
7	30.1	31.3
Sample 11		
2	34.2	34.6
12	34.2	35.0
4	34.4	34.7
13
7	30.6	31.8
Sample 12		
2	30.7	30.8
12	29.0	31.2
4	27.2	29.2
13
7	27.1	30.6
Sample 13		
2	24.1	24.2
12	24.0	24.2
4	17.6	18.4
13
7	22.0	22.7
Sample 14		
2	30.2	30.8
12	30.1	31.0
4	27.9	28.2
13
7	28.6	29.4
Sample 15		
2	27.8	27.9
12	27.5	28.6
4	23.9	26.1
13
7	28.6	29.4

accurate analyses, they are not so in terms of the sensitivity of the insoluble bromide test. Further work is required before the hexabromide test can be accepted with any degree of certainty. Motion was made, seconded, and carried that no further work be done on this hexabromide method because it has been demonstrated to be inexact and unreliable.

Note. Spectrographic determinations were made by Drs. Urbain, Kauffman, and Lingard in the Research Laboratories of Swift & Company.

CONGEAL POINT

The committee has done considerable work in an attempt to standardize some method for the congeal point. It was found that the methods in use in the industry were much alike in principle but varied in detail. Therefore, these details were standardized and samples submitted to several committee members. The method in general was as follows: The temperatures, apparatus, and lighting were standardized and a definite quantity of sample was stirred to the clouding point in a water-cooled bath. The sample was then transferred to an air-cooled bath, and the thermometer fixed in one position and allowed to remain stationary until the temperature increased to a maximum.

It has been the practice of some to use a congeal point procedure which is according to the A.O.C.S. titer method except that the test is made on the glycerides instead of on the fatty acids. The samples sent out were run by both methods. Some of the results are shown in Table III.

It is apparent that neither procedure is satisfactory. Further work is planned.

UNSAAPONIFIABLE MATTER

Time has not permitted much work on the unsaponifiable method, although two samples were sent out. These samples were run by the official A.O.C.S. method, the continuous extraction method (3), and the English S.P.A. method (1). The results are shown below:

Laboratory	Continuous Extraction		Official A.O.C.S.		S.P.A.	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
14	1.49	1.44	1.22	1.18	1.85	1.81
8	1.16	1.10	1.10	1.28
15	1.29	1.02	1.21	0.95
16	1.22	1.19	1.25	1.22
6	1.31	1.36	1.25	1.27
7	1.18	1.27	1.05	1.06
	1.06	1.23	1.10	1.04

Dr. Fitelson of this committee, who is referee on oil, fats, and waxes for the A.O.A.C., comments as follows:

We are now conducting A.O.A.C. collaborative work on methods for unsaponifiable matter, and it appears, from the results obtained so far, that the S.P.A. method will be recommended as the official A.O.A.C. method. Although the continuous extraction method may be satisfactory for many fats, we are convinced that the S.P.A. method has wider applicability and gives higher and more accurate results.

Two members reported no significant differences between results when the extract was dried according to the A.O.C.S. official procedure and in a vacuum oven at 80° C., providing the latter was continued to constant weight. Additional work is required.

TABLE OF INTERPRETATION OF F.A.C. COLOR STANDARDS

About one year ago this committee published a table indicating the visual relationship in intensity between the F.A.C. color standards. It is now recommended that this table be incorporated in the method for the evaluation of color using the F.A.C. color standards (Table IV).

F.A.C. COLOR COMPARATOR

The committee has been considering the adoption of some instrument which would furnish standard lighting conditions and

Table IV. Relationship between F.A.C. Color Standards

F.A.C. Tube No.	Tubes Listed Below Are Equal to or Lighter Than the Corresponding Tube in the Left-Hand Column
1	1
3	1, 3
5	1, 3, 5
7	1, 3, 5, 7
9	1, 3, 5, 7, 9
11	1, 3, 5, 7, 9, 11
11A	1, 3, 5, 7, 9, 11, 13, 11A
11B	1, 3, 5, 7, 9, 11, 13, 11A, 11B
11C	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 11A, 11B, 11C
13	1, 3, 5, 7, 9, 11, 13, 11A
15	1, 3, 5, 7, 9, 11, 13, 15, 11A, 11B
17	1, 3, 5, 7, 9, 11, 13, 15, 17, 11A, 11B
19	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 11A, 11B, 11C
21	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 31, 33, 11A, 11B, 11C
23	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 31, 33, 35, 11A, 11B, 11C
25	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 31, 33, 35, 37, 11A, 11B, 11C
27	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 31, 33, 35, 37, 39, 11A, 11B, 11C
29	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 11A, 11B, 11C
31	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 31, 11A, 11B, 11C
33	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 31, 33, 11A, 11B, 11C
35	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 31, 33, 35, 11A, 11B, 11C
37	1, 3, 5, 7, 9, 11, 13, 17, 19, 21, 23, 25, 31, 33, 35, 37, 11A, 11B, 11C
39	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 31, 33, 35, 37, 39, 11A, 11B, 11C
41	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 31, 33, 35, 37, 39, 41, 11A, 11B, 11C
43	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 11A, 11B, 11C
45	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45, 11A, 11B, 11C

a uniform method of reading F.A.C. colors. One such instrument was constructed by the Fisher Scientific Co., Pittsburgh, Pa., according to the design of Whyte (5) and circulated to several members of the committee. This model was not satisfactory. Mr. Whyte then submitted an improved modification of his original instrument which was also sent to several members of the committee. The principal objections raised to this instrument were that the sample and standards are not viewed under identical conditions of illumination, and that light from standards other than the one selected for the comparison may reach the observer's eye. The committee plans to go further in its search to find a suitable instrument with which to read F.A.C. colors.

TITER STIRRING DEVICE

The committee examined a mechanical stirring device for titers which was made by the Fisher Scientific Co., Pittsburgh, Pa. This unit was motor-driven and permitted vertical stirring of three samples of fatty acids at a time. With a few exceptions, the apparatus permitted stirring as required by the A.O.C.S. method. The ratio of stirring did not exactly conform to requirements. The Transite top of each individual bath needed redesigning so as to allow easy addition or removal of water. Several samples were stirred in this instrument and the results obtained compared with figures obtained by the official method. The agreement was satisfactory. Several minor suggestions were made, all of which were passed on to the Fisher Scientific Co.

MISCELLANEOUS

The committee has been requested to study some procedure by which better to evaluate fats for soap production with respect to color. This problem is being considered but the committee has no data to present now.

The following people have collaborated with the committee in some part of this program: G. W. Agee, J. J. Ganucheau, and B. W. Beadle.

LITERATURE CITED

- (1) *Analyst*, 58, 203 (1933).
- (2) *Oil & Soap*, 10, 105 (1933).
- (3) *Ibid.*, 15, 287 (1938).
- (4) Riemenschneider, Turer, and Speck, *Ibid.*, 20, 169 (1943).
- (5) Whyte, *Ibid.*, 19, 199 (1942).



