BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

Analytical *Industrial and Engineering Chemistry* Edition

Published by the American Chemical Society

EDITORIAL OFFICE:
Room 706, Mills Building,
Washington, D. C.
TELEPHONE: National 0848
CABLE ADDRESS: Jiechem (Washington)

PUBLICATION OFFICE: Easton, Pa.
ADVERTISING DEPARTMENT:
419 Fourth Ave.,
New York, N. Y.
TELEPHONE: Lexington 5608

Editor: HARRISON E. HOWE
Assistant to Editor: N. A. PARKINSON
Associate Editor: E. P. PARTRIDGE
(1440 East Eark Place, Ann Arbor, Mich.)

Volume 2 APRIL 15, 1930 Number 2

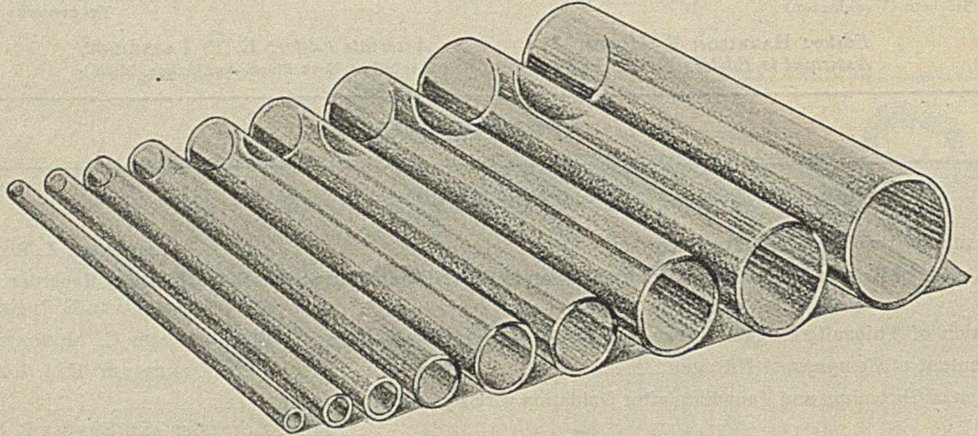
CONTENTS

Entered as second-class matter at the Post Office at Easton, Pa., under the Act of March 3, 1879, as 40 times a year. Industrial Edition monthly on the 1st; News Edition on the 10th and 20th; Analytical Edition on the 15th of January, April, July, and October. Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918.

Subscription to nonmembers, INDUSTRIAL AND ENGINEERING CHEMISTRY, $7.50 per year. Foreign postage $1.50, except to countries accepting mail at American domestic rates and to Canada. ANALYTICAL EDITION only, $1.50 per year, single copies 50 cents, to members 40 cents. NEWS EDITION only, $1.50 per year. Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, Mills Building, Washington, D. C. The Council has voted that no claims will be allowed for copies of journals lost in the mails, unless such claims are received within sixty days of the date of issue, and no claims will be allowed for issues lost as a result of insufficient notice of change of address. "Missing from files" cannot be accepted as the reason for honoring a claim.

20,200 copies of this issue printed

A MORE UNIFORM PYREX TUBING



DIMENSIONS and PRICES

Size o.d. mm.	Variation ±o.d.mm.	App. wall mm.	App. lbs. per ft.	App. lbs. per case	Price per lb.
5	0.5	.8	0.0156	25	$1.00
6	0.5	1.	0.0234	50	.90
7	0.5	1.	0.0284	50	.90
8	0.5	1.	0.0331	50	.90
9	0.5	1.	0.0378	50	.90
10	0.5	1.	0.0426	50	.80
11	0.5	1.	0.0472	50	.80
12	0.5	1.	0.0520	50	.80
13	0.5	1.2	0.0669	50	.90
14	0.5	1.2	0.0727	50	.90
15	0.5	1.2	0.0783	50	.90
16	0.5	1.2	0.0840	50	.90
17	0.5	1.2	0.0891	50	.90
18	0.5	1.2	0.0953	50	.90
19	0.5	1.2	0.1010	50	.90
22	1.0	1.5	0.1454	50	.96
25	1.0	1.5	0.1667	50	.96
28	1.0	1.5	0.1879	50	.96
32	1.5	1.8	0.2300	50	1.10
35	1.5	2.	0.2825	50	1.10
38	1.5	2.	0.3081	50	1.36
41	1.5	2.	0.3689	50	1.36
45	1.5	2.	0.4065	50	1.36
48	1.5	2.	0.4349	50	1.36
51	1.5	2.	0.4632	50	1.66

WE are now prepared to furnish PYREX tubing with a closer selection than has heretofore been available. The tubing is more uniform and the wall has been made lighter, which materially reduces the price because the user gets more feet per pound. The lighter wall makes an improved tubing for lamp working purposes. Further important changes are,

1. Packed in original cases.
2. Subject to same consumer discount as PYREX Laboratory Glassware.
3. Standard cases containing tubing cut in approximate five foot lengths are now available through your regular dealer.

Note: Light and heavy wall tubing formerly listed will be discontinued, but may be obtained on special order. Prices on application.

We reserve the right to ship three or five foot lengths when less than standard case quantities are ordered.

Industrial and Laboratory Division

CORNING GLASS WORKS, Corning, N. Y.

New York Office: 501 Fifth Avenue

T. M. PYREX Reg. U. S. Pat. Off.

NEW MODEL

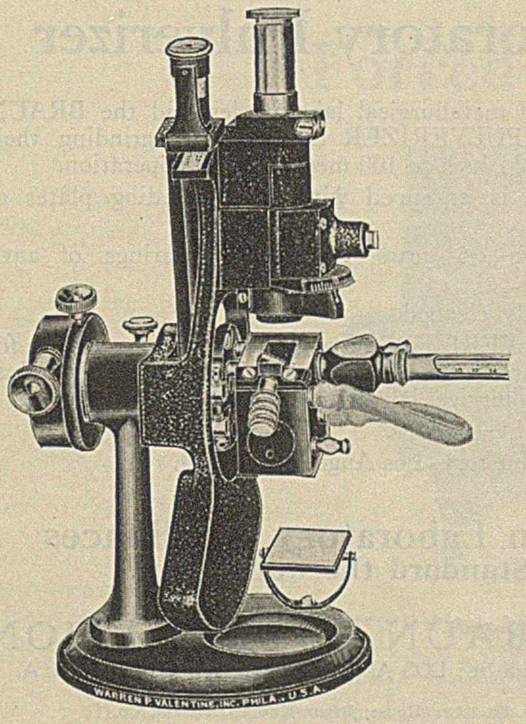
VALENTINE REFRACTOMETERS

INTEGRAL CONSTRUCTION

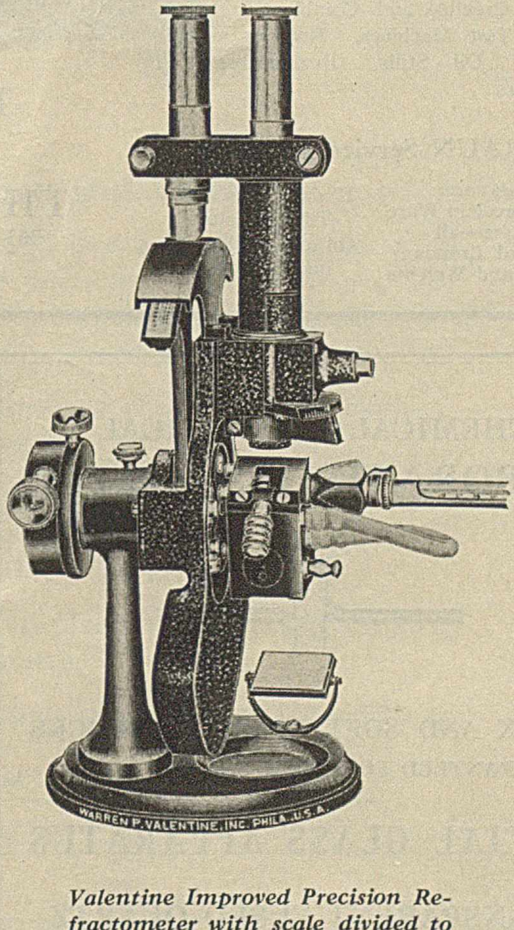
EASY MANIPULATION

PRECISE SETTING

ACCURATE RESULTS



Valentine Precision Refractometer with scale of refractive indices divided to the 3rd decimal and reading to the 4th by estimating tenths of the smallest division. F. O. B. Philadelphia . . . $200.00



Valentine Improved Precision Refractometer with scale divided to the 4th decimal and reading to the 5th decimal by estimating tenths of the smallest division. F. O. B. Philadelphia $250.00

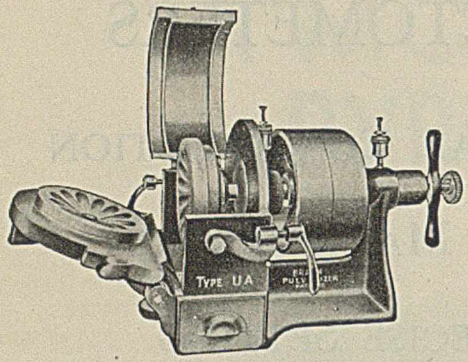
A partial list of users includes the following:

University of Minnesota—Division of Agricultural Biochemistry
South Dakota State College of Agriculture and Mechanic Arts—Division of Agriculture
State of Michigan—Department of Agriculture
Department of Commerce—Bureau of Standards
Chicago, Burlington & Quincy R. R.—Bureau of Tests
University of Pennsylvania
University of Nebraska—Department of Agriculture
Indiana State Teachers' College—Terre Haute, Ind.

WARREN P. VALENTINE, INC.

BANKERS TRUST BUILDING
PHILADELPHIA, PA.

PULVERIZING YOUR LABORATORY SAMPLES
WITH SPEED IN THE
BRAUN Type UA
Laboratory Pulverizer



BRAUN Products Include:

Chipmunk Crusher, UA Pulverizer, Iron Ore and Coal Grinders, G-H Consistency Testers, Electrolytic Outfits, Furnaces—Muffle Crucible and Combination, Flotation Test Machines, Rotarex Asphalt Tester, Oil Stills, Evaporators and Samplers.

BRAUN Service Includes:

Pyrex Glassware
Coor's Porcelain Ware
Filter Paper—all Standard Brands
Balances and Weights
Hydrometers and Thermometers
Oil and Asphalt Testing Equipment.

Industrial and metallurgical laboratories find the BRAUN TYPE UA PULVERIZER essential for grinding their samples from ¼ inch to 100 mesh with one operation.

The machine is equipped with 8-in. grinding plates of special alloy.

Straight drive—no gears—replaceable bearings of anti-friction metal.

All parts easily cleaned.

BRAUN PULVERIZERS have rendered efficient service for many years, and will be found in the most important industrial and metallurgical laboratories throughout the world.

Shipping weight—275 lbs.

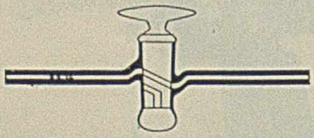
Price F.O.B. Factory, Los Angeles, **$135.00.**

Braun Laboratory Appliances
Standard the world over!

THE BRAUN CORPORATION
363 New High St., LOS ANGELES, CALIFORNIA, U. S. A.

San Francisco House: Braun-Knecht-Heimann Co.

CHEMICAL AND PHYSICAL
LABORATORY SUPPLIES



PYREX AND SOFT GLASS STOPCOCKS
GUARANTEED FOR HIGH VACUUM WORK

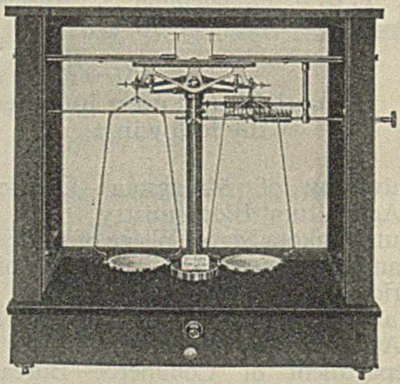
SPECIAL GLASS APPARATUS

TRANSPARENT FUSED QUARTZ
TUBING AND ROD IN STOCK
QUARTZ APPARATUS TO ORDER

Catalogue sent on request

MACALASTER BICKNELL COMPANY
CAMBRIDGE MASS.

USE AN AINSWORTH



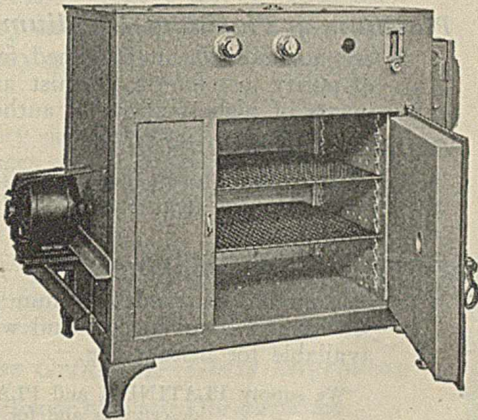
HIGH SPEED BALANCE
For your routine weighing
THE MULTIWEIGHT CARRIER

carries all fractional weights which being units of mass may at any time be adjusted against your laboratory standards.

Ask for Bulletin A-36.

WM. AINSWORTH & SONS, INC.
THE PRECISION FACTORY
2151 Lawrence St. Denver, Colo.

FREAS' ELECTRIC OVENS
with
Forced side draft



These ovens are a radical departure from our former models.

The air currents moving through ports of varied proportion in the sides of the chamber have a uniform sweeping movement over the samples unimpeded by the presence of numerous samples on other shelves.

The advantages of forced air draft in the drying of samples are too well known to require comment.

The ovens have passed the experimental stage, having been made to order for more than two years, thirteen of them being in use in the different laboratories of a single purchaser.

The frames are of welded steel in place of aluminum, making a much more rigid and durable apparatus.

We shall be pleased to answer such questions as may occur to our friends.

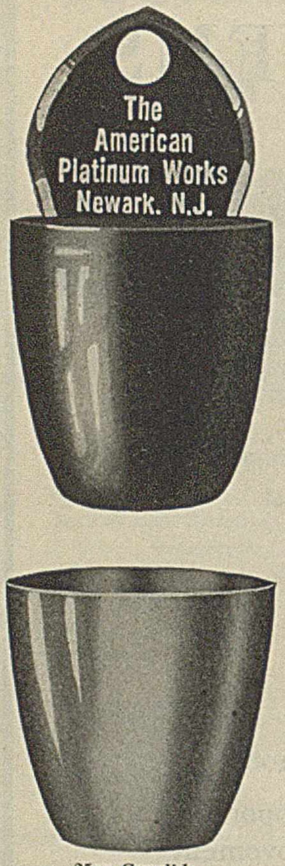
Price List

NO.	INSIDE DIMENSIONS	WATTAGE	PRICE
	TEMPERATURE RANGE: 70° – 180° C.		
601	12″ x 12″ x 12″	700	$250.00
621	18″ x 18″ x 18″	1500	350.00
641	36″ x 18″ x 24″	1900	450.00
	TEMPERATURE RANGE: 150° – 260° C.		
605	12″ x 12″ x 12″	1500	$275.00
625	18″ x 18″ x 18″	2100	385.00
645	36″ x 18″ x 24″	2700	500.00

Also other models with various modifications in design

(4079)

E. H. SARGENT & CO.
155-165 East Superior Street · · · CHICAGO, ILL.
LABORATORY SUPPLIES
Est. 1852



25cc Crucible

APW

. . . . . Lowest since 15 Years!

PLATINUM

Platinum
now available at prices that make the use of substitutes a dubious economy especially when considering, in addition, the long life and high returnable value of old wares.

Platinum or Platinum-Rhodium Laboratory Wares
are made of platinum refined for its specific purpose to a grade of purity just for the chemist and conforming with the requirements of highest chemical authorities.

Platinum-Rhodium-Alloy
is preferred for general routine work for added mechanical strength, low degree of volatilization and minimum chemical losses.

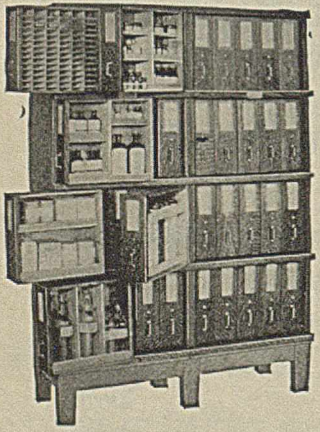
Exchange and Remaking
of your old worn-out platinum wares will add to their length of service at a nominal cost and will always keep your entire stock available for instant use.

We supply PLATINUM and PLATINUM METALS of every description and for every purpose.

Ask for our Catalog E-15 describing our full line of apparatus.

THE AMERICAN PLATINUM WORKS
N. J. R. R. AVE. AT OLIVER ST.
NEWARK, N. J.

IS YOUR LABORATORY NEAT?



It Can Be
If The
SCHWARTZ
SECTIONAL
SYSTEM
Is Installed

SAVES TIME,
MONEY
AND SPACE.

Supplies and Apparatus Always Kept in Best Condition

Write For Our *NEW* Booklet

"How to Store and Catalog Chemicals, Re-Agents, Science Materials and Samples"

SCHWARTZ SECTIONAL SYSTEM
INDIANAPOLIS, INDIANA

LABORATORY REAGENTS
Analysis
STERLING CHEMICALS
Certified
OF THE HIGHEST PURITY

STERLING'S ANALYSIS-CERTIFIED
Reagent Chemicals, C.P.
Mol. Wt. Care+Skill=Quality Grms.

CERTIFICATE OF ANALYSIS
Analysis is not enough--
insist on certification.

Each lot of Sterling's
Analysis-Certified bears the
signature of the chemist who
made the analysis.

Get this added protection
on your laboratory shelves.

W.H. Ketchledge CHEMIST
LOT NO.______ MADE IN U. S. A

STERLING PRODUCTS COMPANY
EASTON, PENNA.

NEW! INTERCHANGEABLE

Ground Glass Connections

MADE OF EITHER PYREX OR FLINT GLASS.
Seventeen sizes. The very latest for laboratory and plant. Reduces laboratory expense and saves stock room space.

The inner and outer cones of every size are ground together so that they are changeable. Single pieces can be replaced by giving the size number. CONFUSION IS ELIMINATED as each individual piece is numbered.

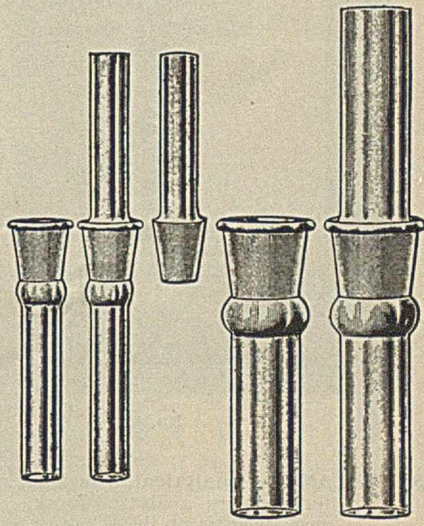
Joints are made to be interchangeable with German standard sizes.

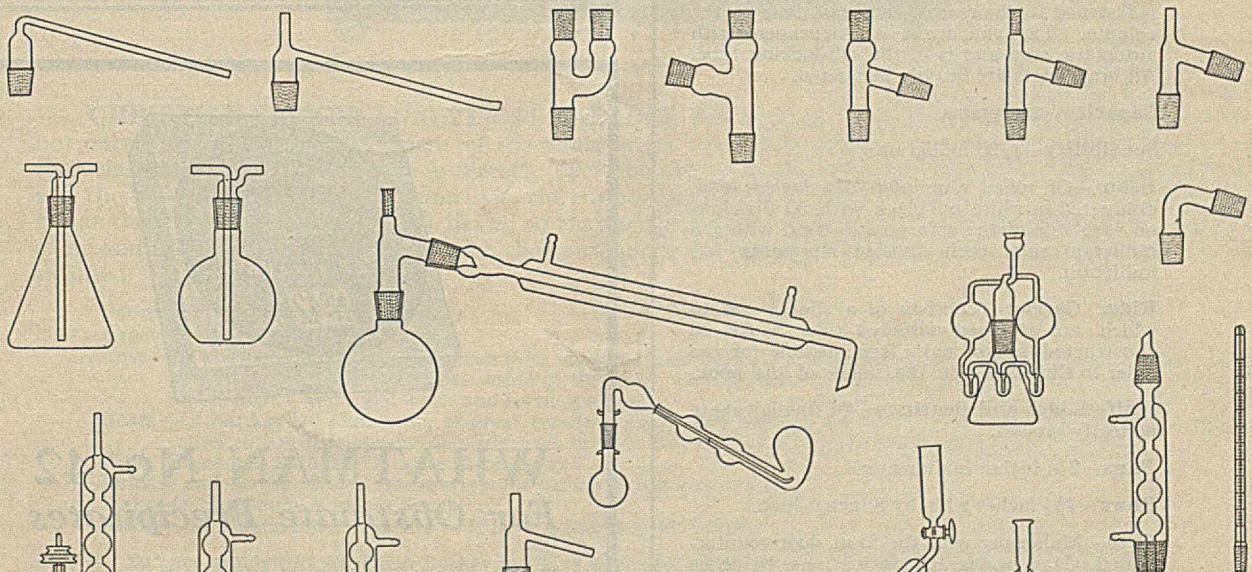
For further data and prices write for booklet showing the different apparatus which we are making with these joints.

Expert Glass Blowing—Glass Grinding—Glass Engraving

Send us your sketch or blue print for quotation.

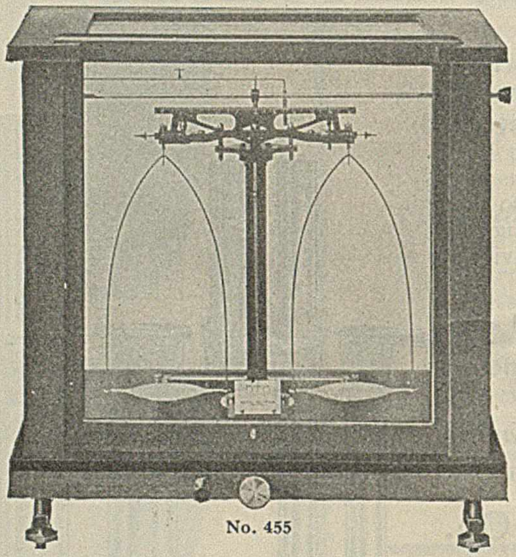
Scientific Glass Apparatus Co.
Laboratory Supplies & Chemicals
49 Ackerman St., Bloomfield, N. J.





ANALYTICAL BALANCE

College Model
for
Quantitative Analysis and Research



No. 455

455 **BALANCE—Analytical,** a medium priced balance for ordinary analytical work. The releasing mechanism is of the fallaway type with three-point suspension for the beam. A spirit level is fastened to the rear of the brass base of the column. The pan arrest is independent with automatic stop and is of the self-locking type. All brass parts are heavily lacquered.

Capacity—100 grams.

Sensibility—1/20 milligram.

Beam—Of rolled aluminum 6½ inches long, graduated in white on black with 50 divisions on each side of the zero point. Used with a 5 milligram rider each division represents 1/10 milligram.

Rider Carrier—Consists of a sliding rod to which are attached patented rider hooks, so constructed as to make it impossible for the rider to slide back on the shank of the hook.

Knife Edges and Bearings—Of Russian agate perfectly ground.

Pans—2⅝ inches in diameter.

Bows—4⅛ inches wide by 8 inches high.

Case—Mahogany with the front door counterpoised. Dimensions, 16¼ inches long, 15 inches high, and 9¼ inches wide.

Price—With slate base................75.00

456 **BALANCE—Analytical,** same as No. 455, but with plate glass base.......................85.00

Immediate delivery from stock.
Refer to Catalog "C" for additional Laboratory Apparatus.

THE
CHEMICAL RUBBER COMPANY
Laboratory Apparatus and Chemicals
West 112th Street and Locust Ave.
Cleveland, Ohio

New Catalog

Merck's Laboratory Chemicals

This Catalog contains a complete list of our newly restandardized C. P. and Reagent Chemicals. They conform to or exceed in purity the well known and widely recognized "Standards of Murray" (1927 edition). The analysis of each C. P. and Reagent is given in the Catalog and shown on the container label.

Write for Catalog

MERCK & CO. INC.
MANUFACTURING CHEMISTS
RAHWAY, N. J.
New York Philadelphia St. Louis
In Canada: MERCK & CO. Limited, Montreal

WHATMAN No. 42
For Obstinate Precipitates

You know them, those obstinate, fine precipitates that seep through any but the most uniformly close Filter Papers.

For such bugbears, use WHATMAN Filter Paper No. 42, close textured, low ash, ideal for freshly precipitated Barium Sulfate, Metastannic Acid, etc.

Leading Oil, Coal, Metallurgical, Fertilizer and other Laboratories running Sulfurs, Tins, etc. regularly have long been standardized on No. 42.

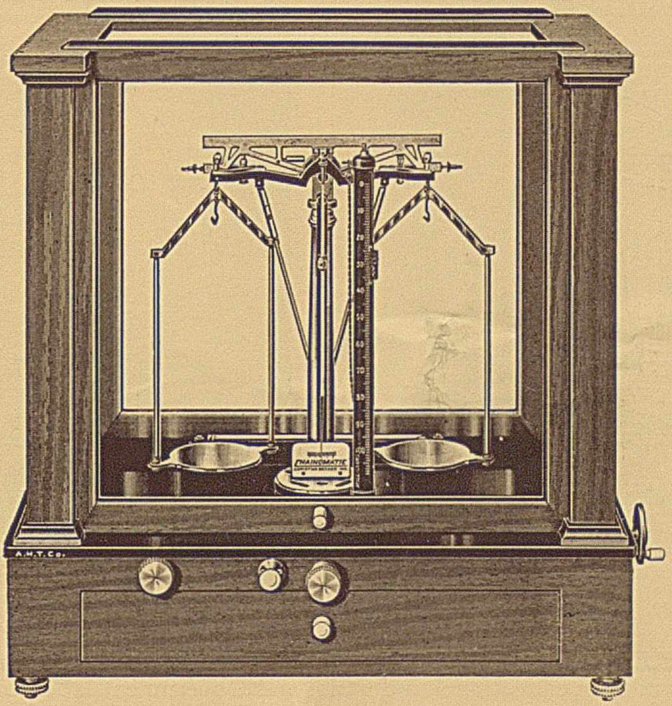
Let us send you samples

H. REEVE ANGEL & CO., INC.
7-11 Spruce St. New York, N. Y.

BECKER

ANALYTICAL BALANCES

IN OUR STOCK FOR IMMEDIATE SHIPMENT



1886-C.

CHRISTIAN BECKER ANALYTICAL BALANCE NO. 9, with special beam arrest (patented) which not only insures positive alignment of the agate edges with their respective bearings, but is so designed that the center agate knife edge is directly over the center of the column. Since the beam arrest arms and the beam pivot about a common axis, the supporting points of the arrest arms move through the same arc as the supporting points of the beam, so that contact between edges and bearings always remains the same and the shifting of the beam, with the consequent dulling of the agate edges and bearings, is thereby avoided.

Sensitivity—$^1/_{20}$th mg with full load.
Capacity—200 grams in each pan.
Case—Of polished mahogany, with glass sides and top, front sliding frame counterpoised, rear frame removable. With polished black plate glass base inside of the case. Outside dimensions, $19^1/_4$ inches long, $11^3/_4$ inches deep, 20 inches high. With vial levels and leveling screws.
Beam—Of hard rolled aluminum, of great tensile strength and uniform density; 7 inches long, graduated from 0 in center to 100 divisions on each side, each division corresponding to $^1/_{20}$th mg when using a 5 mg rider.
Knife Edges and Planes—Of agate throughout.
Release and Arrest—Independent arrest for pans with automatic stop.
Pans—Of aluminum, 3 inches diameter.
Arches—Of aluminum, $4^1/_4$ inches wide by $8^1/_2$ inches inside height.

1886-B.	Balance, Analytical, Christian Becker No. 9, as above described, with Auto-Dex attachment (see page 3) but without weights. With three 10 mg riders	195.00
	Code Word	*Aolce*
1886-C.	Ditto, No. 9 but with Chainomatic feature in addition to Auto-Dex Attachment	235.00
	Code Word	*Aolcg*

ARTHUR H. THOMAS COMPANY

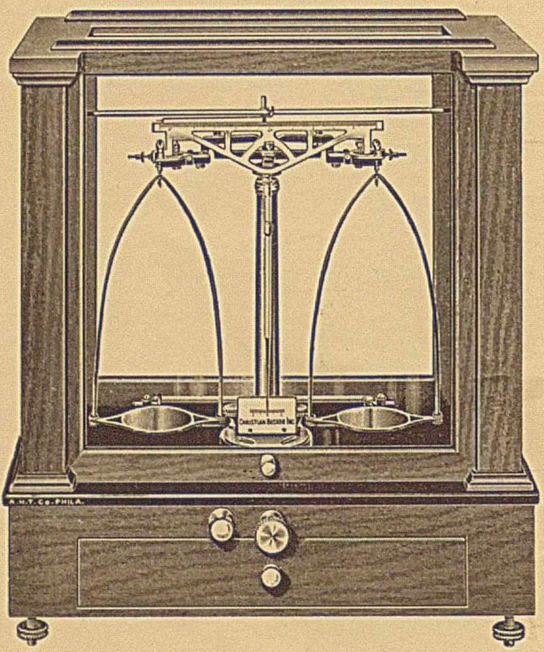
RETAIL—WHOLESALE—EXPORT

LABORATORY APPARATUS AND REAGENTS

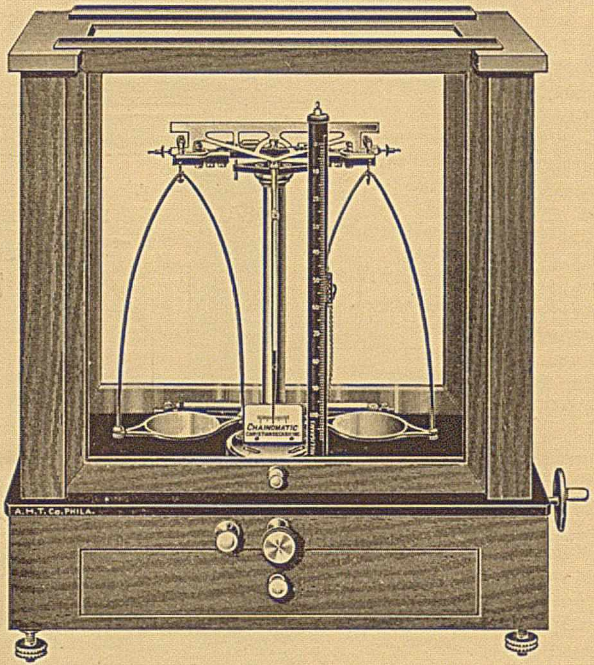
WEST WASHINGTON SQUARE
PHILADELPHIA, U. S. A.

Cable Address, "BALANCE," Philadelphia

BECKER
ANALYTICAL BALANCES



1870.



1882. (See text on opposite page.)

CHRISTIAN BECKER ANALYTICAL BALANCE NO. 8-A. An American-made balance of high reputation, for years popular in educational, industrial and Government laboratories.

Sensitivity—$^{1}/_{20}$ milligram with full load.
Capacity—200 grams in each pan.
Case—Of polished mahogany, with glass sides and top and with front sliding frame counterpoised, and with a polished black plate glass base inside of the case. Outside dimensions 16$^{1}/_{4}$ inches long, 18$^{1}/_{2}$ inches high, 9 inches deep; inside dimensions 13 inches long, 13 inches high, 6$^{3}/_{4}$ inches deep.
Beam—Of hard rolled aluminum alloy of great density and tensile strength, 7 inches long with graduations in black from 0 to 5 mg in $^{1}/_{10}$ths on both sides of the central knife edge.
Knife Edges and Planes—Of agate throughout.
Release and Arrest—Independent arrest for pans with automatic stop.
Pans—Of polished German silver, 2$^{3}/_{8}$ inches diameter.
Arches—Of polished German silver wire, with 4-inch spread.
Riders—Each balance is furnished with three 10-mg riders.

1870. Balance, Analytical, Christian Becker No. 8-A, as above described, without weights, but with three 10-mg riders.......... 150.00
Code Word.......... *Aoiuz*

CHRISTIAN BECKER ANALYTICAL BALANCE NO. 15. This is a high-grade analytical balance at moderate price, but which meets all ordinary needs of analytical work.

Sensitivity—$^{1}/_{10}$ milligram with full load.
Capacity—200 grams in each pan.
Case—Of polished mahogany, with glass sides and top and with front sliding frame counterpoised, and with a polished black plate glass base inside of the case. Outside dimensions 16$^{1}/_{4}$ inches long, 18$^{1}/_{2}$ inches high by 9 inches deep; inside dimensions 13 inches long, 13 inches high, 6$^{3}/_{4}$ inches deep.
Beam—Of hard rolled aluminum alloy, oxidized black, 6 inches long, with white graduations from 0 to 5 mg in $^{1}/_{10}$ths on both sides of the central knife edge.
Knife Edges and Planes—Of agate throughout.
Release and Arrest—Independent arrest for pans with automatic stop.
Pans—Of polished German silver, 2$^{1}/_{2}$ inches diameter.
Arches—Of polished German silver wire, with 4-inch spread.
Riders—Each balance is furnished with three 5-mg riders.

1872. Balance, Analytical, Christian Becker No. 15, as above described, without weights, but with three 5-mg riders. 110.00
Code Word.......... *Aojpi*

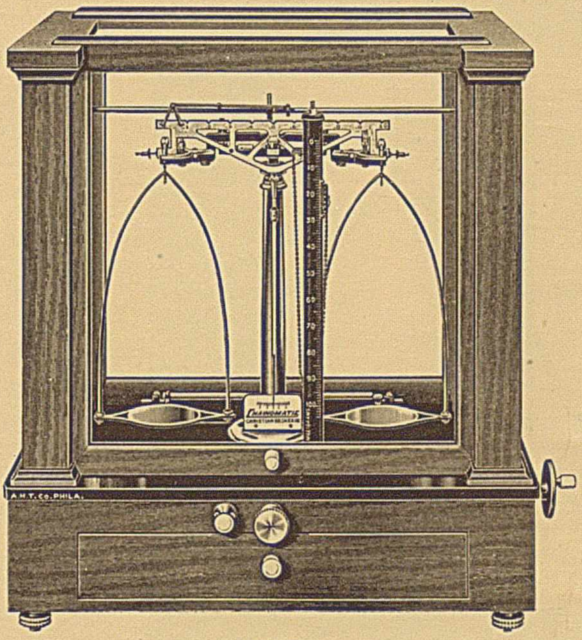
CHRISTIAN BECKER ANALYTICAL BALANCE NO. 16. Identical with Christian Becker No. 15 Balance as to capacity, sensitivity and all important specifications, but with somewhat simplified construction in order to reduce cost, i. e., the omission of the drawer in the mahogany base, the substitution of a black slate base for the polished glass plate, and a central pillar finished in dull black. Recommended as an unusual balance value.

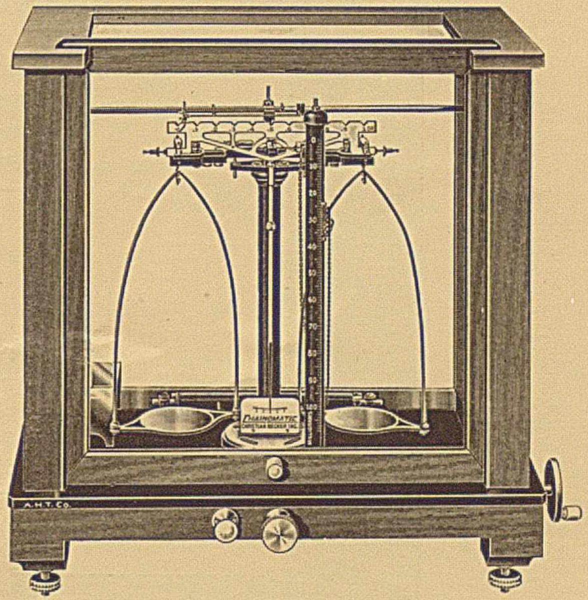
1874. Balance, Analytical, Christian Becker No. 16, as above described, without weights, but with three 5-mg riders. 90.00
Code Word.......... *Aojsc*

ARTHUR H. THOMAS COMPANY, PHILADELPHIA, U. S. A.

BECKER

ANALYTICAL BALANCES


1885-F.


1886-A.

CHAINOMATIC ANALYTICAL BALANCES, Christian Becker. Of the same general construction as the corresponding balances described on opposite page, but with Chainomatic Attachment which eliminates the use of riders and small weights up to 100 milligrams. Weighing is accomplished by means of a gold filled chain, with links of uniform weight, suspended between the beam and a vernier system. The vernier, which reads to 0.1 milligram, is operated by a crank outside the case to the right.

			Code Word
1880.	Balance, Analytical, Christian Becker Chainomatic No. 8-A; identical with 8-A described on opposite page, but with chainomatic attachment. Without weights	190.00	*Aokhy*
1882.	Ditto, No. 15 Chainomatic	150.00	*Aokux*
1883.	Ditto, No. 16 Chainomatic	130.00	*Aolal*

AUTO-DEX ATTACHMENT (Movable Index), **Patented,** for Christian Becker Analytical Balances. The movable index is controlled by a thumb wheel situated at the left hand side of the front of the balance case above the drawer. See illustration of No. 1886-C on page 1. A slight turn of the thumb wheel moves the index plate to the left or right, as required, until the indicator or pointer is coincident with zero of the index.

This attachment proves a great time saver, as it obviates the necessity of touching the adjusting nut, or of recording the rest point, since the rest point and the zero point are always coincident. It also protects the agate edges from wear as it avoids the necessity of frequent release of the balance.

			Code Word
1884.	Balance, Analytical, Christian Becker No. 8-A, with Auto-Dex Attachment as above described, but without weights	160.00	*Aolbe*
1884-A.	Ditto, No. 8-A Chainomatic, with Auto-Dex Attachment	200.00	*Aolbj*
1885.	Ditto, No. 15, with Auto-Dex Attachment	120.00	*Aolbl*
1885-A.	Ditto, No. 15 Chainomatic, with Auto-Dex Attachment	160.00	*Aolbm*
1885-B.	Ditto, No. 16, with Auto-Dex Attachment	100.00	*Aolbt*
1885-C.	Ditto, No. 16 Chainomatic, with Auto-Dex Attachment	140.00	*Aolbu*

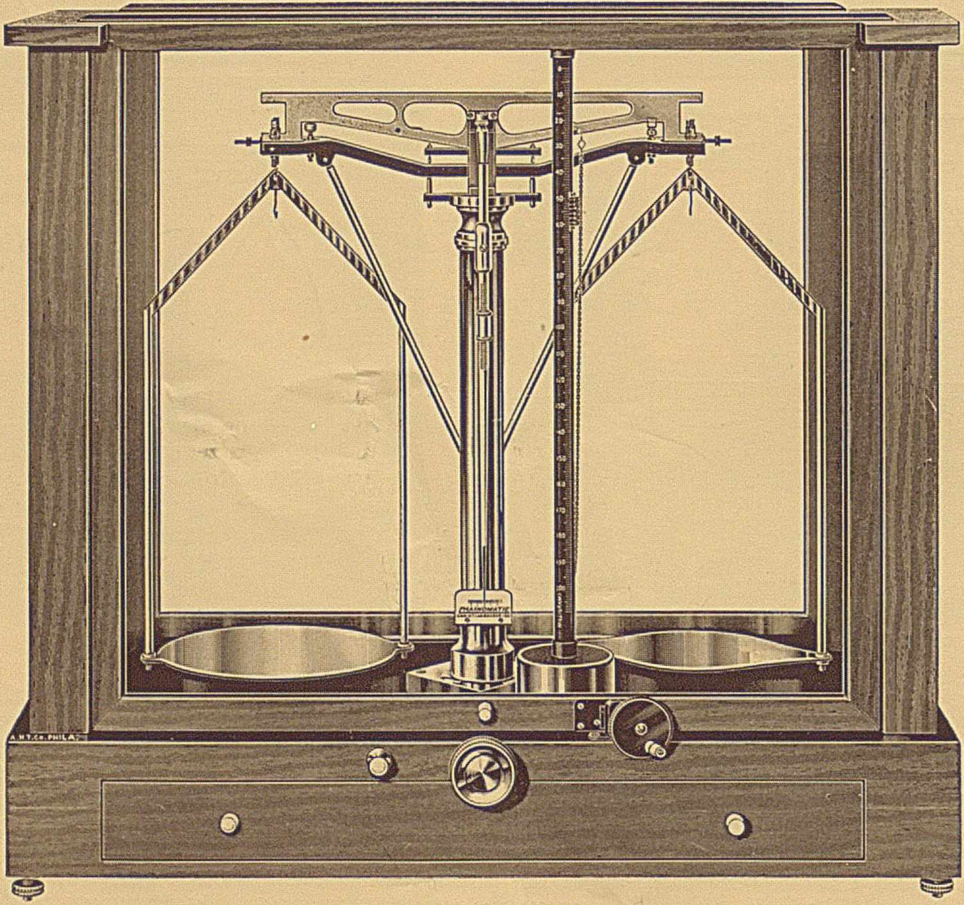
GRADUATED NOTCHED BEAM. Christian Becker Chainomatic Balances are furnished with notched beam graduated from left to right, 0 to 1 gram in 100 mg graduations. This feature, in combination with the Chainomatic Attachment, results in a balance in which the use of all weights from 0.1 mg to 1.1 grams are entirely eliminated. Construction is otherwise identical with Nos. 8-A, 15 and 16.

			Code Word
1885-F.	Balance, Analytical, Christian Becker Chainomatic No. 8-A, with Graduated Notched Beam, as above described, but without weights	210.00	*Aolby*
1886.	Ditto, No. 15 Chainomatic, with Graduated Notched Beam	170.00	*Aolca*
1886-A.	Ditto, No. 16 Chainomatic, with Graduated Notched Beam	150.00	*Aolcd*

ARTHUR H. THOMAS COMPANY, PHILADELPHIA, U. S. A.

BECKER

ANALYTICAL BALANCES



1886-D.

CHRISTIAN BECKER ANALYTICAL CHAINOMATIC BALANCE NO. 14, Improved Model. Specially adapted for the calibration of volumetric flasks, the arches having an unusually large clearance. This is a new execution of the old No. 14 Balance recommended for its large capacity and high sensitivity.

Sensitivity—$^{1}/_{5}$th milligram.
Capacity—2 kilos in each pan.
Case—Of polished mahogany, with glass sides and top, front sliding frame counterpoised, rear frame removable. With spirit level and leveling screws. Outside dimensions over all 30 inches long, 27$^{1}/_{2}$ inches high, 14 inches deep.
Beam—Of bronze, of great tensile strength and uniform density; 14 inches long. Graduated on each side from $^{1}/_{5}$ mg to 20 mg. Will sustain full load without flexure and maintain adjustment through varying temperature changes.
Chainomatic Attachment—See discussion on page 3.
Knife Edges and Planes—Of agate. All edges are entirely freed from the bearings when the balance is arrested.
Pans—Of brass, 8 inches diameter.
Pan Arrest—Independent arrest for pans with stop.
Arches—Of brass; inside dimensions 8$^{1}/_{2}$ inches wide by 16 inches high.

1886-D. Balance, Analytical, Christian Becker Chainomatic No. 14, as above described, without weights.......... 350.00
Code Word.......... *Aolcl*

ARTHUR H. THOMAS COMPANY

RETAIL—WHOLESALE—EXPORT

LABORATORY APPARATUS AND REAGENTS
WEST WASHINGTON SQUARE
PHILADELPHIA, U. S. A.