Uniformity of temperature, $\pm 0.01^\circ\text{C}$. Temperature range from several degrees above cooling water to 60°C .

● This water bath is applicable to all laboratory operations requiring close regulation of temperature.

The central circulating and heating tower applies heat at the point of most rapid circulation of water. This efficient application of heat combined with the complete and rapid circulation of the bath medium eliminates stratification and creation of permanent gradients. Temperature uniformity throughout all areas of the bath is within $\pm 0.01^\circ\text{C}$.

Of the total surface area of the bath which is approximately 190 square inches, only 15 square inches is occupied by control equipment. All remaining space is entirely free for insertion of vessels.

Except for the inlet and outlet tubes of the cooling coil, the wall of the Pyrex glass container is free of obstructions. Unrestricted observation of immersed vessels and measurement of capillary rise, liquid flow, etc., can be made easily and accurately.

A cooling coil is supplied and should be used when operating temperatures are less than 3°C above average room temperature. A compact constant water level device attached to the wall of the container permits rapid overflow and replacement of water displaced by immersed apparatus.

Both central tower and cooling coil are easily removed for cleaning Pyrex glass container. The central circulating and heating tower merely lifts out of the bath.

S-84805 WATER BATH—Constant Temperature, Full Visibility, 0.01° , Sargent, (Patent No. 2,037,993) Consisting of container, the central circulating and heating unit with motor, the Sargent mercurial thermoregulator, a cooling coil and constant level device, the Sargent zero current relay unit complete with cord and plug for connection to standard outlet and with cable for connection to the water bath. Temperature range from several degrees above that of the cooling water to about 60°C . Diameter, 16 inches; height, 10 inches; water depth, $9\frac{1}{2}$ inches; temperature uniformity, $\pm 0.01^\circ\text{C}$. For operation from 115 volt, 60 cycle single phase circuits\$150.00

S-84815 Ditto. But for 115 volt D.C. circuits\$155.00

S-84825 Ditto. But for 230 volt, 60 cycle, single phase circuits.....\$150.00

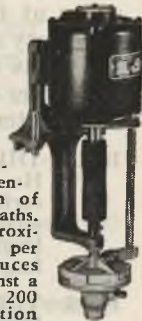
S-84835 Ditto. But for 230 volt, D.C. circuits.....\$155.00

ACCESSORIES

S-84847 CONSTANT HEAD DEVICE. A simple, inexpensive unit to provide constant rate of flow of water passing through the cooling coil of a bath, thus minimizing variations in temperature uniformity caused by fluctuation in pressure of cooling water. Made entirely of Pyrex glass. Each\$6.00



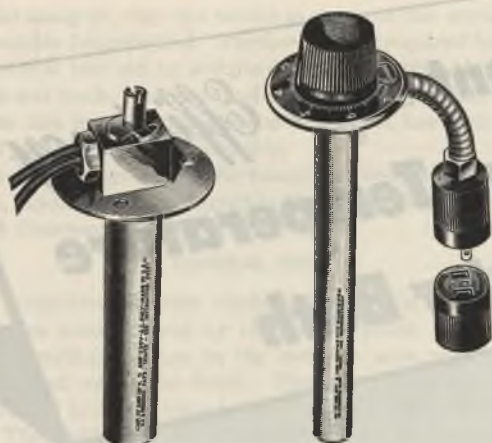
S-71565 PUMP—Water Circulating. For circulating temperature controlling water from bath through water jacketed apparatus. Designed for suspension from rim of Sargent water baths. Flow rate, approximately 4 liters per minute. Produces circulation against a water head of 200 cm. For operation from 115 volt, A.C. 60 cycle circuits. Each\$45.00



E. H. SARGENT & CO., 155-165 East Superior Street, Chicago 11, Illinois

Michigan Division: 1959 East Jefferson, Detroit 7, Michigan

S A R G E N T
 S C I E N T I F I C L A B O R A T O R Y S U P P L I E S



16813

16814

WIDE-RANGE THERMOREGULATORS

Based on an entirely new principle, this "Thermoswitch" offers extreme sensitivity, wide range, rugged construction, and moderate price. It is recommended for controlling temperatures to 0.1° F in incubators, ovens, water baths, etc.

It is constructed with two silver contacts mounted on, but electrically insulated from, curved nickel-iron struts of low expansion coefficient. This assembly is then suspended under tension in a seamless metal tube. Changes in temperature cause the shell to expand or contract and to exercise more or less tension on the struts, causing the contacts to make or break.

The separation of the contacts is approximately 20 times the lineal expansion of the outer shell, resulting in a slow-break action, free from vibration. The contacts are sealed within the shell, eliminating any trouble from moisture, dirt, or tampering.

The "Thermoswitch" covers a range from -100 to $+400^{\circ}$ F. Adjustment is made by turning the screw at the top. For A. C., a relay is seldom necessary since the contact rating is 10 amperes at 115 volts or 5 amperes at 230 volts. A suitable condenser should be used for D. C. The contacts close on temperature decrease.

16813—THERMOREGULATOR, Flange Head Type. Has three tapped holes for mounting on any flat surface by means of screws. The shell can be inserted through a $5/8$ " diameter hole. Approximate length below flange head, $3 3/8$ ". Fitted with 14" long asbestos impregnated lead wire. 6.00

16814—THERMOREGULATOR, All-Purpose Type. The head is fitted with dial and knob and an armored cable is provided to permit ready disconnection of the electrical load. Immersion length approximately $7 3/4$ "; diameter $5/8$ "; with 3" armored cable and midget connector. 10.00

**WILL CORPORATION, ROCHESTER,
NEW YORK**

Offices and Warehouses

BUFFALO APPARATUS CORP., Buffalo, N. Y.

WILL CORPORATION, 596 Broadway, New York City

HELLIGE COLORIMETERS

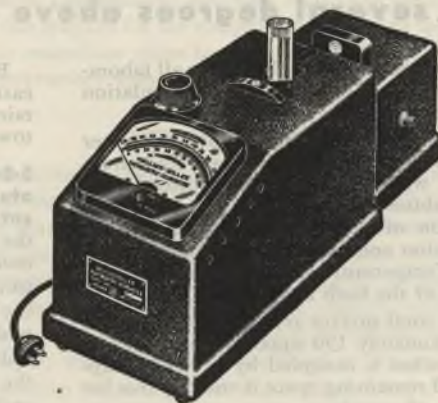
for
VISUAL
and
PHOTOELECTRIC
COLORIMETRY