Cable Address, "BALANCE," Philadelphia

Analytical Industrial and Engineering Chemistry Edition
Published by the American Chemical Society

Volume 2 APRIL 15, 1930 Number 2

A High-Sensitivity Absolute-Humidity Recorder[1]

Crandall Z. Rosecrans

Leeds & Northrup Company, 4901 Stenton Ave., Philadelphia, Pa.

An apparatus has been developed for measuring and recording the amount of water vapor in the air, which is suitable for recording humidities from zero up to saturation within a temperature range from −100° to about 200° C. From 0 to 10 per cent at 25° C. its accuracy is ±0.05 per cent relative humidity. This apparatus is based on the measurement of the thermal conductivity of water vapor and air mixtures, and is continuous reading. A commercial modification of this apparatus is in successful operation, although it is not yet perfected for general plant use.

Methods of Measuring Humidity

NUMEROUS devices have been used for the measurement of water vapor in the atmosphere, each of which has certain advantages peculiar to itself and is adapted for use under particular conditions.

The wet-and-dry-bulb hygrometer has been used to measure atmospheric humidity since 1813, and in meteorological and industrial work it is generally accepted as a standard to the practical exclusion of all other methods. It is well known, however, that the device is very inaccurate in its elementary form, and that many refinements must be made to render its readings reliable. In addition, it is unsuited for the determination of humidities below about 20 per cent at 25° C., while at lower humidities errors in wet-bulb temperatures cause serious errors in readings of relative humidity. On the other hand, the wet-and-dry-bulb hygrometer is also unsuited for observations at high temperature on account of the difficulties involved in keeping the wick wet. It is, of course, completely useless above 100° C. Under best conditions reproducible, results may be obtained, but an absolute error of less than ±2 per cent cannot be assured. Errors of ±5 per cent or more may occur if the wet sack around the wet bulb is not in good condition, or either the relative humidity or the temperature is low; at humidities approaching saturation the error may exceed 18 per cent (*9*). However, within the range of 20 to 100 per cent relative humidity at temperatures ranging from 10° to 60° C., it fulfils a definite place in humidity measurements. The device has only recently been made self-recording by the use of platinum resistance thermometers and an ingenious combination of electrical circuits (*1*).

The dew-point hygrometer depends for its action on the determination of the temperature at which dew forms on a polished metal surface which is cooled by the evaporation of ether or by similar means. Reference to tables or curves then gives the relative humidity for a given air temperature and dew point. This apparatus is evidently not adaptable for modification as a self-recording instrument. Moreover, it is difficult to attain the low temperatures necessary to obtain precipitation of moisture in air originally at 25° C. and with a relative humidity of less than 10 per cent.

The hair hygrometer (*3*) shows a tendency to give higher and higher readings as time elapses, owing to the permanent elongation of the hair kept under tension. No data are available regarding the accuracy attainable at humidities below 10 per cent at 25° C., but Griffiths shows that when hair hygrometers were subjected to humidities of the order of 5 per cent at about 20° C. a permanent change occurred, indicating that the hairs had stretched.

The cotton hygrometer described by Griffiths depends for its operation on the maintenance of a water-soaked cotton winding around a resistance thermometer. It is therefore subject to the same limitations as the wet-and-dry-bulb hygrometer.

If the humidity remains constant, it can be determined to within ±0.1 per cent of its true value by absorbing the water vapor from a known volume of air in a weighed absorption tube. Such accuracy is only made possible by the exercise of special precautions. Under ordinary conditions, however, errors of 2 to 3 per cent may be expected with this method, and with a rapidly varying humidity it is practically useless, giving only an average value during the time of observation.

Heretofore no commercial method has been available for continuously measuring and recording the amount of water vapor in air over a wide range of relative humidities, with an accuracy approximating that obtainable with the absorption method. A request was recently made by Bell System engineers for an apparatus suitable for measuring and recording low humidities within a temperature range of 25–50° C. (77–122° F.) and sensitive to changes of about 0.05 per cent relative humidities. After consultation with the engineers of the Bell Telephone Laboratories, the task of constructing a suitable apparatus was undertaken, with the understanding that A. C. Walker of that organization would calibrate the apparatus. Doctor Walker's work in this connection is published in a companion paper (*10*).

The dew-point apparatus, cotton hygrometer, and chemical absorption methods cannot at present be made recording, at least in satisfactory form. The hair hygrometer would operate within the desired range of humidity, but would certainly not meet the requirements of accuracy. Distinct possibilities were offered by the thermal-conductivity method, and it is the purpose of this paper to show how the unique character-

---

[1] Received December 9, 1929.

istics of this method are particularly adapted for the measurement of extremely low humidities (0.1 to 10 per cent relative humidity at 25° C.). The adaptation has been carried far enough to demonstrate its success as a semi-commercial plant installation. This method can be adapted readily for recording continuously relative humidities from 0 up to saturation; from 0 to 10 per cent at 25° C. the accuracy approximates ±0.05 per cent relative humidity. In general, it is capable of making determinations at temperatures ranging from −100° C., or lower, to about 200° C., if all constituents of the mixture being measured remain in the gaseous phase.

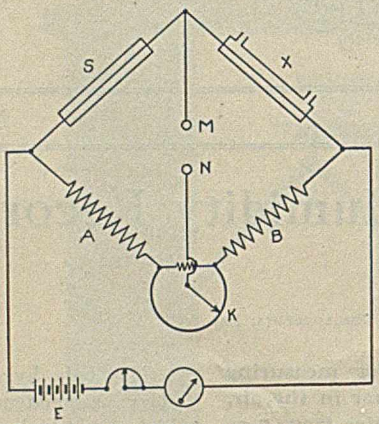


Figure 1—Simple Gas-Analysis Circuit

Thermal-Conductivity Method for Gas Analysis

Koepsel (*5*) in 1908 first described apparatus for determining concentrations of hydrogen in air by the thermal-conductivity method. Shakespear (*8*) made various improvements on the device of Koepsel, and with Daynes (*2*) made an elaborate theoretical investigation of the method. Palmer and Weaver (*6*, *12*) investigated various types of gas-analysis cells and electrical circuits and applied the method to the analysis of a variety of gaseous mixtures.

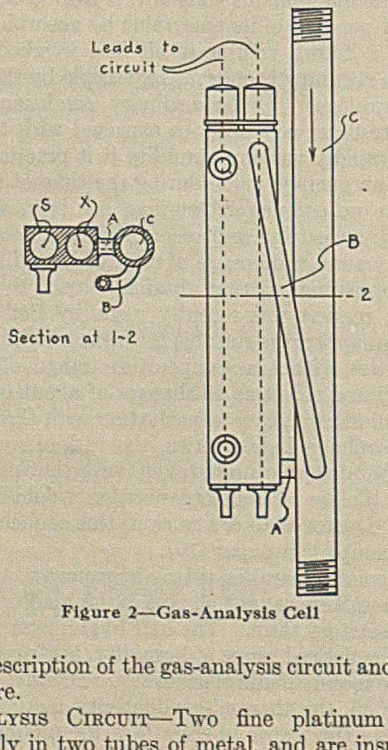


Figure 2—Gas-Analysis Cell

A brief description of the gas-analysis circuit and cell will be repeated here.

Gas-Analysis Circuit—Two fine platinum wires are placed axially in two tubes of metal, and are insulated from the metal. One tube is sealed with dry air in it. The other tube is connected so that the gas to be analyzed passes through it and over the wire. The two wires are connected in a Wheatstone bridge circuit as shown in Figure 1. *S* is the sealed wire, or standard, and *X* is the wire exposed to the gas to be analyzed. *A* and *B* are the other arms of the Wheatstone bridge, and *K* is a slide wire for adjusting the bridge to a balanced condition as desired. If current from the battery, *E*, is passed through the bridge network, the fine platinum wires are heated. Assume that dry air is passed through the cell *X*, and that the bridge is balanced by an adjustment of the slide wire. Now if a gas of higher thermal conductivity than air—water vapor, for example— is passed through the *X* cell, the temperature of the *X* wire will decrease, as the heat will be conducted away from the wire at a higher rate, owing to the higher thermal conductivity of the water vapor. As the temperature of the *X* wire decreases its resistance also decreases, and the bridge becomes unbalanced. The unbalanced potential across the terminals *M*-*N* is measured by a recording potentiometer. Thus it is evident that a calibration of the apparatus can be made, using the variation of the unbalanced potential as an index of the percentage of the water vapor passing through the cell *X*.

Gas-Analysis Cell—The simple gas-analysis cell consists essentially of two cylindrical tubes, through which the platinum wires are stretched. The cell as actually used is shown diagrammatically in Figure 2. The two tubes *S* and *X* are formed by drilling holes in a solid block of metal, and are 0.375 inch (9.53 mm.) in diameter and 4.5 inches (11.4 cm.) in length. The wires are sealed into the tubes at the top by glass-platinum seals. Heavy platinum is used as lead-in wire; the fine platinum wire, 0.002 inch (0.05 mm.) in diameter, is gold-soldered to the lead-in wires.

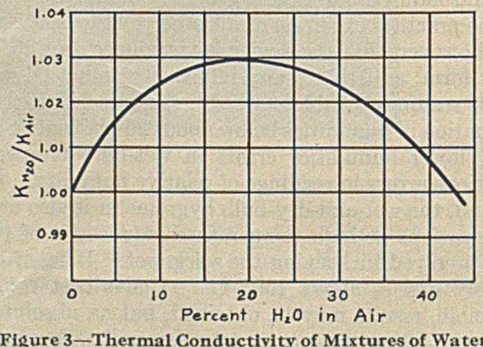


Figure 3—Thermal Conductivity of Mixtures of Water Vapor and Air. Results of Grüss and Schmick

The outstanding feature (*7*) of the cell, as shown in Figure 2, is the method of admitting gas to the *X* or analyzing wire. The gas sample is passed continuously downward through the tube C. A small portion of the sample passes through the tube A into the gas cell, *X*. Here it is heated by the fine platinum wire, which attains a temperature of approximately 210° C., and consequently rises. It passes out of the cell at the top, through the diagonal tube, *B*, and reënters the main gas-sample tube, *C*, at a point opposite the opening *A*, through which it entered the cell *X*. The action of the gas is thus a by-passing of a small amount of the sample flowing in the tube *C* through the analyzing cell *X*. This flow of gas is produced by the difference in weight of the two columns of gas—one in the cell *X* at high temperature and one in the tube *B* at lower temperature. The essential fact, however, is that the tubes *A* and *B* join the main gas-sample tube, *C*, opposite each other. Thus there is practically no pressure difference between the inlet and the exit of the cell *X*, and the flow through the cell *X* is dependent only on the platinum-wire temperature, being practically independent of the velocity of gas flow through the tube *C*.

Thermal Conductivity of Water Vapor

Values of the thermal conductivity of water vapor have been given from calculations based on the specific heat and viscosity. Recently, however, Grüss and Schmick (*4*) have determined the conductivity of mixtures of water vapor and air with considerable accuracy. Figure 3 shows the thermal conductivity of water vapor and air mixtures, referred to air as unity, at a mean temperature of 82.2° C., from the results of Grüss and Schmick. Based upon theoretical considerations, these investigators give for the equation of the curve of Figure 3:

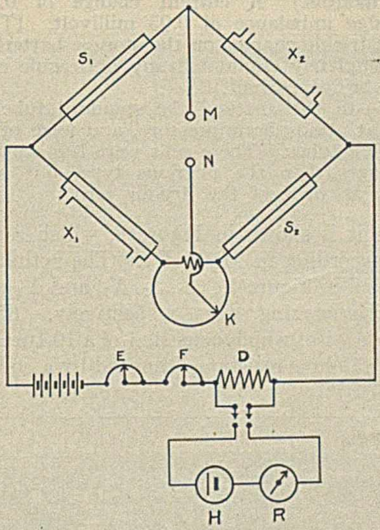


Figure 4—Actual Circuit of Apparatus

$$\left(\frac{L_2}{L_1}\right) = \frac{1}{1 + \frac{P_2}{P_1}1.357} + \frac{0.85}{1 + 0.491\frac{P_1}{P_2}}$$

where L_2 and L_1 are conductivities of two mixtures and P_2 and P_1 are the partial pressures of water vapor and air, respectively.

It was desired to have the recorder accurate to ±0.05 per cent relative humidity over a range from 0 to 10 per cent relative humidity at 25° C. Calculating the thermal conductivity of a mixture of water vapor and air at this upper limit of 10 per cent at 25° C. from the previous equation, we obtain 1.00116 referred to air as unity. The difference between 1.0000 and 1.00116 represents the limits within which the recording apparatus should function. This range is determined, however, for the gaseous mixture at 82.2° C., while in the thermal-conductivity cell described here the mean gas temperature is about 100° C. Since the temperature coefficient of thermal conductivity of water vapor is not known, even approximately, it is possible only to estimate the sensitivity of the gas-analysis cell from the value derived from the work of Grüss and Schmick. A sensitivity of ±0.05 per cent relative humidity is therefore equivalent to a change of the order of 0.0000058 in the thermal conductivity of the gaseous mixture.

Thermal-Conductivity Apparatus

The principal difficulty in designing an instrument of this type is to obtain sufficient sensitivity of the gas-analysis cells to work satisfactorily over such narrow limits of thermal-conductivity change. In order to increase the degree of unbalance of the Wheatstone bridge for a given change of cell-wire resistance, four cell tubes were used, arranged in the circuit as shown in Figure 4. Two cell wires, X_1 and X_2, were exposed to the air gas-water mixture, while the other cell wires, S_1 and S_2, were surrounded by dry air. By the use of this device the potential drop at *M-N*, measured by the potentiometer recorder, is twice that which would be obtained by the simple circuit of Figure 1. An attempt was also made to increase the potential drop at *M-N* (Figure 4) by increasing the current supplied to the bridge.

Serious difficulties were soon found due to variable readings on constant-humidity air, or on even dry air. The readings varied rapidly, sometimes increasing, sometimes decreasing. Accordingly, a potentiometer was connected across the bridge to measure the unbalanced potentials, and an attempt was made to measure the change of the reading per minute, by taking readings every 15 seconds. A constant-humidity gas mixture was used during all this work. Since the unbalanced potentials are functions of the bridge current, the final results of the above tests as plotted in Figure 5 are shown in millivolts per minute per milliampere of bridge current. In this way all values are strictly comparable in absolute magnitude, since the effect of the increase of the bridge current in increasing any unbalanced potential is eliminated by dividing the drift in millivolts per minute by the bridge current.

Various values of bridge current were used, ranging from 500 to 800 milliamperes. The curve of Figure 5 shows very strikingly the sudden increase in the drift at 650 milliamperes. This increase represents a total lack of reliability or reproducibility of the readings. As stated above, all readings were taken on a gas of constant humidity. The drifts took place in either a positive or negative direction. The sudden increase in the rate of drift at about 650 milliamperes is very probably due to the sudden setting up of rapid and variable convection currents within the cell tubes themselves when the wire temperature exceeds a certain critical value. This theory seems reasonable, since all other known factors which vary with the bridge current have been eliminated. This critical value of temperature is a function of the cell diameter also. For the final design, therefore, the current used was 600 milliamperes.

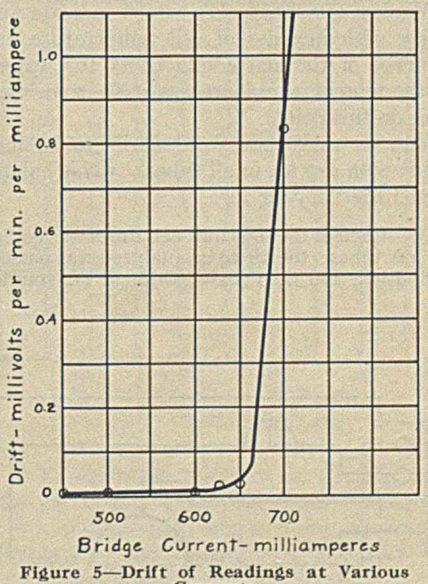


Figure 5—Drift of Readings at Various Currents

The variation of sensitivity with current is based upon two facts.

(1) An increase of bridge current will obviously cause an increase in the potential measured across the terminals *M-N* (Figure 4) for a given degree of unbalance of the bridge. This effect is purely electrical.

(2) If the curves of thermal conductivity versus temperature for water and air diverge with an increase of temperature, the sensitivity of the instrument will increase with higher bridge currents since the difference of thermal conductivity of the gases being analyzed will be greater. On the other hand, if the curves of thermal conductivity converge with increasing temperature, the instrument will become less sensitive with increasing temperature.

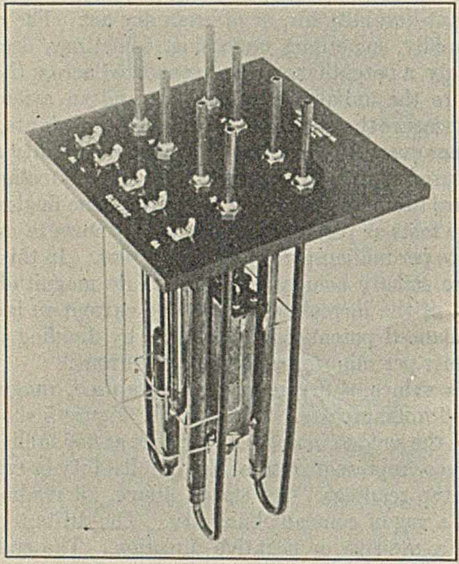


Figure 6—Cell Unit

The effects may be additive or subtractive. From the results of Walker (*10*, Table II), which indicate an increase of sensitivity with increase of cell temperature, it appears that the curves of thermal conductivity for water and air diverge as the temperature increases. No experimental data are available on this point.

Three methods were used for securing a balance of the bridge circuit with dry air in all tubes. (This balance condition is termed the "dry-air zero.")

Method 1—Each of the four unit cell tubes was equipped with convection flow tubes; the air to be analyzed was passed through the X tubes, dried, and then passed through the standard tubes, in series. This method gave the most satisfactory results, because the cell is practically independent of temperature changes and is relatively insensitive to small changes in the current supplied to the bridge. More important, however, is the fact that changes in the concentration of gaseous components other than water vapor which may be present in the mixture have no effect upon the readings, since such changes affect all four arms of the bridge equally. This is true, of course, only when water vapor is the only constituent removed by the drying train interposed between the X and S tubes of the cells.

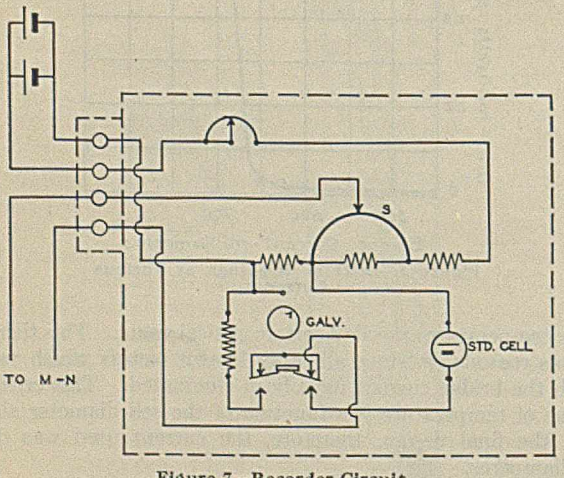


Figure 7—Recorder Circuit

Method 2—In this method the two standard tubes were filled with purified, dried air and were sealed. The X tubes were provided with convection flow tubes, and the air to be analyzed passed only through these in series. A change of 0.1° C. in the cell temperature (the cells being enclosed in a constant-temperature bath) caused a bridge unbalance of 0.1 millivolt, equivalent to about 0.5 per cent relative humidity at 25° C. (This sensitivity to changes of cell temperature was found to be of minor importance in a plant installation, since the controlled oil-bath temperature remained constant to ±0.01° C. for several months.) A current change of 0.001 ampere caused a bridge unbalance of 0.05 millivolt. (The use of a direct-current trickle charger on the storage batteries supplying the bridge completely eliminated any noticeable errors due to variations of bridge current.)

Method 3—In this method the standard tubes were filled with dry air at atmospheric pressure, and were protected with open-end drying tubes. These cells were less sensitive to temperature changes than the previous type, but were unsatisfactory owing to drift of the dry-air zero.

The cell unit is shown in Figure 6, which represents the set-up used according to Method 1. The actual circuit employed is shown in Figure 4. S_1, S_2, X_1, and X_2 represent the standard and analyzing wires, respectively. K is the zero balancing slide wire, which consisted of a 10-turn Kohlrausch slide wire of 6.5 ohms resistance shunted by a coil of 0.5 ohm. E and F are coarse and fine battery-current rheostats; the current was adjusted to the proper value by balancing the potential drop across a coil, D, against that of a standard cell, H, using a small reflecting galvanometer as an index of the balance point. For convenience, all the component parts of the apparatus, except the battery and the cells, were mounted in a single control box.

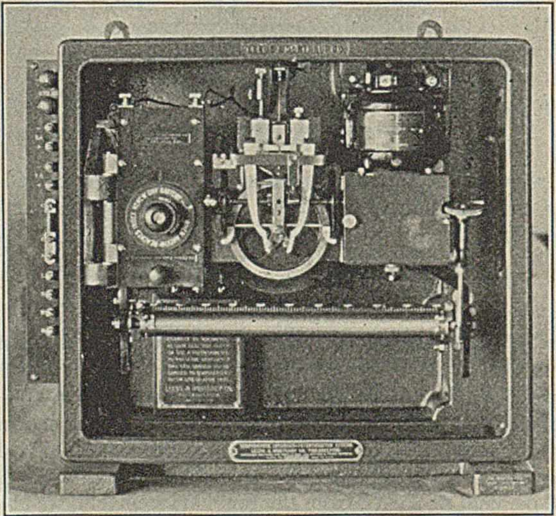


Figure 8—Recorder (Front)

Recorder

The recording potentiometer is connected to the terminals M-N.

The instrument first used was a standard potentiometer-type recorder specially modified to cover a range of 0 to 2 millivolts. Its circuit is shown in Figure 7. The attainment of this low range was made possible by the use of a recorder galvanometer of much higher sensitivity than those usually produced. Figure 8 shows the front of the type of recorder used, and Figure 9 gives a view of its rear working parts. The recorder constitutes in effect a galvanometer, a slide-wire resistance, and a mechanism set in motion by the galvanometer to shift a contact point along the slide wire. The balance point is determined by the absence of current in the galvanometer, at which time the self-balancing mechanism ceases to act.

The disk on the rear of the recorder (Figure 9) carries the slide wire, *S*, of Figure 7. If the potentiometer is not balanced, current flows through the galvanometer, deflecting it and actuating the balancing mechanism. This mechanism turns the slide-wire disk under the contact which may be noted at the top of the disk. The movement of the disk produces an adjustment of the potentiometer, and this automatic adjustment continues until the potentiometer voltage balances the voltage to be measured. At this time the galvanometer returns to its zero position and the balancing mechanism ceases to act. Thus the position of the slide wire *S*, referred to its fixed contact slider, is a measure of the unknown voltage, in this case the unbalanced voltage of the gas-analysis bridge. A small cable attached to a pulley on the shaft carrying the slide wire moves a pen back and forth across a chart. The position of the pen thus indicates the magnitude of the unknown voltage. The chart is in rectangular coördinates, the humidity scale being 10 inches (25.4 cm.) in width.

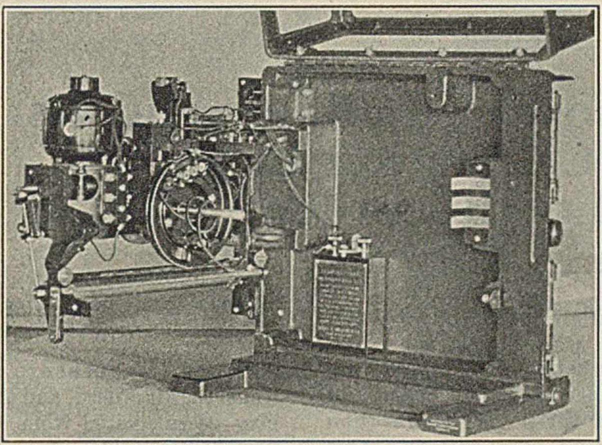


Figure 9—Recorder (Rear)

Calibration

The gas-analysis cells were connected to the calibration apparatus described by Walker (*10*) and air at various constant known humidities was passed through the cells. Recorder readings taken for various humidities furnish data from which a calibration curve similar to that of Figure 10 can be plotted. This curve represents the relation between millivolts as measured on the recording potentiometer and per cent relative humidity at 25° C. It was taken on a set of cells operated according to Method 1; they were placed in an oil bath at 40.1° ± 0.01° C.

Method for Recording Higher Humidities

It was desired to use the range of the recorder to measure humidities other than those included in the narrow range of 0 to 10 per cent relative humidity at 25° C.

It was at first thought that a multiple-range recorder would be the simplest solution of the problem, but it was found possible to calibrate the Kohlrausch slide wire, *K*, in terms of relative humidity at 25° C. That is, by using the recorder galvanometer as an index of zero current condition (the recorder being set at zero on the scale), it was possible to plot a curve of slide-wire reading (*K*) versus relative humidity at 25° C. Walker (*10*) describes this procedure in detail.

A multiple-range recorder was finally constructed, however, which enables the user to measure humidity using a single gas-analysis cell and recorder, in the following ranges: 0–10, 0–20, 0–50, and 48–98 millivolts. The first two ranges will cover from dry to saturated air at 25° C. The last two ranges are useful for measurements of high humidities at higher temperatures. The absolute precision and accuracy are, of course, reduced at the higher ranges.

Accuracy

On the 10 per cent range the recorder is sensitive to a change of ±0.02 per cent relative humidity at 25° C. The accuracy is ±0.05 per cent relative humidity at 25° C. For an instrument of such a low range this accuracy is far better than any heretofore obtained on a self-recording apparatus, and is sufficient for the purpose for which it was designed. Further work in progress bears promise of increasing the accuracy by a considerable amount.

Further Uses of the Apparatus

While the application of thermal-conductivity apparatus to the determination of water vapor is particularly successful in this case, where very low humidities are to be measured, it also should have a considerable field in applications where greater ranges of humidities are to be measured. This is particularly true where it is desired to measure and record humidities in an enclosure without introducing any water vapor by the use of the measuring apparatus, as would be done if the wet-and-dry-bulb thermometer were used. The greatest advantage of the apparatus is, of course, that it is continuous reading and no intermittent sampling is necessary.

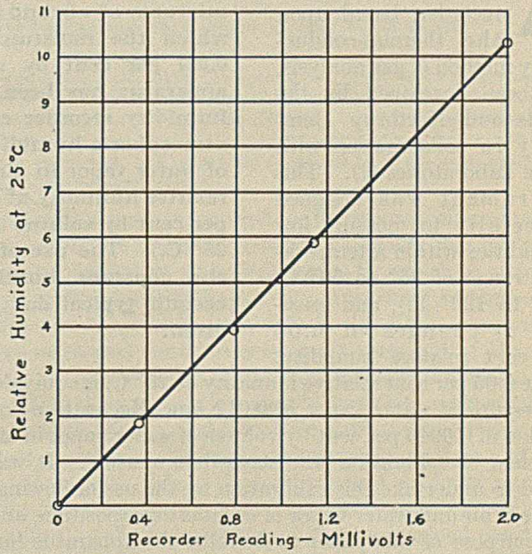


Figure 10—Calibration Curve

Further uses for the thermal-conductivity humidity apparatus are found where it is desired to measure water-vapor content at very high or very low temperature. Above the boiling point of water the usual forms of humidity apparatus cannot be used. For example, the thermal-conductivity method might well be applied to the determination of moisture in dry kilns used in various processes. Likewise, even if the temperature of a gas mixture is below the freezing point of water, the thermal-conductivity method will still give reliable indication of the amount of water vapor present in the mixture. Walker and Ernst (*11*) have given a method of determining the moisture in high-pressure tanks of nitrogen, using the apparatus described.

Conclusion and Acknowledgment

The apparatus described has performed satisfactorily in the Bell Telephone Laboratories. A commercial modification has been in successful operation for a year. It is, however, somewhat in the laboratory stage of development as yet, and a considerable amount of work is necessary in order to make the apparatus suitable for general plant use. In this connection, the kindness of the Bell Telephone Laboratories, and particularly A. C. Walker, must be acknowledged, as calibration of the apparatus would have been very difficult without the calibration apparatus which was developed by Doctor Walker.

Literature Cited

(1) Behr, *J. Optical Soc. Am.*, **12**, 623 (1926).
(2) Daynes, *Proc. Roy. Soc. (London)*, **97A**, 273 (1920).
(3) Griffiths, *Proc. Phys. Soc. London*, **34**, v–xcii (1921–22).
(4) Grüss and Schmick, *Wiss. Veröffentlich. Siemens-Konzern*, **7**, 202 (1928).
(5) Koepsel, *Ber. physik. Ges.*, **10**, 814 (1908); **11**, 237 (1909); *Z. chem. Apparat.*, **3**, 377, 401 (1908).
(6) Palmer and Weaver, Bur. Standards, *Tech. Paper* **249** (1924).
(7) Peters, U. S. Patent 1,504,407 (1924).
(8) Shakespear, *Proc. Phys. Soc. London*, **33**, 163 (1921); U. S. Patent 1,304,208 (1919).
(9) Shaw, *Trans. Roy. Soc. Canada*, **10**, 85 (1916).
(10) Walker and Ernst, IND. ENG. CHEM., Anal. Ed., **2**, 134 (1930).
(11) Walker and Ernst, *Ibid.*, **2**, 139 (1930).
(12) Weaver, Palmer, Frantz, Ledig, and Pickering, IND. ENG. CHEM., **12**, 359 (1920).

Preparation of Air of Known Humidity and Its Application to the Calibration of an Absolute-Humidity Recorder[1]

A. C. Walker and E. J. Ernst, Jr.

BELL TELEPHONE LABORATORIES, 463 WEST ST., NEW YORK, N. Y.

An apparatus is described whereby constant flowing mixtures of air and water vapor may be prepared, in which the moisture content varies not more than 0.001 per cent by volume, over long periods. This apparatus has been utilized to calibrate a sensitive humidity recorder capable of continuously recording atmospheric humidities up to 2.9 per cent by volume of water vapor in air (equivalent to about 95 per cent relative humidity at 25° C.) with a sensitivity of 0.0016 per cent by volume (0.05 per cent relative humidity at 25° C.). The use of the recorder in connection with the constant humidity apparatus is described and certain typical data illustrating the performance are given.

AN absolute-humidity recorder, based upon the thermal-conductivity method of gas analysis, has been developed by the Leeds and Northrup Company in collaboration with these Laboratories (*4*). This instrument was designed especially to measure low humidities within a temperature range of 25° to 50° C. (77° to 122° F.), and sensitive to changes of 0.05 per cent relative humidity. Since 0.05 per cent relative humidity at 25° C. is equivalent to a pressure of water vapor of 0.012 mm. Hg, or to a concentration of 0.0016 per cent by volume of water vapor in air, the problem of calibration was somewhat unusual. It was decided to undertake this calibration by the use of flowing mixtures of air and water vapor of constant composition, and it is the purpose of this paper to describe the apparatus for providing such flowing mixtures and to give calibration data of the humidity recorder together with details of operation.

Apparatus for Preparing Definite Atmospheric Humidities

In 1925 an apparatus was described (*3*) whereby constant flowing mixtures of air and carbon dioxide were prepared, in which the carbon dioxide content varied not more than 0.0005 to 0.001 per cent by volume for long periods. Flowing mixtures of constant humidity have been obtained with a similar apparatus, the principle involved being to mix dry air in fixed proportions with nearly saturated air. The apparatus differs in but one essential detail from that used to provide air-carbon dioxide mixtures; the moist air is obtained by bubbling air through a tower containing distilled water and this tower must be maintained at a fixed temperature to secure a constant degree of saturation.

The apparatus yields a mixture of constant absolute humidity. The relative humidity of a given mixture depends upon the temperature at which the air is used, and this may be calculated from vapor-pressure tables (*2*).

The arrangement of the constant-humidity apparatus is shown in Figure 1.

OPERATION—Air at about 250 mm. of mercury above atmospheric pressure is rapidly and almost completely dried by passage through A_1, a 20-liter carboy containing 5 liters of sulfuric acid. This air is then delivered to the apparatus at nearly constant pressure, determined by the pressure head, *M*. Part of the air stream passes through V_2 to be more completely dried by sulfuric acid in A_2, and by phosphorus pentoxide or Dehydrite (*5*) in *B*, after which acid impurities are removed by calcium oxide in *C*.

Note—If Dehydrite (magnesium perchlorate trihydrate) is used instead of phosphorus pentoxide, the supply pressure of the air can be much lower, and the pressure head, *M*, may be of oil instead of mercury. The oil pressure head is much more quiet and steady than that using mercury.

That most of the drying takes place in A_1 is shown by the fact that the absorbent in *B* needs replenishing but once or twice a year, and the acid in A_2 but once in 3 or 4 months. The rate of flow of dry air to the mixture reservoir, *J*, is measured by the flowmeter, *D*. The remainder of the air, not delivered through V_2, is by-passed through V_1 to *E*, where it is saturated to a constant moisture content by bubbling through distilled water. *F* is a trap to remove entrained water, and the moistened air joins the dry-air stream at *H* after passage through the flowmeter, *G*. The mixture thus formed is of definite moisture content determined by the rates of flow through *D* and *G* and the degree of saturation in *E*. Mixture is delivered at constant rate through the flowmeter *K* for use, simultaneously if necessary, in the calibration of the humidity recorder through V_3, equilibrium experiments through V_4, and gravimetric analyses through the flowmeter *Q* and V_5.

Sufficient air must be supplied to the apparatus to provide adequate quantities of mixture, not only for equilibrium ex-

---

[1] Received December 9, 1929.

periments and analyses, but also an excess bubbling to waste from each of the constant-pressure overflow tubes, *M*, *N*, *O*, and *P*, to insure constant pressures in the various parts of the system. Changes of 1 to 2 inches (2.5 to 5 cm.) in the level of water in the bath, *L*, have appreciably no effect upon the rates of flow through *D* and *G*, and therefore do not affect the mixture composition, since these rates of flow depend, not upon the total hydrostatic heads, but only upon the differential heads fixed by the relative positions of the three adjustable tubes, *N*, *O*, and *P*. To secure the necessary constancy of head the overflow tube *P* is essential; without it the composition of the mixture will vary somewhat with variation in the amount used, which affects slightly the pressure at the exit side of the flowmeter *K*. It is advisable to arrange for a constant flow through *K* continuously, by means of the valve V_4, which, when no equilibrium experiment is in progress, may be adjusted so as to maintain the same pressure drop through *K*.

Distilled water is supplied to *E*, as needed, from the reservoir *E′*. This may be refilled without interrupting the operation of the apparatus. *L* is maintained at constant temperature to provide constant water-vapor pressure in the moist air stream. This is accomplished by the heater lamp, *I*, and adjustable thermostat, *T*. Bubbling from *N*, *O*, and *P* provides adequate stirring to maintain *E* at a constant temperature within ±0.05° C. For high humidities, temperature variations of *E* should not exceed ±0.01° C., and this is accomplished with a motor stirrer in *L*.

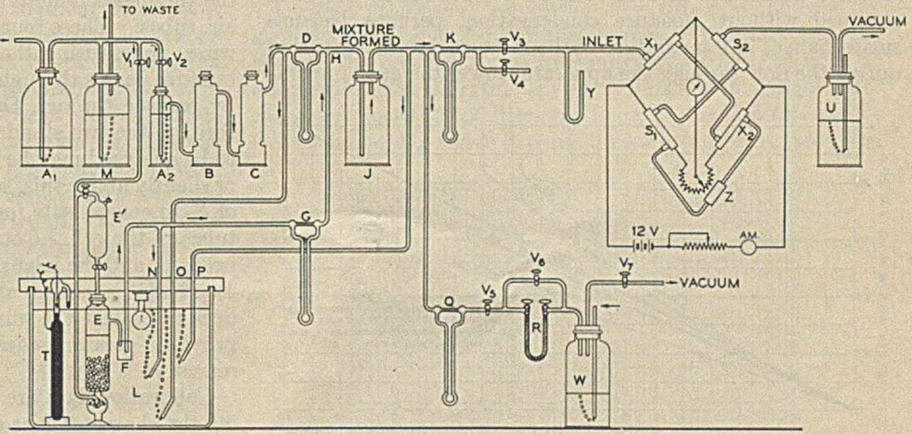


Figure 1—Apparatus for Preparing Constant Mixtures of Air and Water Vapor

Factors Determining Humidity of Mixture

The humidity of the mixture depends upon several factors, the most important being (1) the temperature of the water in *E;* (2) the rate of flow of dry air through *D* and (3) of wet air through *G;* (4) changes in the height of water in *E* causing changes in the pressure distribution in the system and consequent composition changes; (5) the efficiency of saturation in *E*, which depends upon the complexity of the path taken by the bubbles of air, the rate of flow, and the length of the water column.

Considering these factors separately:

(1) A change of 0.1° C. in the temperature of water in *E* causes a change in the mixture compositions of 0.04 and 0.6 per cent relative humidity at 6 and 80 per cent relative humidity (25° C.), respectively. With the temperature control provided—i. e., 0.01 to 0.05° C.—the effect of temperature variations may be considered negligible at any humidity.

(2 and 3) The rates of flow through *D* and *G* are easily controlled by the overflow tubes in *L*, and mixtures of definite composition may be reproduced readily, as will be shown later.

(4) A change of 2.5 to 5 cm. (1 to 2 inches) in the total head of about 18 cm. (7 inches) of water in the saturator *E* is without perceptible effect upon the mixture composition, and greater changes than this need not occur if reasonable care is taken.

(5) Overnight records of operation and gravimetric analyses of the mixture on succeeding days show that the efficiency of saturation of the air passing through *E* is constant for a given setting of the apparatus. For all rates of flow used in this work, the degree of saturation of the air passing through *E* has been found to be between 93 and 96 per cent; e. g., the effluent air from *E* is 93 to 96 per cent relative humidity at the saturator temperature, and for a given set of conditions the efficiency is constant to less than 0.5 per cent. Glass beads in *E* aid materially in giving these high values of saturation efficiency.

Note—In preparing mixtures of high humidity the rate of air flow through *E* is a maximum. Under these conditions, moisture is observed to condense in the glass tube leading from the trap *F* to the flowmeter *G*, owing perhaps to the increased expansion of the gas at the higher rates of flow. Usually this condensation is confined to that portion of the tube immersed in the water bath, *L*, but when the water-bath temperature is more than 2° to 3° C. below that of the room this condensation occurs for a distance of about 2 cm. above the water level. This results in fluctuations of about 0.5 per cent in the mixture humidity, due to the effect of room-temperature variations. This difficulty was eliminated by inserting a small porous plug of glass wool in the glass tube about 2 inches (5 cm.) below the water level, and by placing an electric lamp (10-watt) beside the tube where condensation occurs.

A calibration curve is required for the analysis flowmeter, *Q*. Similar curves are desirable, but not necessary, for the other flowmeters, since they are useful guides by which to estimate the settings for a specific humidity. The simplest method of securing air of definite humidity is to make gravimetric analyses of several mixtures provided by settings of *D* and *G* covering the whole range of moisture content which may be used. With these data it is a simple matter to estimate flowmeter settings for a specific mixture with sufficient accuracy for most purposes. Accurate gravimetric analyses of the estimated mixture should then be secured, and the mixture may be reproduced with extreme accuracy when desired, provided only that the temperature of *E* is maintained constant.

The procedure for analyzing the mixture gravimetrically is as follows:

> Mixture is drawn through the weighing tube *R* by vacuum applied at V_7, at a constant rate observed by the flowmeter, *Q*, and fixed by the vacuum head, *W*. Dehydrite is used in *R* as the absorbent, with a small layer of phosphorus pentoxide in the outlet arm to reduce the moisture in the effluent air to a negligible amount.
>
> *Note*—The use of Dehydrite simplifies the analysis of air for moisture at high humidities, since it does not become gelatinous on absorbing relatively small amounts of water. With phosphorus pentoxide, the pressure drop through *R* changes during an analysis so rapidly as to require almost continuous readjustment of the vacuum head, *W*. That Dehydrite is an efficient absorbent for this purpose is shown by an analysis of air at 75 per cent relative humidity at 25° C. Approximately 0.3 gram of water was absorbed in *R* during the test with no change in weight of a second weighing tube containing phosphorus pentoxide connected in series after *R*.
>
> For high humidities the instant of starting an analysis should be observed as accurately as possible, since the duration of the test is usually 20 to 30 minutes. This is accomplished as follows: *R* is placed in position and air passed through it until *W* is adjusted for a suitable rate through *Q* and *R*. The tube *R* is then weighed and replaced. The mixture is by-passed through V_6 to

W until the proper differential is secured in *Q*. Flow is then diverted quickly through *R*, reducing the error in the time of starting an analysis to a negligible amount.

Mixtures containing as little as 0.0019 and as much as 2.9 per cent by volume of water vapor were obtained with this apparatus as used in the writers' laboratory. These values correspond to 0.06 and 95 per cent relative humidity at 25° C., respectively. Absolute humidities higher than 2.9 per cent of water vapor by volume may be secured readily by increasing the temperature of *E* and maintaining the remainder of the apparatus above this temperature to prevent condensation. Relative humidities greater than 95 per cent have not been obtained without moisture condensation, perhaps because small changes in temperature of the mixture due to expansion during the flow through the apparatus lower the gas temperature below its dew point even though the surrounding room or thermostat is maintained at a temperature theoretically equivalent to 95 per cent relative humidity for this mixture.

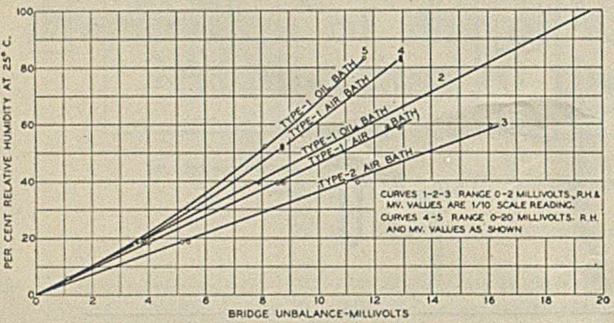


Figure 2—Calibration Curves

It was possible to secure much higher rates of flow of dry air than of wet air with the particular arrangement used in this laboratory, since the rate of bubbling through *E* limited the amount of wet air much more than the resistance through *B* and *C* restricted the flow of dry air. The maximum wet air flow was about 60 liters per hour, that for dry air, 600 liters per hour, and this dry-air flow was materially increased when Dehydrite was substituted for phosphorus pentoxide in *B*.

Reproducibility and Constancy of Mixtures

The reproducibility of the air-water mixture may be gaged from the following experiment.

Two gravimetric analyses, made on successive days, of air furnished by certain settings of the flowmeters gave 0.73 and 0.75 per cent relative humidity at 25° C. Six days later these flowmeter settings were repeated, the apparatus having been used in the meantime to provide several other humidities. The gravimetric analysis of the mixture was 0.74 per cent relative humidity.

The constancy of composition obtained with this apparatus is shown in Table I. During the entire period over which these results were obtained the apparatus was operated continuously, day and night, at this one humidity.