**DIRECT
READER
HELLIGE-
DUBOSCO
COLORIMETER**

EMBODIES
AN UNUSUAL
COMBINATION
OF 10
STRIKING
FEATURES

*Write for Bulletin
250-A, Dept. I.*



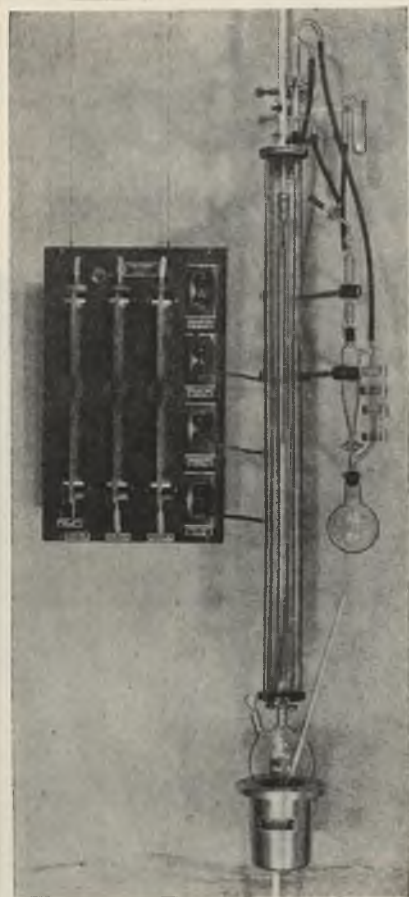
**HELLIGE - DILLER
PHOTOELECTRIC COLORIMETER**

A self-contained colorimeter emphasizing the three primary considerations of accuracy, foolproofness and universality. This precise instrument for accurate and ALWAYS reproducible colorimetric determinations has already proved to be the solution of numerous extraordinary and difficult colorimetric problems. No standards are required.

Write for Bulletin 400, Dept. I.

**HELLIGE
INCORPORATED**

3718 Northern Blvd. Long Island City 1, N. Y.



PRECISE LABORATORY FRACTIONATION

An efficient and versatile laboratory fractionation column assembly with a new method of adiabatic temperature control for precise fractionation of many types of organic liquid mixtures.

Covered by United States and foreign patents.

FEATURES:

1. Fractionation efficiency up to 50 theoretical plates.
2. Fractionation charges from 2 cc. to 5000 cc.
3. Temperature range from room temperature to 400°C. (752°F.).
4. New precision device for adiabatic temperature control.
5. Atmospheric or vacuum fractionation.
6. Three interchangeable fractionating columns.
7. Improved spiral packing.
8. Rapid fractionation with complete visibility.
9. Easily operated with a minimum of experience.

For additional experimental results, method of operation, and details, see article, "Efficient and Versatile Laboratory Fractionation Column Assembly," by F. Todd, *Ind. Eng. Chem., Anal. Ed., Volume 17, page 175, 1945.*

Write for reprint and TECHNICAL BULLETIN 100 for detailed information and prices.

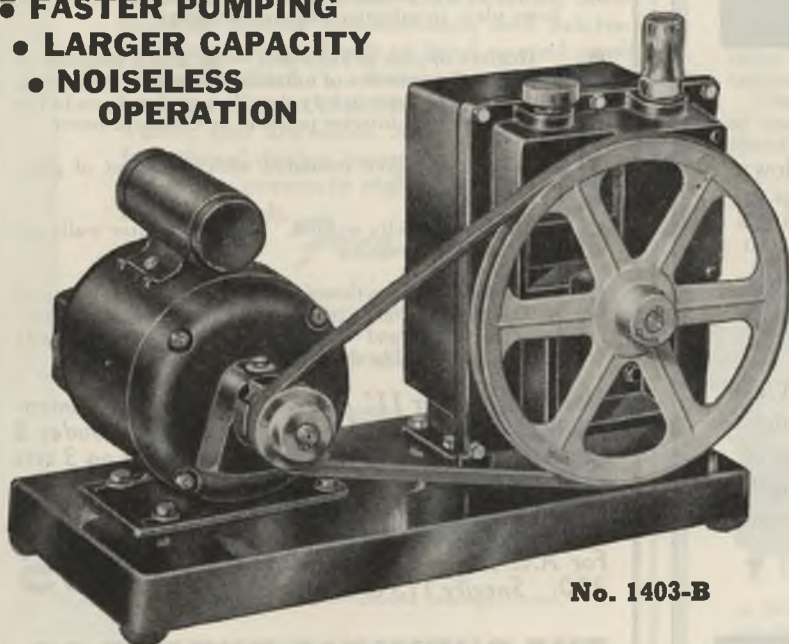
TODD SCIENTIFIC GLASS APPARATUS CO.

Designers and manufacturers of special scientific laboratory apparatus.

DREXEL HILL, PA.

Better Performance--Greater Durability

- FASTER PUMPING
- LARGER CAPACITY
- NOISELESS OPERATION



No. 1403-B

WELCH DUO-SEAL VACUUM PUMPS

A matchless Fore-Pump for diffusion and molecular-drag pumps. Perfectly suited for distillation.

VACUUM GUARANTEED

0.005 mm Hg, or 5 microns.

FREE AIR CAPACITY

1700 ml per second (102 liters per minute)
—510 ml per second at 5 microns.

OPERATES AT 375 R.P.M.

ONLY 1400 ml (3 pints) OIL REQUIRED

Write for FREE 32-page booklet on Welch Duo-Seal Pumps and Vacuum Techniques.



Cat. No. 1403 Duo-Seal Vacuum Pump..... \$100.00

Cat. No. 1403-B With 1/2 H.P. 110 Volt A.C. Motor mounted on Base..... \$145.00

W. M. Welch Scientific Company
1518 Sedgwick Street Established 1880 Chicago 10, Illinois, U.S.A.

ABSORPTION CELLS



The Recognized Standard
of Dimensional Precision

★

Fused—Not Cemented

Windows and bodies are fused into one continuous mass, without joints, cement, or flux. Windows can not become detached.



Available in
Pyrex
Corex "D"
Fused Quartz

12 Styles
373
Standard
Sizes



- Parallelism of Faces of Each Window: ± 5 minutes.
- Windows Flat Over Entire Area to Within 6 Wavelengths.
- Parallelism of Liquid-Glass Interfaces: ± 0.025 to ± 0.01 mm.
- Inside Length (Between Faces of Windows) Held to Unusually Close Tolerances: From $\pm 1\%$ to ± 0.005 mm. of nominal length. Actual mean length marked on each cell to nearest 0.001 mm.

★ Fully Described in Bulletin P-2130 ★

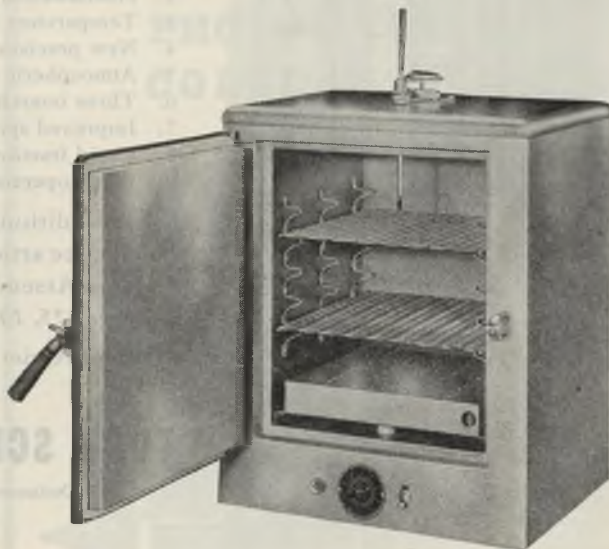
AMERICAN INSTRUMENT CO.

8010 GEORGIA AVENUE • SILVER SPRING, MARYLAND

Theelco

UTILITY OVEN

... the finest electrically heated constant temperature laboratory oven in the moderate price field ...



Note these Superb Features

- 1 Inherent sensitivity of sealed hydraulic thermostat plus or minus $\frac{1}{2}^{\circ}$ C. Fully enclosed silver contact points. No open sparking or arcing.
- 2 Nickel-chromium heating coils on asbestos refractories, in a separate compartment, covered by a diffuser plate to safeguard against drippage.
- 3 Heaters operate at black-heat — an added measure of safety in the presence of inflammable gases. Self-opening latch pulls door tightly shut, but springs open in the event of sudden interior pressure or explosive burst.
- 4 Cabinet and door insulated with a blanket of glass wool.
- 5 All-metal, rigidly welded. Inner and outer walls are rust-resisting steel.
- 6 Fresh air enters through intake port at bottom of oven, passes through heater bank, into working chamber; is discharged through ceiling ports and exits through adjustable shutter.

Working chamber 11" x 11" x 11". Overall dimensions 16 $\frac{1}{2}$ " wide, 16" deep, 25" high. Includes 2 latticed metal shelves adjustable for height on 3 sets of brackets to permit pulling half-way out; thermometer holder; ventilating shutter, hazard-safe door latch, Neon pilot lamp, cord and plug. For A.C. single phase, or D.C. Wattage, **\$85** 300. Specify 115 or 230 volts.....

THE CHEMICAL RUBBER CO.

Scientific Equipment, Analytical Chemicals, Laboratory Supplies
HANDBOOK OF CHEMISTRY AND PHYSICS

2310 Superior Ave. N. E. • Cleveland 14, Ohio

"The Fountain of Youth"
FOR YOUR COMPANY



...technical research properly organized for profit!"

It really pays to give your research men the best in laboratory furniture. For, as you surely know, a well-equipped laboratory pays for itself over and over again. Both in approved products at lower production costs and in developing profitable new products.

In laboratory furniture, the best means Steelab — the fireproof furniture with exclusive lock-jointed construction, ball-bearing drawer suspensions, and micro-leveling device. Built of lead coated copper alloy steel . . . finished with enamel highly resistant to acids, alkalis, solvents, water, and abrasion. An achievement in functional design, every Steelab unit provides the precisely right stage for profitable research.

Free

Send for new Catalogue and Manual — over 224 pages and 800 illustrations, in which you find ways to:

- (1) Plan and lay out your own laboratory.
- (2) Save time and money in setting up your laboratory.
- (3) Help you solve laboratory equipment problems.
- (4) Choose the proper scientifically designed, precision built laboratory equipment.



Send for your copy of this valuable catalogue today.

LABORATORY FURNITURE CO., INC.

Manufacturers and Engineers of Scientific Laboratory Equipment for Over a Quarter Century

37-18 Northern Boulevard, Long Island City, N.Y.

then pioneers . . . now leaders

ACCELERATED TESTING
for
WEATHERING
and FADING
OF MATERIALS



ATLAS TWIN-ARC WEATHER-OMETER

... twice the speed of single arc machine

Faithfully duplicates the combined weathering effects of sunlight, rain, heavy dew and thermal shock; accelerated to reduce years of actual weathering to a few days of testing.

The new Twin-Arc Weather-Ometer is equipped to take large size specimens in order to meet the new Federal Specifications demanding accelerated weathering tests. Full automatic control of light and water periods is provided by the Atlas cycle timer unit which can be set to meet standard and special requirements of weathering tests. A direct reading thermal regulator, automatic shut-off switch and a running time meter are included as standard equipment. After setting exposure cycles on the control panel, the Weather-Ometer can be safely left in continuous operation overnight without attention except to replace carbons once in 24 hours.

The Atlas Weather-Ometer proves the durability of materials under exact conditions of weathering found in actual use in outdoor exposure.

ATLAS FADE-OMETER



The recognized standard testing machine for determining the fastness to light of any material or finishes. Specimens are rotated around the Atlas Enclosed Violet Arc — the closest approach to natural sunlight — in masked holders. Automatic temperature control to within $\pm 3^\circ$ F. and humidity regulated by a constant reservoir according to requirements of tests. Operation is completely automatic without attention from operator; can be left in continuous operation overnight.

★ Originators and sole manufacturers of accelerated testing devices for a quarter of a century. The Atlas Fade-Ometer, Weather-Ometer, Launder-Ometer are the accepted standard accelerated testing machines all over the world.

ATLAS ELECTRIC DEVICES CO.

361 West Superior Street, Chicago 10, Illinois

LaMotte Testing Equipment

*to Control Corrosion
in Your Plant*



Conservation of materials from corrosion is more important today than ever before. The LaMotte Research Department has developed LaMotte pH, chlorine and other corrosion control testing equipment to assist in solving this problem. Write for our Special Corrosion Control Report.

LaMotte Chemical Products Co.

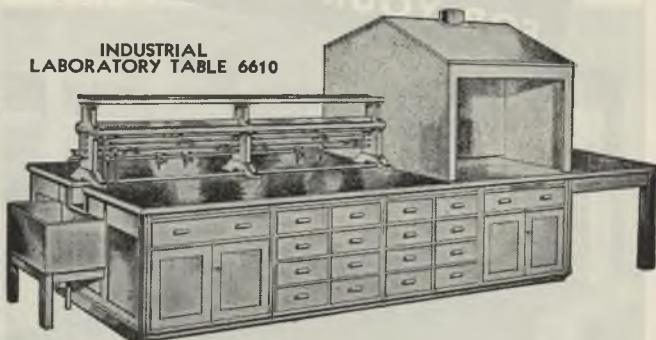
Dept. "F," Towson 4

Baltimore, Md.

PETERSON'S 50 YEARS OF QUALITY

*Supports
Your Judgment*

INDUSTRIAL
LABORATORY TABLE 6610

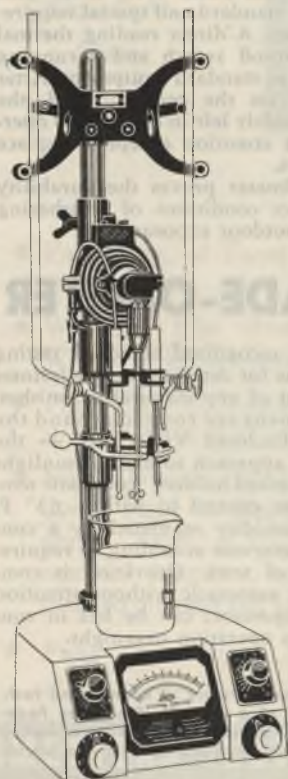


Whenever you specify Peterson Laboratory furniture you know your judgment is supported by the experience of the concerns in the field . . . plus the fact that you cannot go wrong on a make that has maintained a reputation for quality for half a century!