Table I—Constancy of Composition of Air-Water Mixture

(Gravimetric analyses)

DATE	RELATIVE HUMIDITY AT 24.4° C.
	Per cent
2/ 8/29	75.0; 75.3; 75.3; 75.1
2/ 9/29	74.8; 74.9[a]
2/11/29	75.1; 75.3
2/13/29	75.2
2/14/29	75.3
2/15/29	75.3; 75.1
2/16/29	75.1
Average	75.14

[a] The analyses made on February 9 were probably slightly low as the bubbler was but half full of water. Excluding these two results, the maximum deviation from the average was only 0.16 per cent relative humidity.

The constancy of these results is the more striking when it is considered that the air is at a high relative humidity. Below 10 per cent relative humidity at this temperature the mixture varies less than 0.05 per cent relative humidity; or the variations of water content are less than 0.002 per cent of the volume of air.

Humidity Recorder Calibration

A schematic diagram of the thermal-conductivity bridge circuit, which is the essential feature of the humidity recorder, is shown in Figure 1. X_1 and X_2 are the analyzing tubes of the thermal-conductivity cell; S_1 and S_2 the standard, or dry air, tubes. These four tubes contain fine platinum resistance wires, constituting the arms of a Wheatstone bridge. The mixture passes through the analyzing tubes in series, is dried by passage through Dehydrite in *Z*, and continues in series through the two standard tubes. For many purposes the air to be analyzed may be available only at atmospheric pressure or slightly above this, so that vacuum is required on the outlet of S_2 to compensate for the pressure drop through *Z* and the tubes of the cell. Constant flow is obtained with a vacuum head, *U*, and the inlet pressure is observed by the manometer, *Y*. Nujol is used in all flowmeters and manometers, since it does not affect the mixture composition and its low density provides greater sensitivity than could be obtained with mercury.

Calibration data are given in Tables II, III, and IV, showing the characteristics of the humidity recorder when used in three different ways.

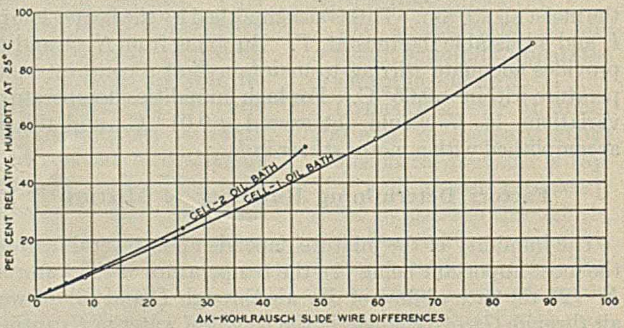


Figure 3—Δ*K* Calibration Curves

Table II is for the most sensitive, low-range recorder (0 to 2 millivolts). The upper limit of water-vapor content which can be analyzed directly with this instrument is between 6 and 10 per cent relative humidity at 25° C., depending upon the sensitivity of the cell. The lower limit is about 0.05 per cent relative humidity at this temperature.

Table II—Calibration Data for 0 to 2 Millivolt Range

TYPE 1 CELL				TYPE 2 CELL	
Oil Bath		Air Bath		Air Bath	
Mv.	*% R. H.*	*Mv.*	*% R. H.*	*Mv.*	*% R. H.*
0.36	1.85	0.40	1.85	0.54[a]	1.85
		0.38	1.85	0.52	1.85
0.79	3.95	0.86	3.95	1.10	3.95
		0.88	3.95	1.14	3.95
1.14	5.88	1.25	5.88	1.61	5.94
		1.29	5.88		
2.00	10.30				

[a] The greater sensitivity of this cell over that of type 1 in the air bath is thought to be due to the size of the platinum resistance wires. A very small reduction in wire diameter results in materially increased sensitivity.

Table III contains data on a multiple-range recorder for the 0 to 20 millivolt range. This instrument, having four ranges—0 to 2, 0 to 20, 0 to 50, and 48 to 98 millivolts—may be used to measure, directly, mixtures containing moisture contents up to saturation at temperatures well above 40° C. Table III contains a calibration up to only about 90 per cent relative humidity at 25° C., this being substantially the limiting concentration available with the humidity apparatus as operated by the writers. In each range the recorder has about the same percentage sensitivity, this being approximately 1 per cent of the observed value.

Table III—Calibration Data for 0 to 20 Millivolt Range

Type 1 Cell

Oil Bath		Air Bath	
Mv.	*% R. H.*	*Mv.*	*% R. H.*
1.15	5.88	1.22	5.88
8.15	52.3	8.75	52.3
		8.75	51.6
11.7	83.2	13.0	83.2
		13.0	82.7

Table IV contains calibration data up to about 90 per cent relative humidity at 25° C., using the sensitive, low-range scale (0 to 2 millivolts), but utilizing an offset zero secured by unbalancing the cell bridge with the Kohlrausch slide wire (*4*). This method permits the use of the most sensitive range of the recorder for measuring high humidities. It has the advantage of showing small variations in gas composition with almost the same sensitivity as that obtainable with the single-range (0 to 2 millivolts) recorder when used directly on air of low moisture content. Its disadvantage is that the potential unbalance as determined by the offset slide wire zero cannot be measured directly in millivolts.

Table IV—ΔK Calibration

Type 1 Cell Oil Bath			Type 2 Cell Oil Bath		
Ko[a]	Δ*K*	*% R. H.*	*Ko*[a]	Δ*K*	*% R. H.*
513.8	8.6	6.30	473.2	2.6	2.34
	59.9	55.3		5.5	4.86
	87.5	88.1		26.2	24.05
				47.6	52.3

[a] Dry air.

Two types of thermal-conductivity cell were used in the experimental calibrations recorded in these tables. Type 1, the more stable and practical cell, was equipped with convection flow tubes on all four cell tubes and the gas to be analyzed was dried after leaving the analyzing tubes before passing to the standard tubes. Type 2 was equipped with convection flow tubes on the analyzing tubes only; the standard tubes were sealed and contained dry air. (For a more detailed discussion of the cell construction see the paper by Rosecrans, *4*.)

The data in Tables II and IV refer to cells of both types, while those in Table III refer to only type 1 cell. All three tables include comparisons of the cell sensitivity when maintained at constant temperature in an oil bath and in an air bath. All experiments were made with the cells at 40.1° C.; the air bath was constant to ±0.025° C., and the oil bath to ±0.01° C.

The curves in Figure 2 are plotted from the data of Tables II and III. The unit values of abscissa and ordinate are as shown for the 0 to 20 millivolt curves, but should be read as one-tenth of these values for the 0 to 2 millivolt curves. The relation between the per cent relative humidity and bridge unbalance is nearly linear up to 10 per cent relative humidity, this being equivalent to about 0.78 per cent by volume of water vapor. Above this concentration the relation deviates appreciably from a straight line, the sensitivity decreasing with increasing moisture content. Cells of type 2 must be maintained at constant temperature to ±0.01° C., since the pressure of the dry air sealed in the standard tubes may change with greater temperature changes by an amount sufficient to alter appreciably the thermal conductivity of the dry air and consequently the resistance of these reference arms of the bridge. Cells of type 1 are not sensitive to changes of 10° C. in the temperature of the surrounding thermostat. It is therefore somewhat surprising that the calibration curves (Figure 2) of type 1 cell differ appreciably in oil and in air baths, although maintained at the same surrounding temperature. Thermocouple measurements of the external surface temperatures of the copper blocks containing the cell tubes showed that these surfaces were 1.5° C. higher in the air bath than in the oil bath. Consequently the bridge arms are at a slightly higher temperature in the air bath, for a given bridge current, than in the oil bath, owing to the lesser temperature gradient between wires and surrounding walls of the cell. This results in increased cell sensitivity with increased cell temperature and suggests that the temperature coefficients of thermal conductivity of air and water vapor diverge with increasing temperature. No data are available by which to calculate this change in sensitivity.

Owing to the use of convection flow tubes on the cells designed by the Leeds & Northrup Company, the rate of flow of gas and the pressure at the tube entrances appear to have no effect upon the calibration curves. This was investigated for rates of from 10 to 100 liters per hour, and for inlet pressures from 2 mm. of Hg above to 5 mm. below atmospheric pressure.

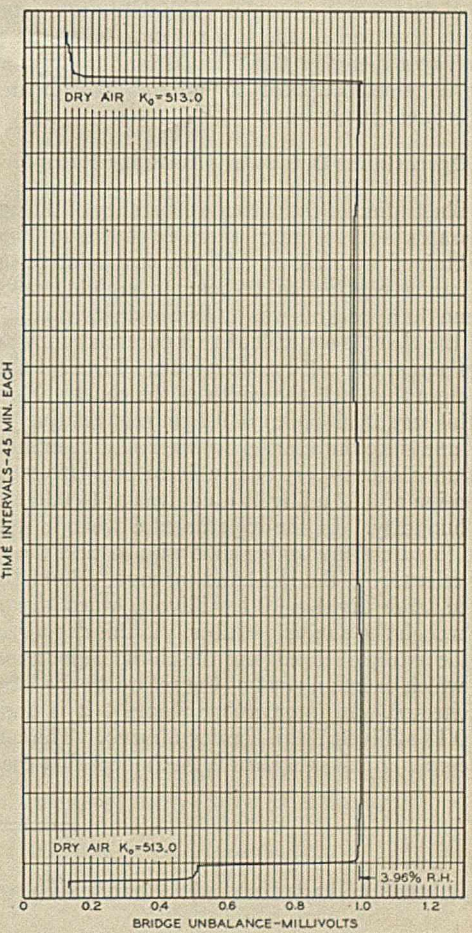


Figure 4—Record as Obtained with Humidity Recorder

The procedure used to secure the Δ*K* data of Table IV, shown graphically in Figure 3, is as follows: The humidity recorder is operated on dry air until constant conditions are assured. The recorder motor is stopped so that the galvanometer pointer swings freely. Air of known humidity is passed through the cell, causing the pointer to be displaced in the direction of increasing humidity. It is then brought back to the mid-position by rebalancing the bridge circuit with the Kohlrausch slide wire. Final adjustment is made with the motor running so that the line drawn on the chart is a continuation of the initial record with dry air. The difference, Δ*K*, between the setting, *K*, thus obtained on the

Kohlrausch slide-wire drum and that initially secured with dry air, *Ko*—i. e., $\Delta K = K - Ko$—is proportional to the humidity. As may be expected from the complexity of the relations in the unbalanced bridge circuit, the curve in Figure 3 is distinctly non-linear.

The non-linear relation observed in Figure 2 is consistent with the results of Grüss and Schmick (*1*), who showed that the thermal conductivity of air increases with the addition of small amounts of water vapor. Their curve of conductivity ratio, L_m/L_{air}, vs. p_{H_2O} exhibits a maximum at a composition of p_{H_2O} = 20 per cent by volume. Further addition of water vapor decreases the ratio until at about 40 per cent by volume of water vapor the mixture conductivity (L_m) is less than that of dry air (L_{air}). On this basis the per cent relative humidity–millivolt curves in Figure 2 should bend towards the relative humidity axis, as observed. The maximum in the curve of Grüss and Schmick is far above the range investigated here and their lowest observation is at 7.1 per cent by volume of water vapor, so that quantitative comparison between the two sets of data is not possible. The data are in qualitative agreement, however, in the two respects—that the pressure of water vapor increases the thermal conductivity, and that the first increments appear to have slightly greater effect than subsequent increments.

Operational Details of Humidity Recorder

As an illustration of the extreme constancy of the humidifying apparatus and recorder, there is shown in Figure 4 a record obtained with air at 3.96 per cent relative humidity (25° C.) in a continuous 16-hour (overnight) test during which time the apparatus was under no supervision. The full width of the chart is equivalent to a potential unbalance of 2 millivolts across the cell bridge circuit. Figure 4 shows but slightly more than half the width of the chart. For the cell used in this test, 2 millivolts = 9.2 per cent relative humidity (25° C.), and since the relation between relative humidity and millivolt unbalance is very nearly linear over this range, each small division of 0.02 millivolt is equivalent to 0.092 per cent relative humidity. In the experimental work it was found desirable to adjust the bridge slide wire so that the recorder pen was offset from the left-hand, or zero, side of the chart about one large division (0.1 millivolt) when dry air was passed through the analyzing tubes. If this dry air zero line were at the extreme left edge of the chart, an increase in cell current, which causes a shift of the record to the left, would not be detected. In interpreting Figure 4 it is understood that the 0.13 millivolt line is the dry-air zero. The constancy of the recorder circuit is evident from the fact that the dry-air zero obtained at the end of the 16-hour run is almost identical with the initial zero of 0.13 millivolt. The spacing of the horizontal lines on the chart corresponds to time intervals of 45 minutes, and the ready response of the recorder to changes in humidity of the analyzed air is evident. (The break in the record at about 0.52 millivolt during the first few minutes of this test corresponds to a humidity of 1.75 per cent or 0.35 millivolt.) The constancy of the humidity supplied by the air apparatus is evident from the record on 3.96 per cent air. The initial and final values for this air were identical, being 0.99 − 0.13 = 0.86 millivolt. During the night a slight downward drift occurred, followed by a similar upward drift. The total magnitude of this drift was 0.02 millivolt. Since 0.01 millivolt is equivalent to about 0.04 per cent relative humidity, the deviation from the mean value of 0.85 millivolt for the 16-hour run was less than 0.05 per cent relative humidity, this being the estimated sensitivity of the humidity recorder. Further evidence of constancy was obtained in a continuous test on air at low relative humidity over a period of one week. Current adjustments were made but once a day, and dry-air zero settings were taken but three times during the week. These dry-air zero settings differed by only 0.01 millivolt.

For satisfactory operation of this recorder the current through the cell bridge must be closely controlled, since a variation of 0.001 ampere causes a bridge unbalance of about 0.05 millivolt. In the work described in this paper the current used was 0.600 ampere. The constant drain of this amount of current from a 12-volt, heavy-duty storage battery caused a slow drift in the voltage, necessitating frequent readjustments of the current. This drift was eliminated by the use of a continuously operated charging current of 0.6 ampere, supplied from a 110-volt d. c. line through a resistance such that the potential drop across the battery terminals gave the balancing current. A properly designed a. c. vacuum-tube or oxide type rectifier may be used where d. c. is not available.

Acknowledgment

Acknowledgment is made to H. H. Lowry for valuable suggestions in the development and calibration of the humidity recorder.

Literature Cited

(1) Grüss and Schmick, *Wiss. Veröffentlich. Siemens-Konzern*, **7**, 202 (1928).

(2) International Critical Tables, Vol. III, p. 212 (1928).

(3) Johnston and Walker, *J. Am. Chem. Soc.*, **47**, 1807 (1925).

(4) Rosecrans, Ind. Eng. Chem., Anal. Ed., **2**, 129 (1930).

(5) Smith, Ind. Eng. Chem., **16**, 20 (1924).

Standardization of Thiosulfate against Standard Permanganate Solution

In our paper entitled "Cupric Oxide as a Standard in Iodimetry" [Ind. Eng. Chem., Anal. Ed., **1**, 68 (1929)], data were given in Table IV for the normality of a thiosulfate solution, as determined by titration against standard permanganate, which were uniformly about 0.15 per cent lower than the mean found with six other standards. This result is at variance with the findings of W. C. Bray on the basis of a critical investigation of this method [*J. Am. Chem. Soc.*, **46**, 2206 (1924)]. Since the time of publication we have been in correspondence with Professor Bray, who suggested that we make a new series of titrations in an endeavor to ascertain the cause of the discrepancy. The work was done with new solutions, and a fresh stock of Bureau of Standards sodium oxalate was drawn upon to standardize the permanganate solution. Strict attention was also paid to the conditions of the titration as determined by Professor Bray. The thiosulfate solution was standardized against cupric oxide as well as electrolytic copper deposited on platinum cathodes. As a result we have been able to reproduce the normality of this thiosulfate solution, by titration against permanganate, to within ±0.07 per cent. Whether the above-mentioned probable sources of error or other unknown causes were responsible for our previous low results, we are now convinced that permanganate solution is equally as trustworthy as the other iodimetric standards employed in our investigation.

T. F. Buehrer and C. Morgan Mason

The University of Arizona
Tucson, Ariz.

January 22, 1930

Moisture Content of Compressed Nitrogen[1]

A. C. Walker and E. J. Ernst, Jr.

Bell Telephone Laboratories, 463 West St., New York, N. Y.

THE absolute-humidity recorder, which was described in a previous paper (*2*), has been used in this laboratory for several experimental purposes, one of which merits special mention.

Nitrogen in tanks under high pressure (150 atmospheres or 2200 pounds per square inch, maximum pressure) has been used commercially for certain drying purposes. Unless special manufacturing processes are used, liquid water always is present in the tanks and the compressed gas is saturated with water vapor at the tank temperature. The drying efficiency of the gas is affected but little by the presence of liquid water in the tank, since the saturated, compressed gas is reduced to but 1 per cent relative humidity when expanded to atmospheric pressure from the maximum tank pressure. However, the drying efficiency decreases with decreasing tank pressure, and a chart of increasing humidity of the expanded gas against decreasing tank pressure is of value in determining below what pressure the humidity of the gas becomes undesirably high. Such a chart is difficult and laborious to prepare by ordinary gravimetric analyses, but a continuous record of the increasing humidity may be obtained rapidly and accurately with the humidity recorder.

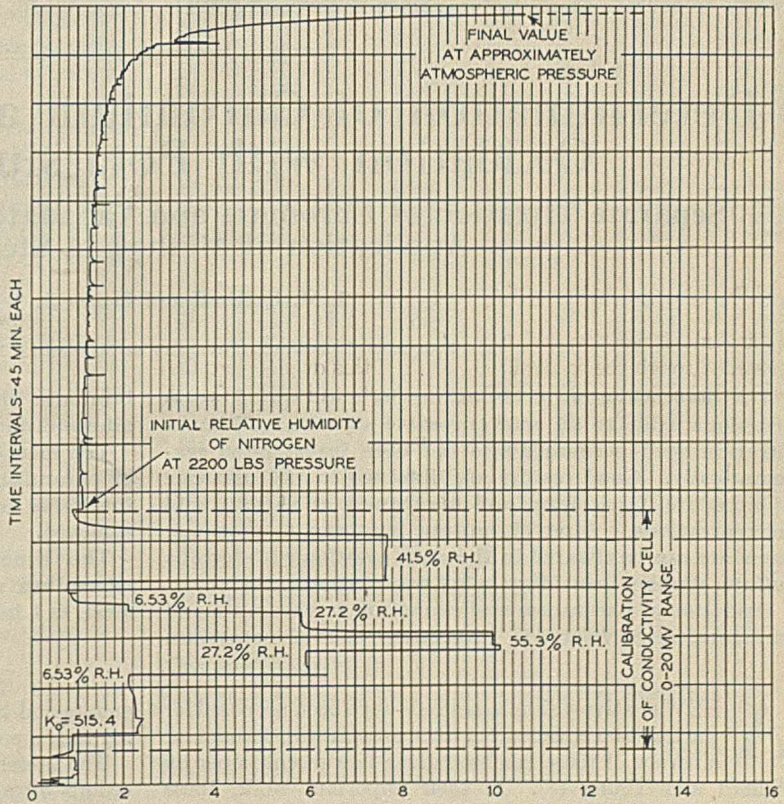


Figure 1

Method of Analysis

Nitrogen was discharged to waste through a measuring flowmeter at a rate of approximately 600 liters per hour, this being sufficiently rapid to exhaust the contents of a full tank (6250 liters or 220 cubic feet of the gas at atmospheric pressure) in one day, but slow enough to prevent cooling of the reducing valve and connections to an undesirable degree. A small portion of this gas was by-passed through the thermal-conductivity cell, at constant pressure, and a continuous record was obtained of the increasing moisture content of the gas.

Results

Figure 1 shows the chart obtained with a tank of commercially available nitrogen which contained some liquid water, although the excess water which could be removed by inverting the tank and blowing off was first discharged. The chart also includes the data from which the humidity-recorder calibration curve was prepared for this work. Sharp peaks occur in the tank record at irregular intervals. These were coincident, in nearly all cases, with readjustments made in the reducing valve to compensate for the drop in tank pressure. The sudden change in pressure during an adjustment to restore the rate to its proper value probably caused droplets of water, condensed in the tank connections owing to the cooling of the expanding gas, to be carried on and vaporized in the gas stream, with momentarily increased humidity.

Since the horizontal lines on the chart indicate time intervals of 45 minutes each, the tank pressures corresponding to different values of humidity may be estimated directly.

These data are given in Table I together with calculated values of relative humidity of the gas expanded to atmospheric pressure from the different tank pressures. These calculated values are based on the assumption that the water-vapor pressure within the tank remains at saturation during the experiment. This assumption, while being the simplest, is probably not justified, since it is doubtful if the saturation pressure of water vapor is maintained in the tank. The slow rate of evaporation of liquid water to compensate for actual loss of water vapor with the expanded gas, together with the cooling effect, should operate to reduce the water-vapor content of the gas in the tank below the initial saturation value. It is evident, therefore, that the values calculated on the basis of the saturation of the gas within the tank would be too high. However, it is to be noted from the data of Table I that above 3 atmospheres the observed values are still higher than the calculated values, indicating inapplicability of the laws of partial pressures for this system. This discrepancy between observed and calculated values has been noted in other cases. It is of the same nature as that observed by Bartlett (*1*), and is qualitatively accounted for by him by assuming that the compressed gas acts as a solvent for water vapor. The difference between the observed and calculated values decreases with decreasing tank pressures and below 3 atmospheres the ob-

---

[1] Received December 9, 1929.

served values are lower than the calculated values, which fact may be attributed to the withdrawal of increased amounts of water vapor at the lower pressures together with a small lag in the humidity recorder. The final observed humidity of 60 per cent is but a rough approximation. No attempt was made to reduce the flow through the flowmeter during the last few minutes of the experiment to approach equilibrium conditions more closely, since for the purpose of this work it was sufficient to determine that the drying efficiency of compressed nitrogen decreases rapidly as the tank pressure decreases.

Table I—Moisture Content of Nitrogen at Atmospheric Pressure after Expansion at 24° C. from High-Pressure Containers in Which Liquid Water Is Present

TIME AFTER START	TANK PRESSURE		RELATIVE HUMIDITY Obsd.	RELATIVE HUMIDITY Calcd.
Minutes	*Atm.*	*Lbs./sq. in.*	*Per cent*	*Per cent*
0	150	2200	1.0	0.66
235	75	1100	2.0	1.32
353	37.5	550	3.4	2.60
411	18.8	275	6.0	5.05
441	9.4	137.5	12.0	9.62
453	4.7	68.8	19.0	17.6
463	2.35	34.4	27.5	29.9
466	1.18	17.2	40.0	45.9
467[a]	1.0	14.7	44.0	50.0
470[a]	0	0	60[a]	100.0

[a] Approximate.

Table II contains experimental data obtained with a tank of nitrogen subjected to special manufacturing processes. Integration of these data indicates that even in this case the expanded gas contained 2 grams of water as compared with a total of 4.5 grams in the gas obtained from the tank which was known to contain excess water. Since it seems impossible that these 2 grams of water existed in the vapor phase, one must conclude that the precautions taken to exclude water in the manufacturing processes were insufficient. In this second case, also, the final value of the relative humidity of the gas expanded to atmospheric pressure is only approximate. Since no satisfactory assumption can be made as to the degree of saturation of the gas initially, no significant value of expected relative humidity can be calculated for purposes of comparison. These data, which have been obtained with specially dried nitrogen, make it evident that for most drying purposes the less carefully prepared gas should be nearly as satisfactory as the "dried" gas, provided that the tank is not completely discharged.

Table II—Moisture Content of Nitrogen at Atmospheric Pressure after Expansion at 24° C. from High-Pressure Containers in Which No Liquid Water Is Present

TIME AFTER START	TANK PRESSURE		RELATIVE HUMIDITY (Obsd.)
Minutes	*Atm.*	*Lbs./sq. in.*	*Per cent*
0	150	2200	0.78
235	75	1100	1.55
353	37.5	550	1.75
411	18.8	275	2.16
441	9.4	137.5	2.75
453	4.7	68.8	3.25
463	2.35	34.4	3.96
466	1.18	17.2	4.65
470[a]	0	0	6.5[a]

[a] Approximate.

Literature Cited

(1) Bartlett, *J. Am. Chem. Soc.*, **49**, 65 (1927).
(2) Rosecrans, Ind. Eng. Chem., Anal. Ed., **2**, 129 (1930).

Determination of Chromium and Vanadium after Oxidation with Potassium Bromate[1]

Separate Titration of Chromate and Vanadate in the Same Solution and Application of Method in Steel Analysis

I. M. Kolthoff and Ernest B. Sandell

School of Chemistry, University of Minnesota, Minneapolis, Minn.

The determination of chromium by addition of excess arsenious oxide to an acid chromate solution and back-titration with permanganate has been investigated systematically. Good results are obtained in the presence of vanadate, ferric iron, and manganese at various acid concentrations. After chromium has been determined, vanadate can be titrated in the same solution with ferrous sulfate, diphenylbenzidine being used as indicator.

Oxidation of chromium and vanadium to chromate and vanadate, respectively, is effected by use of potassium bromate; the excess bromate is removed by boiling with ammonium sulfate.

The method can be applied to the rapid determination of chromium and vanadium in alloy steels. Tungsten interferes in the titration of vanadium and must be removed.

The time required for the total determination of chromium and vanadium, including dissolving of the steel, is 1 hour or less.

. . . .

A FEW relatively simple methods have been proposed for the titration of vanadium when present with chromium; a review of these has been given in a recent paper by Willard and Young (*8*). In their important work, these authors oxidize chromium and vanadium by the persulfate method and, after removing the excess of persulfate, titrate the sum of chromate and vanadate with ferrous sulfate either according to the potentiometric or the usual method, in the latter case with diphenyl benzidine as an indicator. Vanadium, when present with chromium, can be oxidized selectively by potassium bromate in the presence of sufficient hydrochloric acid to prevent the oxidation of the chromium. The excess of bromate is removed by boiling with ammonium sulfate and the vanadate titrated with ferrous sulfate according to the potentiometric or usual method.

The present writers have tried to simplify the above procedure by applying a reducing agent which would reduce chromate but not vanadate. This was accomplished by using arsenious oxide as a reagent. Since the reduction of the chromic acid takes place rather slowly, an excess of arsenious trioxide is added and this is then titrated back with potassium permanganate. A slight reduction of the vanadate by the excess of arsenious acid would not affect the results since the vanadyl salt would be oxidized again by permanganate. After back-titration with permanganate, the vanadate can be determined with ferrous sulfate according to the directions of Willard and Young (*8*).

---

[1] Received December 23, 1929.

Determination of Chromic Acid with Arsenious Oxide under Different Conditions

Spitalsky (*7*) first made use of arsenious acid in the determination of chromium. In brief, his method of procedure was to add an excess of arsenious oxide to a hydrochloric acid solution of dilute chromate and after 20 to 25 minutes to back-titrate the excess of arsenite with potassium bromate using methyl orange as indicator. Lang (*4*) determined chromium in a similar manner, titrating the excess of arsenious acid with potassium permanganate in the presence of chloride and a trace of potassium iodide or iodate as catalyst; in the absence of iodide or iodate the reduction of MnO_4^- to Mn^{++} does not take place smoothly at room temperature. Zintl and Zaimis (*10*) have described the determination of chromium by direct potentiometric titration of chromate with arsenious acid; vanadate is determined in the same solution (after reduction of chromic acid) by titration with ferrous sulfate, the end-point being found potentiometrically. The same workers have applied a modification of this method to the determination of chromium and vanadium in steel (*11*). The procedure given necessitates the removal of all except traces of manganese, and preferably iron, before titrating chromate and vanadate with arsenious acid and ferrous sulfate, respectively. The end points are detected potentiometrically; in order that chromic acid may be titrated with arsenious acid, the presence of a few tenths of a milligram of manganese as a catalyst is necessary. Lang and Zwĕrina (*5*) have also described a method involving the use of arsenious acid and ferrous sulfate for the direct determination of chromium and vanadium in steel. Chromium is titrated with arsenious oxide potentiometrically in the presence of much manganese and a trace of potassium iodide or iodate.

It would seem advantageous to have at our disposal a simple method by which chromium and vanadium could both be determined by visual titration, not involving the detection of the end points potentiometrically. The development of such a method will be described, especially with reference to its application in the analysis of steel; the influence of various factors which affect the method will be discussed.

An excess of standard arsenious acid is added to an acid solution of chromate and vanadate to reduce chromate to chromic salt; titration of the excess arsenious acid by permanganate gives the amount of chromium present. Vanadium is then determined in the same solution by titration with ferrous sulfate, diphenylbenzidine being used as indicator.

DETERMINATION OF CHROMIUM—*Materials Used.* Potassium dichromate: 0.1 *N* solution prepared from recrystallized salt dried at 200° C.

Ammonium metavanadate: 0.025 *N* solution, standardized by reducing with sulfur dioxide and titrating the hot vanadyl solution with potassium permanganate.

Arsenious acid: 0.1 *N* solution prepared by weighing out B. of S. arsenic trioxide (99.97%).

Potassium permanganate: 0.1 and 0.025 *N* solutions, standardized against either sodium oxalate or arsenious oxide.

Ferrous sulfate: 0.025 *N* in approximately 0.1 *N* sulfuric acid.

Potassium iodide (catalyst): 1/400 *N*; 1 or 2 drops in each titration.

Procedure. Varying amounts of dichromate were taken and the acidified solution, having a volume of 50 to 75 cc., was treated with a slight excess of arsenious acid and after standing for 5 to 10 minutes the excess of the latter was titrated with 0.1 *N* permanganate, 1 or 2 drops of 1/400 *N* potassium iodide solution being present. The amounts of acid, chloride, iron (as ferric alum), and vanadium (as ammonium vanadate) present are specified in the tables. When iron was present in the solution to be titrated, 5 to 10 cc. of 85 per cent phosphoric acid were always added to give a more easily discernible end point with permanganate. In determinations 40 to 49, Table I, the only chloride present was that introduced with the standard solution of arsenious acid which contained 10 cc. of 12 *N* hydrochloric acid per liter—i. e., under the conditions of the experiment, the solution to be titrated with permanganate contained approximately the equivalent of 0.25 cc. of 12 *N* hydrochloric acid.

Table I—Chromate Titrations: Effect of Chloride, Acid Concentration, Ferric Iron, and Vanadate

No.	Cr Taken	Fe^{+++} Present	V Present	Chloride Added	12 *N* H_2SO_4	Chromium	
						Found	Error
	Gram	*Grams*	*Gram*	*Cc.*	*Cc.*	*Gram*	*Gram*
				12 *N* HCl			
1	0.0445	...	...	..	25	0.0426	−0.0019
2	0.0445	...	...	..	25	0.0436	−0.0009
3	0.0445	...	...	..	8	0.0419	−0.0026
4	0.0445	...	...	10	..	0.0445	0.0000
5	0.0445	...	...	10	..	0.0444	−0.0001
6	0.0445	...	...	10	25	0.0444	−0.0001
7	0.0445	...	...	10	25	0.0444	−0.0001
8	0.0445	...	...	2	25	0.0444	−0.0001
9	0.0445	...	...	1	25	0.0446	+0.0001
10	0.0445	...	...	1	25	0.0445	0.0000
11	0.0445	1.5	...	..	25	0.0415	−0.0030
12	0.0445	1.5	...	..	25	0.0429	−0.0016
13	0.0445	0.1	...	1	25	0.0442	−0.0003
14	0.0445	0.7	...	1	25	0.0443	−0.0002
15	0.0445	1.5	...	1	25	0.0443	−0.0002
16	0.0445	...	0.01	..	25	0.0431	−0.0014
17	0.0445	...	0.025	1	25	0.0446	+0.0001
18	0.0445	...	0.05	1	25	0.0441	−0.0004
19	0.0433	1.5	0.025	..	25	0.0426	−0.0007
20	0.0433	1.5	0.025	..	5	0.0429	−0.0004
21	0.0445	1.5	0.025	..	25	0.0436	−0.0009
22	0.0445	1.4	0.075	..	25	0.0435	−0.0010
23	0.0445	1.5	0.025	1	25	0.0444	−0.0001
24	0.0445	1.5	0.050	1	25	0.0444	−0.0001
25	0.0445	1.5	0.025	1	25	0.0444	−0.0001
26	0.0433	2.0	0.050	1	25	0.0431	−0.0002
27	0.0173	1.5	0.025	1	25	0.0171	−0.0002
28	0.0433	1.5	0.025	1	5	0.0432	−0.0001
29	0.0433	1.5	0.025	1	10	0.0433	0.0000
30	0.0433	1.5	0.025	1	50	0.0431	−0.0002
				NaCl			
				Gram			
31	0.0433	1.5	0.025	0.1	5	0.0432	−0.0001
32	0.0173	1.5	0.025	0.05	5	0.0173	0.0000
33	0.0035	1.5	0.025	0.05	5	0.0030	−0.0005
34	0.0035	1.5	0.025	0.05	5	0.0030	−0.0005
				Conc. 12 *N* HCl			
				Cc.			
35	0.00173	2.0	0.025	4	5	0.00177	+0.0004
36	0.0433	1.5	0.060	1	25	0.0433	0.0000
37	0.0445	...	...	10	..	0.0447	+0.0002
38	0.0445	...	...	10	..	0.0445	0.0000
39	0.0445	...	...	10	..	0.0446	+0.0001
40	0.0445	...	...	[a]	10	0.0444	−0.0001
41	0.0445	...	...	[a]	30	0.0446	+0.0001
42	0.0445	...	...	[a]	30	0.0445	0.0000
43	0.0445	...	...	[a]	20	0.0443	−0.0002
44	0.0445	...	0.02	[a]	20	0.0445	0.0000
45	0.0445	0.7	...	[a]	5	0.0442	−0.0003
46	0.0445	0.7	...	[a]	25	0.0444	−0.0001
47	0.0445	0.6	0.025	[a]	10	0.0445	0.0000
48	0.0445	0.6	0.06	[a]	25	0.0444	−0.0001
49	0.0445	0.6	0.025	[a]	40	0.0446	+0.0001
50	0.0445	...	...	30	..	[b]	......

[a] Chloride from As_2O_3 only.

[b] End point could not be distinguished.

Table II shows the influence of time on reduction of chromate with arsenite.

Table II—Influence of Time of Standing before Back-Titration of As_2O_3

No.	Cr Taken	Fe^{+++} Added	V Added	12 *N* HCl	12 *N* H_2SO_4	Time of Standing	Chromium	
							Found	Error
	Gram	*Grams*	*Gram*	*Cc.*	*Cc.*	*Min.*	*Gram*	*Gram*
1	0.0445	...	...	2	25	90	0.0444	−0.0001
2	0.0445	...	...	0.5	30	10	0.0446	+0.0001
3	0.0445	...	...	0.5	10	10	0.0446	+0.0001
4	0.0445	...	...	0.5	30	1	0.0445	0.0000
5	0.0445	...	0.025	0.5	30	180	0.0444	−0.0001
6	0.0445	...	0.015	0.5	10	1	0.0443	−0.0002
7	0.0445	0.6	...	0.5	25	15	0.0444	−0.0001
8	0.0433	1.5	...	1	25	2	0.0431	−0.0002
9	0.0433	1.5	0.025	1	5	15	0.0432	−0.0001
10	0.0433	1.5	0.025	1	5	1	0.0434	+0.0001
11	0.0035	1.5	0.025	2	5	1	0.0033	−0.0002
12	0.0035	1.5	0.025	3	5	2	0.0034	−0.0001
13	0.0173	1.5	0.025	1	25	30	0.0171	−0.0002

The manganous salt present during the determinations given in Table III was added as pure manganous sulfate.

Table III—Determination of Chromium in Presence of Manganese, Iron, and Vanadate

No.	Cr Taken	Fe^{+++} Present	V Present	Mn^{++} Present	Acid			Chromium	
					12 *N* HCl	12 *N* H_2SO_4	H_3PO_4 (85%)	Found	Error
	Gram	*Grams*	*Gram*	*Gram*	*Cc.*	*Cc.*	*Cc.*	*Gram*	*Gram*
1	0.0441	...	..	0.005	1	10	10	0.0439	−0.0002
2	0.0433	1.5	..	0.005	1	25	..	0.0431	−0.0002
3	0.0433	1.5	0.05	0.007	1	25	..	0.0431	−0.0002
4	0.0441	...	..	0.050	1	6 *N* 15	10	0.04385	−0.00025
5	0.0441	2.5	..	0.050	0.5	20	10	0.0436	−0.0005
6	0.0441	2.5	..	0.070	0.5	30	10	0.0435	−0.0006

Discussion of Results. The reduction of dichromate by arsenious acid is fairly rapid. In solutions which are 1 normal (or more) in acid, the reduction is complete in 1 minute if 1 or 2 cc. of excess arsenious acid are added (Nos. 4, 6, 10, and 11, Table II). The presence of chloride is necessary in the back-titration of arsenious acid with permanganate; in the absence of chloride, even when catalyst is present, the results of the titration are low. These observations confirm in some respects the observations of Lang (*4*). The amount of chloride that need be added, however, is small, as little as 0.05 to 0.1 gram in 50 cc. being sufficient (Nos. 31 and 32, Table I). Even at chloride concentrations as high as 1 or 2 normal a good end point is obtained with permanganate; increasing the chloride concentration much above this gives a fleeting end point. Varying the acidity of the solution from 1 normal to more than 6 normal has no effect on the results within experimental error. Iron and vanadium are without influence. Experiment 5 in Table II shows that no interference by vanadate occurs even if the excess of arsenious trioxide is titrated back after 3 hours' standing. When iron is present in large amounts, phosphoric acid should be added in order that a sharp end point may be obtained with potassium permanganate.

When large amounts of manganese are present in solution with chromic acid, a brownish color appears in the solution soon after the addition of a little arsenious acid in spite of the presence of the catalyst, potassium iodide, and has a tendency to persist, especially when iron is present, after a slight excess of arsenious acid has been added. After standing for a short time (usually less than 1 minute) with a slight excess of 0.1 *N* arsenious acid, the murky color of the solution disappears and the normal bluish green color appears. When potassium iodide is not present as catalyst, the brown color due to trivalent manganese disappears only with extreme slowness after addition of excess arsenious acid. The addition of a trace of potassium iodide is, therefore, unconditionally necessary in the presence of manganese.

The color change in titrating with permanganate is from bluish green to blue. A deepening of the color indicates the end point. The results given in the tables have not been corrected for the color effect of the chromic salt; the excess of permanganate required to give a perceptible end point in the colored solution under the conditions described (40 mg. chromium in 100 cc., etc.) corresponds to a correction of about +0.1 mg. chromium in the amount found. The end point can easily be detected with an accuracy of a drop of 0.1 *N* permanganate. The observation of the end point is incomparably better than in cases where the reduction is accomplished with ferrous sulfate instead of arsenious trioxide in the presence of vanadate. It is for this reason that the writers prefer this procedure to that described by Hamner (*1*) and ecommended by the Bureau of Standards for routine analysis (February 7 1922).

Knop (*3*) has recently described the use of several new oxidation-reduction indicators in titrations with permanganate. The applicability of two of these, Eriogrün B and Setopalin, to the detection of the end point in the titration of excess arsenious acid with permanganate for the determination of chromate was tested. One-half a cubic centimeter of a 0.1 per cent solution of each indicator, respectively, was added to the acid solution (1 or 2 *N*) of chromic salt containing arsenious oxide; titration was then made with 0.025 *N* permanganate. The end point thus obtained (color change from green to bluish) was more distinct than that with permanganate alone, but the relatively high acidity of the solution evidently is detrimental to the full utility of the indicators. At lower acidities (below 0.5 *N*) both indicators are very useful. The general procedure for the titration of chromate and vanadate will be described later.

Determination of Vanadate by Titration with Ferrous Sulfate with Diphenyl Benzidine as Indicator

A brief study was made of the method of determining vanadic acid by titration with ferrous sulfate using diphenylbenzidine as indicator according to the procedure given by Willard and Young (*8*).

Titrations of vanadic acid were made at a volume of 50 to 100 cc. with 0.025 *N* ferrous sulfate which had been standardized against potassium permanganate. Vanadium was present as ammonium vanadate. The concentration of the diphenylbenzidine indicator used was 0.1 per cent in concentrated sulfuric acid. Sodium acetate was added in the form of the trihydrate. (Table IV)

In agreement with the results of Willard and Young (*8*), it was found that the color change at the end point in the titration of vanadic acid in the absence of sodium acetate was slow, although good results could even then be obtained if

Table IV—Titration of Vanadate

No.	V Taken	Cr Present	Fe^{+++} Present	0.1 *N* As_2O_3 Added	Acid Present		Sodium Acetate Added	Diphenylbenzidine Added (0.1%)	Time before Titrating	Vanadium	
					6 *N* H_2SO_4	H_3PO_4				Found	Error
	Gram	*Gram*	*Grams*	*Cc.*	*Cc.*	*Cc.*	*Grams*	*Cc.*	*Min.*	*Gram*	*Gram*
1	0.0280	..	...	...	5	5	5	0.8	5	0.0278	−0.0002
2	0.0280	..	...	...	5	10	5	0.6	0	0.0278	−0.0002
3	0.0280	..	...	...	5	5	0	0.5	0	0.0278	−0.0002
4	0.0280	..	...	...	5	5	8	0.5	5	0.0278	−0.0002
5	0.0280	..	...	...	10	5	8	0.5	5	0.0279	−0.0001
6	0.0280	..	...	...	10	5	8	0.5	5	0.0279	−0.0001
7	0.0280	..	1.5	...	10	5	8	0.5	5	0.0278	−0.0002
8	0.0280	..	1.5	...	10	5	0	0.5	0	0.0279	−0.0001
9	0.00224	..	1.5	...	10	10	0	0.5	0	0.00233	+0.00009
10	0.00224	..	1.5	...	10	10	0	0.5	0	0.00229	+0.00005
11	0.00224	..	1.5	...	10	10	10	0.5	5	0.00210	−0.00014
12	0.00224	..	1.5	...	5	10[a]	12	0.5	5	0.00216	−0.00008
13	0.00224	..	1.5	...	5	5[a]	12	0.5	5	0.00213	−0.00011
14	0.00224	0.03	...	...	5	10	8	0.5	5	0.00221	−0.00003
15	0.00224	0.03	1.5	...	5	10	8	0.5	5	0.0022+	0.0000
16	0.00224	0.03	...	0.1	5	10	8	0.5	5	0.0022	0.0000
17	0.00224	0.03	1.5	0.1	5	10	8	0.5	5	0.0022	0.0000
18	0.00224	0.03	1.5	0.5	5	10	8	0.5	3	0.0218	−0.00006

[a] 2 cc. 12 *N* HCl also present.

Table V—Simultaneous Determination of Chromate and Vanadate

No.	Cr Taken	V Taken	Fe Present	Acidity			Conditions of Vanadium Titration			Chromium		Vanadium	
				H_2SO_4 (6 *N*)	H_3PO_4	HCl (concd.)	Sodium acetate added	Diphenylbenzidine (0.1%)	Time of standing	Found	Error	Found	Error
	Gram	*Gram*	*Grams*	*Cc.*	*Cc.*	*Cc.*	*Grams*	*Cc.*	*Min.*	*Gram*	*Gram*	*Gram*	*Gram*
1	0.0433	0.00224	...	5	10	2	10	0.5	3–5	0.0434	+0.0001	0.00238	+0.00014
2	0.00346	0.0280	...	5	10	2	10	0.5	3–5	0.00338	−0.00008	0.02787	−0.00013
3	0.0433	0.0280	1.5	5	10	2	15	0.5	3–5	0.0430	−0.0003	0.0282	+0.0002
4	0.0433	0.0280	1.5	5	5	2	12	0.5	3–5	0.0432	−0.0001	0.0281	+0.0001
5	0.0433	0.0112	1.5	5	10	2	12	0.5	3–5	0.0432	−0.0001	0.0113	+0.0001
6	0.0433	0.00224	1.5	5	10	2	12	0.5	3–5	0.0430	−0.0003	0.00248	+0.00024
7	0.0433	0.00224	1.5	5	10	2	12	0.5	3–5	0.0431	−0.0002	0.0023	+0.0001
8	0.01732	0.00336	3	5	10	2	10	0.5	3–5	0.01724	−0.00008	0.00340	+0.00004
9	0.01732	0.00224	1.5	5	5	2	10	0.5	3–5	0.01730	−0.00002	0.00235	+0.00011
10	0.01732	0.0280	1.5	5	10	2	10	0.5	3–5	0.01728	−0.00004	0.02794	−0.00006
11	0.0433[a]	0.00224	1.5	5	10	2	10	0.5	3–5	0.0430	−0.0003	0.00248	−0.00024

[a] In this determination 5 mg. Mn^{++} were present.

care was exercised in addition of reagent near the end point. It is advisable, however, to add sufficient sodium acetate to react with the sulfuric and hydrochloric acid present; approximately 5 grams of $NaC_2H_3O_2.3H_2O$ can be allowed for each cubic centimeter of concentrated sulfuric acid and 1.5 grams for each cubic centimeter of concentrated hydrochloric acid. In the calculation of the results given in Table IV, the volume of ferrous sulfate was corrected for the indicator blank by adding 0.03 cc. to the volume of 0.025 *N* ferrous sulfate used for each 0.1 cc. of 0.1 per cent diphenylbenzidine solution added, this being the value given by Willard and Young (*8*). In agreement with the statement of these authors it was found that, in the presence of tungstic acid, the blue color of diphenylbenzidine does not appear and the titration of vanadium is rendered impossible.

It appears that more than traces of arsenious acid partially reduce vanadate on standing (compare determinations 16, 17, and 18, Table IV).

Combined Determination of Chromate and Vanadate

In the determinations of both chromium and vanadium the solution had a volume of 50 to 75 cc. and contained the amounts of chromate, vanadate, ferric alum, acid, and chloride indicated in Table V; 1 or 2 drops of 1/400 *N* potassium iodide were always added at the beginning. Tenth-normal arsenious acid was added from a buret until the color of the solution became bluish green; then a few cubic centimeters were always added in excess. After having stood for a few minutes, the excess of arsenious acid was titrated with 0.025 *N* permanganate and from this volume the amount of chromium present was found. One drop of 0.1 *N* arsenious acid was then added to reduce any small excess of permanganate that might be present. After addition of the amounts of sodium acetate trihydrate and 0.1 per cent (in concentrated sulfuric acid) diphenylbenzidine given in the table, the solution was allowed to stand for the length of time indicated. The titration of vanadium was then made by slowly adding 0.025 *N* ferrous sulfate until the blue color of the liquid changed to green. In the calculation of the quantity of vanadium present, the indicator correction was assumed to be 0.03 cc. 0.025 *N* ferrous sulfate per 0.1 cc. 0.1 per cent diphenylbenzidine, this correction being added to the volume of 0.025 *N* ferrous sulfate actually used.

From the results in Table V it may be concluded that the following general procedure will give satisfactory results.

Standard Solutions Required—*Arsenious acid:* 0.1 *N*, preferably prepared by weighing out 4.947 grams of pure arsenic trioxide and dissolving in 40 to 80 cc. of 1 *N* sodium hydroxide and diluting nearly to 1 liter. Hydrochloric acid is added until the solution is neutral or slightly acidic and finally the solution is made up to exactly 1 liter. If pure arsenic trioxide is not at hand, an approximately 0.1 *N* solution is prepared from the best product and standardized against permanganate. The solution of arsenious acid to be standardized should be about 1 normal in hydrochloric acid; 1 or 2 drops of 1/400 *N* potassium iodide are added. Potassium permanganate is run in (not too rapidly) until the faintest pink tinge appears in the liquid. The end point is excellent.

Potassium permanganate: 0.025 *N*, standardized against pure arsenious acid or pure sodium oxalate.

Ferrous sulfate: 0.025 *N* in approximately 0.1 *N* sulfuric acid.

Determination of Chromate—The solution in which chromium and vanadium are to be determined may conveniently have a volume of 100 cc. and should not contain more than 0.05 or 0.075 gram of chromium in this volume. The acidity of the solution should be at least 1 normal; 1 or 2 cc. of concentrated hydrochloric acid, or its equivalent, should be present, as well as 1 or 2 drops of 1/400 *N* potassium iodide. In case iron is present 5 to 10 cc. of 85 per cent phosphoric acid must be added. Standard arsenious acid is slowly run into the solution of chromate and vanadate from a buret until the color becomes bluish green; a few cubic centimeters in excess are then added. In case much manganese is present, the appearance of the bluish green color may take some time. Therefore, 5 minutes should elapse between the addition of arsenious acid and the beginning of the back-titration with permanganate; in most cases when the quantity of manganese present is small, it is sufficient to allow the solution to stand for 1 or 2 minutes to effect complete reduction of chromate. The excess of arsenious acid is now titrated by slowly running in potassium permanganate; the end point is indicated by a sudden deepening in color of the green chromic solution to bluish green. The end point may be recognized to within 1 or 2 drops of 0.025 *N* permanganate without difficulty if not much more than 0.05 gram of chromium is present per 100 cc.

Determination of Vanadate—To remove a possible slight excess of permanganate, 1 drop of arsenious oxide is added. Vanadium is now determined essentially according to the directions of Willard and Young. Approximately 5 grams of sodium acetate trihydrate are added for each cubic centimeter of concentrated sulfuric acid present (including also the sulfuric acid of the indicator to be added) and 1.5 grams for each cubic centimeter of 12 *N* hydrochloric acid, and thereafter 0.5 to 1.0 cc. of 0.1 per cent diphenylbenzidine (in concentrated sulfuric acid). The solution is allowed to stand for 5 minutes and is then titrated slowly with 0.025 *N* ferrous sulfate. Special care should be taken to add the ferrous sulfate dropwise near the end point. The color change is from blue to green or bluish green, the change being sharper the less chromium is present in solution. To correct for the indicator blank add 0.03 cc. for each 0.1 cc. of diphenylbenzidine indicator present to the volume of 0.025 *N* ferrous sulfate used in the titration. In case tungstic acid is present, it must be removed before vanadate can be titrated with diphenylbenzidine as indicator (*8*).

Oxidation of Chromic and Vanadyl Salts with Potassium Bromate

The oxidation of chromic salts to chromic acid and vanadyl salts to vanadic acid can be effected by the use of potassium persulfate as oxidizing agent, and this is the reagent ordinarily used in determining the sum of chromium and vanadium in steels (*2*, *6*, *9*). In the present investigation the possibility of using potassium bromate as the oxidizing agent was studied. Potassium bromate has already been utilized by Willard and Young (*8*) as a reagent for the oxidation of vanadyl salts to vanadic acid in hydrochloric acid solution without affecting chromic salts.

In the experimental work to be described, the oxidation of chromium was carried out in a solution acidified with sulfuric and phosphoric acids. At low acid concentrations the oxidation is so slow that it is not conveniently applicable. It was found, however, that small amounts of manganese greatly increased the speed of the reaction, since in the presence of phosphoric acid the trivalent (and quadrivalent) forms of manganese catalyze the oxidation of chromic salts to chromic acid. After the oxidation has been completed, it is necessary to destroy all excess of bromate and to decompose the manganic phosphate still present. For this purpose ammonium sulfate was used. The higher oxidation states of manganese are quickly reduced to Mn^{++} in hot solution, but it was found that a complete decomposition of bromate at 100° C. was difficult to attain after a moderate period of boiling even though the presence of manganese is decidedly favorable. Thus, after boiling for 15 minutes with about 3 grams (excess) ammonium sulfate in the presence of 3 cc. of concentrated sulfuric acid and 10 cc. of phosphoric acid and 5 to 10 mg. of Mn^{++} in 100 cc., the solution still contained enough bromate to give an error of about +0.5 mg. in the amount of chromium found. It was found, however, that, after most of the bromate had been destroyed by boiling for a few minutes with ammonium sulfate, the last traces could be eliminated by adding a small amount of hydrochloric acid. If 5 grams ammonium sulfate were added to a solution containing 5 cc. of concentrated sulfuric acid, 5 to 10 cc. of phosphoric acid (85 per cent), and 1 cc. of concentrated hydrochloric acid with 1 gram of potassium bromate, no bromate was left after boiling for 10 to 15 minutes (methyl orange test).

The results recorded in Table VI were obtained by oxidizing a 100-cc. portion of chromic and vanadyl salts (obtained by reducing dichromate and vanadate with sulfur dioxide) containing the stated amounts of acid and manganese (as manganous sulfate) with 2 grams of pure potassium bromate. In determinations 1 to 6 boiling with potassium bromate was continued for 10 minutes, in determinations 7 to 18 for only 5 minutes. Five grams of ammonium sulfate were then added to the solution; after most of the bromine had been boiled out, 10 cc. of 1 *N* hydrochloric acid were added and boiling was continued until starch-iodide paper was no longer colored. After cooling, chromate and vanadate were determined as already described. In all cases when iron was present enough additional phosphoric acid was added after oxidation to make the total amount present about 10 cc. of 85 per cent acid. After the addition of 2 drops of 1/400 *N* potassium iodide and a small excess arsenious acid (usually only a few cubic centimeters), the solution was allowed to stand 3 to 5 minutes or until it was bluish green with no murky color, which would be due to trivalent manganese.

Table VI—Oxidation of Cr^{+++} and VO^{++} with Potassium Bromate and the Determination of Chromium and Vanadium according to the Proposed Method

No.	Cr Taken	V Taken	Fe Present	Mn Present	Acid Present		Chromium		Vanadium	
					H_2SO_4 (concd.)	H_3PO_4 (85%)	Found	Error	Found	Error
	Gram	*Gram*	*Grams*	*Gram*	*Cc.*	*Cc.*	*Gram*	*Gram*	*Gram*	*Gram*
1	0.0441	....	...	0.004	3	10	0.0435	−0.0006	....	......
2	0.0441	....	...	0.004	3	10	0.0435	−0.0006	....	......
3	0.0441	....	1.0	0.005	3	10	0.0434	−0.0007	....	......
4	0.0441	....	...	0.005	8	10	0.0433	−0.0008	....	......
5	0.0441	....	...	0.005	3	10	0.0435	−0.0006	....	......
6	0.0441	....	...	0.005	1	4	0.0439	−0.0002	....	......
7	0.0441	....	...	0.010	1	5	0.0439	−0.0002	....	......
8	0.0441	....	2.5	0.010	1	5	0.0442	+0.0001	....	......
9	0.0441	....	...	0.005	2	2	0.0441	0.0000	....	......
10	0.0441	....	...	0.025	3	2	0.0439	−0.0002	....	......
11	0.0441	....	2.5	0.035	3	1	0.0440	−0.0001	....	......
12	0.0441	....	...	0.005	5	5	0.0439	−0.0002	....	......
13	0.0441	0.0112	...	0.005	2	2	0.0438	−0.0003	0.0112	0.0000
14[a]	0.0441	0.0112	2.0	0.050	3	10	0.0442	+0.0001	0.0110	−0.0002
15	0.0441	0.0112	2.0	0.050	2	5	0.0438	−0.0003	0.0110	−0.0002
16	0.0176	0.0112	2.0	0.040	2	4	0.0175	−0.0001	0.0112	0.0000
17[a]	0.0882	0.0280	2.0	0.050	2	10	0.0882	0.0000	0.0282	+0.0002
18	0.0176	0.0280	...	0.050	3	3	0.0176	0.0000	0.0281	+0.0001

[a] Vol. 200 cc. instead of 100 cc.

Note—At the Minneapolis meeting of the AMERICAN CHEMICAL SOCIETY September, 1929, H. H. Willard described the favorable properties of 70 per cent perchloric acid as an oxidizing agent. In concentrated solution chromium and vanadium can be oxidized to chromic acid and vanadic acid, respectively, by boiling with perchloric acid. After the completion of the oxidation, the perchloric acid need not be removed; by simply diluting with water its oxidizing properties practically disappear and it will not interfere in the titration of chromate and vanadate. In this way it may be possible to avoid the use of potassium bromate entirely. See also Lichtin, IND. ENG. CHEM., Anal. Ed., **2**, 126 (1930).

It will be seen that, when the acidity is high, the amount of chromium found is too low. This may be attributed to the decomposition of chromic acid by boiling with Cl^- in the presence of the amounts of acid given. Decreasing the acid concentration improves the results. It had been the original intention to maintain a rather high concentration of phosphoric acid in the solution during oxidation to prevent the precipitation of manganese dioxide, which dissolves rather slowly when boiled with ammonium sulfate. In the presence of smaller amounts of phosphoric acid (2 to 5 cc. per 100 cc. of solution) there is more or less precipitation of manganese during the 5-minute period of boiling required for oxidation, depending upon the amount of manganese present. When ammonium sulfate is added and the liquid boiled, manganese dioxide will be dissolved by the combined action of ammonium ion and phosphoric acid. Only when 50 mg. or more of manganese are present is complete solution of manganese dioxide effected with difficulty at phosphoric acid concentrations of 3 or 4 cc. per 100 cc. The hydrochloric acid added to decompose the residual bromate will, of course, also attack manganese dioxide.

Determination of Chromium and Vanadium in Steel

The results of the analyses of different steels given in Table VII were obtained by the following recommended procedure:

For steels containing chromium to the extent of 1 per cent a 2- to 3-gram sample is taken and for higher contents correspondingly less. The weighed sample is transferred to a 250-cc. Erlenmeyer flask; 25 cc. water are added and then 1.5 cc. of concentrated sulfuric acid for each gram of steel, allowing 1 to 2 cc. in excess, and 3 or 4 cc. of 85 per cent phosphoric acid. To hasten solution of the steel, the liquid is boiled. When solution is complete, sufficient concentrated nitric acid is added dropwise to oxidize iron to the ferric condition; about 1 cc. per gram of steel is sufficient. The solution is now boiled to expel the oxides of nitrogen and sufficient water added to make the total volume approximately 100 cc. One or two grams of pure potassium bromate are then added and the solution is boiled for 5 minutes. Five grams of ammonium sulfate are cautiously added in small portions to the solution (which should again have been brought to approximately 100 cc.); the solution is boiled until most of the bromine has been expelled. Then 10 cc. of 1 *N* hydrochloric acid are added and boiling is continued until starch-iodide paper is no longer colored. After cooling to room temperature, 5 to 8 cc. of 85 per cent phosphoric acid and 1 to 2 drops of 1/400 *N* potassium iodide are added; 0.1 *N* arsenious acid is run in slowly from a buret until the color of the solution has become bluish green and finally 2 to 3 cc. in excess. The analysis is then continued as described above for the combined determination of chromate and vanadate.

Table VII shows that the proposed method gives satisfactory results.

Table VII—Analyses of Bureau of Standards Steels according to the Proposed Method

STEEL	BUREAU OF STANDARDS VALUES		VALUES BY PROPOSED METHOD	
	Chromium	Vanadium	Chromium	Vanadium
	Per cent	*Per cent*	*Per cent*	*Per cent*
30	1.35	0.21	1.343 1.353	0.220 0.214
30[a]	1.04[a] 1.01[b]	0.21	1.005 0.998	0.207 0.212
30[b]	1.03	0.208	0.99	0.206
32	0.89	..	0.930 0.941	0.018

[a] Persulfate oxidation.
[b] Permanganate oxidation.

Literature Cited

(1) Hamner, *Met. Chem. Eng.*, **17**, 206 (1917).
(2) Kelley and Conant, J. Ind. Eng. Chem., **8**, 719 (1916).
(3) Knop, *Z. anal. Chem.*, **77**, 125 (1929).
(4) Lang, R., *Z. anorg. allgem. Chem.*, **152**, 205 (1926).
(5) Lang, R., and Zwěrina, *Z. Elektrochem.*, **34**, 364 (1928).
(6) Lundell, Hoffman, and Bright, Ind. Eng. Chem., **15**, 1064 (1923).
(7) Spitalsky, *Z. anorg. Chem.*, **69**, 179 (1911).
(8) Willard and Young, Ind. Eng. Chem., **20**, 764 (1928).
(9) Willard and Young, *Ibid.*, **20**, 769 (1928).
(10) Zintl and Zaimis, *Z. angew. Chem.*, **40**, 1286 (1927).
(11) Zintl and Zaimis, *Ibid.*, **41**, 543 (1928).

The Testing of Automotive Rubber Parts Assembled under Compression[1]

Part I—Deflection under Compression

Franz D. Abbott

Firestone Tire and Rubber Company, Akron, Ohio

Present-day test specifications on automotive rubber parts are not only incomplete and misleading, but entirely lacking in uniformity. This is particularly true of compression and permanent-set tests on automotive mechanical rubber parts assembled under compression. Consequently, an effort has been made to show the urgent need for unification of such methods.

Data are presented in Part I to show that high tensile is no criterion of relative resistance to compression set and that hardness is not a measure of deflectability. In addition, deflection and permanent set under compression are greatly influenced by the size and shape of the test piece, the method of cutting the sample, the gage and methods of measuring it, and condition and kinds of surfaces in contact with the test piece.

Compression and compression-set testing equipment are discussed, and some newly designed laboratory equipment is described. One piece of apparatus, the compressetometer, has been found extremely useful in making deflection, hysteresis, and set tests. These tests may be performed under constant load or constant distortion. The constant-load (spring) compression-set clamp is suggested as a suitable laboratory standard for permanent-set testing under compressive loads.

....

In keeping with the rapid strides in the automobile industry, an almost endless variety of rubber mechanical goods is being used in motor-car manufacture. As a result there has arisen a great variety of tests and test specifications, many of which are worthless for evaluating the parts under consideration. In fact, some of these specifications, particularly those requiring compression- and permanent-set tests, are often defeating the purpose for which they were written. The authors of these specifications have either presupposed a uniformity in testing equipment and details of tests, and hence have very briefly stated the tests, or else, through a lack of appreciation of the many factors influencing the results, have failed to include such important details as size of test piece, gage, etc. Consequently many inferior stocks may pass these specifications if the testing conditions are carefully chosen. There are generally other requirements, such as tensile, elongation, etc., to preclude the possibility of passing certain very low-grade stocks, but even these requirements do not offer an absolute safeguard against inferior quality, for a very high tensile, for example, does not

[1] Received July 3, 1929; revised paper received December 2, 1929. Presented before the Division of Rubber Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

necessarily mean high quality in a good motor-support or shock-insulator stock. Undoubtedly modulus, stress, and elongation at break, and also percentage change in physical properties after aging are important in evaluating many rubber parts, and would be to a certain extent for automobile mechanical goods also, were it not practically impossible to perform many of these tests on the rubber parts themselves owing to their peculiar shape and size. In many cases it may prove necessary to have the producer furnish with each shipment laboratory test slabs of the same stock for tensile, deflection, and set tests. In general, these test pieces will be given that cure which produces the maximum desired physical property rather than one identical with that of the part in question. This procedure makes it possible for an unethical producer to furnish samples of stock apparently identical in composition, yet of far better physical properties than those possessed by the parts included in the shipment. The question of equivalent cure is also very important and "mechanicals" will often necessarily differ greatly in cure from such test slabs.

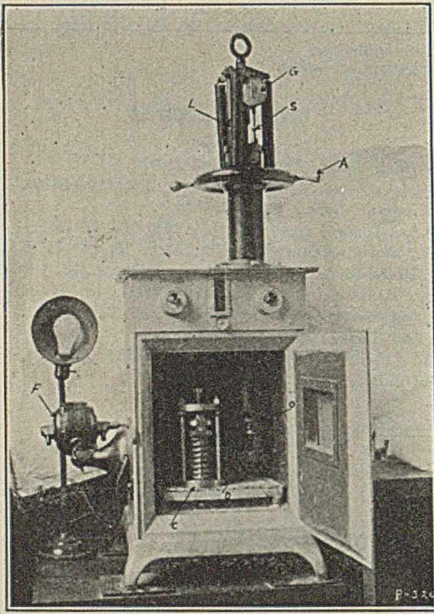


Figure 1—Compressetometer

To date it has been impossible to establish any true mathematical relationship between the results of tensile tests and those of many of the other mechanical tests. Goodwin and Park (*4*) have shown that the abrasion resistance of a tread compound cannot be judged merely by its tensile data. Likewise the writer (*1*) has shown that the data of tensile tests will not serve to evaluate properly the resistance of a stock to flexure under compression. In view of the above facts, it seems advisable to perform such tests as simulate, partly at least, service conditions.

Probably one of the most important groups of automobile mechanical rubber goods is that including parts assembled under compression, such as bumpers, engine and radiator pads, shims, shock insulators, torque insulators, etc. Nevertheless, most investigators appear to have almost wholly disregarded compression testing, particularly hysteresis and permanent set under compressive loads. Recently, however, Birkitt and Drakeley (*3*) have published some very interesting results of work on compression testing. Their data show that gage, area of test piece, and slippage all influence compression results, but apparently the results reported have only slightly, if at all, affected compression and permanent-set testing methods. Their tests were conducted at unusually high pressures per unit area. Ariano (*2*) also has experimented with molded cylinders of vulcanized rubber compressed in the direction of the axis between parallel plates. The apparatus could compress the cylinders to 45 per cent of their original height. His paper consists of a somewhat mathematical discussion of the form of the compression curve and some factors influencing it, but does not give details concerning laboratory procedure. Neither of these papers, however, attempts to correlate the factors studied with permanent set under compression.

Hippensteel (*5*) recently described a rubber compression-testing machine, which is capable of tests at considerably higher loads than are necessary for ordinary laboratory tests.

Early in the study of automotive rubber parts used to absorb vibration, the author was confronted with the necessity for a suitable device for conducting laboratory tests under compression, either at constant load or constant deflection, in order to compare resistance to flexure under compression with permanent set under compressive loads. Such a device (Figure 1) was then designed, as a co-testing device with the compression flexometer (*1*). The latter may be described as a dynamic flexure-compression testing device, while the new instrument, called a "compressetometer" may be considered as a static compression testing device inasmuch as permanent set and fatigue tests are performed under steady loads. The compressetometer is suitable for tests at loads up to 228 kg. (500 lbs.), which is a reasonable laboratory range. The capacity may be increased by substituting heavier springs. This device is much less expensive than the machine discussed by Hippensteel and furthermore makes possible many special tests, particularly tests at high and low temperatures.

Description of Compressetometer

The compressetometer, which is mounted in an electric oven, produces compressive loads on test pieces by means of three tension springs, placed outside the oven in order to avoid heat effects as much as possible. By turning the hand wheel, *A*, in a clockwise direction, the springs are made to pull a plunger, *B*, down onto a sample resting on the bottom plate, *D*. Loads are measured in 5-lb. units on the scale, *L*. The gage, *G*, measures deflections in thousandths of an inch. The spindle, *S*, can be adjusted to various heights to get the correct zero point on the deflection gage for various thicknesses of test pieces. A high degree of accuracy is possible, especially when testing small round disks cut from slabs, merely by lowering the plunger and noting the position at which it just touches the test piece. More positive accuracy is obtained, however, by first running the plunger down as far as it will go, setting the deflection gage to that reading corresponding to the thickness of the sample to be tested, and then raising the plunger and inserting the sample. The latter method is used in all research and special or comparison tests. A fan, *F*, provides circulation of air. A thermometer is so inserted through the orifice, *O*, that readings can be

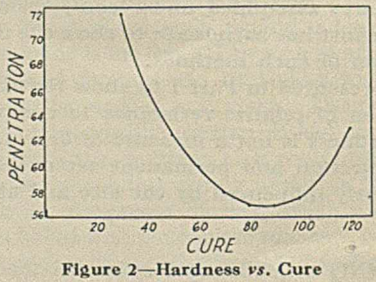


Figure 2—Hardness *vs.* Cure

taken through the glass in the door. As a special precaution in some cases, particularly in getting heat tests started, the thermometer is inserted from the front so that its bulb rests on the plate, *D*. In order to avoid errors due to temperature effects when standard permanent-set tests are made, it is necessary to insert the test piece between metal plates (at room temperature) with surfaces similar to those in the permanent-set equipment used. These are then placed in the compressetometer, which is already at the test temperature, and the required load is imposed on the test piece.

The majority of compression tests in this laboratory have been performed with the above equipment. Although the compressetometer is relatively easy to operate at loads up to 500 lbs., plans have been made to motorize this equipment for tests at higher loads. The instrument is also to be autographic so that complete hysteresis curves will be obtainable.

Method of Testing

In conducting compression and hysteresis tests, the loading and unloading are performed at the same arbitrarily fixed rates. In general, during the first half of the loading cycle, distortions are read at every 11.5 kg. (25 lbs.) or less, depending upon the size of the test piece, and finally at every 23 kg. (50 lbs.) as the slope of the curve becomes steeper (as $\Delta y/\Delta x$ increases). For unloading data, readings are taken at each of the distortions recorded during loading.

TESTS AT CONSTANT LOAD—In performing permanent-set tests at constant loads, the test piece is put into the compressetometer under the proper temperature conditions and compressed to the required load. There is an immediate fatigue effect, as shown by a change in the distortion during the first few minutes after the maximum load is reached. The rate of this change decreases rapidly, and this means a change in load. Consequently, for the first few minutes, and much less frequently for the next 3 or 4 hours, or even during most of the test, the hand wheel is so regulated that the load is kept constant. The drop in load over a 24-hour period due to fatigue of the samples is very small, particularly when the gage is approximately 0.635 cm. (0.250 in.) (normal or average gage for most set tests), so that continued load adjustments are unnecessary except in the most exacting tests. A change of 0.25 cm. (0.1 in.) or 40 per cent based on 0.635-cm. (0.250-in.) gage, in the position of the plunger causes a variation in the load of only approximately 3.18 kg. (7 lbs.) and no high-grade stock of this gage will show a distortion fatigue of 40 per cent in a 24-hour test at 70° C. at ordinary test loads. The error due to neglecting the actual fatigue effect is low, but depends on the load-deflection ratio of the spring used.

TESTS AT CONSTANT DISTORTION—If tests are to be run at constant distortion, the hand wheel must be run back to much lower loads than the initial maximum. Consequently, frequent adjustments are necessary, particularly at first. The fatigue effect may result in a 50 per cent drop in the load in these distortion tests.

CHECK CALIBRATIONS—The compressetometer is also used to check calibrations of the springs used in compression-set clamps (Figure 1, *C*). The base, *D*, is removed and another base containing a well to receive the spring is substituted. The compressetometer itself is calibrated by means of dead weights hung from the ring shown at the top after inverting the instrument. The instrument is first removed from the oven and suspended by a hook screwed into the base, *D*.

Relation of Hardness to Deflection under Compressive Loads

Hardness has been one of the most frequently discussed tests to be applied to mechanical goods. In the past no universally adopted instrument of any reasonable accuracy has been available to the trade. As commonly used, the term "hardness" refers to the resistance of the surface and adjoining layers of the rubber to a relatively small penetrating point of definite size when subjected to an arbitrarily determined load obtained either by means of springs or a dead weight. The Pusey and Jones plastometer, which represents the dead-weight type, is quite unwieldy for rapid routine tests. On the other hand, the spring type of instrument is easy to operate and speedy enough for production tests or for checking shipments. However, probably the most widely known instrument of this type is limited in accuracy, not only within a single instrument itself, but also when comparing one instrument with another. This is brought forcibly to our attention by frequent statements on purchasing specifications for automotive mechanical rubber parts, such as "the hardness of this part shall be such and such a value, as determined by or on the instrument in this laboratory." A subcommittee of Committee D-11 (on rubber products) of the American Society for Testing Materials is making a study of hardness-testing instruments of the penetration type and sponsoring the development of a dead-weight instrument for use primarily as a reference standard. It will probably be found desirable for the A. S. T. M. instrument to be sufficiently flexible for routine testing also.

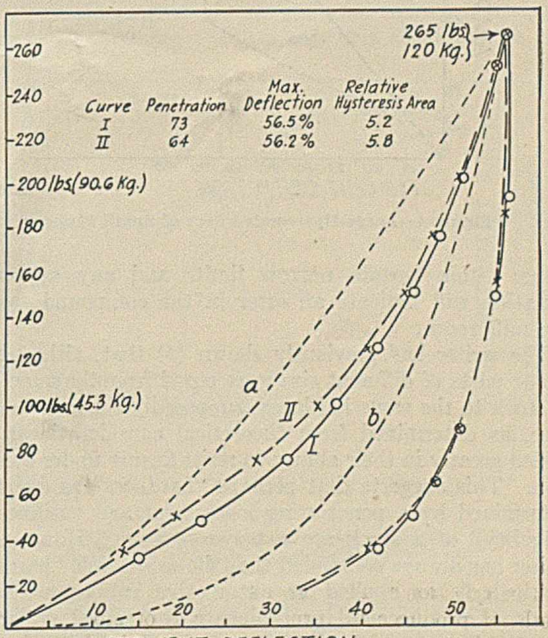


Figure 3—Load Deflection Curves of Two Disks of Penetration 73 and 64, Respectively

Without further discussing the advantages and disadvantages of the various penetration types of instruments, it will suffice here to state that "hardness" figures in this report were obtained by means of the Firestone penetrometer (*8*). This instrument measures the amount of penetration of a ball point of standard size, subjected to a definite load obtained by means of an accurately calibrated spring. Penetration values are directly measured and accurately indicated in thousandths of an inch (A. S. T. M. hardness values per specification D314-29T).

Although the penetrometer is invaluable for certain work, hardness data are not satisfactory for judging the cure of a part. This is shown in Figure 2. The average penetration values of slabs marked in code were used in plotting this curve. It is seen that in passing from an undercure of 60 minutes to an overcure of 112 minutes at 148° C. the penetration varies only four points, which is well within the tolerance on most specifications. However, the penetrometer is valuable in checking cured slabs of this stock (No. 4), and also many other stocks, in that each cure will have a penetration value within certain narrow limits and any appreciable variation will indicate an error in the compound room or the mill room.

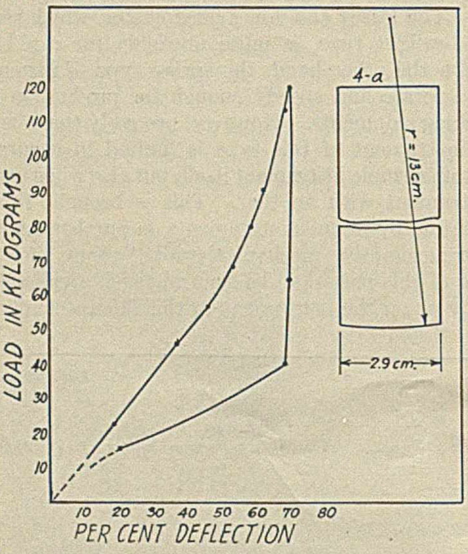


Figure 4—Large Hysteresis Effect of Small Plunger

The writer has previously shown (*1*) that, although two motor parts of different size were cured from the same batch of stock to the same hardness (supposedly the same state of cure, as determined from theoretical considerations), they varied greatly in their ability to resist flexure under compression. This suggests that perhaps "hardness" as commonly determined by a penetrating instrument and "stiffness" or "rigidity" of a stock are not synonymous. However, the writer has always contended that the expression "hardness," particularly as applied to automotive rubber mechanical goods, *should* be used to designate the actual stiffness or deflectability as determined by a suitable compression test.

Large slabs often vary considerably in hardness (penetration). Theoretically, of course, all portions have received the same cure. Since penetration instruments produce low elongations, it has been considered that modulus data (and perhaps tensile) might likewise show up differently on such portions of the slab. To date it has been possible to show only a shade of difference, if any, in the modulus and tensile values for such portions. Data already obtained tend to show that the softer portions possess a slightly lower modulus at 400 per cent elongation. It is reasonable, of course, to assume that the variation in modulus at such elongations would probably be very small if the variations in hardness were due to but slight differences in cure of the surface tested.

Note—Since presentation of this paper, proof has been secured that there is no difference in cure as determined by combined sulfur data, but probably hardness variations are due to different stress conditions at the surface at various places in the slab owing to variations in stressing (flow) during cure.

Figure 3 shows load-deflection curves (I and II) of two disks of a stock of hardness values 73 and 64, respectively. Tests were made on round disks of 1.9 cm. (0.75 in.) diameter. It will be noted that the maximum deflections under 42 kg. per sq. cm. (600 lbs. per sq. in.) are practically identical, although from the penetration data one would hardly expect such results. The energy absorbed during loading is less for the test piece of high penetration. The hysteresis area is likewise somewhat lower.

Note—The area beneath the deflection curve and that between the deflection and the recovery curves are called, respectively, "relative energy of loading" and "relative hysteresis area" throughout this article, inasmuch as such data have not been converted into absolute units of energy.

Additional proof that hardness as determined by a penetrating instrument does not necessarily specify the true stiffness (hardness) of a stock is given in Table I. Tests 1 and 2 show decidedly different maximum deflections for both sizes of test disks, although there was no difference in penetration. On the other hand, 1 and 3, both on optimum cures as determined by maximum tensile, possessed the same stiffness, or maximum deflection data on both disks. Tests 2 and 4, an undercure and an optimum cure, respectively, differ widely in penetration but show no difference in maximum deflection at 182 kg. (400 lbs.) on a round disk of 6.45 sq. cm. (1 sq. in.) area. However, at 42 kg. per sq. cm. (600 lbs. per sq. in.) on a 1.9-cm. ($^3/_4$-inch) disk there is a difference in the maximum deflection values.

Table I—"Hardness" *vs.* Deflection

TEST	STOCK	CURE AT 148° C.	PENETRATION	MAXIMUM DEFLECTION	
				At 42 kg./sq. cm. on 1.9-cm. disks	At 28 kg./sq. cm. on 2.9-cm. disks
		Minutes	*0.001 in.*	*Per cent*	*Per cent*
1	1	70	60	49.8	34.1
2	2	30	60	52.2	41.2
3	11	90	50	50.2	34.2
4	3	90	99	61.5	43.1

We can thus assume that two stocks entirely suited for a given purpose might possess the same deflectability in a given test, yet vary beyond certain specified penetration values. This can readily be seen from curves *a* and *b*, Figure 3. These are theoretical curves for possible high- and low-modulus stocks that would possess approximately the same maximum deflection. Such curves which cross or meet after starting out with definitely different slopes are not unusual in compression tests. Indeed, Somerville and Ball (*7*) have shown that stress-strain curves based on tensile data likewise may cross.

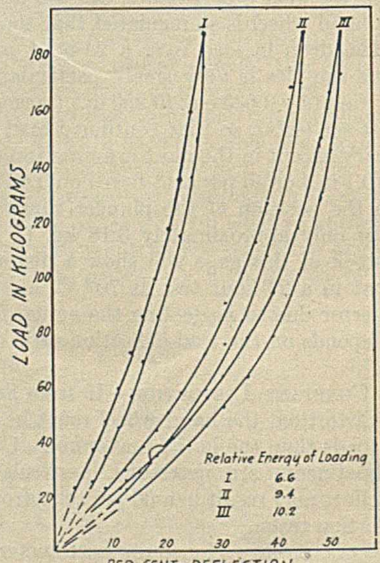


Figure 5—Effect of Gage on Compression Tests

Influence of Size of the Test Piece on Compression Tests

The size of the sample under compression influences both the accuracy of the individual tests, and accuracy depending on the "spread" between the results of different tests. The principal source of error in the first case is "cupping" or actual difference in size of the dies. The degree of cupping will depend upon the contour of the face of the die, method of applying the load, condition of the surface of the sample and die (whether wet or dry), and gage of the test piece. The possible errors in results due to an error of 0.076 cm. (0.031 in.) in the diameter of the test piece due to cupping or size of the die vary from 12.3 per cent on a disk of 1.9 cm. (0.75 in.) diameter to only 5.5 per cent on a 2.9-cm. (1.14-in.) disk.

Cupping on a 1.9-cm. disk of a pure-gum stock (No. 1 of the present A. C. S. Physical Testing Committee) has been found to amount to 0.127 cm. (0.05 in.) on a sample of 0.72-cm. (0.285-in.) gage. Evidently the standard test piece should be more than 1.9 cm. (0.75 in.) in diameter. It will be readily seen, however, that the larger the test piece the less will be the spread between results. A careful consideration of the various factors involved is necessary before setting a standard.

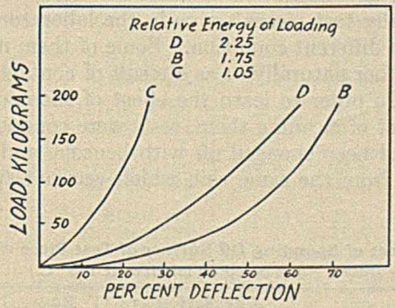


Figure 6

The use of plungers (anvils), rather than subjecting the whole test disk to the compressive load, eliminates the error due to the cupping effect but may involve even more serious errors. Cutting due to sharp edges of the plungers is quite serious at relatively high loads, and this influences slippage. In addition, different test pieces are subjected to different stresses per unit volume by use of the plunger. Consequently, at high distortions at least—i. e., loads of 42.2 kg. per sq. cm.—on small plungers of 1.9 cm. (0.75 in.) diameter and even slightly larger, the test is so severe that it produces abnormal compression results. It is true that motor supports and other parts assembled under compression are commonly considered as loaded to a constant load per unit area—or, owing to the low percentage deflections to a constant load per unit area—but in reality they are assembled at practically constant deflection. A 5.9-cm. (2.32-in.) round disk cut from a slab of motor-support stock No. 5 of 0.545-cm. (0.214-in.) gage was deflected only 7 per cent by a load of 227 kg. (500 lbs.). Therefore, tests on disks large enough to insure sufficient accuracy are much more comparable to service conditions and fairer to all grades of stock than the constant-area tests as secured by plungers. Furthermore, the percentage distortion in tests at constant load per unit volume is more in line with service assembly compression.

Table II—Effect of Various Sizes of Plungers on Square Test Pieces of Same Area of Overhang
(Stock No. 6, cured 12 minutes at 160° C.; all tests at 19.3 kg. per sq. cm. (275 lbs. per sq. in.)

Diameter of Plunger		Area under Load	Gage	Volume under Load		Final Gage	Max. (Final) Load	Load per cc. Based on:		Increase in Load	Max. Deflection	Relative Hysteresis Loss
				Original	Final			Original thickness	Final thickness			
Cm.	*In.*	*Sq. cm.*	*Cm.*	*Cc.*	*Cc.*	*Cm.*	*Kg.*	*Kg.*	*Kg.*	*Per cent*	*Per cent*	
1.9	$^{3}/_{4}$	2.84	0.595	1.69	1.27	0.447	550	32.4	43.0	32.7	24.8	0.6
2.38	$^{15}/_{16}$	4.45	0.564	2.51	1.89	0.425	863	34.2	45.5	33.0	24.8	2.45
2.90	$1^{9}/_{64}$	6.45	0.595	3.84	2.87	0.445	125	32.4	43.5	33.6	25.2	5.4
3.81	$1^{1}/_{2}$	11.40	0.587	6.7	5.55	0.485	222	32.7	39.7	21.1	17.3	4.55

In a further effort to show that it was advisable to use a test piece of larger diameter than the 1.9-cm. (0.75-in.) round disk a series of tests was arranged wherein the area under compression varied from 2.94 sq. cm. (0.44 sq. in.) to 11.4 sq. cm. (1.77 sq. in.). In order to eliminate the variable introduced by cutting the samples by means of a steel die, the steel plunger method was used. In each case a square test piece was cut of such a size that the area was 8.05 sq. cm. (1.25 sq. in.) greater than the contact area of the plunger, in order to get approximately the same supporting action by the surrounding rubber. It is possible that the amount of overhang should be based upon the relative circumferences of the test pieces under compression rather than be set at the same excess area. The results are reported in Table II.

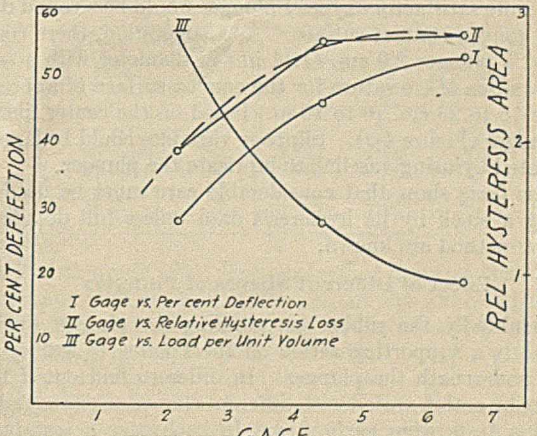


Figure 7—Effect of Gage on Per Cent Deflection Relative Hysteresis Area, and Load per Unit Volume

The hysteresis data were secured by plotting percentage deflection against load. A more complete analysis would involve the use of both loads per unit area and loads per unit volume. In general, a small plunger shows a larger hysteresis value than actually exists. This increased hysteresis area with the smaller plungers may be explained somewhat on the basis of the increased load per unit volume and also by means of an experiment with a very thin sheet of pure gum. If such a sheet is stretched with the finger nearly to the point of rupture, it is found that the stresses are somewhat similar in effect to surface tension—viz., the small volume of rubber over the end of the finger tends to form to the rounded portion of the finger and seemingly to cling to it. At very high loads a plunger of 1.9 cm. (0.75 in.) diameter has penetrated the rubber to such a degree that the test piece seems to cling to the plunger as the loads are released, and consequently there is a high hysteresis area. The proof of this theory is found in experiments run on small plungers at much higher loads. In Figure 4 we see that the unloading curve descends abruptly for a considerable period, causing a large hysteresis area. When the major portion of the load has been released, there is an abrupt decrease in the distortion value. This point indicates the stress above which the sample clung to the

Table III—Effects of Various Shapes of Plungers
(Area of plungers, 6.45 sq. cm. (1 sq. in.), stock No. 2 cured 10 minutes at 160° C.)

Type of Plunger	Gage		Max. Deflection	Relative Hysteresis Area	Final Gage		Stress per Unit Volume				
							400 lbs./sq. in.		28 kg./sq. cm.		Increase in load
							Original	Final	Original	Final	
	In.	*Cm.*	*Per cent*		*In.*	*Cm.*	*Lbs./sq. in.*		*Kg./sq. cm.*		*Per cent*
2.9 cm. dia.	0.230	0.585	24.4	5.15	0.174	0.442	1740	2300	122	162	32.2
2.54-cm. cube	0.232	0.590	25	4.1	0.174	0.442	1720	2300	122	162	33.7
Annular ring (1.9 cm. i. d.)	0.232	0.590	29.7	4.3	0.163	0.415	1720	2460	115	173	43.0
2.9-cm. dia. disk of rubber	0.219	0.555	29.2	2.75	0.155	0.394	1820	[a]	128	[a]	0

[a] 400 lbs. per sq. in. based on the final area would have required a final load of 565 lbs., or an increase of 41.3 per cent in load per unit volume.

plunger. The lower maximum distortion and the high hysteresis area for the largest plunger show that the slippage factor influences the results greatly.

This effect in the use of the plunger is decidedly detrimental, and plungers of small size, particularly at high loads, have been found to give greater errors than buttons or disks cut from flat sheets. Although the corners might be rounded to a certain extent for all anvils, the question of uniformity of this construction presents a serious objection. It would seem that a more satisfactory type of plunger would be a round disk with a convex contact surface. As a suggestion, there could be used a plunger 2.9 cm. (1.14 in.) in diameter with a suggested radius of curvature for the convex surface of approximately 15 to 25 cm. (6 to 10 in.) based on the center line of the plunger (Figure 4-*a*). Slippage variables could be largely eliminated by using vaseline to lubricate the plunger.