LEONARD PETERSON & CO., Inc.

1222-34 FULLERTON AVE.

CHICAGO 14, U. S. A.



Made in U. S. A.

Leitz

G & D

ELECTRO-TITRATOR

A universal Electro-Titrator using a highly stable and sensitive voltmeter circuit designed by Dr. R. L. Garman and Dr. M. E. Droz for determinations of end-points in electrometric neutralization titrations (including pH determinations), oxidation-reduction titrations, and precipitation titrations.

Some of its outstanding advantages are:

1. Variable sensitivity up to a maximum of 40 millivolts per inch of needle deflection.
2. Battery operated, uses as little as 0.25 watts; fluctuations in the power supply are completely eliminated.
3. Direct reading meter with $3\frac{3}{8}$ " linear scale permits continuous readings of voltage changes.
4. Compact, sturdy design.

Used for control work and research work in leading laboratories throughout the country.

E. LEITZ, Inc., 730 Fifth Ave., New York 19, N. Y.

Please send us ELECTRO-TITRATOR pamphlet No. 1283

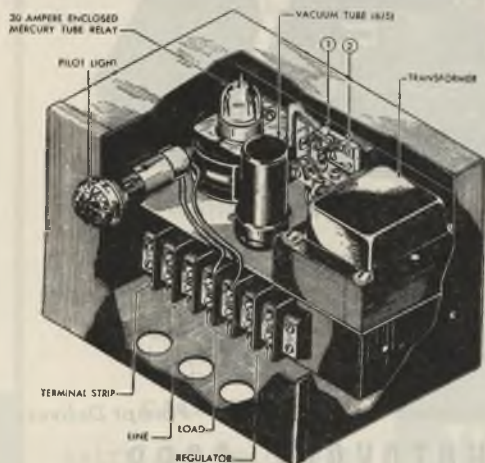
(Dept. IEC-EE)

Name

Address

City.....State.....

The Modern ELECTRONIC RELAY



Advantages of this new modern electronic relay are years ahead of the usual magnetic relay. For temperature control or other applications in the laboratory or plant, it has many outstanding features.

- Does not spark on "make" or "break."
- Because regulator contacts and mercury surface are kept clean, there's no fouling or erosion.
- Regulators will last indefinitely.
- Gives increased sensitivity and better performance with any of the usual bi-metallic regulators. No sticking or pitting.
- Is applicable wherever extremely light contact pressures on the regulator or pilot device must control operation of a heater, motor, or other electrical unit.
- Is safe, silent and simple to install.
- Will operate at many times the sensitivity of ordinary relays.
- Will handle up to 30 amperes on load circuit.
- Is equipped with convenient pilot light.
- Only two micro amperes (1/500,000 amp.) will operate the relay through the regulator circuit.

Relay is supplied "normally closed." Power is cut off when regulator contacts are closed and vice versa. Operations can be reversed by switching wire connectors 1 and 2 on primary relay.

Catalog No. J40313—Electronic Relay for 110-120 volts, 60 cycle current, **\$39.50**
Dimensions 7" x 5" x 5".....

For current supply other than 110-120 volts—60 cycles, for higher load capacities than 3300 watts or special applications, please inquire.

ARTHUR S. **LAPINE** & COMPANY
LABORATORY APPARATUS & REAGENTS - INDUSTRIAL CHEMICALS

109 W. Hubbard St.,

Chicago 10, Illinois

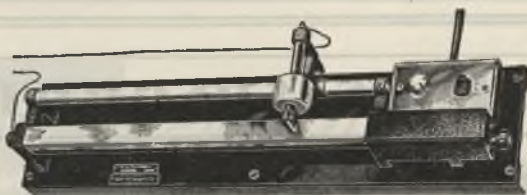
Yes... These Are All PARR INSTRUMENTS

Serving the Engineering Chemist for 45 Years



PARR
Needle Valve

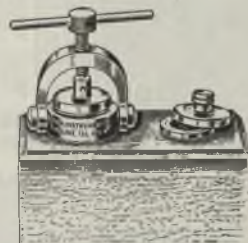
Instruments are only as good as the materials and workmanship that go into them. For 45 years, Parr instruments have been especially designed and produced under specifications of extreme exactness to incorporate the highest available quality of material and workmanship. That's why you're safe in putting your instrument problems squarely up to PARR.



The DENNIS Melting Point Apparatus

PARR INSTRUMENTS
Built For Accuracy
Precision and
Durability

Parr Instruments are modern in design and of sturdy construction — built to give years of service. Take advantage of Parr's 45 years experience in fine instrument manufacture. Familiarize yourself with the many advantages offered by Parr Instruments.



PARR
Micro Bomb

For complete information about PARR Instruments see your dealer or write direct to the factory

PARR INSTRUMENT COMPANY - Moline, Ill.

CHEMICAL AND SCIENTIFIC PORCELAIN WARE



Basic equipment
OF ALL
MODERN TESTING
LABORATORIES

COORS
U.S.A.

COORS PORCELAIN COMPANY
GOLDEN, COLORADO

LUMETRON

Photoelectric COLORIMETER and FLUORESCENCE METER

A high precision instrument of unusual flexibility for all tests involving . . .

TRANSMISSION
FLUORESCENCE
TURBIDITY
U. V. ABSORPTION



Mod. 402EF for determination of Vit. B₁ and B₂

Also

Colorimeters	Densitometers
Reflection Meters	Smoke Meters
Glossmeters	Vitamin A Meters
Continuous-Flow Colorimeters	

Write for Literature

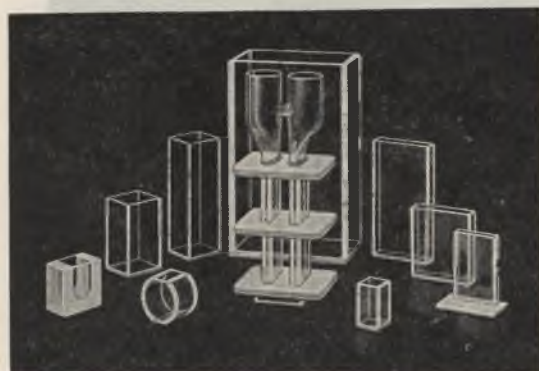
Prompt Delivery

PHOTOVOLT CORP.

95 Madison Ave.

New York 16, N. Y.

GLASS ABSORPTION CELLS



Sole manufacturer in the
★ United States of fused ★
Electrophoresis Cells.

Makers of complete
Electrophoresis Apparatus

Literature sent
Upon Request

OF FINE QUALITY

made by *Klett*

Fused in an electric furnace with cement that is acid, alkali and solvent resistant.

Optical Flat Walls. Many stock sizes are available. Special sizes made to order.

KLETT SCIENTIFIC PRODUCTS

KLETT-SUMMERSON PHOTOELECTRIC COLORIMETERS •
COLORIMETER NEPHELOMETERS • FLUORIMETERS • BIO-
COLORIMETERS • ELECTROPHORESIS APPARATUS •
GLASS STANDARDS • KLETT REAGENTS

Klett

MANUFACTURING CO., 177 East 87th Street, New York, N. Y.



THE SYMBOL OF SATISFACTION IN LABORATORY EQUIPMENT

PLATINUM

CRUCIBLES

WIRE

FOIL

GAUZE

DISHES

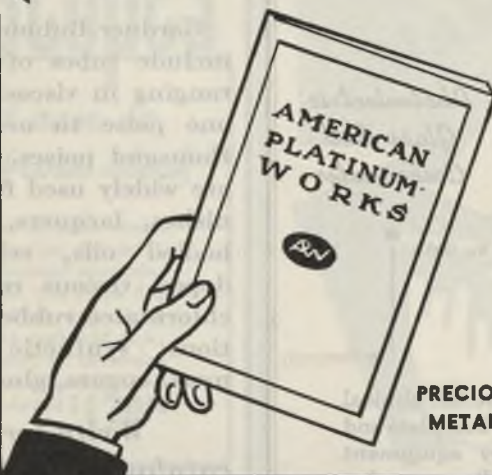
TUBING

SPONGE

BLACK

CALORIDES

SALTS AND SOLUTIONS



SEND for our Catalogue IE-17 listing our standard products for chemical laboratories.

PRECIOUS METALS



SINCE 1875

THE AMERICAN PLATINUM WORKS

N. J. R. R. AVE. at OLIVER ST.

NEWARK 5, N. J.

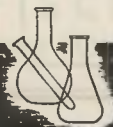
Available NOW!

Order Early to Avoid Disappointment!

- ★ COLEMAN pH ELECTROMETER
..... Model 3 A ..\$180.00
..... Model 3 D ..\$235.00
- ★ COLEMAN UNIVERSAL SPECTRO-
PHOTOMETER..... Model 11... 340.00
- ★ COLEMAN PHOTOFLUOR-
OMETER..... Model 12... 220.00
- ★ WACO SEPARATOR,
for Semi-Micro..... 34.50
- ★ MIDGET MUFFLE FURNACE..... 44.00

Write for new **FREE** Edition of **CURVES** and **REFERENCES**, exact references for newest colorimetric and spectrometric analyses.

Bulletin IE5.



WILKENS-ANDERSON CO.
111 NORTH CANAL STREET • CHICAGO 6, ILLINOIS

STREAMLINED!



New LINDBERG LABORATORY FURNACES

- NEW** in appearance and construction. Design harmonizes with other modern lab equipment.
- NEW** "stepless" control that gives any desired heat within the range of the unit.
- NEW** convenient, manually operated door like those used on industrial furnaces.
- NEW** rugged heating elements, low voltage type — higher operating temperatures — longer life — fewer replacements.

Write for informative bulletin.

Buy More War Bonds

SCHAAR & COMPANY

Complete Laboratory Equipment

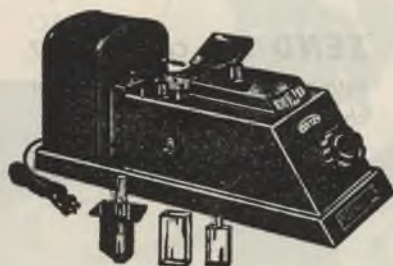
754 WEST LEXINGTON STREET

CHICAGO, ILLINOIS

Klett

Photometers

Klett-Summerson



Photoelectric
Glass Cell
Colorimeter

No. 900-3

For the varied needs of industrial, clinical and agricultural laboratories. Complete and self contained—no accessory equipment necessary. Fused cells for readings on solution depths of 2.5, 10, 20, and 40 mm. Selective light filters available.

The Klett Fluorimeter



No. 2071

Designed for the rapid and accurate determination of thiamin, riboflavin, and other substances which fluoresce in solution. The sensitivity and stability are such that it has been found particularly useful in determining very small amounts of these substances.

To further increase its adaptability a separate circuit and scale is provided for colorimetric determinations.

KLETT SCIENTIFIC PRODUCTS

ELECTROPHORESIS APPARATUS • BIO-COLORIMETERS
GLASS ABSORPTION CELLS • COLORIMETER NEPHELOMETERS • GLASS STANDARDS • KLETT REAGENTS

LITERATURE SENT UPON REQUEST

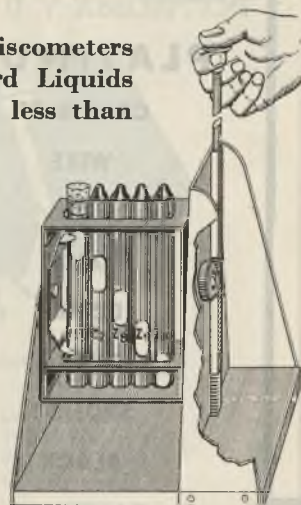
Klett Manufacturing Co.
179 EAST 87TH STREET NEW YORK, N. Y.



**VISCOSITY
READINGS**
*in a few seconds
to a few minutes!*

Gardner Bubble Tube Viscometers include tubes of Standard Liquids ranging in viscosity from less than one poise to over one thousand poises. They are widely used for varnishes, lacquers, heavy bodied oils, cellulosic dopes, viscous resin or chlorinated rubber solutions, synthetic polymers, sugars, glues, etc.

*Write for
catalogs and prices!*



Henry A. Gardner Laboratory, Inc.

APPARATUS DIVISION: 4723 ELM ST., BETHESDA, MD.



FINE ANALYTICAL FILTER PAPERS

SINCE EIGHTEEN FIFTY-SIX



CARL SCHLEICHER & SCHUELL CO.

Plant and Laboratories: SOUTH LEE, MASS.

Executive Offices: 116-118 WEST 14th STREET
NEW YORK, N. Y.



NOW AVAILABLE

without
WPB approval

Microscopes

This model can be delivered from stock

Cat. No. 6325—Bausch & Lomb Model BA-8 Microscope for medical, industrial, hospital and commercial laboratories. Vertical monocular body. Rack and Pinion coarse adjustment, Lever-Type fine adjustment. Built-in mechanical stage, Rack and Pinion substage. Achromatic Objectives: 10X (16 mm) 0.25 N.A., 43X (4 mm) 0.65 N.A., and 97X (1.8 mm) oil immersion 1.25 N.A. Triple nosepiece. Huygenian eyepieces: 5X and 10X. Abbe condenser 1.25 N. A. In hardwood **\$170⁰⁰** carrying case.....