These facts show that considerable care must be used in judging a stock by its hysteresis data unless full details of the test method are known.

Effect of Different Shapes of Plungers

Undoubtedly the rubber surrounding the plunger during test exerts a supporting action on the volume of rubber directly underneath the plunger. In order to find out if this supporting action varied with different shapes of plungers the following tests were performed. In each case a test piece 3.2 cm. (1.5 in.) square was used. The various plungers were placed on the center of the respective test pieces. In the case of the square plunger, the sides were parallel to those of the test piece. The data are given in Table III. Although the maximum deflection data at 28 kg. per sq. cm. (400 lbs. per sq. in.) for the round disk, the square block, and the annular ring increased, in the order named, nevertheless these values check within 3 per cent distortion. The 2.9-cm. (1.14-in.) round disk of rubber suffered the same maximum deflection as the sample with the annular ring, although in the latter case the maximum load was 43 per cent greater. Evidently the test volume under the ring was able to carry this 43 per cent increase in load because of the supporting action of the rubber not directly under the plunger.

The slightly greater maximum deflection found in the test with the annular ring over that for the other plungers can be explained on the basis of flow into the hole in this plunger.

Factors Influencing Slippage and Consequent Effects on Deflection and Hysteresis Data

Birkitt and Drakeley (*3*) have shown that the percentage deflection is dependent upon the ease of slipping at the surfaces of the test piece and the testing equipment, and also that, with almost perfect slippage as secured by vaseline, variations in the thickness have little or no effect on the maximum percentage deflection. Although it is true that there is at most very low slippage in the assembly compression of motor supports and many other parts, slippage certainly does condition the results of deflection tests. It is later shown that considerably more slippage occurs with a chromium-plated surface than with the polished steel surfaces. To date all routine tests of deflection comparisons in the compressetometer have been conducted with the test piece in contact with polished steel surfaces. These are cleaned before each test with a metal polish, the surplus of which is immediately wiped off with a clean dry cloth.

Undoubtedly test pieces arrive in the laboratory with the surfaces in a different condition. Some of them may be oily or greasy, either naturally or as a result of contact with such materials. In order to learn the effect of such surfaces and also the effect of cleaning them, tests were conducted with a disk that had been sponged off with benzene and also on a similar disk from the same slab which was not sponged off. (Table IV)

Table IV—Effect of Sponging Off Surface of Test Piece with Benzene
(Stock No. 2 cured 30 minutes at 148° C.)

Gage		Surface	Deflection at:			Relative Hysteresis Area	Load to Deflect 18.7 %	
			5.55 kg. per sq. cm.	28 kg. per sq. cm.	42 kg. per sq.cm.			
Cm.	*In.*		%	%	%		*Kg.*	*Lbs.*
0.61	0.240	Sponged[a]	21.2	51.2	57.5	1.6	13.6	30
0.612	0.241	Natural	25.3	51.0	56.9	0.3	10.5	23

[a] An undercure (highly bloomed) was used, but the test piece was not sponged sufficiently to remove all the bloom.

The greatest difference is noted at low loads per unit area, while at very high loads the results are very close. Probably the outstanding effect was that the hysteresis area of the unsponged sample was much less than that for the sponged sample. This is entirely in keeping with the theory of the effect of slippage—poor recovery due to friction.

Unless otherwise specified, all the tests recorded elsewhere in this paper were on test pieces with the natural surfaces.

Effect of Thickness on Compression Tests

The influence of gage on compression testing has been ignored in the literature, with the exception of the work of Birkitt and Drakeley (*3*). Although their paper pointed out that the percentage deflection under equivalent loads per unit area is the same for test pieces of different gage provided perfect slippage occurs, it seems doubtful if gage variation has been generally considered as a source of error in specifications requiring such tests. The data in this paper are offered because in compression testing of motor supports or similar products little slippage actually occurs and, as previously mentioned, practically no slippage occurs in the service assembly.

Table V gives some data on two stocks that have been cured in a press in large slabs approximately 1 meter square. The slabs were cured 20 minutes at 160° C. (320° F.). It will be noted from the penetration data that the test disks showed no difference in cure (a poor criterion), although in the case of stock No. 7 it is quite possible that the thicker portion was enough below the cure of the thin section to give the results noted. However, the nature of stock No. 5 was such that the optimum cure (maximum tensile) could have been obtained anywhere from 14 to 20 minutes at the temperature used. Consequently, it is doubtful if the thicker portion of this stock is undercured or the thinner portion overcured. It will be noted that the thicker portions gave deflection values consistently higher than those for the thinner test pieces. This is to be expected when we consider that we have not provided for slippage of the test pieces over the contact surfaces of the testing equipment. Consequently a thicker sample will have more freedom of movement than a thinner sample (on a percentage-volume basis). The same general result is found in the study of compressive loads on short versus long columns.

Table V—Effect of Gage on Compression and Hysteresis Data

Stock	Cure at 160° C.	Penetration	Gage		Deflection at:		Relative Hysteresis Area
					5.55 kg./sq. cm.	28 kg./sq. cm.	
	Min.	*0.001 in.*	*Cm.*	*In.*	*Per cent*	*Per cent*	
					1.9-cm. round disk		
	20	88–9	0.627	0.247	25.5	47.4	1.0
		90	0.765	0.301	27.9	50.9	0.5
5	20	...	0.606	0.239	15.1	36.0	3.5
			0.740	0.291	16.8	41.9	2.85
					2.9-cm. round disk		
7		88–9	0.660	0.260	18.0	38.5	4.0
		90	0.772	0.304	18.7	40.5	1.5
5		...	0.615	0.242	8.26	30.1	7.1
			0.726	0.286	7.7	31.8	6.8

Another peculiarity is that the hysteresis area of the thin test piece was always greater than that for the thick piece. There are two possible explanations for this. In the first place, the thinner test piece was subjected to a greater load per unit volume—i. e., greater fatiguing stresses. Elementary mechanics furnishes the second explanation. It is known that a body which least resists a force is the least affected permanently by that force. Therefore, the thin pieces must have offered greater resistance to the deflecting force, for we find that they were deflected a lesser amount. In other words, there was a greater ratio of stress to strain in the thinner than in the thicker test piece. Because of this, it is to be supposed that the thinner samples were under a somewhat greater fatiguing action. In addition, it is known, that the thinner section actually was subjected to greater stress per unit volume than the thicker one, yet, as noted previously, was deflected to a less extent (was in a condition of less strain) principally because of less slippage per unit volume. Furthermore, in this case the ratio of deflection due to slippage and actual deflection of the rubber inside the test piece is greater for the thin test piece. Hence, there is less tendency to recover upon unloading, with a consequent greater hysteresis area.

Further proof of the above theory as to why a thick test piece suffers less hysteresis loss than a thin sample is found in the action of a pure-gum stock as compared with a highly compounded stock. In general, the pure-gum stock has a lower hysteresis loss, at least for the first hysteresis loop and even in the flexometer test, because it resists the compressing force to a lesser degree and also offers less internal resistance to molecular re-allocation. In Table VI are recorded some data for the load-deflection curves of a pure-gum stock (No. 2) and the same stock loaded with 15 volumes of carbon black (No. 9). In each case the 30-minute cure was an undercure. The loading curves for the disks 1 and 3 were almost identical (absorption of the same amount of energy) with the same maximum deflection. Nevertheless the relative hysteresis area of the pure-gum stock was 0.3 as compared with 2.75 for stock No. 9. In each case the 60-minute cure was approximately the optimum, yet for the pure gum we note a decided increase in the hysteresis area, whereas there is very little increase for stock No. 9.

Table VI—Load-Deflection Data for Pure-Gum Stock (No. 2) and Stock Containing Carbon Black (No. 9)

(1.9-cm. round disks at 120 kg.)

Stock	Disk	Cure at 140° C.	Penetration	Gage		Max. Deflection	Relative Hysteresis Area
		Min.	*0.001 in.*	*Cm.*	*In.*	%	
2	1	30 (under)	105	0.557	0.241	56.9	0.3
	2	60 (opt.)	100	0.562	0.243	61.8	3.9
9	3	30	84	0.593	0.257	56.8	2.75
	4	60 (opt.)	74	0.565	0.244	52.0	3.05

At first it would seem that no further proof of the above explanation is necessary. However, in the following series the opposite relation is shown for the hysteresis data. An explanation is presented with the data.

In the above series of tests the question of identical cure arises, particularly when the gage variation is considerable. In order to avoid this difficulty, it was decided to take 2.38-cm. ($^{15}/_{16}$-in.) disks of 0.55-cm. (0.94-in.) gage slabs of stock No. 8 cured 25 minutes at 160° C. Deflection and hysteresis data were first obtained on a single disk, then on a sample piled two disks high, and finally on a third sample three disks high. The piled samples appeared under load as single thick disks. However, it is known that greater slippage must have occurred between the rubber surface in contact with rubber than between the rubber-to-metal surfaces. Proof of this is given later from compression-set tests conducted under similar conditions. The data of these tests are given in Table VII with curves in Figure 5.

From this table we can see that increased gage means

Table VII—Effect of Gage on Compression Tests

Gage		Total Volume under Compression		Max. Deflection at 42 kg.	Relative Hysteresis Area	Relative Energy of Loading	Load per Unit Vol.		No. of Layers
Cm.	*In.*	*Cc.*	*Cu. in.*	*Per cent*			*Kg./cc.*	*Lbs./cu. in.*	
0.55	0.216	2.46	0.15	27.8	1.85	6.6	7680	2780	1
1.1	0.436	5.92	0.30	45.8	2.75	9.4	3810	1380	2
1.65	0.651	7.38	0.45	52.7	2.85	10.2	2580	933	3

Table VIII—Effects of Repeated Deflection

[Original gage 0.63 cm. (0.249 in.); final gage, 0.625 cm. (0.246 in.)]

Loop	Deflection at:				Load Loss at Max.		Load to Deflect (1.5 cm.) 24%		Relative Hysteresis Area	Load Drop at:					
	22.6 kg.		163 kg. (max.)							0.05 cm.		0.10 cm.		0.15 cm.	
	Cm.	*In.*	*Cm.*	*In.*	*Kg.*	*Lbs.*	*Kg.*	*Lbs.*		*Kg.*	*Lbs.*	*Kg.*	*Lbs.*	*Kg.*	*Lbs.*
1	0.025	0.010	0.165	0.065	11.4	25	150	330	17.7	17.7	39	27.2	60	33.6	74
2	0.038	0.015	0.168	0.066	11.4	25	134	295	9.6	..	..	15.0	33	20.5	45
3	0.035	0.014	0.169	0.0665	..	..	135	297	8.4	9.1	20	12.1	27	17.7	39
9	0.033	0.013	0.165	0.065	11.4	25	138	303	8.1	7.7	17	14.1	31	15.0	33

greater percentage deflection and greater hysteresis area, in spite of the fact that the thicker disks carried smaller loads per unit volume. This last may seem quite anomalous until consideration is given to some possible curves as shown in Figure 6. If two stocks give deflection curves as in *D* and *B* (a hard and a soft stock, respectively) yet are both fairly deflectable, it is seen that it is entirely possible for the stiffer stock, *D*, to possess a higher hysteresis loss than the more deflectable stock, especially if it is assumed that complete hysteresis loss occurs at the maximum deflection. On the other hand, in case of a very stiff stock which deflects only a small amount and suffers 100 per cent hysteresis loss after reaching maximum deflection, as in curve *C*, it is easily possible for the hysteresis loss to be less than that for a highly deflectable stock, *D* or *B*. It is assumed that these tests are all conducted to the same maximum load. The application to the tests in Table VII is very easy merely by assuming that these curves apply to disks of different gage instead of disks from different stocks. The major cause of the higher hysteresis loss for higher gages is, however, the increased resistance to slippage (as in Part II).

The data in Figure 7 show that per cent deflection, relative hysteresis area, and load per unit volume in constant maximum-load tests vary with gage (data shown in Table VI and Figure 5). Curve I shows that the percentage deflection, as well as the hysteresis area, is approaching a maximum with increase in gage.

The outstanding feature of the whole matter is that the hysteresis area depends on the cure, the gage, the slippage, and the location of the load-deflection curve. It is again evident that great care is needed in judging a stock by hysteresis data.

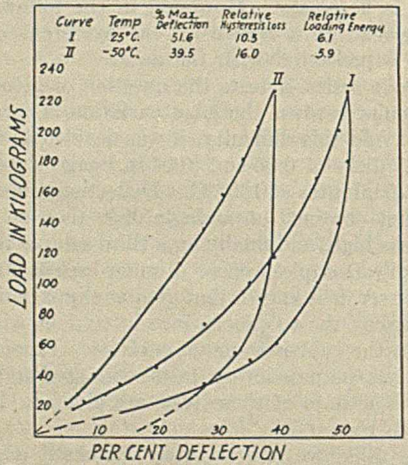


Figure 8—Low-Temperature Compression Test

Effect of Extreme Cold in Deflection and Hysteresis Tests

Additional proof of the preceding discussion is found in tests run on a sample at normal temperature and then subjected to severe cold. The sample, which was tested cold, naturally had stiffened up considerably and consequently suffered less deflection; in other words, it resisted the compression force to a greater extent. It was found that the hysteresis loop for low temperatures was greater than for higher temperatures. In the tests here recorded a sample of No. 10 stock was cut from a shock insulator. This test piece was cut for flexometer tests (*1*) and was 1.43 cm. (0.56 in.) wide by 4.12 cm. (1.63 in.) long by 2.86 cm. (1.13 in.) high. The lower end of the compressetometer together with the test piece was immersed in a mixture of carbon dioxide snow and acetone for several hours previous to the test. Changes in the freezing mixture were made from time to time to keep the temperature at approximately −50° C. The curves for the deflection tests on this sample, both at normal and at low temperature, are shown in Figure 8.

At extremely low temperatures, as is to be expected, the deflection curve, from the beginning, is much more nearly a straight-line function of the compressing load than the curve for the higher temperature tests. The loading curve shows a similarity to that of a steel spring. In other words, the rubber very nearly obeys Hooke's law. This is the only example of this phenomenon encountered in the work herein reported, and is only relative, for the size of the test piece and conditions of the test determine the relation between the load and the deflection for any given stock. However, owing to the great hysteresis loss of this sample (for a single impact or compression) it has greater absorbing power than the spring because the spring would recover directly. The tests on the cold sample were made after it had been tested at room temperature.

In Figure 8, although there was considerable difference in the percentage deflection at the maximum load, the energy of loading, as measured by the comparative areas under the loading curve for each case, was approximately the same. The relative return of energy as measured by the area of the loops was approximately 60 per cent less for the cold sample.

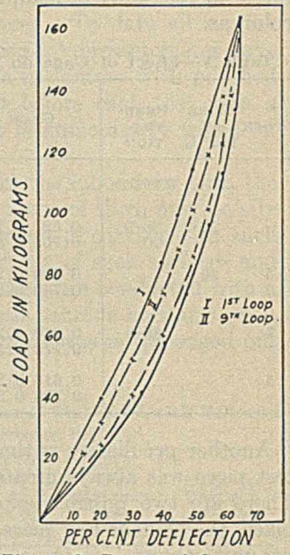


Figure 9—Repeated Compression Tests

In order to determine whether the rubber suffered any serious effects from this test, the test piece was taken immediately from the cooling solution and run in the flexometer at 50 per cent distortion. The test piece rapidly warmed up to approximately 70° C. and after 10 minutes' flexing was removed. No failure or appreciable set could be detected.

In the above it was assumed that the previous test at room temperature on this sample had no effect on the piece as later tested in the cold. These tests were run 24 hours apart. This assumption is justified as shown by data presented in the next section. Furthermore, data on impact tests on bumpers, given in Part II of this paper, show that very little change in hysteresis loss occurred after several hundred deflections at 54 per cent distortion.

Effect of Repeated Compression on Results of Compression Tests

Repeated hysteresis tests under compression show a similarity to repeated stretch tests (*6*) in that the greatest area is found for the first loop and reaches a fairly constant value for the third loop. Undoubtedly, continual fatigue occurs to a greater or less extent depending on the stock. A direct comparison of data of repeated tensile tests with data of repeated compression tests cannot be made without considering the question of the relative loads per unit volume and whether repeat tests have been made at constant maximum load or constant maximum distortion.

Table VIII gives deflection and hysteresis data for the first, second, third, and ninth tests on 2.3-cm. round disks of stock No. 4 cured to the optimum. The original area of this test piece was 4.16 sq. cm. (0.645 sq. in.) and loadings were to 38.5 kg. per sq. cm. (550 lbs. per sq. in.). The hysteresis loss or area in the first loop is shown to be considerably greater than that for the second loop, which in turn is somewhat greater than that for the third loop. In other words, the hysteresis loop is continually getting smaller, but very little difference is noted after the third cycle has been made. The data for load loss, which is the drop in load at maximum loading for 1 minute, show that this stock is fairly resistant to fatigue effects. The values for load drop represent the respective decreases in load, for the given distortions, for the unloading curves as compared to the loading curves, and are an indication of the relative decreases in hysteresis areas with repeated deflection. Figure 9 shows the curves for the first and for the ninth hysteresis loop. It will be noted that the ninth loop falls entirely within the first. These data are typical of those obtained in many similar tests.

Literature Cited

(1) Abbott, Ind. Eng. Chem., **20**, 853 (1928).

(2) Ariano, *India Rubber J.*, **76**, 207 (1928).

(3) Birkitt and Drakeley, *Trans. Inst. Rubber Ind.*, **1**, 368 (1926); **3**, 462 (1928).

(4) Goodwin and Park, Ind. Eng. Chem., **20**, 706 (1928).

(5) Hippensteel, *India Rubber World*, **78**, 55 (1928).

(6) Schidrowitz, "Rubber," p. 236 (1911).

(7) Somerville and Ball, *Rubber Age*, **24**, 490 (1929).

(8) Zimmerman and Brown, Ind. Eng. Chem., **20**, 216 (1928).

Part II—Compression-Set and Some Special Tests

In Part II the main factors necessary to be considered in formulating a compression-set test are described and a proposed compression-set test is briefly outlined. The constant-load test is preferable to a constant-deflection test. To secure the true relative properties of stocks, it is recommended that the surfaces be lubricated with vaseline. Tests for special cases, such as the flexometer test and an impact test for bumpers, are also described.

AS MENTIONED in Part I, many automobile mechanical rubber parts are assembled wholly or in part under compression. In the first class are motor supports, body and fender shims, radiator pads, spring shackles, torque insulators, etc. Axle and spring bumpers, grommets, tubing, and other parts are so installed that portions of them are under compression to a greater or less degree, and so belong to the second class. All such parts in time acquire permanent set as a result of compressive forces. Set under compression has been considered of such serious consequence that motor-car manufacturers insist that such parts shall withstand some sort of a compression or permanent-set test. Unfortunately there are a great many such tests requested in specifications, although they all aim to determine the same answer—namely, the quality of the part tested. Under properly controlled conditions a single test can be made to furnish all the information desired which is the resistance of the part to permanent set when under a compressive load.

Constant Distortion *vs.* Constant Load

Compression-set tests can be made under conditions of constant distortion or constant load. Although the former is the simpler, particularly as regards equipment, the writer believes that permanent-set tests on the various stocks or rubber parts to be assembled under compression should be conducted under constant load.

Probably one of the simplest devices for the test at constant distortion is made from two parallel steel plates clamped together by means of four bolts passing through the plates near the corners (*A*, Figure 1). The distortion of the test piece is determined by holding a scale beside the clamp. This is a grievous source of error. In *B* (Figure 1) a step toward greater accuracy has been made in providing a constant zero point for measuring the distance between the two plates. The scale can be put flush on the bottom plate and thus there is a single point of error in measuring the distortion. Even these distortion measurements are probably not accurate to within ±0.025 cm. (0.016 in.). This is only a 6 per cent error based on a gage of 0.635 cm. (0.250 in.) for the test piece. But the slope of the load-deflection curves for a 1.9-cm. (0.75-in.) round disk near the maximum load in a standard test conducted at 42 kg. per sq. cm. (600 lbs. per sq. in.) is much greater than the slope at the low loads. The above maximum load produced a deflection of 0.322 cm. (0.127 in.) on a test piece of stock No. 6 cured 12 minutes at 160° C. (320° F.). An error in the maximum distortion of but ±0.025 cm. (0.01 in.) would amount to a variation in the load from 107 kg. (236 lbs.) to 136 kg. (300 lbs.). These data correspond to deflections of 0.298 cm. (0.117 in.) and 0.348 cm. (0.137 in.) taken from load-deflection curves. This is a variation in load of approximately 12 per cent. An additional variable—drop in load due to fatigue—also exists.

Consider the case of a soft and a harder stock, each compounded and used for motor-support service, and also of a third stock which is much stiffer yet likewise a high-quality stock. Some relative compression data for these stocks are given in Table I.

If all tests were conducted at 37.3 per cent deflection, a load of 120 kg. (265 lbs.) would be imposed on stock No. 11, whereas less than two-thirds of this amount would be imposed on stock No. 5. Stock No. 14 is even more deflectable and at 18.7 per cent deflection it carries only approximately one-fourth the load carried by No. 11. Inasmuch as the gage of the No. 11 sample was about 16 per cent greater than that for the other samples, this stock was favored in the series and a sample of approximately 0.57 cm. (0.225 in.) gage would have required a higher load than 120 kg. (265 lbs.) for 37.3 per cent deflection as used in the above comparison.

In tests run at a constant maximum load the actual loads per square centimeter under a maximum load of 120 kg. (265 lbs.) show that No. 11 is being stressed only 38 per cent more than No. 14, instead of 350 per cent more as was the case in tests under constant distortion.

In order to consider the constant-load tests to have been made at the same load per cubic centimeter, let us assume that the original gage of all stocks was the same. This would mean that those stocks which in the table have a gage higher than No. 14 would actually show in the table even greater variations from that stock. To summarize, a soft stock experiences a less load per unit area due to a greater percentage deflection, but the same load per unit volume. This decrease in load is nearly proportional to the final area resulting from a decrease in thickness. On the other hand, in the case of constant-deflection tests the hard stock may require three to four times as much load, or even more, to deflect to the same amount as the soft stock. If, as above, we assume that all stocks in Table I had the same original gage, the figures in the last two columns will represent loads per unit area during test.

Table I—Comparative Deflection of Hard and Soft Stocks[a] Loaded to Maximum of 42 kg. per sq. cm. (600 lbs. per sq. in.) Based on Original Area

Stock	Cure		Hardness (Penetration)	Max. Deflection at 120 kg.	Gage		Volume	Final Area	Actual Load per sq. cm. at Max. Load of 120 kg.	Relative Load to Give Deflection of:	
					Orig.	Final				18.7%[b]	37.3%
	Min.	° C.	0.001 in.	%	Cm.	Cm.	Cc.	Sq. cm.	Kg.	Kg.	Kg.
14	25	320	100	54.8	0.562	0.254	1.6	6.3	19.1	8.2	37.8
5	12	320	63	45.4	0.576	0.315	1.64	5.2	23.0	18.2	68.2
11	60	298	38	37.3	0.68	0.426	1.93	4.55	26.5	36.4	120.0

[a] 1.9-cm. (0.75-in.) disks used.

[b] Approximate assembly deflection of a certain car support, but on larger areas.

Compression-Set Clamp

The above discussion has disregarded actual changes or fatigue of the test piece during the test. For both constant load by spring clamps and constant distortion the stock which suffers the more rapid fatigue will be benefited to the extent that it will be resisting the smaller final load per unit area. This effect is negligible in a properly designed spring clamp, as has been shown by tests in the compressetometer. Evidently a constant-load device is a necessity. If a spring clamp is used, a suitable means for measuring deflection of the springs (loads) is likewise a necessity.

Probably the simplest type of constant-load equipment is based on one of the constant-deflection clamps described above. If the tie bolts are longer, a short compression spring can be inserted between the plates of the clamp. The test piece is then put on a steel disk placed on top of the spring and loaded by compression of the spring. Here again there is a fairly large error in measuring by means of an ordinary loose scale or caliper and scale. One such type of set clamp which has come into use has a short clutch spring about 7 cm. (2.75 in.) long, which distorts 0.95 cm. (0.38 in.) under 120 kg. (265 lbs.) load. It has been shown that percentage deflection increases during tests by an amount equivalent to the fatigue of the test piece. This may amount to as much as 0.127 cm. (0.05 in.) on a 0.635-cm. (0.25-in.) sample, and may cause an error of approximately 13.0 per cent based on the spring distortion of 0.95 cm. (0.38 in.).

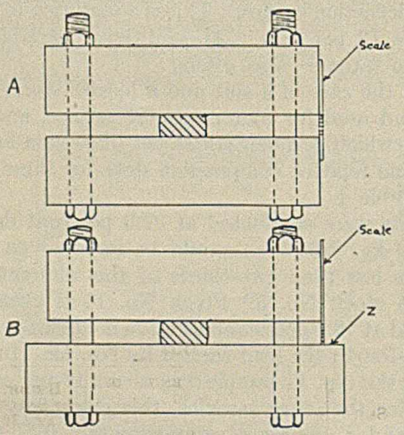


Figure 1—Constant-Deflection Compression-Set Clamps
A—Double zero-error
B—Constant zero-setting at *Z*

In order to provide an easier operating and more accurate device, the writer designed the small compression-set clamp shown in Figure 2 (also shown in Figure 1, Part I). This clamp is provided with a spring 10.1 cm. (4 in.) long, which deflects 1.9 cm. (0.75 in.) at 120 kg. (265 lbs.). The error due to the change in distortion caused by the fatigue of the sample has been cut 50 per cent. Likewise the percentage error arising from an error in measuring this spring deflection has been decreased. For convenience the clamp is provided with a depth gage with a scale graduated in hundredths of an inch. The gage is rigidly attached to the clamp, and hence is much more satisfactory than a loose scale. Load-deflection data are then obtained for each spring and suitable curves are constructed so that the clamp can be set to a definite scale reading for a given desired load. A magnifying glass is used in reading the scale. A single nut control increases the ease of operation and permits uniform deflection throughout the test piece.

Comparison of Tests Using Plunger and Rubber Disk

It can readily be seen that both the constant-deflection clamp and the constant-load clamp can be used to test either small buttons cut direct from the samples (constant-volume tests) or to make constant-area tests by means of a small plunger or anvil. The relative merits of the plunger versus the round rubber disk method were discussed in Part I. The same arguments against the plunger are valid here. Some comparative compression-set tests were also made.

All tests were started in clamps originally at room temperature and were of 66 hours' duration at 70° C. All test pieces were 1.9 cm. in diameter and were cut from the same slab of stock No. 14, cured for 50 minutes at 148° C. The load was 42 kg. per sq. cm. (600 lbs. per sq. in.). All disks were sponged off with benzol and dried. The original gage was determined by a R. & S. gage with 1-cm. (0.39-in.) diameter foot, the final gage by a B. & S. No. 2 micrometer caliper 0.396-cm. (0.16-in.) diameter foot after a 30-minute recovery. In the exceptional case of a warped disk the average of the minimum and maximum gage was measured 0.15 cm. (0.08 in.) from the edge of the disk.

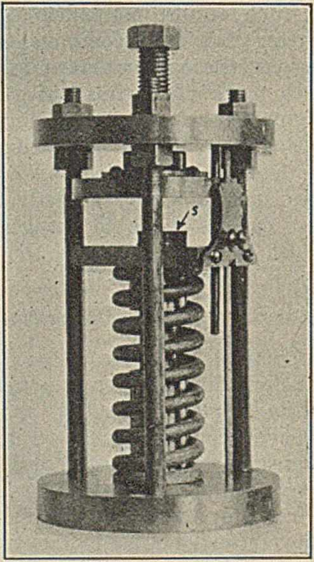


Figure 2—Compression-Set Clamp
S—Test disk

The results are given in Table II. The final load per unit volume is 59.4 per cent greater in case of the plunger method with an increase of 40 per cent in permanent set. This would tend to show that percentage increase in set is not in the same ratio as percentage increase in load per unit volume and hence the error is slight for small differences in the latter. In addition, "cupping" occurs in the lower side of the test piece in the plunger method at high loads (over 42 kg. per sq. cm. or 600 lbs. per sq. in.). This should preclude the use of an ordinary thickness gage unless it is provided with a small foot and also a small pedestal to support the test piece.

Table II—Comparison-Set Tests Using Disk and Plunger

CLAMP	MINIMUM GAGE			SET	VOLUME		LOAD PER CC.	
	Orig.	Final	Loss		Orig.	Final	Orig.	Final
	Cm.	*Cm.*	*Cm.*	%	*Cc.*	*Cc.*	*Kg.*	*Kg.*
DISK:								
1	0.658	0.470	0.178	28.6	1.87	1.87	1050	1050
2	0.674	0.508	0.166	24.6	1.91	1.91	1040	1040
				Av. 26.6				
PLUNGER:								
1	0.665	0.420	0.245	37.0	1.85	1.19	1045	1670
2	0.665	0.417	0.248	37.4	1.85	1.118	1045	1670
				Av. 37.2				

Dead-Weight *vs.* Spring Compression-Set Clamps

Without doubt a properly arranged dead-weight equipment should be more nearly capable of 100 per cent accuracy in load than the spring clamp. However, in order to eliminate frictional "wobble" troubles such equipment should be vertical acting, as in Figure 3, *A*, instead of "horizontal acting" as shown in *B*. A dead-load device is unwieldy and liable to error due to a sudden application of the load (slippage errors). For testing a piece 12.9 sq. cm. (2 sq. in.) in area at 28 kg. per sq. cm. (400 lbs. per sq. in.) using 364 kg. (800 lbs.), for example, some hydraulic or pneumatic equipment would be much more convenient than the actual weight method. However, for the sake of simplicity and for practical accuracy, the constant-load spring clamp is very satisfactory when properly designed, and the adoption of some fairly compact device, such as shown in Figure 2, would be an important step forward in the program of unification of methods of testing.

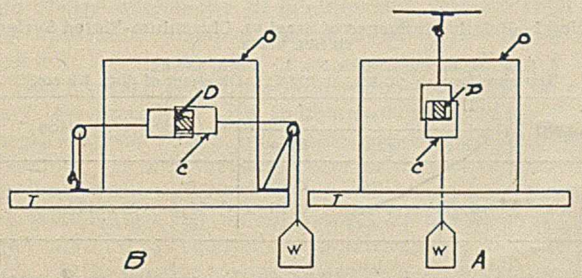


Figure 3—Dead-Weight Constant-Load Clamps

O—Oven
T—Table
D—Test disk
C—Telescopic test clamp

The question has been raised as to the effect of repeated use on the calibration curve of the springs used in the constant-load clamps. Figure 4 shows that deflections of a new spring at 120 and 182 kg. (265 and 400 lbs.), respectively, were 1.7 and 2.59 cm. (0.67 and 1.03 in.), whereas after almost 3 months of continual use at loads between these two values for periods varying from 22 to 72 hours at 70° C., the distortions were, respectively, 1.9 and 2.76 cm. (0.7 and 1.09 in.). Of course other calibration curves were necessary in the meantime, but most of the change occurred within the first few tests at the higher load, and hence probably could have been avoided by a dead-weight test before calibration. It is considered that most of this change occurred in the thin ground-down portions of the last coil at each end of the spring.

Another question has been raised as to the variation between calibration at room temperature and at the standard test temperature (70° C.). In Figure 5 it is shown that at 182 kg. (400 lbs.) there is less than 0.038 cm. (0.015 in.) weakening at 70° C. as compared with the value at 24° C., whereas at 120 kg. (265 lbs.) there is practically no error. This is quite within the experimental error in most spring clamps in use.

It has been claimed (private communication to the author) that the spring clamp gives higher compression-set results than the dead-load method "due to the stiffening action resulting from the heat-expansion of the spring." Others have maintained that heat tends to weaken the spring. The latter view is strengthened by the curve in Figure 5. In fact, the variation due to temperature in the load-deflection curve of the type of spring used in the clamps shown is probably far within the other errors inherent in any small, compact non-precision instrument of this type.

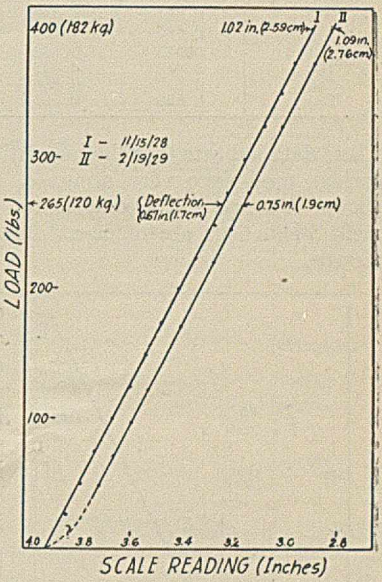


Figure 4—Calibration of Constant-Load Spring

Note—For present purposes a precision instrument is considered only as one which will measure distortions of load or gage of the sample to within 1 per cent and 0.0025 cm. (0.001 in.), respectively.

It is true that there is an apparent stiffening of the spring during a compression-set test which may amount to as much as 0.127 cm. (0.05 in.) increase in length at 120 kg. (265 lbs.) in tests on 1.9-cm. (0.75-in.) disks cut from slabs of approximately 0.635-cm. (0.25-in.) gage. This is due, however, to fatigue of the stock, and in fact the load is really falling instead of increasing. Some data are given in Table III. The tests were conducted at 70° C. at 136 kg. (300 lbs.) on 2.9-cm. disks of 0.95-cm. stock. The error in load is less than 3 per cent, and is less on lower gages and at higher loads. For two samples tested simultaneously the error is doubled.

Table III—Error in Spring Load Due to Failure of Test Piece

CLAMP	SAMPLE GAGE	SET	COMPRESSED LENGTH OF SPRING			HEIGHT OF SPRING AT 136 KG.	AV. INCREASE IN LENGTH
			Orig.	Final	Increase		
	Cm.	%	*Cm.*	*Cm.*	*Cm.*	*Cm.*	%
1	0.965	11.1	7.62	7.7	0.08	2.135	3.0
2	0.966	9.2	7.6	7.65	0.05	2.135	

It was shown in Part I that the load falls when test pieces stand under constant distortion due to the fatigue in the rubber. Even greater fatigue occurs in the constant-load spring clamp, because the load is greater than that necessary for a constant-distortion test. A large change in distortion of the test piece allows the spring to expand slightly with an appearance of stiffening; hence the load in a spring clamp is continually decreasing with increasing fatigue, but this load drop is quite negligible. Since the load drop is doubled if two samples are tested in the same clamp, only one test should be made at one time in each clamp.

The accuracy of spring calibrations as determined by data obtained from tests on 1.9-cm. pieces tested at 42 kg. per sq. cm. for 24 hours at 70° C. in different clamps is shown in Table IV. All the disks were cut from the same slab of stock (No. 15 cured 20 minutes at 160° C.) and readings were checked independently by two observers. Final gage measurements were made by a small-foot (No. 2) B. & S. micrometer caliper.

Table IV—Comparison of Accuracy of Calibration of Various Clamps

Clamp	Gage			Set
	Original	Final	Loss	
	Cm.	*Cm.*	*Cm.*	%
A-1	0.702	0.572	0.030	18.5
	0.695	0.562	0.033	19.1
A-2	0.691	0.550	0.041	20.6
	0.695	0.565	0.030	19.0
B-1	0.675	0.542	0.033	19.9
B-2	0.678	0.542	0.036	20.2
B-3	0.678	0.526	0.052	22.5
B-4	0.695	0.555	0.040	20.4

These data indicate that the calibration curves for the various springs used were very accurate. The duplicate tests in clamps A-1 and A-2 likewise show very satisfactory agreement when tests are made at different times in the same clamps.

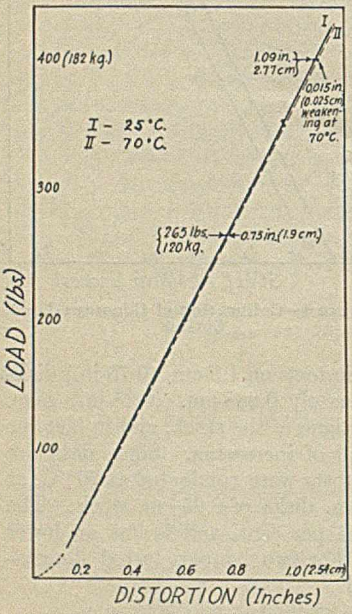


Figure 5—Effect of Heat on Spring Calibration

The slope of the spring-calibration curve has a definite effect on the accuracy possible with the constant-load clamp. It is doubtful if any spring should be used at test loads of 182 kg. (400 lbs.) or under if the slope of its calibration curve is greater than that noted in this paper. Owing to the increased relative distortion at low loads due to the ground-down spring ends, the slope is arbitrarily set for data between 120 and 182 kg. (265 and 400 lbs.). Thus the original slope of the calibration curve (Figure 4) for the spring was 3.86, whereas the final value was 3.97. A maximum value of 4.5 might be set, but is probably high, and any value lower than 3.75 prevents use over a wide load range.

For high-load clamps this laboratory is using springs calibrated to 455 kg. (1000 lbs.) with a maximum slope of 6.5.

Note—Since presentation of this paper clamps of 1800 kg. (4000 lbs.) capacity have been secured.

Influence of Gage and Slippage and Factors Influencing Slippage

Variation in the gage of the test piece has an enormous effect on permanent-set tests under compression. The effect on single disks of variable gage is magnified in tests conducted on pieces formed by "piling" disks. Table V gives data of permanent-set tests conducted similar to deflection tests recorded in Table VII, Part I, except that the set tests were of 24 hours' duration at 70° C. under 188 kg. (414 lbs.) in the compressetometer.

Greater slippage (distortion) occurred at the rubber-to-rubber surfaces and evidently the increase in area of the middle disk on test 3 alone accounts for the increased set, for it was subjected to less load per unit area and also per unit volume than specimens in tests 1 and 2. In Part I it was shown by percentage-deflection data that lubricated samples distorted the most, as a result of surface slippage. Evidently control of slippage is of prime importance in true set tests as well as true deflection tests.

Various surfaces affect the slippage to different degrees. Accordingly compression-set tests were made to determine the effect of a lustrous chromium plate on polished steel. In one experiment two test disks of 1.9 cm. diameter were separated by a bright chromium-plated spacer during tests in polished steel clamps. In each case the final diameter of the surface in contact with the steel plate was 1.9 cm., whereas that in contact with the chromium surface was 2.16 cm. This represents over 22 per cent increased area with the chromium surface. Practically no slippage occurred at the polished steel surface.

Table V—Influence of Gage Variation on Compression-Set

Test	Original Gage		Volume under Load	Relative Load per cc.	Compression-Set	
	Each disk	Total			Each disk	Total average
	Cm.	*Cm.*	*Cc.*	*Kg.*	%	%
1	0.508	0.508	2.30	80	19.6	19.6
2	0.488 0.470	0.958	4.26	62	23.2 26.0	24.6
3	0.445 0.361 0.445	1.251	5.57	32.6	30.0 43.2 30.0	34.4

Table VI shows set data obtained when both surfaces of the test pieces were in contact with polished steel and bright chromium-plated surfaces, respectively. In this laboratory bright chromium-plated contact surfaces have been made a standard because it is easier to keep them in a uniform condition. All constant-load clamps have been chromium-plated all over. The results are so satisfactory that such a procedure is recommended for adoption as standard.

Table VI—Relative Influence of Steel *vs.* Chromium-Plated Surfaces in Set Tests

A. S. T. M. hardness stock No. 1. Load, 120 kg.
Test specification, 20 hrs. at 70° C. Diameter of disk, 1.9 cm.

Clamp	Gage			Set	Surface
	Orig.	Final	Loss		
	Cm.	*Cm.*	*Cm.*	%	
A-1	0.726	0.596	0.13	17.8	Chromium plate
A-2	0.726	0.615	0.11	15.4	Steel

Birkitt and Drakeley (*3*, Part I) reported more nearly ideal slippage in deflection tests when pieces were lubricated with vaseline but they made no mention of set tests. Table VII shows the increased set resulting from the use of a thin film of white vaseline on the round 1.9-cm. test disks subjected to 42 kg. per sq. cm. for 24 hours at 70° C. as compared with normal tests.

Table VII—Effect of Lubrication of Test Piece

Cure at 148° C.	Compression-Set	
	Normal surface	Vaseline
Minutes	%	%
30	17.3	27
45	16.6	26.5
60	14.7	18.7
75	15.8	20.4

Here again set is affected more by the physical distortion, or relative displacement within the test piece, than by load per unit volume or unit original area. Consequently, in a test to determine the true deflectability and set the rubber should be lubricated.

Duration of Compression-Set Tests

Increased duration of the test naturally produces increased set, but there seems to be nothing gained by setting up a standard of duration greater than 22 hours at 70° C., which is universally accepted as the standard aging temperature.

Table VIII shows the values for percentage set on 1.9-cm. disks of stock No. 16 (cured 25 minutes at 160° C.) when subjected to 120 kg. for various periods at 70° C.

Table VIII—Effect of Duration of Tests on Compression-Set

TEST	DURATION	ORIGINAL GAGE		COMPRESSION-SET (AV. OF 2 TESTS)
	Hours	*Cm.*	*In.*	*Per cent*
1	8	0.62	0.245	14.3
2	21	0.615	0.242	24.25
3	25$^{1}/_{3}$	0.617	0.243	25.5
4	48	0.62	0.245	31.0
5	72	0.62	0.245	37.0

Inasmuch as daily routine tests are often desirable, this laboratory is standardizing on a 22-hour test. This allows a 2-hour change-over period, which is sufficient to take care of several clamps and allows the clamps to reach room temperature, which is desirable for the sake of uniformity. The 22-hour standard will facilitate testing by speeding up tests and in having a definite time each day for the work.

Measurement of Original and Final Gage of Test Pieces

The measurement of the final gage after subjecting the test piece to the compressive load is very important. In most methods cupping occurs on the top or bottom surface or both, as a result of slippage. In all tests in this laboratory, and those herein reported except tests with the ring method mentioned later, the original gage has been measured by a Randall and Stickney gage with a 1.9-cm. (0.75-in.) diameter foot acting under a dead load of 200 grams (0.44 lb.), whereas the final gage was obtained by a No. 2 Brown and Sharpe micrometer 30 minutes after removal from the test apparatus. Samples were allowed to cool on an oak desk top.

This recovery period has been considered ample for ordinary test procedure. No trouble is experienced in getting checks with the B. & S. micrometer caliper even by different operators. In order to compensate for the lack of a pressure-foot load, 0.001 inch (0.025 mm.) is deducted from the reading obtained by the touch system. If the distortion has been uniform, as required in this laboratory and made possible by the single-nut control constant-load clamps, little experience is necessary for the operator to get the minimum gage reading that just allows no-load slippage between the micrometer feet. A small-foot R. & S. gage with a similar small-foot pedestal or table for the test piece is necessary for accurate work if the micrometer is not used, but the latter is more economical and just as accurate if made a standard procedure. The No. 2 B. & S. micrometer is not satisfactory for measuring the gage at the center of test pieces of large diameter because the anvil does not protrude far enough from the frame. A micrometer similar to B. & S. No. 30 R. & S. is needed, but with a micrometer larger than the No. 2 the accuracy has been impaired.

Other Permanent-Set Methods

Where service assembly involves compression a compression-set test is more logical than any type of tension-set test, whether at repeated constant distortion or repeated constant load. The procedure of holding at either a definite elongation or elongating load and then determining the set after a certain recovery period likewise finds small favor for, although such tensile methods may differentiate between stocks, only by checking against set results under compression or actual service is it possible to find out if such results have any meaning as to service under compression. After all, shims, supports, and similar parts fail principally due to one or two causes (or both)—namely, structural deterioration or loss in gage.