SCHAAR & COMPANY

Complete Laboratory Equipment

748 W. LEXINGTON STREET CHICAGO 7

For RESEARCH ahead

get the

Wide-Range

Flow-Test Kit



YOU can't perceive *ahead of time* what turn your research will take or exactly what flow rate measurements you will require. But you can save yourself a fretful delay by ordering *ahead of time* the Wide-Range Flow-Test Kit of laboratory rotameters. This handy Kit covers a range of 2.0 cc/min. to 7.5 g.p.m. of water and 60.0 cc/min. to 14.0 c.f.m. of air, or their equivalents in other fluids. With this Kit on the shelf, you will not have to shelve any project requiring accurate flow rate measurement.

To be prepared for research ahead, send for Bulletin 32-E which gives the full details.

FISCHER & PORTER CO.
3504 COUNTY LINE ROAD HATBORO, PA.

Double Header Clean-Out MANOMETER

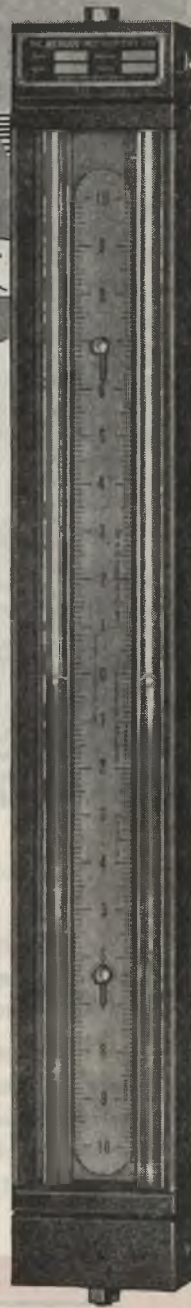


This instrument is distinctive among clean-out U type manometers because of its *double* head—removable clean-out heads at both top and bottom. These heads are easily disconnected permitting quick and frequent cleaning of complete instrument.

The manometer (Model B-1275) has a large bore Pyrex tubing of $\frac{7}{16}$ " inside diameter which gives a flat indicating fluid meniscus. Bold numerals and graduations facilitate distant reading. Scale is adjustable.

B-1275 is designed for maximum line pressure of 100 lbs. per sq. in. It has holes for mounting to wall or panel. Ask for Catalog C-11 giving other features of this outstanding instrument.

THE MERIAM INSTRUMENT CO.
10952 MADISON AVENUE • CLEVELAND 2, OHIO
WESTERN DIVISION:
1418 WILSON AVE., SAN MARINO, 9, CALIF.
IN CANADA: PEACOCK BROS., LTD., MONTREAL



MERIAM ★
★ Instruments
ESTABLISHED 1911

MANOMETERS, METERS AND GAUGES FOR THE ACCURATE MEASUREMENT OF PRESSURES, VACUUMS AND FLOWS OF LIQUIDS AND GASES

ACCURACY



Everytime IN YOUR LABORATORY

SINGLING OUT a pre-designated target and striking it with uncanny accuracy . . . that's what our airmen achieve with the new science of "pin-point" bombing.

FOR THE SAME "on target" accuracy in the laboratory, many chemists count on Baker & Adamson Reagents—the *precision* chemicals for today's exacting analytical requirements. The high purity and constant uniformity of each B&A Reagent are built in throughout every stage of manu-



facture—from initial processing of raw materials down to the last of many exclusive B&A production controls.

AS A RESULT, each product has the "Baker & Adamson Quality" that means *accuracy* to chemists throughout America . . . the accuracy you can get by specifying "B&A" on your next order of laboratory chemicals.

Setting the Pace in Chemical Purity Since 1882



BAKER & ADAMSON

Division of GENERAL CHEMICAL COMPANY, 40 Rector St., New York 6, N. Y.

Sales and Technical Service Offices: Atlanta • Baltimore • Boston • Bridgeport (Conn.) • Buffalo
Charlotte (N. C.) • Chicago • Cleveland • Denver • Detroit • Houston • Kansas City • Los Angeles
Minneapolis • New York • Philadelphia • Pittsburgh • Providence (R. I.) • San Francisco • Seattle
St. Louis • Utica (N. Y.) • Wenatchee • Yakima (Wash.)

In Wisconsin: General Chemical Wisconsin Corporation, Milwaukee, Wis.

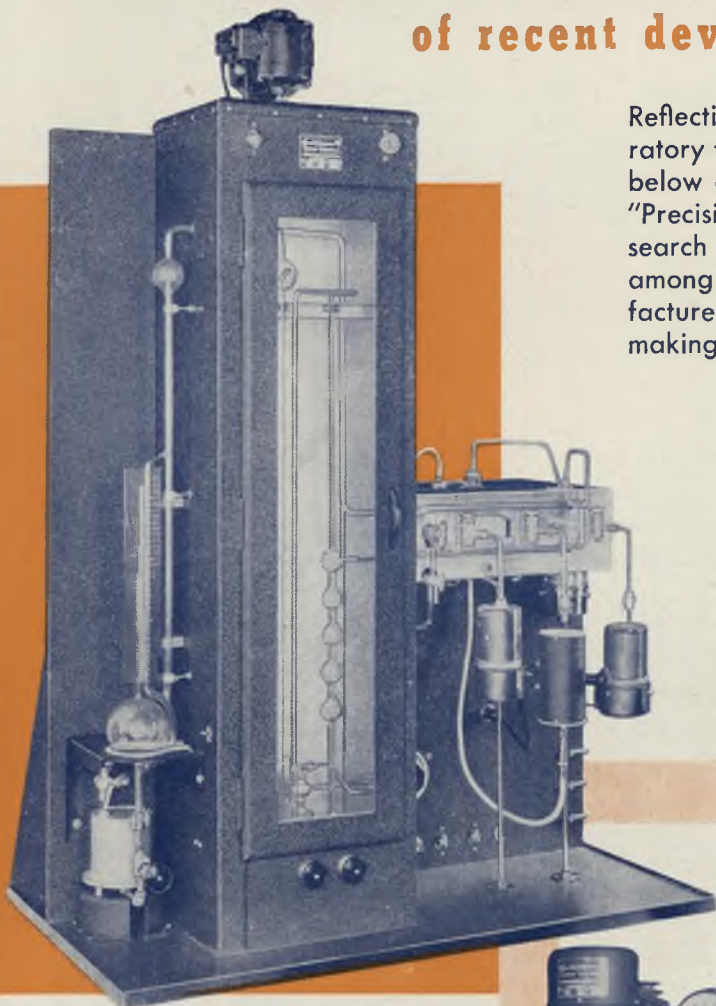
In Canada: The Nichols Chemical Company, Limited • Montreal • Toronto • Vancouver

*Reagent
and Fine
Chemicals*

A "PRECISION" FOURSOME

of recent developments for your laboratory

Reflecting the latest technological developments in laboratory techniques for vital research, the four units shown below are representative examples of the versatility of "Precision" Equipment Engineering. If you have a research problem, you will undoubtedly find the solution among the more than 3,000 items of "Precision" manufacture. Keep abreast of these latest developments by making sure your name is on our mailing list.