A cold-flow test depending upon exudation of rubber through the opening in an annular ring has occasionally been used in place of the compression-set test. The ring test finds little to warrant its adoption because:

(1) The flow into the opening depends upon the condition of the edges of the ring surfaces and of the rubber and ring.

(2) The flow occurs early in the test and, although it is more or less permanently held owing to the conditions of the test, it is not necessarily a criterion as to whether or not the support will suffer compression-set, inasmuch as in service assemblies usually very little percentage flow occurs.

(3) There are inaccuracies inherent in the method of measuring the relative displacement into the hole in the ring.

(4) The necessary sample—at least greater than the 3.44 cm. (1.355 in.) o. d. of the ring—cannot be secured from many automotive rubber parts.

(5) The test requires 48 hours to give a percentage value for the cold flow equivalent to that secured in 24 hours by the disk method. Lessening the time would greatly decrease the accuracy of the ring test and is inadvisable.

Requirements of a Compression-Set Test

A satisfactory compression-set test should be formulated only after due consideration of the following factors:

MATERIAL TESTED

(1) Within what limits of thickness do samples fall?

(2) Within what limits of hardness do samples for a particular product fall?

(3) Is any consideration taken of such ingredients as paraffin, etc., which might give a surface with a lubricating effect?

TEST PIECE

(1) What is the size (diameter or other dimensions) of the test piece?

(2) How are the test-piece dimensions secured? Are they (*a*) molded; (*b*) cut by a steel die,* by blow with a hammer, or by pressure as in an arbor press; (*c*) cut by a cork-borer; or (*d*) by the spinning or motor-drill method?

(3) Is the slab or die wet before the test pieces are cut?

TESTING CLAMPS

(1) Does the device produce constant distortion?

(2) Does the device give a constant load obtained by springs? Are the springs inside or outside of the oven, and what is the load-deflection ratio of the spring?

(3) Does the device give a constant load obtained by dead weight, and is the test piece assembled in a horizontal or vertical position?

(4) What is the speed of (*a*) compression; (*b*) releasing the load?

(5) Is slippage in the clamps controlled by (*a*) lubrication of contact surface; (*b*) a polished contact surface; or (*c*) plated (chromium, etc.) contact surfaces?

(6) Is the clamp at room temperature or test temperature when the test pieces are inserted and the load is applied?

(7) If a constant-distortion device, how is the distortion measured?

(8) If a constant-load device, how is the load measured?

(9) What kind of an oven is used in the test? Is the temperature automatically controlled, and is the air changed regularly or circulated by a fan?

OTHER CONDITIONS OF TEST

(1) What are the temperature limits of the test?

(2) How long is the test (22 to 72 hours, etc.)?

(3) Is the test piece removed from the clamps at once after removal from the oven?

(4) Does the test piece recover on glass, wood, or a metal surface?

(5) How soon after removal from the clamp is the final gage measured?

(6) How is the final gage measured (R. & S. gage or micrometer caliper)? State the size of both contact feet or surfaces of the gage.

(7) Can the method be universally adopted without highly complicated equipment?

(8) Are there any special factors peculiar to the part to be tested or to the laboratory equipment that must be considered?

Suggested Method for Compression-Set Test

Cut two round disks of the same gage, preferably less than 1.27 cm. (0.5 in.) from the part in question by means of a steel die with an arbor press, giving accurately an area of 1 sq. in. (6.45 sq. cm.) without lubrication of the test piece or die. Compress between bright chromium-plated surfaces in a constant-load clamp at room temperature to 28 kg. per sq. cm. (400 lbs. per sq. in.). The maximum slope of the load-deflection curve of the spring for providing the load shall be 4.5 for a 182-kg. (400-lb.) spring or 6.5 for a 455-kg. (1000-lb.) spring.

Keep the clamps with the test piece in a 70° C. oven provided with a fan for air circulation for 22 hours, and then immediately remove the test piece from the clamp. Take the final gage at the center of those test pieces which are not irregularly deflected by means of a small-foot micrometer caliper similar to B. & S. No. 2 not less than 30 or more than 35 minutes after removal from the testing device. Compression-set is reported as the percentage decrease in gage based on the original thickness as determined by the standard Randall & Stickney gage or No. 2 B. &. S. micrometer caliper.

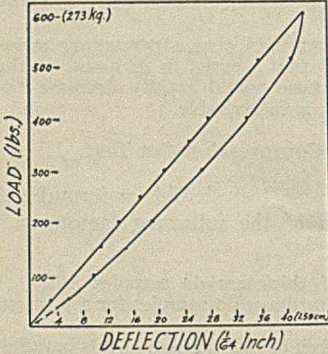


Figure 6—Shear Hysteresis

For true comparative results of the quality of the stocks test disks should be lubricated, but this involves difficulties not worth encountering except for research and stock development since service compression is without slippage. Hence lubrication of the test disk is not included in the above.

Additional Tests on Auto Mechanicals

In the automobile assembly most rubber parts used under compression, particularly those used to absorb vibration, suffer, in addition to the compressive load, repeated dynamic stresses of impact, flexure, or shear, or perhaps all three. Flexure, impact, and shear tests have been used in this laboratory for evaluating such parts as spring shackles and torque insulators, bumpers, and certain types of motor supports. Figure 6 shows the load deflection, or shear, curve obtained in a test on a vertical type of metal-rubber motor support which is fast replacing compression supports.

Figure 7 shows a device for repeated compression tests on bumpers. Various stocks, cured in the form shown in *A*, are subjected to 44 impacts each minute, either for a definite period or until failure occurs. In the former case hysteresis and deflection tests, before and after the test, are used to judge the ability of the stock to withstand impact. Most tests have been run at approximately 54 per cent deflection, which for stock No. 11, cured 60 minutes at 147° C., required 590 kg. (1300 lbs.). Some data obtained on various cures of three stocks are given in Table IX. In every case the maximum deflection at the 227-kg. (500-lb.) load increased as a result of the impact test, whereas there was a decrease in the relative hysteresis area. Comparing the optimum cures of the first two stocks, it will be noted that stock No. 11 showed less change in hysteresis loss than stock No. 12. The former is the more efficient stock. Furthermore, the relative drop in hysteresis loss with increased cure was less for No. 11 than for No. 12. Even though the optimum cure of No. 11 was impacted for 5 hours, the relative hysteresis loss was intermediate between the lower and higher cures. In the case of No. 12 the 5-hour impact test had increased the change in hysteresis loss beyond that obtained for either the under- or the over-cure, indicating that this stock had absorbed more internal energy, or at least had acquired a certain amount of set, and consequently was requiring less energy per deflection as the test progressed. The 45-minute cure of No. 12 had started to fail before the end of the 5-hour test. This is taken as further proof of the logic of the hysteresis theory especially when we consider that no failure occurred with the 40-minute cure of No. 11 when impacted 7 hours more. Likewise the drop in hysteresis loss in this latter case was no more than for the overcure.

In the case of stock No. 13 failure had occurred before the end of the $1^1/_2$-hour impact period. This test piece is shown in Figure 7.

It might prove more sound technically to impact the bumpers under constant load or to a constant energy absorption value each time. However, the matter of imposing actual loads of approximately 455 kg. (1000 lbs.) at the rate used in this test offers serious difficulties for the ordinary laboratory type of equipment. Furthermore, if a compounded stock meets other requirements for motor-support

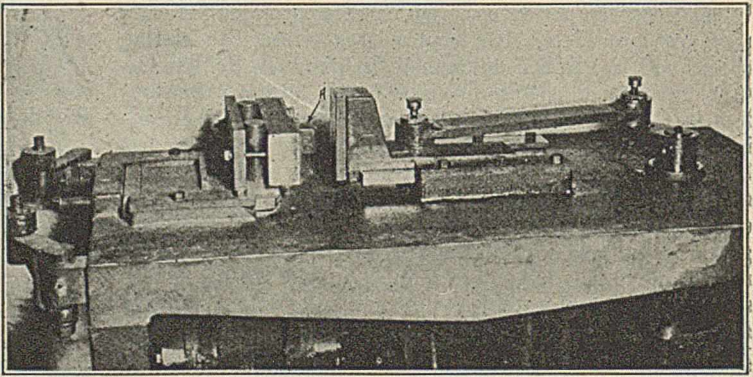


Figure 7

Table IX—Repeated Compression Tests on Bumper Stocks—44 Impacts per Minute

Stock	Cure	Penetration		Duration of Impact at 54%	Maximum Deflection at 227 kg.		Approx. Relative Hysteresis Loss		Decrease in Hysteresis Area
		Before impact	After impact		Before impact	After impact	Before impact	After impact	
	Min.	*0.001 in.*	*0.001 in.*	*Hours*	%	%	%	%	%
11	40	54	..	$1^1/_2$	32.4	33.9^a	43	36	7^a
	60	50^b	49	5	29.6	32.5	50	41	9
	80	53	50	$1^1/_2$	32.8	33.8	54	43	11
12	30	49	48	$1^1/_2$	28.6	31.4	47	38	9
	45	48^b	47	5^c	28.4	30.3	52	38	14
	60	49	50	$1^1/_2$	30.2	32.8	56	45	11
13	20	55^b	55	$1^1/_2$	38.5	..	..	..	..

[a] The maximum deflection and relative hysteresis loss values after 7 hours' additional impact were 33.4 and 32 per cent, respectively.
[b] Considered as optimum cure.
[c] Had "failed" (internal crack up from bottom and also in from the side) before the end of a 5-hour test.

stocks, it should be satisfactory for bumpers if it passes the above impact test.

In the case of No. 11 and No. 12 the results should be entirely comparable, particularly for the optimum cures, for they showed the same stiffness as determined by load-deflection data.

For shock and torque insulators and also the vertical type of motor supports, the flexometer test, with or without compression to correspond to service conditions, is undoubtedly valuable, and laboratory tests have been made on this basis. Results of the flexometer tests have been found much more satisfactory than tests on the entire shackle.

The above-mentioned impact and flexure tests require special equipment and consequently are not recommended for the general run of automobile mechanicals assembled under compression, but rather only for special products. For motor supports, body shims, and similar parts it would seem advisable, as previously stated, to perform tests such as deflection and compression-set, since these can be performed on the parts themselves or on test pieces cut therefrom.

Notes

(1) Tests recorded in this paper have been on stocks of moderate or relatively good resistance to compression-set. For torque-resisting purposes under compression, stocks have been developed with practically no set as determined by the method suggested.

(2) Trouble has not been taken to make metric units (obtained as slide rule derivations of standard English data) check perfectly, since the slight discrepancies do not interfere with the point to be proved.

(3) Committee D-11 of the A. S. T. M. has approved a tentative method of test for the hardness of rubber. This is published in the 1929 Proceedings of the society (D314-29T).

Acknowledgment

The writer wishes to acknowledge his indebtedness to E. B. Babcock, Erle C. Zimmerman, and N. A. Shepard, who have coöperated to make possible the investigations herein reported.

Cholesterol as a Measure of Egg Yolk in Milk Products[1]

Lincoln M. Lampert

Research Laboratory, Golden State Milk Products Company, San Francisco, Calif.

A method for the determination of cholesterol in dairy products is described.

The cholesterol content of several dairy products and of dried, frozen, and fresh egg yolk has been determined.

If the normal sterol content of a food product is known, an index to the amount of egg yolk added to that product may be found by determination of the total sterol content.

The increasing use of egg in milk products and the enactment of legal regulations specifying the minimum amount of egg solids permitted in certain products has developed a need for an adequate method of routine analysis for egg solids. The lipoid phosphorus method is usually employed for this determination. Preliminary work with this method showed considerable variation when the gravimetric procedure was employed. Better results were had with the colorimetric procedure for lipoid phosphorus. Since cholesterol occurs in considerably larger quantities in egg than in milk products, it occurred to the writer that cholesterol might serve as a point of attack for the solution of the problem. In contrast to the lipoid phosphorus, cholesterol is stable and quite well defined chemically, and it can be separated and estimated accurately. Theoretically it would appear that cholesterol has desirable properties for the purpose in hand.

A review of the literature revealed only meager work done on this question. Cappenberg (*3*) suggested the use of cholesterol for the determination of egg yolk. Later Berg and Angerhauser (*1*) made the same suggestion and gave six analyses of egg in which the cholesterol was determined. Buchanan (*2*) made a historical review of the methods used by various investigators, and concluded that Cappenberg and Berg and Angerhauser "propose cholesterol as a means of determining egg solids. This method has not been applied practically."

This information, coupled with previous studies, convinced the writer that the use of cholesterol as a quantitative index for the amount of egg added to milk products offered inviting possibilities.

Determination of Cholesterol

Cholesterol may be determined gravimetrically as the digitonide or colorimetrically. Digitonin is an expensive reagent and often difficult to procure. The colorimetric method of Steinle and Kahlenberg (*10*) was thought to offer some advantage, such as permanence of color, over the well-established Liebermann-Burchard procedure, but the correct cobalt-blue color was only obtained with pure cholesterol. The color usually obtained by this method on the material extracted from milk products ranged from purple to gray. This led to the adoption of the Liebermann-Burchard method as the more desirable procedure.

A standard solution of cholesterol was made of cholesterol purchased from Pfanstiehl. This was compared colorimetrically with a sample of specially purified Kahlbaum's cholesterol and also determined as the digitonide. The cholesterol digitonide gave a recovery of 99 per cent in the Pfanstiehl product, and both samples gave identical colorimetric reactions.

Owing to the limited amount of digitonin available, only a few control determinations were made with it to check the colorimetric values. In all cases the agreement was good.

The material extracted by ether from the unsaponifiable portion of the fat is called "cholesterol" throughout this paper, although it contained small quantities of unidentified substances.

Unless otherwise stated, all analytical data given are the results of at least two determinations of cholesterol.

Procedure—The sample was extracted by the Mojonnier modification of the Roese-Gottlieb method. The sample was weighed into a Mojonnier extraction flask. Ten-gram portions were taken for milk products, two grams for skim-

---

[1] Received October 26, 1929.

milk powder, and 0.5 gram for butter samples. When egg products were examined, 0.3 gram of the dry yolk or 1 gram of the fresh or frozen yolk was taken. In all cases at least three extractions were made. Sufficient water was added to make the total volume about 12 ml., and then 2 ml. of strong ammonium hydroxide solution was well mixed with the sample. Ten milliliters of ethyl alcohol were added, and the flask was shaken for $^1/_2$ minute, after which 25 ml. of ethyl ether were added and again shaken for $^1/_2$ minute. Next 25 ml. of petroleum ether were added and the flask was shaken for $^1/_2$ minute. If an emulsion formed, it was broken by the addition of a few milliliters of alcohol. After centrifuging or allowing to stand a few moments, the clear ether layer was poured into a dry 250-ml. beaker and evaporated nearly to dryness upon a hot plate. The succeeding extractions were made in the same manner, except that only 5 ml. of alcohol were added. The combined extracts were evaporated until the residual liquid became cloudy owing to the insolubility of the fat in the remaining alcohol. The residue was then saponified by a method modified from that of Kerr and Sorber (*7*). To the residue in the beaker 15 ml. of 95 per cent alcohol were added and brought to a boil. To this was added 1 ml. of a solution made by adding 100 grams of potassium hydroxide to 100 ml. of water. The beaker was covered with a watch glass and allowed to boil about 10 minutes. After cooling 30 ml. of ethyl ether were added so as to wash down the sides of the beaker and mix thoroughly with the contents. The ether suspension was carefully transferred to a conical separatory funnel. Another 30-ml. portion of ether was added to the beaker and likewise transferred to the separatory funnel. Next the beaker was washed with two successive 25-ml. portions of distilled water, added slowly to the separatory funnel. The funnel was rotated gently but not shaken, in order to prevent the formation of a stubborn emulsion. When an emulsion formed, a few milliliters of alcohol were added to break it. Separation took place rapidly and the soap solution was withdrawn. The ether layer was washed three times with 50-ml. portions of distilled water, or until it was alkali-free, as shown by testing the aqueous portion with phenolphthalein indicator. The ether portion was next transferred to a 50-ml. beaker and carefully evaporated to dryness, preferably on a steam bath. The clear yellow oil-like residue was dissolved in chloroform, transferred to a volumetric flask, and diluted to exactly 50 ml. The solution was always clear, but at times had a slight yellow tint due to the presence of carotinoid·bodies.

For colorimetric determination of the cholesterol, 10 ml. of the chloroform extract were taken in a dry test tube and 2 ml. of acetic anhydride were added. Then 0.2 ml. of concentrated sulfuric acid was added and the tube inverted several times to mix the contents. The tube was stoppered and let stand exactly 15 minutes in the light by which it was to be examined. It was then compared with the standard, made from ice cream of known egg content, pure cholesterol, or fresh egg yolk. No satisfactory permanent color standard has yet been found.

Very good results were obtained with a series of solutions prepared from ice-cream mix of known composition. If kept tightly stoppered, in the dark, these solutions appear to keep indefinitely. For ordinary work a series increasing by 0.5 per cent egg yolk from 0.0 to 4.0 per cent was found useful.

The same results may be obtained by using pure cholesterol as a standard, in which case a solution containing 0.0005 gram per milliliter is prepared. A standard may also be made by extracting by the above method 1 gram of the carefully separated and well-mixed yolks of three or four large fresh eggs. Two milliliters of this solution diluted to 10 ml. with chloroform equal 0.04 gram of egg yolk. This amount of egg yolk was found to contain 0.00054 gram of cholesterol. By taking various amounts of this solution and diluting to 10 ml. with chloroform, standards covering a wide range can easily be prepared.

Samples of ice cream containing no egg or very small additions of egg exhibited a yellow-gray tint when examined for cholesterol. This color is similar to that obtained at times in the cholesterol determination of blood. In most cases this off-color did not interfere with a very close approximation of the egg content. Should difficulty be experienced, recourse may be made to a method suggested to the writer by Rollin G. Myers (*8*), who used a similar procedure for the determination of minute amounts of ammonia in blood. The method was to add to the unknown a small known amount of the standard, bring to volume, and determine the cholesterol. The result minus the amount added was that originally present.

Cholesterol Content of Some Milk Products

Milk, cream, condensed milk, butter, skim milk, condensed skim milk, and skim-milk powder are the chief milk-product constituents found in ice cream. In order to obtain a quantitative measure of added egg solids by the determination of cholesterol, it is necessary to know the amount of cholesterol added to the mix by these products.

The literature has few references to the sterol content of milk products. The data in Table I are taken from "The Fundamentals of Dairy Science" (*9*).

Table I—Cholesterol Content of Milk Fat

AUTHORITY	CHOLESTEROL
	Per cent
Klostermann and Opitz	0.075
Boemer	0.3116 to 0.4066
Kirsten	0.36 to 0.43

Kirsten also reports that the breed and age of the animals and the type of their feeds has little influence upon the cholesterol content of the milk fat.

Two valuable sources of information giving the cholesterol content of milk products are Denis and Minot (*4*) and Fox and Gardner (*5*). The average findings of these authors is given in Table II.

Table II—Average Cholesterol Content of Some Milk Products

AUTHORITY	PRODUCT	AVERAGE FAT	AVERAGE CHOLESTEROL	AVERAGE CHOLESTEROL IN FAT
		Per cent	*Per cent*	*Per cent*
Denis and Minot	Milk	4.07	0.0145	0.356
Fox and Gardner	Milk	3.65	0.0126	0.343
Fox and Gardner	Milk	3.86	0.0151	0.3635
Fox and Gardner	Condensed milk	9.16	0.0303	0.328
Fox and Gardner	Skimmed milk	0.187	0.0037	1.912
Fox and Gardner	Butter milk	0.511	0.0101	1.977

Table III—Cholesterol Found in Some Milk Products

PRODUCT	FAT	CHOLESTEROL	CHOLESTEROL IN FAT	AVERAGE CHOLESTEROL IN FAT
	Per cent	*Per cent*	*Per cent*	*Per cent*
Milk:				
(*a*)	3.3	0.012	0.333	0.346
(*b*)	3.9	0.017	0.359	...
Cream	32.3	0.075	0.232	0.232
Evaporated milk	7.87	0.031	0.393	0.393
Buttermilk	0.59	0.01	1.69	1.69
Condensed skim milk (32% solids):				
(*a*)	0.32	0.009	2.81	2.49
(*b*)	0.56	0.012	2.16	...
Butter fat:[a]				
(*a*)	...	0.23	0.23	0.257
(*b*)	...	0.29	0.29	...
(*c*)	...	0.25	0.25	...
Skim-milk powder (three samples)	1.00	0.02	...	2.00

[a] The amount of cholesterol found in dry filtered butter fat was more than expected. In order to check this determination, the butter fat (*a*) giving 0.23 per cent cholesterol was treated with digitonin. The cholesterol digitonide precipitate obtained corresponded to a cholesterol content of 0.20 per cent.

Denis and Minot used the Liebermann-Burchard colorimetric method for determining the cholesterol, while Fox and Gardner used the digitonide method, extracting the fat by the Roese-Gottlieb method. Fox and Gardner believe that, in addition to the cholesterol, free or esterified, which is held by the fat, a certain amount may be present in colloidal solution or even combined with a protein.

The results obtained by the writer, given in Table III, compare favorably with those in Table II.

Cholesterol Content of Egg Products

Samples of fresh, frozen, and dry egg yolk were examined for their cholesterol content. As a check three of the determinations were made with digitonin as well as colorimetrically.

Some ice-cream manufacturers use powdered egg yolk in their mix rather than fresh egg. Fresh or frozen egg yolk is generally preferred in making French ice cream. In some samples of powdered yolk obtained from different sources a low content of cholesterol was found. Investigation showed that some manufacturers of egg products for ice-cream use make for this purpose an egg powder containing added milk proteins or sodium caseinate. The sodium caseinate adds to the viscosity of the ice-cream mix.

Table IV—Cholesterol Found in Some Egg Products

Sample	Product	Moisture	Cholesterol Colorimetric	Cholesterol by Digitonin	Dry Basis
		Per cent	*Per cent*	*Per cent*	*Per cent*
1	Powdered egg yolk	4.98	1.95[a]	1.84	2.05
2	Powdered egg yolk	6.02	2.54	..	2.70
3	Powdered egg yolk	5.70	1.84[a]	1.88	1.95
4	Powdered egg yolk	4.15	1.76[a]	..	1.83
5	Powdered egg yolk	3.66	1.72[a]	..	1.78
6	Powdered egg yolk	3.00	2.55	2.61	2.63
7	Frozen egg yolk	46.66	1.50	..	2.81
8	Yolk from small cold-storage egg	...	1.27	..	..
9	Yolk from large fresh egg	49.61	1.415	..	2.81
10	Yolk from sample 9 dried in vacuum at 135° C. for 40 minutes	...	2.74	..	2.81
11	Yolk from 3 medium-size fresh eggs	...	1.33	..	..
12	Yolk from fresh egg	...	1.38	..	..
13	Yolk from 3 fresh eggs	...	1.40	..	..
14	Yolk from 3 fresh eggs	...	1.33	..	..

[a] These egg powders were evidently not pure, but contained some diluent such as dry skim milk. They were of a very light cream color, whereas samples 2 and 6 were deep yellow in color.

Berg and Angerhauser (*1*) give the average cholesterol content of fresh egg yolk as 1.40 per cent. The results found in this work indicate a value of 1.36 per cent for the whole fresh egg yolk.

Determination of Egg in Ice Cream

It will be seen that in an egg-free mix, cholesterol is added chiefly by those products containing butter fat in appreciable amounts. To obtain a measure of the cholesterol in ice cream, some determinations were made on ice-cream mixes known to contain no added egg products (Table V). These mixes, with four exceptions, were factory made, and contained from 35 to 40 per cent of total solids. The milk solids used were cream and condensed skim milk. Samples 1, 2, 4, and 12 were prepared in the laboratory from cream and skim-milk powder.

Table V—Cholesterol Content of Ice-Cream Mix without Egg

Sample	Fat	Cholesterol	Sample	Fat	Cholesterol
	Per cent	*Per cent*		*Per cent*	*Per cent*
1	8.42	0.030	7	11.77	0.038
2	9.87	0.032	8	11.92	0.037
3	10.26	0.032	9	12.16	0.038
4	10.40	0.035	10	12.50	0.038
5	10.59	0.038	11	13.13	0.039
6	11.50	0.038	12	16.35	0.040

The results on the ice cream examined showed a fairly uniform cholesterol content. The amount of cholesterol found was not absolutely proportional to the fat, but varied in a manner analogous to the cholesterol content of milk, cream, and milk fat.

In order to facilitate the approximation of the cholesterol content of an ice-cream mix, the curve shown in Figure 1 was obtained from experimental data.

By multiplying the fat content of the ice cream by the figures shown in the abscissa the percentage of cholesterol in the no-egg mix is obtained.

Since large amounts of added egg yolk will appreciably add to the fat content of an ice cream, a correction for this extraneous fat should be applied. The average fat content of commercial samples of egg yolk is about 23 per cent. In the calculation of the following formula, which was used to obtain the egg-yolk content of ice cream, the factor used for the cholesterol content of the yolk was 1.36 per cent, and 23 per cent for the fat content.

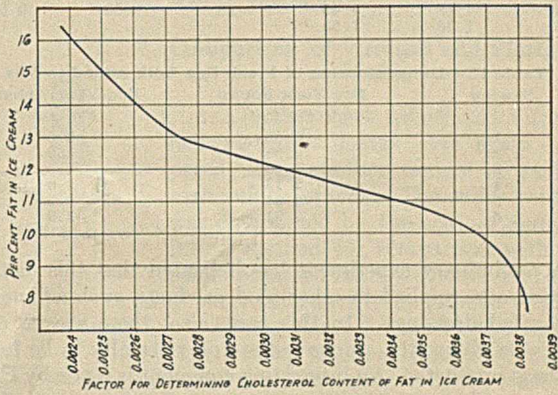


Figure 1—Cholesterol Content of Ice-Cream Mixes

$$\text{Per cent egg yolk} = \frac{73.5\,(a - bc)}{1 - 16.9\,c}$$

where a = total per cent cholesterol found
b = total per cent fat found
c = factor for fat obtained from Figure 1

In order to prove the accuracy of this method for determining egg yolk in ice cream, a number of samples of ice-cream mix were made containing various amounts of fresh, frozen, or powdered egg yolk. The approximate cholesterol content of the no-egg mix was found from Figure 1, and the egg content calculated from the formula given.

Table VI shows the results obtained when powdered egg yolk was added to ice-cream mix known to be egg free, Table VII, the results of analyses of commercial ice cream, and Tables VIII and IX, the results of single determinations on samples the egg content of which was not known to the writer when analysis was made. Some variation in results may be attributed to the difficulty in mixing the small amount of egg homogeneously with the sample, especially with the small lots prepared in the laboratory. All ice creams were plain or vanilla flavored.

Table VI—Determination of Powdered Egg Yolk in Ice Cream

Egg Yolk Added	Cholesterol in Added Egg Yolk Powder	Excess Cholesterol Found in Mix	Egg Yolk Found from Increase of Cholesterol Content
Per cent	*Per cent*	*Per cent*	*Per cent*
1.0	1.84	0.019	1.03
1.0	1.76	0.018	1.02
1.0	1.72	0.018	1.05
2.0	1.84	0.036	1.95
2.0	1.76	0.034	1.93
2.0	1.72	0.034	1.92
0.64[a]	Not known	...	0.72
1.50[a]	Not known	...	1.65

[a] This mix was prepared by N. C. Smith, of the State Dairy Laboratory, by adding powdered yolk to evaporated milk.

Table VII—Determination of Egg in Commercial Ice Cream

Reported Composition	Equivalent Egg-Yolk Content	Egg-Yolk Content Found
	Per cent	*Per cent*
86 lbs. of whole fresh egg in 4500 lbs. mix (1.91 per cent)	0.96	0.93
0.4 to 0.45 per cent powdered yolk	0.8 to 0.9	0.88
20 eggs in 2.5 gallons of mix (about 11 per cent)	About 5.5	5.4

Table VIII—Egg Yolk in Ice-Cream of Unknown Composition

Sample	Egg Yolk Calcd. as Added	Egg Yolk Actually Added	Sample	Egg Yolk Calcd. as Added	Egg Yolk Actually Added
	Per cent	*Per cent*		*Per cent*	*Per cent*
1	None	None	8	4.12	3.83
2	1.00	1.12	9	1.49	1.14
3	4.90	4.83	10	7.49	7.55
4	7.55	7.92	11	0.32	0.39
5	None	None	12	3.65	4.19
6	1.18	1.40	13	0.50	0.50
7	7.33	7.55			

Table IX—Determination of Fresh Egg Yolk Added to Mix

Sample	Egg Yolk Found	Egg Yolk Added
	Per cent	*Per cent*
1	0.55	0.5
2	0.96	1.0
3	1.43	1.5
4	2.13	2.0
5	2.64	2.5
6	2.94	3.0

A preliminary experiment has indicated that this method may also be applied to other food products, such as noodles and salad dressings. In this case, also, there are no data available giving the amount of sterols normally to be found in these products. An interesting comment is made by Hertwig and Bailey (*6*) who, in determining the unsaponifiable matter in wheat flour, pastes, and eggs, found "The unsaponifiable matter obtained from all samples and using all methods responded very satisfactorily to the chloroform sulfuric acid color test for plant and animal sterols."

Acknowledgment

This work was begun while the writer was assistant chemist in the Dairy Laboratory of the California State Department of Agriculture. The writer wishes to acknowledge the assistance and encouragement of C. F. Hoyt, in charge of the State Dairy Laboratory. Thanks are due R. G. Meyers for suggestions in preparing the manuscript and for a sample of pure cholesterol, and to Professor Norton, of the Sacramento Junior College, for temporary use of his colorimeter. The writer is also indebted to A. M. Besemer, director of research of the Golden State Milk Products Company, for aid and suggestions in completing this preliminary report.

Literature Cited

(1) Berg and Angerhauser, *Z. Nahr. Genussm.*, **29**, 9 (1915).
(2) Buchanan, *J. Assocn. Official Agr. Chem.*, **7**, 407 (1924).
(3) Cappenberg, *Chem.-Ztg.*, **33**, 985 (1909).
(4) Denis and Minot, *J. Biol. Chem.*, **36**, 58 (1918).
(5) Fox and Gardner, *Biochem. J.*, **17**, 288 (1923).
(6) Hertwig and Bailey, *J. Assocn. Official Agr. Chem.*, **9**, 122 (1926).
(7) Kerr and Sorber, *Ibid.*, **8**, 91 (1925).
(8) Myers, *J. Biol. Chem.*, **41**, 124 (1920).
(9) Rogers' Associates, "The Fundamentals of Dairy Science," Chemical Catalog, N. Y., 1928, p. 68.
(10) Steinle and Kahlenberg, *J. Biol. Chem.*, **67**, 425 (1926).

Comparison of Fused Silica, Gold, and Platinum Linings for Calorimeter Bombs[1]

Oscar Kenneth Bates

Department of Physics, Massachusetts Institute of Technology, Cambridge, Mass.

The lining for heat of combustion bombs as recommended by the A. S. T. M. "shall have an inner surface of platinum, gold, porcelain enamel, or other material which is not attacked by nitric and sulfuric acids or other products of combustion." This article describes a series of tests made for the purpose of comparing translucent Vitreosil linings with platinum and gold linings in order to determine their ability to resist the action of acids formed during the combustion in the bomb. Samples of coals ranged from a little higher than normal sulfur up to extremely high percentage of sulfur, giving thereby a wide range of results as far as acid formation in the bomb was concerned.

Apparatus and Methods

An Emerson calorimeter bomb of approximately 400 cc. capacity was used. The A. S. T. M. Standard Method D271-29 and the sodium peroxide fusion method for determination of sulfur were employed.

Sodium Peroxide Fusion Method—A 1-gram sample mixed with 15 to 18 grams of sodium peroxide in a nickel crucible suspended in cold water. The mixture was fired by means of a glowing piece of string. The cooled mass was disintegrated in water, acidified with hydrochloric acid, filtered, and barium sulfate precipitated in the usual manner.

The same Emerson bomb, Vitreosil pan, and nickel pan support were used in every test, the only change being in the linings. The water equivalents of the bomb with the different linings were determined.

Comparison of Gold and Vitreosil Linings

The gold lining was approximately 0.004 inch (0.1016 mm.) thick backed by 0.020 inch (0.508 mm.) of silver. The total weight of this lining was 147 grams. The Vitreosil lining weighed 86 grams.

Three samples of coal of varying sulfur content were used. The sulfur content was determined directly by the sodium peroxide fusion method. The results of these tests are given in Table I.

The determinations made with the translucent Vitreosil gave lower heating values with the two samples having a high sulfur content, but with the sample of low sulfur content the results agreed very closely. On the low-sulfur sample the heating values obtained using the Vitreosil and gold linings checked to better than 0.2 per cent. On the coals of higher sulfur content the results with the two types of linings differed approximately 0.6 per cent.

Since lower heating values were obtained with the Vitreosil linings on the high-sulfur coals, it might seem that an error results with the use of this type of lining. Further tests indicate, however, that the results obtained with the Vitreosil linings are the more nearly correct of the two.

Comparison of Gold, Vitreosil, and Platinum Linings

The coal was of a higher sulfur content than those used in the first series of tests. The sulfur was determined by the bomb-washings method.

---

[1] Received December 10, 1929.

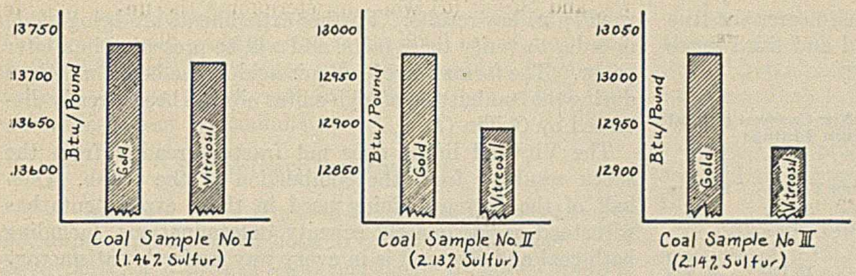
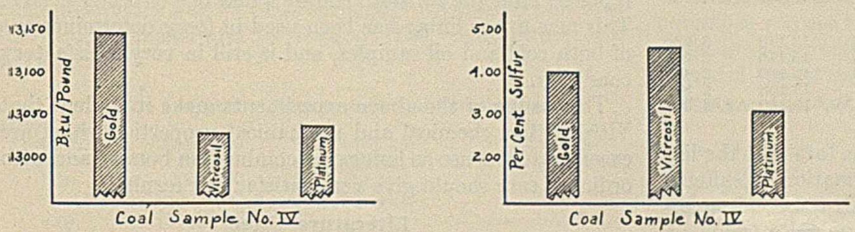
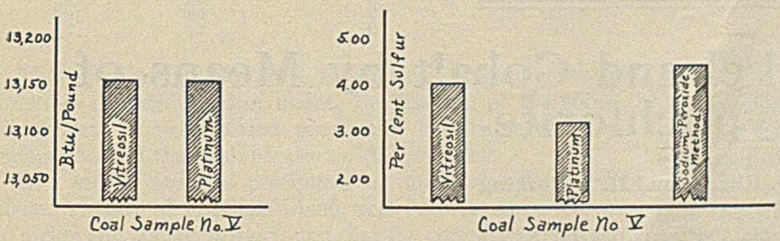


Figure 1—Comparison of Heating Values of Three Samples of Coal as Determined with Gold and Vitreosil Linings



Heating Value
Sulfur Content

Figure 2—Comparison of Heating Value and Sulfur Content of Sample of Coal as Determined with Gold, Vitreosil, and Platinum Linings



Heating Value
Sulfur Content—Sodium Peroxide Method

Figure 3—Comparison of Heating Value and Sulfur Content of Sample of Coal as Determined with Vitreosil and Platinum Linings

These experiments with high-sulfur coal show very good agreement between the heating values obtained with the Vitreosil and the platinum linings. The values determined with the gold lining do not agree very closely but they clearly indicate an appreciably higher heating value than that received with either of the other linings. This was also definitely shown in the first series of tests when the high-sulfur coal was used.

Table I—Comparison of Heating Values of Coals Using Gold and Vitreosil Linings

Lining	Fuel	Temp. Rise	Calcd. Heat Obsd.	Titration Cor.	Sulfur Cor.	Heating Value	
	Grams	*° C.*	*Gram-cal.*	*Cal.*	*Cal.*	*Gram-cal. per gram*	*B. t. u. per lb.*
SAMPLE I—SULFUR CONTENT, 1.46 PER CENT							
Gold	0.9467	3.080	7253	−25	−18	7616	13,710
	1.0060	3.283	7732	−27	−19	7639	13,750
	0.8332	2.724	6415	−23	−16	7652	13,770
	1.2287	4.008	9439	−32	−23	7635	13,740
						Av.	13,740
Vitreosil	0.8195	2.650	6273	−15	−16	7617	13,710
	0.8248	2.673	6327	−18	−15	7631	13,740
	0.7239	2.341	5541	−16	−14	7614	13,710
						Av.	13,720
SAMPLE II—SULFUR CONTENT, 2.13 PER CENT							
Gold	1.1302	3.483	8202	−31	−31	7202	12,960
	0.9289	2.870	6759	−27	−26	7219	12,990
						Av.	12,980
Vitreosil	0.8805	2.690	6367	−24	−24	7177	12,920
	0.9071	2.766	6547	−20	−25	7168	12,900
	0.9246	2.811	6654	−23	−26	7144	12,860
	1.0255	3.142	7437	−23	−28	7199	12,960
	0.7487	2.277	5390	−19	−21	7146	12,860
	0.9283	2.832	6703	−24	−26	7167	12,900
						Av.	12,900
SAMPLE III—SULFUR CONTENT, 2.14 PER CENT							
Gold	0.7801	2.408	5671	−24	−22	7211	12,980
	0.8263	2.557	6022	−24	−23	7233	13,020
	0.8492	2.630	6194	−26	−24	7235	13,020
	0.9105	2.814	6627	−26	−25	7222	13,000
						Av.	13,010
Vitreosil	0.9359	2.867	6786	−23	−26	7198	12,960
	0.8196	2.502	5922	−14	−23	7180	12,920
	0.7766	2.382	5638	−22	−22	7203	12,970
	0.5281	1.615	3823	−14	−15	7184	12,930
	0.8625	2.630	6225	−20	−24	7166	12,900
	0.8423	2.570	6083	−20	−23	7171	12,910
						Av.	12,930

The sulfur content as determined with the Vitreosil lining was much higher than was obtained when either the platinum or gold lining was used. The gold lining gave the intermediate value and the platinum lining the lowest. Without doubt the value obtained using Vitreosil linings is nearest to the true sulfur content of the sample.

Comparison of Vitreosil and Platinum Linings

As a further check translucent Vitreosil and platinum linings were again compared using another sample of coal of high sulfur content. The sulfur content was determined by the sodium peroxide fusion method for comparison with the result obtained from the bomb washings. This series of tests gave results similar to those obtained with the same linings in the second series. The heating values checked very closely, but the sulfur determinations from the washings were quite different. The sulfur content determined from the sodium peroxide method was 4.51 per cent; determined from the bomb washings using the Vitreosil lining, 4.13 per cent, and using the platinum lining 3.30 per cent.

Summary of Results

The heating values of the different coals as determined by the Emerson bomb lined with Vitreosil agreed very closely with those determined using a platinum lining. The values obtained with the bomb lined with gold backed with silver agreed satisfactorily with the Vitreosil lining for samples of low sulfur content, but differed when samples of high sulfur content were used. This indicates that additional heat is evolved by reactions in which the lining plays the important part. This additional heat was not evolved when the Vitreosil and platinum linings were used.

Table II—Comparison of Heating Value and Sulfur Content of Coal (Sample IV) Using Gold, Vitreosil, and Platinum Linings

Fuel	Temp. Rise	Calcd. Heat Obsd.	Titration Cor.	Sulfur Cor.	Heating Value		Sulfur
Grams	*° C.*	*Gram-cal.*	*Cal.*	*Cal.*	*Gram-cal. per gram*	*B. t. u. per lb.*	*%*
GOLD LINING							
1.0467	3.291	7750	−48	−51	7308	13,150	3.72
1.0047	3.175	7477	−47	−52	7341	13,210	3.99
0.6852	2.149	5062	−36	−39	7278	13,100	4.42
0.6729							4.31
					Av.	13,150	Av. 4.11
VITREOSIL LINING							
0.7378	2.295	5433	−35	−41	7261	13,070	4.29
0.6260	1.945	4604	−32	−38	7243	13,040	4.62
0.7069	2.197	5200	−38	−44	7241	13,030	4.73
0.6780							4.86
0.7873							4.76
0.5381							4.68
					Av.	13,050	Av. 4.66
PLATINUM LINING							
0.7757	2.414	5675	−24	−30	7246	13,040	2.96
0.7239	2.251	5292	−23	−29	7239	13,030	3.07
0.6676	2.082	4895	−24	−30	7251	13,050	3.52
0.8018							3.18
					Av.	13,040	Av. 3.21

When the sulfur content of high-sulfur coals is determined by the bomb-washings method, somewhat low values are obtained with all three linings, but those obtained with the vitreosil lining are much the highest and are much nearer the true value. This fact was shown in the second and third series of tests.

Table III—Comparison of Heating Value and Sulfur Content of Coal (Sample V) Using Vitreosil and Platinum Linings

Fuel	Temp. Rise	Calcd Heat. Obsd.	Titration Cor.	Sulfur Cor.	Heating Value		Sulfur
Grams	*° C.*	*Gram-cal.*	*Cal.*	*Cal.*	*Gram-cal. per gram*	*B.t.u. per lb.*	*%*
			VITREOSIL LINING				
0.8832	2.757	6526	−35	−47	7297	13,140	4.06
0.7970	2.491	5901	−32	−43	7310	13,160	4.17
0.8046	2.517	5958	−35	−42	7309	13,160	4.14
1.0050	3.151	7460	−44	−54	7326	13,190	4.16
						Av. 13,160	Av. 4.13
			PLATINUM LINING				
0.7351	2.312	5435	−23	−35	7316	13,170	3.66
0.7770	2.441	5739	−23	−33	7315	13,170	3.26
0.7192	2.256	5304	−23	−32	7298	13,140	3.47
0.7049	2.208	5191	−19	−26	7302	13,150	2.82
						Av. 13,160	Av. 3.30

The cause of these low values may be the fact that the linings act as catalysts differently in the formation of sulfonic acid during the combustion in the bomb. If the bomb washings contained sulfonic acid, soluble barium salts would be formed during analysis, and consequently the determinations would give low results. Further experiments are being made in order to verify these facts, and will be presented in a later paper. The formation of sulfonic acid in the bomb washings during the combustion of high-sulfur oils has been already discussed by Griffin (*1*).

The Vitreosil lining does not fracture readily from the shock resulting from the combustion in the bomb. One-half of the Vitreosil lining used in these experiments has withstood approximately seventy determinations, including both coal and oils, and is in every way perfectly satisfactory and without signs of injury. The other half of the lining fractured slightly after fourteen determinations and was replaced after the thirtieth run by a new one of better design. This new upper lining has been used in forty determinations of both coal and oil samples, and is still in very satisfactory condition.

The results of the above experiments make it evident that Vitreosil has chemical and mechanical properties which are excellent for its use as linings for combustion bombs, and with ordinary care should give very satisfactory results.

Literature Cited

(1) Griffin, Ind. Eng. Chem., Anal. Ed., 1, 167 (1929).

Separation of Nickel and Cobalt by Means of Hypochlorite[1]

F. H. Rhodes and H. J. Hosking

Cornell University, Ithaca, N. Y.