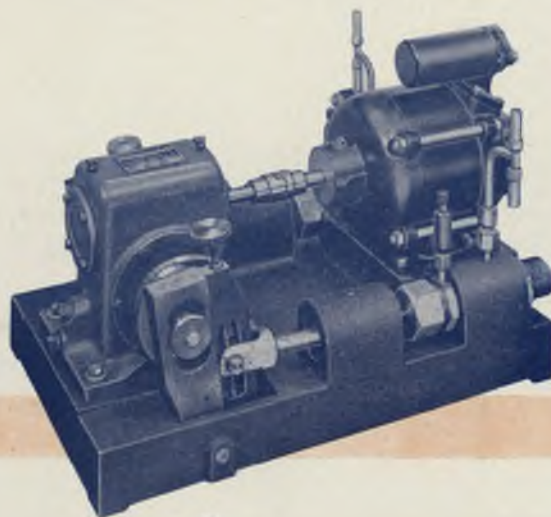


THE "PRECISION"-SHELL SURFACE AREA APPARATUS

The "Precision"-Shell Surface Area Apparatus is designed to facilitate the determination of the surface area of powdered or granular, porous or non-porous, materials according to the method described in the literature by Brunauer, Emmet, and Teller,¹ using low temperature adsorption of nitrogen gas, or the adsorption of other bases such as butane at appropriate temperatures, or by the method described by Harkins and Jura.² This apparatus also can be used for the determination of particle size of non-porous materials and for the evaluation of porosity, and hence apparent density, of certain types of porous materials.

- (1) S. Brunauer and P. H. Emmet, JACS 57, 1754 (1935). See also P. H. Emmet, ASTM Vol. 41, 1941 and Brunauer "The Adsorption of Gases and Vapors", Princeton University Press, 1943.
- (2) W. Harkins and G. Jura, JACS 66, 919, 1356, 1362, 1366 (1944).

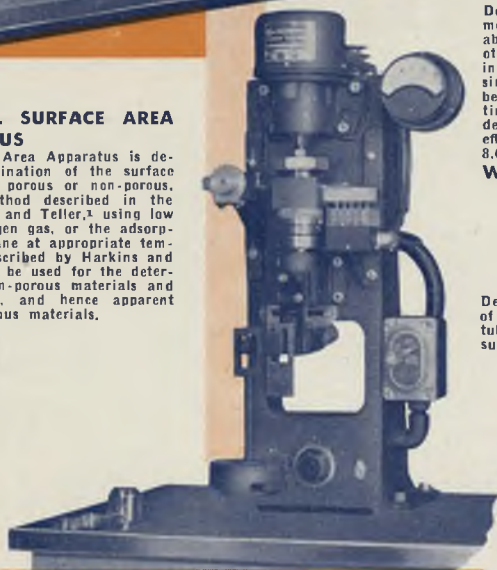
Send for Bulletin T-9970.



"PRECISION" U.O.P. DUPLEX HIGH PRESSURE PUMP, VARIABLE STROKE

Developed in cooperation with the Universal Oil Products Company to meet requirements for a sturdy, continuous duty, high pressure adjustable stroke pump for use in connection with pilot plant operation and other types of experimental work. This pump is of the DuPlex type, with individual cylinders permitting two types of liquids to be pumped simultaneously. Where increased volume is necessary, both cylinders can be piped in parallel. The design of the DuPlex Pump permits continuous operation and will maintain a given flow rate continuously delivering full rated output at maximum rated pressure. Volumetric efficiency throughout the full range is over 90%. Maximum pressure 8,000 lbs.

Write for Bulletin T-9945.



"PRECISION"-SHELL WEAR TESTER

Designed as a companion unit to the "PRECISION"-Shell 4-Ball E.P. Lubrication Tester, the "PRECISION"-Wear Tester utilizes the same basic principle to determine the wearing qualities of lubricants. Wear is measured in terms of average scar diameters under various load and temperature conditions. Tests are reproducible. Reference: Transaction of the A.S.M.E. 44-SA-3. Complete information will be furnished on request. Write for Bulletin T-9814.

"PRECISION"-BLAINE AIR PERMEABILITY FINENESS TESTER

Developed for measuring the fineness of granular materials by means of the air permeability method, this apparatus is analogous to the U tube viscometer in which the liquid in the U tube provides the pressure difference and also serves to indicate the volume of flow. For routine work, the calculations are very simple as the relative fineness can be expressed in terms of the time required for the liquid in one of the manometer arms to fall a definite distance. The apparatus can be calibrated by means of a standard sample of known specific surface. The results of the tests are reproducible. Send for Bulletin 4360 giving theoretical discussion by R. L. Blaine, Associate Mat'l Engineer, National Bureau of Standards. Reprinted from A.S.T.M. Bulletin



See Your Laboratory Supply Dealer

PRECISION

SCIENTIFIC COMPANY
1736-54 N. Springfield Ave., Chicago 47, U.S.A.

Engineers and Builders of Scientific Research and Production Control Equipment



A seaman manning a 2½ meter Range Finder reports range continuously during action.—U. S. Navy Photo.

In testing, the Range Finders are filled with compressed gas and immersed in water to reveal leaks.



The coincidence prism shown here is the most complex of the precision optical parts in a Range Finder.

Giant Range Finders which span the battleship turrets represent two tons of precision optical instrument.



Test chamber duplicates the continuous vibration of the ship and the shock of a broadside of heavy guns.

Accurately aimed naval gunfire knocks out many enemy shore installations to make troop landings safer.



Official U. S. Navy Photos



The War's Toughest Optical Job



When the big guns of America's warships speak, the sea, the sky, and the earth tremble. Enemy shore installations and enemy ships, pinpointed by the accuracy of our gunfire, crumble even as the hopes of the aggressors have crumbled.

Creating and building the optical "eyes" that help to make possible this unerring accuracy is the war's toughest optical job. These eyes are

the giant range finders which span each gun turret and fire control tower. They represent highly complex optical systems, so precise that the allowable deviation of some parts is but one-half second of arc, equivalent to 1" at 6½ miles—systems so rugged that accuracy remains constant under the shock of thundering salvos and continuous ship vibrations.

The production of these giant optical instruments in the quan-

ties needed by the world's greatest Navy is just one of the many tough optical jobs assigned to Bausch & Lomb . . . America's optical headquarters. Bausch & Lomb Optical Co., Rochester 2, New York.

BAUSCH & LOMB

ESTABLISHED 1853