Nickel and cobalt can be separated from each other by fractional precipitation with sodium hypochlorite. The sharpness of the separation may be increased by effecting the precipitation in hot solution, by allowing the precipitated oxide to stand in contact with the solution for a considerable time, and by adding sufficient alkali to neutralize the free acid formed by the interaction between the cobaltous salt and the hypochlorite. Under proper conditions it is possible to precipitate most of the cobalt free from nickel and to leave a final residual solution containing most of the nickel free from cobalt, with but a comparatively small intermediate fraction which contains both elements.

MUCH of the cobalt used in this country is obtained from the complex ores of Ontario, in which the cobalt is associated with nickel, iron, copper, silver, and arsenic. In smelting, the cobalt is concentrated as a complex speiss, which is roasted and leached to produce a solution containing cobalt, nickel, iron, and small amounts of copper and arsenic. From this solution the iron, copper, and arsenic are precipitated by calcium carbonate, leaving a final solution containing nickel and cobalt relatively free from other metals.

The most commonly used methods for the separation of the nickel from the cobalt are based upon the differences in the extent and rate at which the two metals may be precipitated, as their higher oxides, by the addition of oxidizing agents to solutions of their divalent salts. The oxidizing agent commonly used is sodium hypochlorite. This reagent, under proper conditions, precipitates cobalt as a sesquioxide or hydrated sesquioxide (Co_2O_3 or $Co_2O_3.xH_2O$), while from solutions of nickelous salts a mixture of nickel sesquioxide and nickel peroxide (NiO_2) or complexes containing these oxides are obtained. The precipitation of the cobalt proceeds somewhat more readily than does the precipitation of the nickel, so that by properly controlling the conditions it is possible to throw down most of the cobalt relatively free from nickel and to leave in solution most of the nickel relatively free from cobalt.

Despite the industrial importance of this method of separation, there is comparatively little published information as to the effects of various conditions upon the completeness with which the separation may be effected. This investigation was undertaken for the purpose of determining the extent to which nickel and cobalt may be separated by fractional precipitation by sodium hypochlorite and to study the effects of various conditions upon the completeness of this separation.

Materials Used

In the preliminary experiments solutions of pure cobalt sulfate and nickel sulfate were used. The raw material used in the final experiments was a crude mixture of cobalt oxide and nickel oxide presented by the Deloro Smelting and Refining Company, of Toronto, Ont. This material contained: nickel, 17.4; cobalt, 22.6; iron, trace; and calcium, 12.3 per cent. The calcium was present in part as carbonate and in part as sulfate.

The solution of sodium hypochlorite used in the preliminary experiments was prepared by dissolving 50 grams of sodium hydroxide and 10 grams of sodium carbonate in 900 cc. of water, cooling at 10° C., passing chlorine into the solution until 40 grams of chlorine had been absorbed, and finally

---

[1] Received January 12, 1930.

diluting until the solution was 1 normal in oxidizing power. The hypochlorite solution used in the final experiments was prepared in a similar manner but was somewhat more concentrated, being 2.2 normal in oxidizing power and 0.44 normal in respect to alkalinity.

Preliminary Experiments

Two solutions were prepared which were, respectively, 0.5 normal and 1 normal both in cobalt and in nickel. To 25-cc. portions of each of these solutions were added varying amounts of the 1 normal hypochlorite solution. After standing for 1 hour at room temperature each solution was filtered. Each precipitate was washed thoroughly with water and then analyzed for nickel and for cobalt. The results are shown in Table I.

Table I—Effect of Concentration of Solution

Hypochlorite Solution Added	Total Co Pptd.	Total Ni Pptd.	Ratio of Co to Ni in Ppt.
Cc.	*Per cent*	*Per cent*	
	0.5 normal solutions		
10	60	0	100:0
15	75	Trace	99:1
20	87	2.5	97:3
	1 normal solutions		
10	40.5	0	100:0
15	52	0	100:0
20	69	0	100:0
25	77	0	99:1

These results indicate that, in solutions containing equal amounts of cobalt and of nickel, the fraction of the cobalt which can be precipitated practically free from nickel is independent of the concentration of the solution.

In a second series of precipitations, made at 18° C. with 25-cc. portions of solutions which were 0.2 normal in respect to nickel and cobalt, it was found that the completeness of the separation increases with increase in the time of standing after the addition of the hypochlorite. The results are shown in Table II.

Table II—Effect of Time of Standing

Time of Standing after Adding NaOCl	Total Co Pptd. with Only Faint Trace of Ni
	Per cent
5 minutes	40
1 hour	75
24 hours	88

Upon the first addition of the hypochlorite it is possible to precipitate only a relatively small fraction of the cobalt without at the same time throwing down some of the nickel. If sufficient hypochlorite is added to precipitate some nickel along with the cobalt, the precipitated nickelic oxide will react slowly with the cobaltous salt remaining in solution, forming soluble nickelous salt and insoluble cobaltic oxide. The rate at which this reaction proceeds increases with the temperature. For example, when the precipitation is effected at 18° C. and the precipitated oxide is allowed to stand only 5 minutes in contact with the solution, only 40 per cent of the total cobalt is precipitated free from nickel, while when the precipitation is made at 80° C. under otherwise similar conditions it is possible to precipitate 67 per cent of the cobalt substantially free from nickel.

Effect of Alkalinity upon Precipitation

The general over-all equation for the precipitation of cobaltic oxide by hypochlorite may be written:

$$2CoSO_4 + NaOCl + 2H_2O = Co_2O_3 + NaCl + 2H_2SO_4$$

The hydrochloric acid formed by the interaction may interfere with the precipitation by decomposing any hypochlorite which does not immediately enter into the reaction and also by dissolving a part of the cobaltic oxide with the formation of the unstable cobaltic chloride. It is evident that the amount of cobalt which can be precipitated by a given quantity of hypochlorite should be increased by the addition of sufficient alkali to neutralize the hydrochloric acid as fast as formed. The addition of excessive amounts of the alkali will cause the precipitation of nickel along with the cobalt and will thus interfere with the completeness of the separation.

A series of precipitations was made in which varying amounts of 0.15 N sodium hydroxide solution were introduced along with the solution of hypochlorite. In each case 25 cc. of a 1 N hypochlorite solution were added to 25 cc. of a solution of nickel and cobalt sulfates which was 0.25 normal in respect to each element. The precipitations were made at room temperature, and the precipitate was allowed to stand for 24 hours in contact with the solution before filtering. The results are shown by Table III.

Table III—Effect of Adding Sodium Hydroxide with Hypochlorite

NaOH Soln. Added	Total Co Pptd.	Total Ni Pptd.	Ratio of Co to Ni in Ppt.
Cc.	*Per cent*	*Per cent*	
0	88	0	100:1
10	95	1	99:1
20	97	18	84:16
30	100	38	73:27
40	100	49	67:32
50	100	64	61:39
100	100	96	51:49

Fractional Precipitation of Cobalt and Nickel

In any industrial application of this method to the preparation of pure cobalt and pure nickel from solutions that contain both of these metals, it will be necessary to effect the precipitation fractionally, so as to obtain a first precipitate of pure cobaltic oxide, an intermediate fraction which contains both cobalt and nickel, and a final solution carrying nickel free from cobalt. The economic feasibility of this process depends upon the possibility of being able to remove the last traces of cobalt from the solution without at the same time precipitating an excessive amount of nickel, since only in this way would it be possible to obtain a reasonably small intermediate fraction which could be redissolved and added back to the original solution.

To 250 cc. of a solution which was 1 normal in respect to nickel sulfate and cobalt sulfate was added a mixture of 200 cc. of normal 1 N sodium hypochlorite solution and 200 cc. of 0.15 N sodium hydroxide solution. After standing for 2 hours at 70–80° C. with constant stirring, the solution was filtered. To the filtrate was added 100 cc. of a mixture of equal volumes of the solutions of sodium hydroxide and sodium hypochlorite, and the solution was stirred and filtered as before. A third precipitation was then made, using 100 cc. of the mixture of the solutions of sodium hydroxide and sodium hypochlorite. Each precipitate, as well as the final filtrate, was analyzed for nickel and cobalt. The results are shown by Table IV.

Table IV—Fractional Precipitation Data

	1st Ppt.	2nd Ppt.	3rd Ppt.	Final Filtrate
Per cent of total Co	90.0	8:0	2.0	0
Per cent of total Ni	0.1	0:8	3.5	93.7
Ratio of Co to Ni	99.94:0.06	10:1	37.5:62.5	100:0

These results indicate that under proper operating conditions it would be possible to recover, from a solution which contains approximately equal concentrations of cobalt and of nickel, an initial precipitate which contains 90 per cent of the cobalt free from nickel and a final filtrate which contains at least 90 per cent of the nickel free from cobalt, with an intermediate fraction which should contain less than 10 per cent of the total metal present.

Separation on Semi-Plant Scale

To determine whether or not the results obtained in the laboratory can be duplicated on a manufacturing scale, one experiment was made with relatively large quantities of material, using apparatus similar to that which might be employed in actual industrial operation. A solution of cobalt and nickel chlorides was prepared by dissolving the crude mixed oxides (from the Deloro Smelting and Refining Company) in hydrochloric acid. This solution contained 12.8 grams of nickel and 16.6 grams of cobalt per liter—i. e., it was 0.218 molar in respect to nickel and 0.282 molar in respect to cobalt. To 81 liters of this solution were added 26 liters of a solution of sodium hypochlorite which was 2.2 normal in oxidizing power and 0.44 normal in respect to free alkali. Since the hypochlorite solution itself contained free alkali, no additional sodium hydroxide was required in the precipitation. The precipitation was effected at 70–80° C. After the addition of the precipitant, the mixture was stirred for 2 hours and was then filtered through canvas in a plate-and-frame filter press. No particular difficulty was experienced in this filtration. The cake in the press was washed with water. The filtrate was returned to the agitator, and an intermediate fraction of mixed oxides was precipitated by the further addition of 8 liters of the solution of hypochlorite. The precipitate was filtered and washed as before. The original solution, each press cake, and the final filtrate were analyzed for nickel and for cobalt. The results are shown by Table V.

Table V—Fractional Precipitation, Semi-Plant Scale

	ORIG. SOLN.	1ST PPT.	2ND PPT.	FILTRATE
Grams Co	1345	1054	320	None
Grams Ni	1035	7.3	30.8	997
Per cent total Co	100	68	24.0	0
Per cent total Ni	100	0.64	3.0	96.4
Ratio Co:Ni	56.5:43.5	99.37:0.63	91.3:8.7	100:0

These data indicate that the results obtained in the laboratory can, in general, be duplicated in operations on a large scale. That the separation obtained in the semi-plant scale experiment was not quite so complete as was indicated by the laboratory work is due principally to the fact that the washing in the filter press was not so thorough as was the washing in the laboratory experiments. The precipitated cobaltic and nickelic oxides are rather finely divided, but can be filtered very satisfactorily on canvas in any standard filter press.

Improved Method for Determining Volatile Hydrocarbons in Soap[1]

Clarence T. N. Marsh

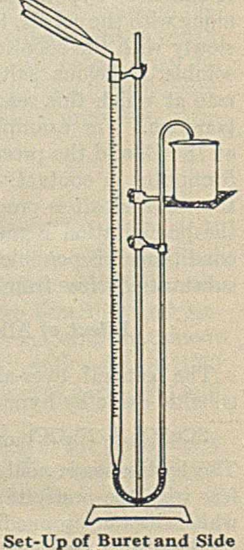
Meat Inspection Laboratory, Bureau of Animal Industry, U. S. Department of Agriculture, Chicago, Ill.

IN THE work of this laboratory it has recently been necessary to examine a large number of samples of so-called "naphtha" soap. Part of the examination consisted in determining the percentage of volatile hydrocarbons or naphtha present. The standard method of the Committee on Methods of Analysis and Specifications of Commercial Soap and Soap Products of the Division of Industrial and Engineering Chemistry of the AMERICAN CHEMICAL SOCIETY (*1*) was followed. By modification in certain details it was found possible to shorten the method, make it more convenient of manipulation, and enhance its accuracy. As the modifications devised materially diminish the difficulty of the determination, a description of them is offered.

The use of calcium chloride, suggested in a footnote in the original method, was resorted to in order to save time and enhance accuracy. A three-hole rubber stopper was used in the flask containing the soap, the third hole being fitted with a 60-cc. open-top, cylindrical separatory funnel, the stem of which was allowed to extend into the flask for about 7.6 cm. (3 inches). This separatory funnel was filled with a solution of calcium chloride of approximately 1.34 specific gravity. Just as the soap solution starts to boil and foam begins to rise in the flask, approximately 15 to 20 cc. of the calcium chloride solution are allowed to run in. This produces a flock of large suspended insoluble particles which tend to keep down the foaming and allow a faster rate of distillation. It may be found necessary to make further addition of calcium chloride solution later in the distillation period in case foam rises too high in the flask.

To collect and measure the recovered naphtha, a 50-cc. Mohr apparatus graduated in 0.1-cc. divisions was used. The bottom of the buret was connected by means of a piece of rubber tubing 15 to 20 cm. (6 to 8 inches) in length to a glass tube of about 7 to 8 mm. outside diameter. This tube, which is approximately 13 cm. (5 inches) shorter than the buret and bent at the top, is held in a vertical position and parallel to the buret by means of a clamp. Its upper end is bent outward and down to deliver liquid into a 1-liter beaker held in position under it by a ring support and clamp. The buret is so placed and adjusted that the condenser tube just touches its inside edge, thus allowing the distillate to run in quietly down the side and not to fall in drops. Before the distillate starts to come over, the buret and side tube are filled with water and so adjusted that water drops from the side tube into the beaker when the level of water in the buret is near the 5-cc. mark.

The naphtha soon appears on the surface of the water in the buret, and at this point a very small particle of powdered oil-soluble red dye is dropped in the buret. This dissolves in and colors the naphtha layer. If the tip of the condenser tube is correctly placed in contact with the buret, the naphtha layer will be quiescent and no trace of red color will appear in the water below it. The water automatically flows into the beaker. When there is no further increase in the volume of the naphtha layer and approximately 800 cc. of water have collected in the beaker, the distillation may be discontinued.



Set-Up of Buret and Side Tubing

[1] Received February 10, 1930.

The side arm may then be raised or lowered to bring the bottom of the naphtha layer to any convenient point and its volume read. The volume of the hydrocarbon oil may be read immediately, as no emulsification or entrapment of hydrocarbon oil in the water takes place. No gain in accuracy is attainable by corking the buret and deferring the reading until the next day.

The accompanying drawing illustrates the set-up of the buret and side tubing and the adjustment of the tip of the condenser to the buret.

Literature Cited

(1) J. Ind. Eng. Chem., **14**, 1159 (1922).

A System of Proximate Chemical Analysis of Plant Materials[1,2]

Selman A. Waksman and Kenneth R. Stevens

New Jersey Agricultural Experiment Station, New Brunswick, N. J.

A system of proximate analysis of plant material is proposed which will enable one, by a series of simple manipulations and by the use of inexpensive apparatus and chemicals, to account for 88 to 95 per cent of the material, including the most important groups of plant constituents. Only the results obtained by direct analysis are recorded. A complete analysis can be carried out, in duplicate, with only 14 grams of dry material.

The method of analysis can be utilized in the study of the chemical composition not only of fresh plant material, but also of decomposed plant residues, such as artificial composts, manures, peats, and forest soils. The method can be used conveniently in following the chemical changes produced in plants in the process of their growth as well as in the course of decomposition of plant residues by microörganisms.

IN investigations involving the chemical composition of plant products, a complete and systematic, even if only proximate, scheme of quantitative analysis of the various organic and inorganic chemical constituents of the plant material, both fresh and decomposed, is frequently needed. This applies not only to problems in plant physiology, plant pathology, agronomy, and animal feeds, but also to soil science problems, especially in the study of the mechanism of decomposition of green manures, stable manures, and artificial manures, as well as of the degradation of organic plant residues in the soil in general.

Because of the complexity of the composition of different plant materials and in view of our limited knowledge of the chemistry of many of the constituents, it is out of the question to propose a system of analysis which would either be complete or could be applied in an unqualified manner to all plant substances. Some of the more abundant plant constituents can be grouped in such a manner, on the basis of both their chemical relationship and their role in plant growth, that their determination should give an insight into the general composition of the plant and offer a basis for further investigation. One cannot expect, however, to account in these analyses for 100 per cent of the constituents of the substance analyzed, provided that the most important chemical groups are not overlooked.

Sources of Error in Analyses of Plant Materials

In carrying out quantitative analyses of plant material, several important errors are frequently made, even if the analysis is only proximate:

(1) Only a few definite groups of chemical constituents are usually taken into consideration, such as the complex carbohydrates—starches, pentosans, celluloses, etc.—proteins, fats, lignins, and mineral substances. A large number of other complexes which frequently form quantitatively important ingredients of the plant material are thereby overlooked. An attempt to make the sum of the constituents accounted for total 100 per cent usually involves several errors of determination. Young plant materials may contain, for example, as much as 15 to 35 per cent of water-soluble substances, including various sugars, organic acids, amino acids, etc.; these substances are only partly accounted for in many systems of analysis (*22*) and are usually not considered at all.

(2) Some of the analyses are based, not upon the determination of definite chemical complexes, but on certain known procedures which give well-known preparations. Cellulose, for example, is usually determined by the Cross and Bevan method, which results, especially in the hands of inexperienced investigators, in a preparation containing, in addition to true celluloses, pentosans, lignins, nitrogen compounds, and mineral substances. Unless all these impurities and perhaps others are accounted for, one can never be certain to what extent the figure recorded actually represents true celluloses. The confusion that may arise can be seen from some analyses of Rege (*23*), who reported that dry poplar wood, consisting of 98.32 per cent organic matter, was made up of 66.3 per cent cellulose, 20.63 per cent pentosan, and 28.44 per cent lignin. In other words, the sum of the three constituents alone is considerably greater than that of the total plant material, and wood also contains various amounts of fats, waxes, resinous materials, nitrogenous substances, mineral substances, and what not, in addition.

(3) There is considerable confusion as to the nature and method of determination of the lignins. Here again one may use the method of hydrolysis of the plant material with concentrated acids which do not act upon lignins, or extract the lignins with an alkali followed by precipitation with an acid, or one may employ special reagents, such as chlorine dioxide, etc., for the oxidation of the lignin. One is never certain whether in these different methods he is dealing with the same chemical complex or with different substances. The acid lignin, obtained by treatment of the plant material with fuming hydrochloric or 72 per cent sulfuric acid, contains mineral substances and certain nitrogenous compounds (protein derivatives), the latter usually not even being accounted for in the analyses. The alkali lignin contains hemicelluloses and nitrogenous complexes, while in the treatment of the plant material with an oxidizing agent for the removal of the incrustants one dissolves, not only the lignins, but also sugars, starches, certain hemicelluloses, and various other substances. Frequently the question is raised as to whether some of the lignin present in plant material may not actually dissolve in dilute acids and even in water, and whether the structure of the lignin molecule is not considerably changed as a result of the treatment with the chemical reagents (*24*).

(4) Confusion exists also in regard to the hemicellulose group. In some cases the pentosans only are determined by the furfural-phloroglucinol method. Frequently some of the material thus obtained represents not only pentosans, but also other furfural-yielding compounds, such as pectins and uronic acids. In some

---

[1] Received January 16, 1930.

[2] Paper of the Journal Series, New Jersey Agricultural Experiment Station, Department of Soil Chemistry and Microbiology.

methods of analysis the hemicelluloses are hydrolyzed by dilute acids and then calculated from the amount of reducing sugar. Some investigators (*9, 18*) even claim that hemicelluloses are not true pentosans or hexosans, but contain acid groups of the uronic acid type.

(5) Another source of uncertainty is found in the numerous foodstuff analyses involving crude fiber determinations. This complex is made up of true celluloses, certain hemicelluloses, considerable lignin, some nitrogenous organic complexes, and certain mineral substances. Without any concise definition of the nature of the substances that one sets out to determine, the results are likely to be confusing.

It is difficult enough to interpret quantitative data obtained in the analysis of fresh plant material when the chemical nature of the substances is more or less known. It becomes doubly difficult when the plant material has undergone a certain amount of decomposition by microörganisms, owing to the great number of substances formed, either intermediary or synthetic, of plant or microbial origin. This results in vague conceptions about "humus" and "humic acids" which cannot increase our knowledge of the processes involved. Here again only a more concise definition of the nature of the substances acted upon by the various reagents and a more complete knowledge of the products resulting from the chemical treatment will throw light upon the natural processes which lead to the formation of the so-called "humus" and bring about a better understanding of its true nature.

Requirements of System of Analysis

The system of analysis described herein is a result of a comparison of the methods proposed at various times for the analysis of celluloses, hemicelluloses, lignins, proteins, and other chemical complexes, with the intention of combining the methods of determination of the various plant constituents, so as to fulfil the following requirements:

(1) The determination was to be based, not upon the loss in weight, but upon the amount of the specific complex actually found.

(2) The quantity of the chemical constituent thus determined should represent a definite minimum whereby one would always feel certain that the substance in question was present in the plant material in at least the amount obtained in the analysis.

(3) The determination should be based as much as possible upon our knowledge of the chemical nature of the complex in question.

(4) The complete analysis of the plant material should be carried out on a small quantity (5 to 10 grams) of material.

(5) The results should check well in the hands of different investigators and no chance should be left for large errors in the manipulation.

(6) The complete analyses must take only a minimum of time.

Existing Methods for Determining Plant Constituents

Before outlining the system of analysis in detail, one must consider the methods now commonly employed for the determination of several of the most abundant groups of plant constituents and indicate the reasons for the selection of the particular method.

TRUE CELLULOSES—The role of celluloses in the transformation of organic matter in the soil cannot be overemphasized. The true celluloses are characterized by various color reactions. They are not hydrolyzed by dilute acids, but are dissolved and later hydrolyzed by concentrated acids (60 to 80 per cent sulfuric or 42 per cent hydrochloric).

Three general methods are available for making a quantitative determination of celluloses:

(1) The chlorination method of Cross and Bevan or one of its various modifications, as well as other similar methods usually employed for the determination of cellulose in certain natural organic materials, especially in the analysis of wood and wood pulp (*26, 27*).

(2) The removal of the lignins from the organic matter with acid sodium sulfite solution, followed by extraction of the cellulose with ammoniacal copper solution and its precipitation with hydrochloric acid. This represents a combination of Klason's (*13*) and Charpentier's (*6, 7*) methods as suggested and developed by Barthel and Bengtsson (*1, 5*).

(3) Hydrolysis of the cellulose-containing material, previously freed from sugars, starches, and hemicelluloses, with concentrated acids, then completing the hydrolysis to glucose by boiling with the dilute acid. The cellulose content is calculated from the amount of reducing sugar formed.

The first two methods are too lengthy and tedious, especially the second method, which requires preliminary extraction with an acid sulfite solution to remove the lignins. This method can, however, be modified considerably by extracting the pentosans and lignins with dilute alkali solution under pressure. This modification is based upon the fact that lignins are soluble in dilute alkali solutions under pressure and upon the observation that when a soil is previously treated with a dilute alkali solution the extraction and precipitation of celluloses are much less difficult. The only danger in the use of dilute alkalies under pressure is the destruction thereby of some of the true cellulose.

Table I shows that by a preliminary treatment of the plant material followed by extraction of the cellulose with ammoniacal copper solution nearly all the cellulose can be recovered; only autoclaving with 5 per cent solution of the alkali results in a loss of cellulose.

Table I—Influence of Preliminary Treatment on Cellulose Content of Paper and Straw

PRELIMINARY TREATMENT	MATERIAL[a]	WEIGHT OF DRY RESIDUE	CELLULOSE CONTENT
		Mg.	*Mg.*
Boiling 1 hour with 50 cc. of 3% NaOH solution	Paper	...	948
	Wheat straw	443	352
Autoclaving 30 minutes at 15 lbs. (1 atm.) pressure with 50 cc. of 5% NaOH solution	Paper	...	868
	Wheat straw	361	325
Autoclaving 15 minutes at 15 lbs. (1 atm.) pressure with 50 cc. 2% NaOH solution	Paper	...	940
	Wheat straw	456	320

[a] 1 gram used in each test.

The outstanding disadvantage of the chlorination methods is that they do not give pure cellulose. Unless the various impurities, both organic and inorganic, are accounted for, the results will be only of relative value.

Using the third method, Ost and Wilkening (*19*) hydrolyzed cotton with sulfuric acid and reported a 95 per cent yield of cellulose, as calculated from the reducing sugar of the hydrolyzate. Willstätter and Zechmeister (*31*) treated cellulose with 41 per cent hydrochloric acid and obtained 96.3 per cent cellulose yield. Monier-Williams (*17*) and other investigators found that cellulose can be hydrolyzed by sulfuric acid theoretically to glucose as required by the equation

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6$$

A yield of 95.1 per cent glucose was thereby actually obtained.

Kiesel and Semiganovski (*12*) were the first to report 100 per cent glucose yield from cellulose by the following procedure: Pure filter paper, in which the moisture and ash content have previously been determined, is treated with 7 to 10 volumes of 80 per cent sulfuric acid (sp. gr. 1.74) for $2^1/_2$ hours at room temperature. The material is then diluted with 15 volumes of water and heated in a water bath for 5 hours. A colorless hydrolyzate is obtained. The glucose is determined by any convenient method. The amount of cellulose is calculated by multiplying the glucose yield by the theoretical figure 0.9. In the case of plant materials a small quantity is first treated with 100 volumes of 2 per cent hydrochloric solution for 3 to 5 hours under a reflux condenser. The residue is filtered, washed first with water and then with alcohol and ether, dried, and treated with 10 volumes of 80 per cent sulfuric acid. After 2$^1/_2$ hours' extraction, 15 volumes of water (on the basis of the amount of acid used) are added and the flask containing the material is immersed for 5 hours in a boiling-water bath. After filtering, the solution is made up to volume and an aliquot portion is carefully neutralized and sugar determined.

Table II—Influence of Preliminary Treatment of Paper with 2 Per Cent Hydrochloric Acid on Cellulose Content, as Determined by Treatment with 80 Per Cent Sulfuric Acid

(Paper used, 500 grams; dry material, 480 mg.)

PRELIMINARY TREATMENT WITH HCl	SUGAR PRODUCED ON TREATMENT WITH H_2SO_4	CELLULOSE RECOVERED
	Mg.	*Per cent*
Autoclaved 1 hour at 120° C.	490	91.9
Steamed 1 hour at 100° C.	509	95.4
Boiled under reflux condenser 5 hours	503	94.3

These results can readily be confirmed, although in most instances the yield of cellulose is found to be 95 to 96 per cent rather than 100 per cent. The influence of preliminary treatment with a dilute hydrochloric acid solution upon the amount of cellulose obtained on subsequent treatment with 80 per cent sulfuric acid is brought out in Table II. These results show that if the extraction is carried out at temperatures not higher than 100° C. the loss of cellulose will be rather small. Wohl and Blumrich (*32*) have shown that the results of the treatment of cotton cellulose with dilute hydrochloric acid depend upon the strength of the acid and length of extraction. In the case of a 0.5 per cent acid solution the loss was 0.77 per cent in 2 hours and 1.38 per cent in 6 hours; in the case of a 3 per cent acid solution, the loss was 3.42 and 5.43 per cent cellulose, as shown by the sugar yield, respectively. Owing to the numerous limitations of the methods of plant analysis and to a lack of a clear understanding of the true chemical nature of the celluloses in the plant materials, the error of 5 or 6 per cent involved may be disregarded. This is especially true if we define celluloses as that group of plant complexes which is hydrolyzed with concentrated acids (42 per cent hydrochloric or 72 to 80 per cent sulfuric) giving glucose as the product of hydrolysis.

HEMICELLULOSES—The methods now available for a quantitative determination of hemicelluloses are based either upon distillation with 12 per cent hydrochloric acid and determination of the furfural by precipitation with phloroglucinol, the weight of the precipitate being taken as a measure of the pentosan content of the material; or upon hydrolysis of the material with hot dilute hydrochloric acid at ordinary pressure and determination of the reducing sugar produced. Both methods are open to considerable criticism. By the phloroglucinol method we determine, not only the pentosans, but the furfural-yielding compounds in general. The sugar produced in the acid hydrolysis may be a result of the hydrolysis of some of the true celluloses, while some of the hemicelluloses may be only partly hydrolyzed.

Uncertainty frequently arises in regard to the action of dilute mineral acids upon the different carbohydrates and allied compounds. Does the acid act only upon hemicelluloses or does it also hydrolyze true celluloses? To what extent does it affect the lignins? What part of the proteins are hydrolyzed? The claim (*10*) that a large part of the celluloses is removed by hydrolysis with dilute acids cannot be taken very seriously, since one is dealing here, not with true cellulose, but with a certain preparation obtained by chlorination of plant material. Since this preparation is rich in pentosan, it is but natural that it should be reduced considerably in quantity when the plant substance has been first treated with dilute acid. The same would apply to the preliminary treatment of the plant material with an alkali solution, which will remove part of the lignin and part of the hemicelluloses.

In order to obtain further information concerning the nature of the carbohydrates acted upon by dilute acids at ordinary pressure and at 100° C. the following experiment was carried out: Nine organic materials, including four fresh plant materials, three composts of plant residues which were kept under controlled laboratory conditions (*29*) at a favorable moisture and temperature, and two forms of peat (*30*), were used for this purpose. The pentosan content was determined in aliquot portions of all the untreated materials. Several 10-gram samples (on a dry weight basis) from each of the nine preparations were treated with 150-cc. portions of a 2 per cent hydrochloric acid solution for 5 hours in flowing steam. The extracts were filtered and washed. The solutions were used for the determination of total reducing sugar and of pentose sugar (furfural determinations). The cellulose and lignin (ash- and nitrogen-free) content of the residual material was then determined by treating aliquot portions of some of the residues left after the first hydrochloric acid extraction with 80 per cent sulfuric acid solution, according to the method outlined later. Some of these residues were treated a second time with fresh 150-cc. portions of a 2 per cent hydrochloric acid for 5 hours in flowing steam. The extracts and some of the residues were then analyzed in a manner similar to that of the residues after the first extraction. The treatment was repeated a third time using some of the residues left after the second hydrochloric acid extraction. The results are given in Table III.

The effect of prolonged treatment of plant substances with hydrochloric acid differs markedly with the nature of the

Table III—Influence of Repeated Extraction of Fresh and Decomposed Plant Materials with 2 Per Cent Hydrochloric Acid upon Hemicellulose, Cellulose, and Lignin Content[a]

(On basis of original material)

MATERIAL	PENTOSAN IN ORIGINAL MATERIAL	ONE EXTRACTION FOR 5 HOURS				SECOND EXTRACTION FOR 5 HOURS				THIRD EXTRACTION FOR 5 HOURS			
		SOLUTION		RESIDUE		SOLUTION		RESIDUE		SOLUTION		RESIDUE	
		Hemi cellulose sugar	Pentoses as pentosan	Cellulose	Lignin	Hemicellulose sugar	Pentoses as pentosan	Cellulose	Lignin	Hemicellulose sugar	Pentoses as pentosan	Cellulose	Lignin
	%	%	%	%	%	%	%	%	%	%	%	%	%
Fresh rye straw	23.91	25.67	24.50	37.57	17.32	3.90	2.73	35.09	15.85	1.76	0.65	32.81	15.83
Rye straw composted 18 months	21.04	23.33	21.50	35.30	25.25	3.71	1.90	31.27	24.30	1.85	0.70	29.37	23.24
Fresh oak leaves	13.66	18.44	12.60	12.19	36.13[a]	1.51	0.91	12.74	34.50	0.66	0.48	12.30	34.27
Oak leaves composted 18 months	10.45	12.67	8.10	8.38	45.43	1.57	0.74	8.10	46.52	0.59	0.45	7.71	46.42
Fresh alfalfa plants	13.88	12.33	8.80	25.25	13.43	3.88	1.54	22.26	12.00	1.24	0.61	22.28	12.09
Alfalfa plants composted 18 months	9.98	8.11	6.60	18.66	19.09	2.26	1.75	18.69	20.73	1.04	0.75	17.00	19.20
Fresh Sphagnum moss	11.05	24.56	9.50	19.66	15.06	2.52	0.63	19.09	12.60	1.92	0.42	17.86	12.73
Highmoor (Sphagnum) peat	11.64	23.44	11.80	17.09	24.83	3.96	0.85	18.73	22.51	3.27	0	...	...
Lowmoor peat	4.81	9.50	3.95	0	50.83	1.22	0.43	0	48.03	0	0	0	...

[a] The lignin content is somewhat high since the preparations were not extracted first with ether and alcohol.

material. It was much more marked in alfalfa plant and Sphagnum moss and peat than in oak leaves. In some plant materials, notably rye straw, the hemicellulose group is made up largely of pentosans, while other plants, especially Sphagnum moss and to a less extent oak leaves, contain a considerable quantity of hexosan hemicelluloses. As a matter of fact both the Sphagnum plant and the Sphagnum peat contain much more hexosan hemicelluloses than pentosans. The same is true in the case of the lowmoor peat, which originated from herbaceous plants.

In the case of some plants—especially alfalfa, both fresh and decomposed, Sphagnum, and decomposed oak leaves—the total pentosan content of the untreated material was found to be greater than the pentose sugar content found in the hydrolyzate, even after prolonged treatment with dilute acids. This would tend to indicate that these materials contain furfural-yielding compounds, which do not yield reducing sugars on hydrolysis with dilute acid.

The loss in cellulose after repeated treatment of fresh and decomposed plant materials with dilute acid usually did not exceed 12 per cent of the total cellulose content. Only in the case of decomposed rye straw was the loss greater. In some cases, however, as in the fresh and decomposed oak leaves, there was no loss at all or very little loss. The loss of lignins due to prolonged treatment with hot dilute acid was also rather small.

Since even a single extraction with dilute hydrochloric acid for 5 hours in flowing steam gave, in the case of most plant materials, both fresh and decomposed, a larger figure for the total hemicellulose content than for the pentosans alone, and since the results for the reducing sugar obtained on hydrolysis represent a more definite group of carbohydrate complexes than the total pentosan results, we may feel justified in adopting the method of hydrolysis at least in the procedure for hemicellulose determination. It is true that some of the sugar on hydrolysis may not come from polysaccharide hemicelluloses but from uronic acid complexes. One may go a step further and determine the amount of uronic acid in the plant material. It is also true that some of the pentoses may be changed to furfural even on boiling with dilute acid. However, for a proximate system of analysis the total sugar obtained on hydrolysis of the plant material with hot dilute acid at ordinary atmospheric pressure is as good a measure as any previously suggested.

For the purpose of a proximate plant analysis, one may define hemicellulose as that group of plant constituents which gives reducing sugars on hydrolysis with hot dilute acids. It is understood, of course, that the free sugars and the starches in the plant material are accounted for otherwise, previous to the acid treatment.

LIGNINS—The methods at present available for lignin determination can be classified into three groups:

(1) Treatment in the cold with concentrated acids—notably fuming (42 per cent) or gaseous hydrochloric acid, 72 to 80 per cent sulfuric acid, or a mixture of these acids (*8, 14, 28, 31*). This treatment hydrolyzes all the carbohydrates, leaving the lignins intact. The digest is then diluted with 15 volumes of water, thoroughly boiled, and filtered. The undigested residue is considered to be lignin. However, it always contains some mineral matter and some nitrogenous complexes; these must always be accounted for (*20*). It is also important that the original plant material be first treated with ether to remove the fats and waxes.

(2) Extraction with an alkali, preferably 4 to 10 per cent sodium hydroxide solution under pressure. The lignin is thus brought into solution and can be reprecipitated by acidifying with hot hydrochloric acid (*4, 16, 21*). It is essential that the hot acid be allowed to act upon the precipitate so as to remove the hexosans and pentosans which are dissolved by the alkali and precipitated by the acid, as shown in Table IV. Some of the lignin is also soluble in cold alkali solution (*2, 3*).

Table IV—Lignin Content of Fresh and Decomposed Plant Materials, as Determined by Alkali Extraction Method and Treatment with Concentrated Acids

(On basis of original dry material)

MATERIAL	EXTRACTED WITH COLD 4% NaOH SOLN., PPTD. WITH HOT HCl		EXTRACTED WITH 4% NaOH SOLN., UNDER 1 ATM. PRESSURE FOR 1 HOUR		TOTAL ALKALI LIGNIN[a]	ACID LIGNIN[b] (80% H_2SO_4)
	Sugar in soln.	Lignin	Sugar in soln.	Lignin		
	%	%	%	%	%	%
Fresh rye straw	15.02	10.52	3.79	3.12	13.64	14.63
Decomposed rye straw	13.28	9.80	2.77	4.96	14.76	18.88
Fresh oak leaves	4.52	6.76	4.94	7.56	14.32	30.30
Decomposed oak leaves	1.52	5.56	3.92	15.16	20.72	42.43
Fresh cornstalks	13.92	8.56	6.56	1.60	10.16	11.28
Decomposed cornstalks	2.80	12.88	2.57	9.24	22.12	23.86
Fresh alfalfa plant	4.94	5.36	2.57	1.60	6.96	10.78
Decomposed alfalfa plant	0	9.08	0	1.20	10.28	15.85
Fresh Sphagnum moss	1.80	0.84	2.98	0.96	1.80	7.33
Decomposed Sphagnum moss	1.12	1.96	4.32	0.64	2.60	8.73

[a] Nitrogen content not accounted for.
[b] Nitrogen and ash accounted for.

Hägglund (*11*) found that, when wood is treated with an alkali and the solution thus obtained is precipitated with hydrochloric or sulfuric acid, lignin equivalent to 21.6 per cent of the wood is obtained. This is to be compared with a yield of 28 to 29 per cent when the same wood is treated with strong acids according to one of the methods previously outlined. A 10 per cent sodium hydroxide solution was found to extract 20.3 per cent of the lignin at room temperature for 24 hours, 29.6 per cent at 100° C. for 3 hours, 45.6 per cent at 120° C. for 5 hours, and 84 per cent of the lignin when extracted with saturated alkali solution for 24 hours at 100° C. The alkali lignin was found to correspond to α-lignin, or that which is precipitated from the sulfite extract of wood with naphthylamine; compounds may be obtained which contain 3 per cent nitrogen. The β-lignin is that part of the alkaline extract which is no longer precipitated by acids. The alkali lignin gives the furfural reaction, indicating the presence of pentoses or pentosans, and contains some ether-soluble substances. Unless a very high pressure (10 atmospheres and 180° C.) is used, the lignin will not be extracted quantitatively by the alkali solution. Even then, however, the yield of acid lignin will be greater than that of alkali lignin (*16*).

(3) The use of oxidizing agents to remove the lignins. König and Rump (*15*) employed a 3 per cent ammoniacal solution of hydrogen peroxide. Schmidt (*25*) recommended the use of a 5 to 6 per cent solution of chlorine dioxide. This reagent does not attack carbohydrates, but oxidizes lignins or substances having a benzene ring and a free hydroxyl group. However, the lignin yield obtained by this method was found to be considerably higher even than that of acid lignin, as the oxidizing agents also oxidize various hemicelluloses.

A detailed study of the three methods for a quantitative determination of the lignin content of various fresh and decomposed plant materials, carried out in the laboratory, brought out the advantage of determining the acid lignin. The alkali lignin gives too low results and the yield varies with the nature and concentration of the alkali, as well as the temperature and time of extraction. The chlorine dioxide lignin gives too high results due to the action of the reagent upon various other plant constituents. The fact that the results obtained by this method are based upon differences in weight of the material before and after the treatment, without a knowledge of the substances removed, makes the method open to further criticism.

Recommended Methods

By combining the above methods for the quantitative determination of hemicelluloses, celluloses, and lignins with the procedure commonly followed in the determinations of the chemical composition of plant materials, the following system of analysis of plant products is outlined. This system has been used successfully in the study of the chemical composition not only of fresh plant materials, decomposed plant residues, but also of peats, forest soils, and other natural organic complexes.

The constituents of the fresh or decomposed plant material are divided into seven general groups—namely (1) ether- and alcohol-soluble fraction; (2) cold- and hot-water soluble fractions; (3) hemicelluloses; (4) celluloses; (5) lignins; (6) proteins, including the various organic nitrogenous complexes, and (7) mineral substances or ash. The results are always calculated on an oven-dry basis of the material.

Note—Since some of the organic nitrogenous complexes are soluble in water, correction must always be made. One may report the water-insoluble nitrogenous complexes as "crude protein."

The determinations of the moisture, ash, and total nitrogen are carried out by the ordinary procedures. For the complete analysis, two 5-gram portions of the material are sufficient.

ETHER EXTRACT—Two 5-gram portions of air-dry material are extracted for 16 to 24 hours, in a Soxhlet apparatus, with sulfuric ether. The solvent is then evaporated to a small volume and the concentrated extract is transferred to constant-weight drying bottles, dried for 12 to 24 hours at 100° C., and weighed. The weight of the residue may be recorded as the ether-soluble portion, or it may be added to the alcohol-soluble material and only the sum of the two recorded.

Table V—Proximate Chemical Composition of Some Fresh Plant Materials
(On basis of dry material)

CONSTITUENT	YOUNG CORN-STALKS	MATURE CORN-STALKS	TIMOTHY HAY	RYE STRAW	OAK LEAVES	NEEDLES OF *Pinus strobus*	*Carex*, GREEN LEAVES	ALFALFA PLANT	CYPRESS WOOD
	%	%	%	%	%	%	%	%	%
Ether- and alcohol-soluble fraction	3.42	5.99	2.90	5.33	9.93	23.92	2.54	10.41	5.45
Cold- and hot-water soluble organic matter	28.27	14.14	16.92	6.26	10.26	7.29	12.56	17.24	3.18
Hemicelluloses	20.38	17.63	22.07	21.10	15.62	18.98	18.36	8.52	11.16
Celluloses	23.05	29.67	26.09	38.62	17.18	16.43	28.20	26.71	37.62
Lignins	9.68	11.28	16.21	14.63	29.66	22.68	21.08	10.78	28.21
Crude protein	2.61	1.98	3.25	0.81	3.47	2.19	7.08	8.13	0.66
Ash	7.40	7.53	5.68	4.18	4.68	2.51	3.30	10.30	0.76
Total	94.81	88.22	93.12	90.93	90.80	94.00	93.12	92.09	87.04

COLD-WATER EXTRACT—The material left after the ether extraction is carefully transferred to a beaker or a 250-cc. Erlenmeyer flask and 150 cc. of distilled water are added; extraction is continued in the cold for 24 hours. The cold aqueous extract is filtered through small filter papers which have been previously dried and weighed; the plant residue is washed with two or 3 portions of cold distilled water. The filtrate and washings are made up to volume. One aliquot portion (usually one-tenth) is used for the determination of reducing sugars by the Bertrand or other convenient method. Another aliquot portion (usually one-third) is placed in a constant-weight silica dish, evaporated on a water bath, and dried at 100° C. to constant weight; the dish is then ignited and weighed again; the difference in the weight of the dish and contents before and after ignition gives the total water-soluble organic matter, while the difference between the weight of the dish after ignition and the original weight of the dish gives the water-soluble ash. A third portion of the extract (one-third) is placed in a Kjeldahl flask, a couple of drops of concentrated sulfuric acid are added, the flask is placed on a hot plate, and the contents are evaporated to a small volume; a determination of total nitrogen is then made using the Kjeldahl method or one of its modifications. If nitrates are present in the plant material, a fourth aliquot portion can now be clarified and nitrates determined by the phenol-disulfonic acid method, or directly by reduction with Devarda's alloy.

HOT-WATER EXTRACT—The plant residue left after the cold-water extraction is returned to the beaker or flask by the use of a fine stream of water. The volume of water is made up to about 150 cc. and the flask is placed on a boiling-water bath for 3 hours, or boiled for that period under a reflux condenser. The contents are then transferred to the original weighed filter paper. The residue is washed two or three times with hot water. The filtrate and washings are made up to volume: two aliquot portions are used for the determination of the hot-water soluble organic matter, soluble ash, and total nitrogen. When it is desired to determine quantitatively the starches in the original plant material, using an enzyme preparation, a separate portion should be employed, since the introduction of the enzyme will interfere with further analysis of the material. The yield of hemicellulose will have to be corrected for the starch content if a separate determination is made of the starches. The cold- and hot-water soluble organic matter can be recorded together or separately.

ALCOHOL-SOLUBLE PORTION—The residue from the hot-water extraction is returned to the flask with 95 per cent alcohol. The volume of alcohol is made up to about 150 cc. and the flask placed on a boiling-water bath or a hot plate and connected with a reflux condenser; digestion is continued for 2 or 3 hours. The extract is filtered through the original filter paper and the residue is washed with hot 95 per cent alcohol. The filtrate and washings of the alcohol extract are evaporated in constant-weight dishes on a water bath, and the alcohol-soluble portion is determined. The residue of the plant material left after the alcohol extraction is now dried at 80–100° C. to constant weight. The difference between the weight of the paper with the residue and that of the original paper gives the weight of the plant material from which the ether- and alcohol-soluble, as well as the water-soluble, portions have been removed. The sum of the weight of these fractions and the weight of the plant substance left should give the quantity of the original dry plant material taken for analysis.

TREATMENT WITH DILUTE ACID—The residue from the alcohol extraction is returned to the original flask and 150 cc. of a 2 per cent solution of hydrochloric acid are added. The flask is placed either in flowing steam or connected with a reflux condenser, and the contents are boiled, using an open flame, for 5 hours. The extract is filtered through the original filter paper and the residue washed thoroughly with water until free from acid. The paper containing the residue is now placed in an oven and dried for 10 to 12 hours at 70–80° C.; the temperature is then raised to 100° C. and drying is continued until constant weight has been attained. The weight of the paper with the residue minus that of the original paper gives the weight of the plant material left after extraction with dilute hydrochloric acid. It is important to record this weight, since it enables us to calculate later the cellulose and lignin content of the original preparation, because the determination of these is carried out on aliquot portions of the material left after the hydrochloric acid extraction.

The acid extract and washings are made up to volume.

An aliquot portion (one-tenth or one-twentieth) is neutralized with 10 per cent sodium hydroxide solution. If a precipitate is formed, it must first be filtered off. The reducing sugars are determined by any convenient method; the total reducing sugar found in the hydrochloric acid extract, when multiplied by the particular dilution, represents the hemicelluloses in the original plant material which have been changed to sugars by boiling with dilute acids. By multiplying the total reducing sugar in the 2 per cent hydrochloric acid extract by 0.9, the hemicellulose content in the original 5-gram portion of the air-dry material is obtained.

Cellulose—Two 1-gram portions from each of the dried residues left after the extraction with 2 per cent hydrochloric acid are carefully weighed out and placed in 300-cc. beakers or Erlenmeyer flasks. If the material is not fine enough, it must be first thoroughly ground, then dried again, and the 1-gram portions weighed out. If the original analysis has been made in duplicate, there will be four 1-gram portions for each plant material. Ten cubic centimeter portions of 80 per cent sulfuric acid are added to the several 1-gram portions of the residue. The acid should thoroughly penetrate the material within a few minutes. If it does not, glass rods should be used for mixing the material thoroughly with the acid. The acid is allowed to act upon the material for $2^{1}/_{2}$ hours in the cold, the mixture being stirred occasionally. At the end of that time 150-cc. portions of distilled water are added to each flask and the contents steamed or boiled under a reflux condenser for 5 hours or autoclaved at 120° C. for 1 hour. The cold concentrated acid transforms all the cellulose into hydrocellulose. This is further hydrolyzed, on boiling with the dilute acid, to reducing sugars. The boiling with the dilute sulfuric acid should be long enough to allow the transformation of all the hydrocellulose and other intermediary substances to glucose. Kiesel and Semiganovski (*12*) found that treatment of cellulose with 80 per cent sulfuric acid, followed by boiling for several hours with the acid diluted with water in the ratio of 1:15, will give a quantitative yield of cellulose in the form of glucose; the amount of glucose thus obtained when multiplied by 0.9 gives the cellulose content of the plant material. These results have been confirmed in this laboratory, although, instead of the 110 per cent glucose, one usually obtains only about 104 to 105 per cent, which indicates that only 95 to 96 per cent of the cellulose is usually accounted for. However, the advantages of this method over all the other methods of cellulose determination are so marked that it is preferred even if the results for cellulose determination are 4 or 5 per cent lower than the actual cellulose content in the plant material. For an accurate cellulose determination it is essential, of course, first to remove from the plant material the pentosans and other hexosans, as was done in this system of analysis by the 2 per cent hydrochloric acid extraction.

The 1-gram portions of material thus treated with sulfuric acid are now filtered through small quantitative filter papers, which have been previously dried and weighed. The residues are thoroughly washed with water until free from acid and placed in a drying oven at 70° C. for 24 hours (temperature may be raised to 100° C. for 1 or 2 hours towards the end). The filtrates and washings are made up to volume. Aliquot portions (one-tenth) are neutralized with 10 per cent sodium hydroxide solution and the reducing sugars determined by the Bertrand or other convenient method. The yield of sugar calculated for the total volume of the filtrate is multiplied by the weight of residual plant material left after the 2 per cent hydrochloric acid extraction, to give the yield of cellulose sugar in the original 5-gram portion of the plant material.

Lignin—The four residues from the sulfuric acid treatment are thoroughly washed, dried, and weighed. Two of the residues are ignited to obtain their ash content and the other two are used for the determination of total nitrogen. The average weight of the residue after the weight of the paper has been subtracted, minus the ash and minus the nitrogen content of the residue multiplied by 6.25, gives the lignin content of the 1 gram of material left after extraction with 2 per cent hydrochloric acid. By multiplying this amount of lignin by the weight of the residue left after treatment with the hydrochloric acid, the weight of the total lignin in the original 5 grams of the plant material is obtained.

Protein—This system of analysis lends itself readily to the determination of several organic nitrogenous fractions. However, for the present no attempt has been made to determine many of these. The nitrogen is differentiated into the water-soluble and water-insoluble. The total nitrogen minus the water-soluble portion is multiplied by 6.25 and the product recorded as "crude protein."

Typical Results by Methods Outlined

Table V contains a series of typical analyses of various fresh plant materials, by the methods outlined above. Table VI contains the analyses of several plant residues that have undergone thorough decomposition by microörganisms, under aerobic conditions and in the presence of additional inorganic salts, and also of several peat preparations.

Table VI—Proximate Chemical Composition of Some Composted Plant Materials[a] and Peat

(On basis of dry material)

Constituent	Corn-stalks	Oak Leaves	Alfalfa Plant	Low-moor Peat	High-moor Peat
	%	%	%	%	%
Ether-soluble fraction	0.35	1.77	0.90	1.10	3.96
Cold- and hot-water soluble fraction	13.47	3.85	17.49	1.24	...
Hemicelluloses	10.74	12.27	8.22	8.95	16.24
Celluloses	4.78	8.92	15.90	0	19.91
Lignins	23.86	44.50	16.08	50.33	38.26
Crude protein	12.97	7.44	9.18	18.72	6.58
Ash	26.63	8.12	24.88	10.13	1.50
Total	92.80	86.87	92.65	90.47	86.45

[a] For periods ranging from 1 to 2 years.

Without going into a detailed discussion of the significance of the results presented in the above two tables, which has been done elsewhere (*29*, *30*), it is sufficient to call attention to the fact that by this system of analysis we are able to account for 88 to 95 per cent of the total constituents of various natural organic materials of plant origin. It enables us, not only to obtain an insight into the chemical composition of the plant substances, but also to follow the course of transformation of the various chemical constituents when these substances are undergoing degradation either in the digestive tract of animals, in the compost heap or in the soil.

Literature Cited

(1) Barthel and Bengtsson, Centralanst., *Meddel.* **300** (1926).
(2) Beckmann and Liesche, *Z. angew. Chem.*, **34**, 285 (1921).
(3) Beckmann and Liesche, *Biochem. Z.*, **121**, 293 (1921).
(4) Beckmann, Liesche, and Lehmann, *Ibid.*, **139**, 491 (1923).
(5) Bengtsson, Centralanst., *Meddel.* **279** (1925).
(6) Charpentier, *Ibid.*, **205, 218** (1920–1921).
(7) Charpentier, "Studien über den Einfluss des Rindvieh- und Pferdestallmistes auf die Zersetzung der Zellulose in der Ackererde," Dissertation, Helsingfors, 1921.
(8) Dore, J. Ind. Eng. Chem., **11**, 556 (1919); **12**, 476 (1920).
(9) Ehrlich, *Z. angew. Chem.*, **40**, 1305 (1927).
(10) Gerhardt, *Plant Physiol.*, **4**, 373 (1929).
(11) Hägglund, *Cellulosechemie*, **5**, 81 (1924); **6**, 29 (1925).
(12) Kiesel and Semiganovski, *Trans. Chem. Pharmac. Inst. Moscow*, **18**, 82 (1927).
(13) Klason, *Ber.*, **56**, 300 (1923).
(14) König and Becker, *Z. angew. Chem.*, **32**, 155 (1919).
(15) König and Rump, "Chemie und Struktur der Pflanzenzellmembranen," Berlin 1914.

(16) Mehta, *Biochem. J.*, **19**, 958 (1925).
(17) Monier-Williams, *J. Chem. Soc.*, **119**, 803 (1921).
(18) O'Dwyer, *Biochem. J.*, **20**, 656 (1926).
(19) Ost and Wilkening, *Chem.-Ztg.*, **34**, 461 (1910).
(20) Paloheimo, *Biochem. Z.*, **165**, 463 (1925).
(21) Powell and Whittaker, *J. Chem. Soc.*, **125**, 357 (1924); **127**, 132 (1925).
(22) Pringsheim, "Polysaccharide," p. 96, Berlin, 1923.
(23) Rege, *Ann. Appl. Biol.*, **14**, 1 (1927).
(24) Riefenstahl, *Z. angew. Chem.*, **37**, 169 (1924).
(25) Schmidt, Hoag, and Sperling, 1922–1925. *Ber.*, **54**, 1860 (1921); **55**, 1530, 1534 (1922); **56**, 23 (1923); **58**, 1394 (1925).
(26) Schorger, J. Ind. Eng. Chem., **9**, 556 (1917).
(27) Schwalbe, "Die chemische Untersuchung pflanzlicher Rohstoffe und der daraus abgeschiedenen Zellstoffe," Hofmann, p. 131, 1920.
(28) Schwalbe, *Papier-Fabr.*, **23**, 174 (1925).
(29) Waksman and Stevens, *Soil Science*, **26**, 113 (1928).
(30) Waksman and Tenney, *Ibid.*, **24**, 275, 317 (1927).
(31) Willstätter and Zechmeister, *Ber.*, **46**, 2401 (1913).
(32) Wohl and Blumrich, *Z. angew. Chem.*, **34**, 7 (1921).

Application of Microscopic Analysis to Mixtures of Metals and Alloys[1]

Willet F. Whitmore and Frank Schneider[2]

The Polytechnic Institute, Brooklyn, N. Y.

In order to employ microscopic qualitative analysis to the fullest extent in industrial work it has been necessary to devise a new system of separation of the metals. A study has therefore been made of the most useful microscopic forms for the identification of certain metals, and the modification of some of the standard crystal forms caused by the presence of other metals has been investigated. Photographs of the characteristic forms obtained with typical mixtures, showing these modifications in form, are submitted.

On the basis of the above, and other considerations, a new plan of qualitative analysis especially adapted to microscopic procedure has been developed. This plan eliminates the use of hydrogen sulfide, shortens the time of analysis, permits working with small amounts of material, and dispenses with half the filtering operations required when the usual wet method of analysis is employed.

THE superiority of the microscopic tests over the ordinary methods of qualitative analysis is obvious when one compares, for example, the microscopic test for tin with the so-called wet-method test. In the latter the presence of tin is confirmed by the reduction of mercuric chloride, and the formation of the insoluble white mercurous chloride constitutes the entire test. In microscopic analysis, on the other hand, the tin itself is precipitated as stannous oxalate and the presence of the tin ascertained, not only by the presence of a precipitate, but also by the color and crystalline form of that precipitate. The time required to make the test is also greatly reduced. It is apparent, therefore, that a system of analysis with such obvious advantages is one of great utility, which should be developed to a high degree of efficiency.

The microscopic identification of an element by chemical methods is accomplished by transposing that element into a known crystalline form possessing a definite color, using any suitable reaction. The substance to be tested is dissolved in a suitable solvent and a drop of this solution is placed on a microscope slide. The reagent is then added to the drop either in solid or dissolved form. The resulting precipitate is observed under the microscope. Since most of the forms suitable for this purpose are salts, one of the well-known reactions for salt formation is generally employed. The most useful of these reactions, so far as chemical microscopy is concerned, is the method of double decomposition. Accordingly in the detection of a basic element, an acid or a soluble alkali salt whose anion combines with the metallic element is added to give a relatively insoluble crystalline product.

The microscopic tests, in their present stage of development, are limited in their applicability, however. The chief difficulty lies in the fact that some of the best reagents can be applied to more than one element and when dealing with mixtures the resulting interferences may seriously interfere with or prevent identification of the constituents. The lack of information on the behavior of the reagents to mixtures has limited the application of microscopic tests to confirmatory tests. Emich (*3*), a noted authority on microscopic methods, says:

> Behrens has applied his methods to separations, which are admittedly not possible in the case of an unknown mixture in which all important elements may be present. Schoorl, therefore, applied the microchemical analysis only to the separation within a group and to the identification of a single ion.

Behrens and Kley (*1*) have used the ordinary methods of separation—i. e., with hydrochloric acid, hydrogen sulfide, etc.—and have used the microscopic tests in place of the usual confirmatory tests. This does not utilize the potentialities of microscopic analysis to the fullest extent.

In order to employ these elegant and sensitive methods of attack, it should be possible, after a study of the interferences, to devise a new method of separation which would conform in ease and speed of manipulation to the final microscopic tests. This can be accomplished by utilizing all the possibilities for identification without further purification and also avoiding numerous filtrations, gas precipitations, etc. Several attempts have been made by other investigators to arrive at this end, but all the proposed methods have at least one serious drawback. Chamot (*2*) gives a plan using group reagents, but no separation is involved. The authors have made a careful study of the effect of these reagents on mixtures of metals and the results of this study show that it is impossible to identify several metals simultaneously except in a few limited cases. The fact that some separation was necessary was recognized by other investigators. Zepf (*6*), Longinescu and Chaborski (*4*), and Martini and Shamis (*5*) suggest plans of analysis but either limit themselves to a small group of metals or do not take the interferences completely into account.

The authors have therefore attempted to furnish a plan of analysis which will provide sufficient separation to prevent interference with the final tests for each element, and include all metals usually encountered in qualitative analysis. The

---

[1] Received November 27, 1929.

[2] This paper is based upon a thesis presented by Frank Schneider in partial fulfilment of the requirements for the degree of bachelor of science in chemistry at the Polytechnic Institute of Brooklyn.

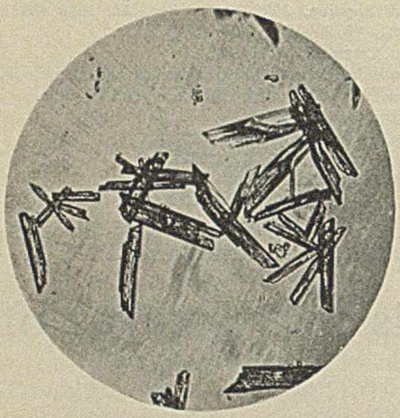


Figure 1—Stannous Oxalate

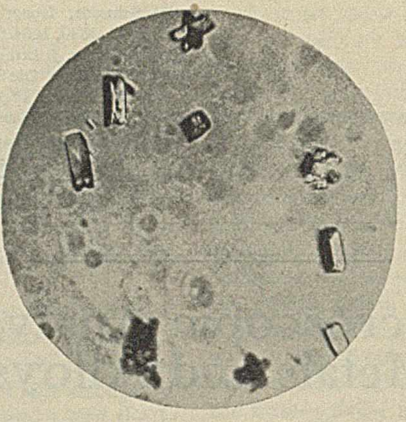


Figure 2—Sodium Antimoniate

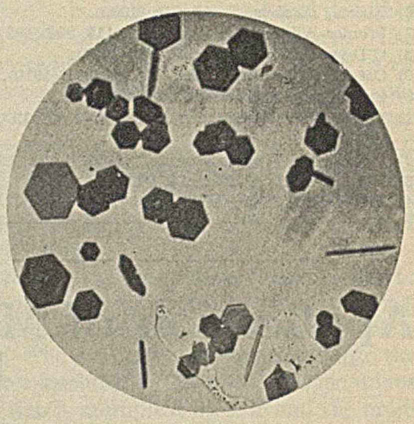


Figure 3—Potassium Bismuth Sulfate

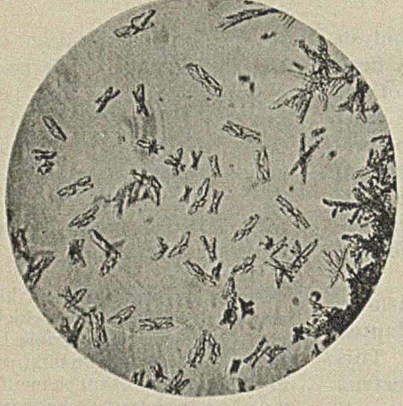


Figure 4—Ammonium Magnesium Arsenate

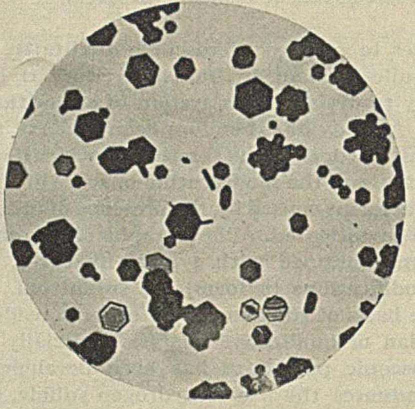


Figure 5—Caesium Bismuth (Antimony Iodide)

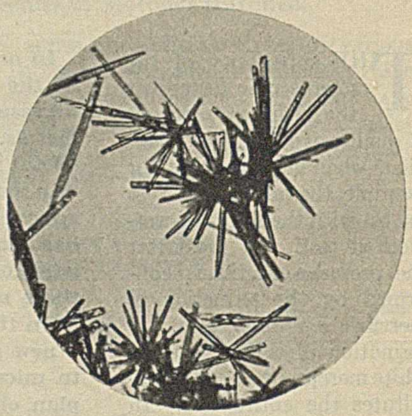


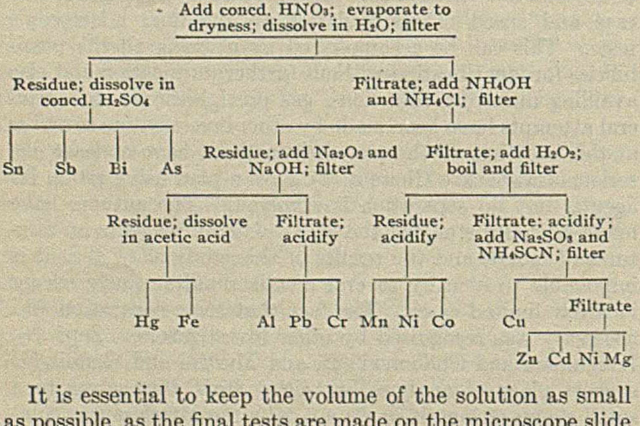
Figure 6—Cobalt Mercurithiocyanate

alkali and alkali-earth groups have been omitted from this scheme, since their identification and separation have been well developed (*1*, *3*).

General Directions

The sample to be analyzed, in shavings or some other finely divided form, should weigh 0.25 to 0.5 gram. If micro-apparatus such as described by Emich (*3*) is available, the amount can be reduced considerably.

Scheme of Analysis



It is essential to keep the volume of the solution as small as possible, as the final tests are made on the microscope slide and a large volume is obviously out of the question. The volume should never exceed 35 cc.

In the filtrations where a large amount is to be handled a small funnel filter and suction or a centrifuge is used, but in making tests on the slides decanting will often suffice. All precipitates should be washed at least twice, the first washings to be joined with the filtrate.

All the final tests for the individual elements are given as recommended by Behrens and Kley (*1*).

Plan of Separation

To 0.25–0.50 gram of the sample in an evaporating dish add concentrated nitric acid and evaporate over a water bath to a moist solid or sirupy liquid condition (1).[3] Add water and evaporate again to a moist state. Extract with hot water, but do not boil. Filter through double filter paper.

RESIDUE—Oxides of tin, antimony, arsenic, and bismuth. Group I.

FILTRATE—Nitrates of iron, chromium, aluminum, lead, zinc, cadmium, copper, cobalt, nickel, magnesium, manganese, and mercury. Add excess ammonium chloride and ammonium hydroxide. Filter. (2)

RESIDUE—Hydroxides of iron, chromium, aluminum, and lead and mercuric amido-nitrate. Group II.

FILTRATES—Nitrates and ammonia salts of zinc, cadmium, copper, cobalt, nickel, magnesium, manganese. Add hydrogen peroxide (3) and boil for five minutes. Filter.

RESIDUE—Oxides of manganese, cobalt, and possibly nickel (4). Group III.

FILTRATE—Nitrates and ammonia salts of zinc, cadmium, copper, magnesium, and nickel. Group IV.

Notes—(1) Care must be exercised to prevent decomposition of the nitrates into insoluble oxides. Practice will enable the analyst to determine for himself the proper state of dehydration.

---

[3] Numerals in parentheses in the Plan of Separation and Analysis of the Groups refer to the notes at the end of each group treatment.

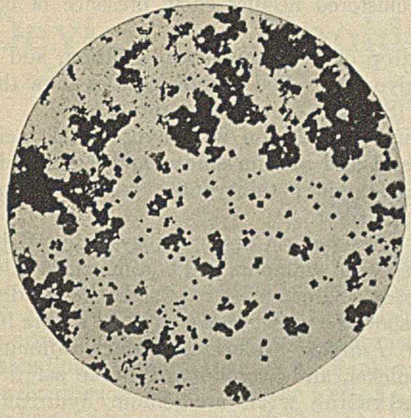


Figure 7—Potassium Copper Lead Nitrate

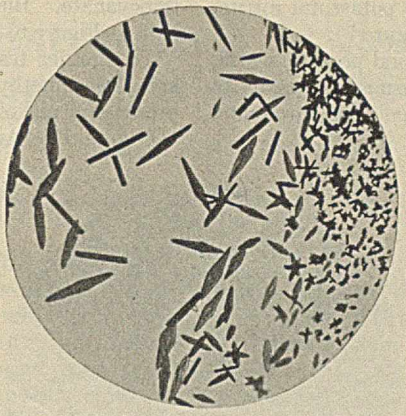


Figure 8—Silver Dichromate

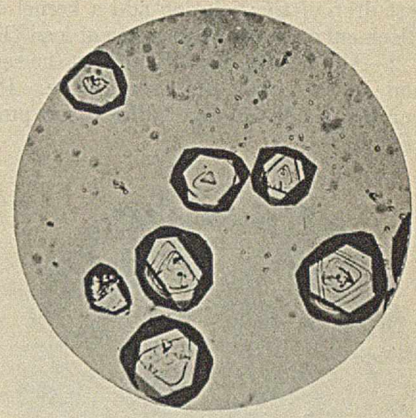


Figure 9—Caesium Aluminum Sulfate

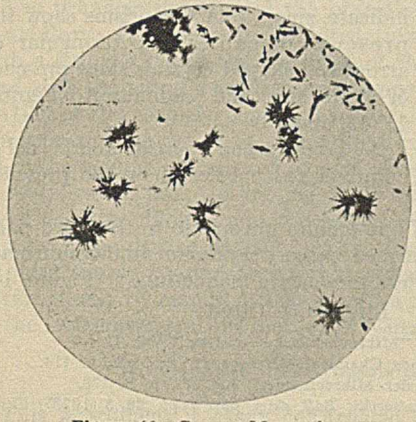


Figure 10—Copper Mercurithiocyanate

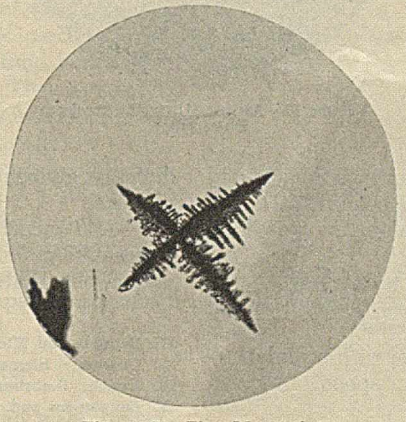


Figure 11—Zinc Mercurithiocyanate

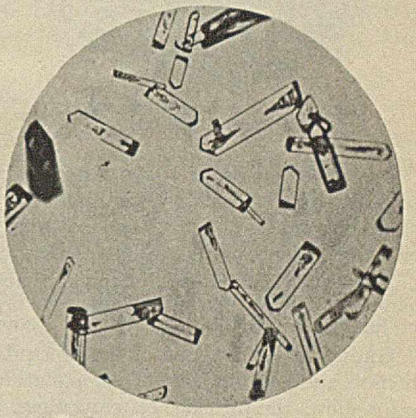


Figure 12—Cadmium Mercurithiocyanate

(2) The volume must be kept as small as possible at this point and the filter covered with a watch glass to prevent oxidation of the manganese.

(3) The solution should contain an excess of ammonium hydroxide at this point and at the end of the boiling. If an excess is not present, more ammonia must be added.

(4) Some nickel may be oxidized at this time, but the oxidation is incomplete and the nickel must therefore be tested for in both groups.

Analysis of the Groups

Group I—The residue from the nitric acid treatment is placed in a small beaker and heated, gently at first, with aqua regia. The solution is then boiled to expel excess nitric acid and divided into two parts. In cases where the tin content of the metal is high, some stannic oxide will remain insoluble after this treatment, but enough tin will go into solution to give a good test for the element in any case.

1—To the first part, water is added and an iron nail dropped in. The solution is slightly warmed to start the action and then is allowed to stand. After about a half hour the clear liquid is decanted and tested for tin with gold chloride or oxalic acid. (Figure 1)

2—The second part is evaporated almost to dryness and divided into three parts (1):

(a) The first part is boiled with a few drops of concentrated potassium hydroxide solution, cooled, and a drop tested on a slide with sodium chloride. It is often necessary to add more sodium chloride, as the amount necessary depends upon the amount of potassium hydroxide used. The characteristic lentil-shaped or prismatic crystals of sodium pyroantimoniate are evidence of the presence of antimony. (Figure 2)

(b) The second part is dissolved in the least possible amount of concentrated sulfuric acid, and a drop of this solution is merged on a slide with a drop of concentrated potassium sulfate solution. Colorless hexagonal plates of potassium bismuth sulfate show the presence of bismuth (2). (Figure 3)

(c) The third portion is dissolved in ammonium hydroxide and filtered or decanted if a precipitate forms. The filtrate is placed on a slide and a kernel of magnesium or calcium acetate added. The characteristic H-shaped crystals of ammonium magnesium arsenate show the presence of arsenic. (Figure 4)

Notes—(1) At this point it may be well to test for the presence of antimony and bismuth with caesium chloride and potassium iodide. Crystals of these two salts are placed at opposite sides of the test drop and the appearance of red or orange hexagons shows the presence of antimony or bismuth or both. (Figure 5)

(2) Sometimes these plates will be circular at first but turn into hexagons later.

Group II—The residue is dissolved on the filter paper in the least amount of dilute hydrochloric acid, washed into a beaker, and sodium hydroxide and sodium peroxide added. The solution is boiled and filtered.

Residue: Group IIA, iron and mercury oxides. Dissolve in hydrochloric acid and take two test drops. To the first add potassium ferrocyanide. Blue precipitate indicates iron. Neutralize the second drop with ammonia and add ammonium thiocyanate and cobalt chloride. Clusters of blue needles show mercury. (Figure 6)

Filtrate: Group IIB, sodium aluminate, chromate, and plumbate. Acidify with acetic acid (1). Divide into three parts:

1—To the first part add copper acetate solution and to a test drop of this solution add a kernel of potassium nitrite. Black cubes show the presence of lead (Figure 7).

2—Add a drop of nitric acid to the second portion, warm, and add a kernel of silver nitrate. Prismatic crystals of varying shades of red indicate the presence of chromium. (Figure 8)

Figure 13—Mercuri-thiocyanates of Zn and Cd (1:1)

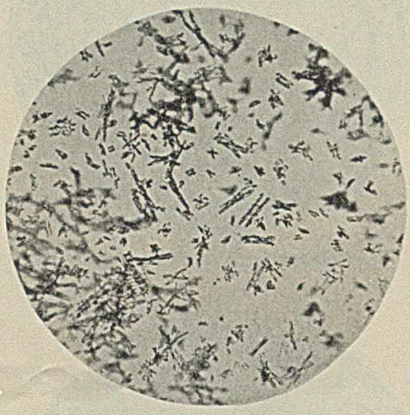


Figure 14—Ammonium Magnesium Phosphate

3—Add a few drops of concentrated hydrochloric acid and to a test drop add a very small amount of concentrated caesium bisulfate solution. The colorless alum crystals indicate the presence of aluminum. (Figure 9)

Note—(1) If lead and chromium are both present, lead chromate will be precipitated upon acidifying the solution and no further tests for these two metals are necessary.

Group III—Fuse part of the precipitate with sodium carbonate and sodium nitrate on a platinum spoon. A green color shows the presence of manganese.

Dissolve the remainder of the precipitate in hydrochloric acid and neutralize with ammonium hydroxide; filter if necessary. To a test drop add a drop of ammonium mercurithiocyanate. Blue clustered needles show presence of cobalt. (Figure 6)

To another test drop of the ammoniacal solution, add a kernel of dimethyl glyoxime. Red or pink needles show the presence of nickel. (See note 4 under Separation.)

Group IV—Acidify the solution with hydrochloric acid and add sodium sulfite and boil. Add ammonium thiocyanate solution, cool, and filter.

Residue: Copper thiocyanate. Dissolve in ammonia and add mercuric chloride. Green clusters of radiating needles show the presence of copper. (Figure 10)

Filtrate: Chlorides of zinc, cadmium, nickel, and magnesium. Make solution alkaline with ammonium hydroxide. Divide into three parts:

1—To the first part add ammonium mercuri-thiocyanate. Feathered crosses indicate zinc; colorless prisms show the presence of cadmium; triangular or arrowhead-shaped crystals show presence of both zinc and cadmium. (Figures 11, 12, and 13)

2—To the second portion add kernel of dimethyl glyoxime. Pink or red needles show the presence of nickel.

3—Add kernel of ammonium phosphate to the third part. Characteristic four-armed feathery crystals of ammonium magnesium phosphate show presence of magnesium. (Figure 14)

Literature Cited

(1) Behrens and Kley, "Mikrochemische Analyse," Vol. I.
(2) Chamot, "Elementary Chemical Microscopy," 2nd ed., p. 414.
(3) Emich, "Lehrbuch der Mikrochemie," 2nd ed., p. 8, 173.
(4) Longinescu and Chaborski, *Bull. chim. pure appl.*, **26**, 3 (1923); *Chem. Zentr.*, **95**, 944 (1924).
(5) Martini and Shamis, "Trabajos al segundo congreso de guimica Buenos Aires," 1924.
(6) Zepf, *Metallbörse*, **13**, 652 (1923).

Substitute for Amalgamation in Testing Bituminous Materials for Melting Point, Ductility, and Float Test[1]

Hans Eisner

Imperial Oil Refineries, Ltd., Sarnia, Ont.

THE melting point (*3*), ductility (*1*, *3*), and float (*4*) tests for bituminous materials are performed in most laboratories by individuals without chemical training, and large quantities of mercury are often left on the plate after amalgamation. Stock (*2*) has shown that 1 cubic meter of air containing 0.001 mg. of mercurial vapor is injurious to health and chronic poisoning will result with prolonged contact. The layer of mercury on the plate when coming in contact with the hot bituminous material gives off poisonous mercurial vapors and, as a result, not only the man who is working with it, but also other people, are affected.

In the writer's laboratory an attempt was made to replace this amalgamated plate. The first experiments were with highly polished plates, in the hope that the sample could be easily removed. These attempts failed, as the asphalt stuck tenaciously to the plate, showing that the mercury forms an isolating film between the asphalt and the plate. The next experiment was to cover the plate with a material which must form a thin layer soluble in water—e. g., glycerol. This gave better results. It was observed, however, that the glycerol would not retain a continuous film if the plate was polished. The application of glycerol to a rough, unpolished plate gave better results. Should the surface of the brass plates be too smooth, the surface should be first cleaned and then etched with acid. On applying the glycerol to the surface prepared in this manner, it was found that the film remained unbroken; in fact, a great improvement over a rough, untreated surface was noted. The molds and rings could be taken off the plate with greater ease than when mercury solution had been applied for amalgamating.

In this laboratory etched plates of brass and stainless steel give perfect satisfaction. All impurities are removed from the surface with solvent naphtha, carbon bisulfide, or carbon tetrachloride before applying the glycerol, one drop of which is quite sufficient to cover one square inch of surface. The quantity of glycerol is small and the worker is, at all times, free from danger of acid burns or mercury poisoning. In this laboratory the amalgamation of plates and molds has been replaced entirely by the use of glycerol.

(1) Am. Soc. Testing Materials, Tentative Method D113–26T (1928).
(2) Stock, *Z. angew. Chem.*, 41, 663 (1928).
(3) U. S. Dept. Agr., *Bull.* 1216, Method 53, p. 81.
(4) *Ibid.*, Method 50, p. 79.

---

[1] Received January 11, 1930.

Device for Rapid Estimation of the Density of Small Amounts of Solids[1]

Earle R. Caley

Department of Chemistry, Princeton University, Princeton, N. J.

In certain investigations it is desirable to determine rapidly the approximate density or specific gravity of small amounts of solids the available weight of which renders the employment of the usual means of making such estimations impracticable. The simple instrument shown in the illustration, which might be termed a "microdensimeter," has been found useful in such cases and is particularly recommended as an aid in the rapid identification of fragments of material.

The principle involved in the operation of this device is elementary. The narrow graduated tube is partially filled with a suitable liquid and the level of the fluid is carefully read with the aid of a reading microscope. Then a weighed portion of the coarsely powdered material is introduced into the tube and the rise of the liquid level in divisions is noted. Since the volume represented by each division is known from a careful calibration, the volume of the sample is thus given, and this value divided into the weight of the sample gives, of course, the desired density. While the principle involved is quite simple, it was found that satisfactory results are obtained only by careful attention to the proper construction of the instrument and the method of using it.

Description of Microdensimeter

This instrument is easily constructed from glass tubing, but it is essential that the tubing selected for the narrow tube be of quite uniform bore and care must be exercised that the uniformity of the part to be graduated is not altered in the operations of closing the tube and forming the upper portion. It is also important that the internal diameter of the graduated tube shall not exceed 2.50 mm. or be smaller than 2.00 mm. A larger diameter means loss of accuracy due to the correspondingly smaller changes in the level of the liquid for a given volume of the solid, while a smaller diameter leads to difficulties due to the inclusion of air bubbles in the tube when it is being filled with liquid. Tubes of smaller diameter than 2.00 mm. also render difficult the ready introduction and removal of the coarse particles and powders that are used for density determinations by this method. The enlarged portion of the tube, which allows the sample to be readily introduced into the smaller part, should be from 1.5 to 2.0 cm. in diameter and about twice as long. It should taper gradually and smoothly into the narrow tube and should have its upper portion so formed that it may be tightly closed with a rubber or glass stopper.

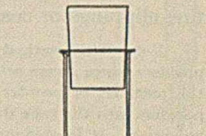
A suitable length of the narrow tube is arbitrarily graduated into a number of divisions spaced not more than 1.0 mm. apart. These graduations must be spaced very evenly and should be etched in lightly to increase the accuracy in reading. The glass part of the instrument used in obtaining the values shown in the tables had a total height of 13.4 cm. The length of the narrow tube was 9.5 cm., the total distance occupied by the 100 divisions being 7.3 cm. The external diameter of the graduated part of the tube was 6.0 mm. and the internal diameter 2.33 mm.

The finished tube is provided with a well-fitting glass or rubber stopper and a base that permits the ready removal of the tube for cleaning and inspection. The completed instrument is calibrated with distilled water at 20° C. in the usual manner. The water for calibrating is most conveniently introduced by means of a pipet with a drawn-out capillary end. The accurate reading of the liquid level in the tube is most conveniently done by means of a 25–50 power reading microscope provided with cross hairs and arranged to slide vertically on an upright stand. With this accessory there is little difficulty in reading tenths of a division on the tube. Less satisfactory results are obtained by using a reading lens owing to the difficulty of avoiding errors due to parallax.

Displacement Liquid

It was found impracticable to employ water as a confining liquid in this instrument, since its high surface tension caused gross errors due to the inclusion of minute air bubbles in the tube and between particles of the solid sample. The most satisfactory displacement liquid is ethyl ether. With this fluid there is rarely any air bubble formation either in the tube or between fragments of the sample and any minute air bubbles present are readily removed by tapping the tube gently. Ethyl ether is also of great practical advantage in making a series of determinations, since successive samples are readily removed from the tube by shaking, and the remaining film of ether evaporates rapidly leaving a clean, dry tube ready for another estimation. Ether further permits the direct estimation of the density of most water soluble substances by means of this method. Alcohol and other liquids of low surface tension may be substituted, but in general these are less satisfactory and should be used only in cases where the material examined is soluble in ether. The only disadvantage in the use of ether lies in its volatility, but the error arising from this source may be made negligible by proper manipulation.

Several experiments demonstrated that it was necessary to use a stoppered tube in order to prevent undue error from the evaporation of the ether even from such a small surface as is exposed in the narrow tube of this instrument. These experiments were conducted by filling the clean, dry tube with ether to different points and making successive readings at 5-minute intervals. Table I shows the increased rate of evaporation from an open tube as compared with that from a closed tube, and it also shows how the rate of evaporation decreases as the length of empty tube above the surface of the liquid is increased. It will also be noted that in the experiment with the closed tube a certain time was required to obtain equilibrium, as might be expected. The latter experi-



Microdensimeter

---

[1] Received December 30, 1929.

ment also demonstrates that when a stoppered and partially filled tube is used the rate of evaporation is too small to effect two successive readings that occur about one minute apart, which is the case in an actual determination. With less volatile liquids, such as alcohol and benzene, it was found that the rate of evaporation in open tubes of this small cross section is negligible for the purposes of this method.

Table I—Rate of Evaporation of Ethyl Ether from the Microdensimeter Tube under Different Conditions

(Temperature, 20° C.)

Elapsed Time	Open Tube Nearly Filled	Open Tube Half Filled	Stoppered Tube Half Filled
Minutes	*Reading*	*Reading*	*Reading*
5	96.1	59.0	56.7
10	95.1	58.4	56.2
15	94.4	58.1	56.0
20	93.7	57.8	55.8
25	92.9	57.4	55.5
30	92.0	57.0	55.3
35	91.2	56.6	55.0
40	90.6	..	54.8
45	..	..	54.6

Procedure for Density Determination

The solid material must first be reduced to particles of suitable size for introduction into the instrument. The method used will vary with the material to be examined. In the case of minerals and crystalline substances a convenient procedure is to crush the material in an agate or steel mortar and select suitable fragments with a forceps as the sample is progressively reduced to smaller particles. The best results are obtained when particles ranging from 0.5 to 1.5 mm. in diameter are taken. In the case of metals or alloys fine clippings or coarse filings may be taken from the sample.

Note—This method is not adapted to determining the density of fine powders, since errors arise from the inclusion of minute air spaces between the particles of powder and there is often difficulty in introducing such powders into the tube due to the tendency of the material to collect at the meniscus. It is obvious that the density of deliquescent and sticky substances cannot be determined by this method owing to their tendency to adhere to the walls of the small tube.

After the sample has been prepared, the tube is filled about half way with pure ether, by means of a small pipet. No air bubbles will be included in the tube if this operation is properly performed, but if any are trapped gentle tapping will cause them to rise to the top. The instrument is then stoppered while the sample is weighed out. The weight to be taken will depend upon the amount of sample available and the probable density of the substance. Ordinarily a sample of from 0.0500 to 0.1000 gram will be chosen for non-metallic materials, while a sample of from 0.2000 to 0.3000 gram is best for metals of high density and their alloys. Useful results in either case, however, can be obtained with smaller samples. As soon as the sample has been weighed out, the liquid level is read to the nearest tenth of a division with the reading microscope. Then the stopper is removed from the tube and the sample is introduced, after which the tube is immediately restoppered. The instrument is then gently tapped several times to bring all of the sample into the liquid and to cause any minute air bubbles that may be present to rise to the surface of the ether. The second reading of the liquid level is made immediately. The interval between the two readings of the liquid level should not be longer than one minute. A simple calculation then serves to give the required density.

There is no need to apply a temperature correction for the expansion of the glass tube over the ordinary range of room temperatures, since the error that might arise from this source is small compared with the other errors of the method. When liquids other than ether are used, care must be taken that sufficient time is allowed for the surface of the tube above the meniscus to dry completely before introducing the sample.

Table II—Rapid Estimation of Densities of Several Non-Metallic Substances Using Small Samples

Sample Taken	Difference between Scale Readings	Displaced Volume	Density Found	Density by Pycnometer
Gram		*Cc.*		
		PURE POTASSIUM CHLORIDE		
0.1297	21.2	0.0657	1.98	
0.1014	16.6	0.0515	1.97	
0.1014	16.5	0.0512	1.98	
0.0913	14.7	0.0456	2.00	
			Av. 1.98	1.99
		PURE SODIUM CHLORIDE		
0.1121	16.6	0.0515	2.18	
0.1071	16.0	0.0496	2.16	
0.1002	15.0	0.0465	2.15	
0.0913	13.6	0.0422	2.16	
			Av. 2.16	2.17
		ICELAND SPAR		
0.1505	17.9	0.0555	2.71	
0.1460	17.4	0.0539	2.71	
0.1091	12.9	0.0400	2.73	
0.1052	12.4	0.0384	2.74	
			Av. 2.72	2.72

Table III—Rapid Estimation of Densities of Several Metals Using Small Samples

Sample Taken	Difference between Scale Readings	Displaced Volume	Density Found	Density by Pycnometer
Gram		*Cc.*		
		PURE ALUMINUM WIRE		
0.1037	12.5	0.0388	2.67	
	12.5	0.0388	2.67	
	12.4	0.0384	2.70	
	12.5	0.0388	2.67	
			Av. 2.68	
0.0962	11.6	0.0360	2.67	
	11.5	0.0357	2.69	
	11.4	0.0353	2.72	
	11.4	0.0353	2.72	
	11.5	0.0357	2.69	
			Av. 2.70	2.70
		PURE ZINC (30-MESH)		
0.3116	14.2	0.0440	7.08	
0.3161	14.3	0.0443	7.14	
0.2971	13.6	0.0422	7.04	
0.2752	12.3	0.0381	7.22	
0.3452	15.8	0.0490	7.04	
			Av. 7.10	7.12
		PURE COPPER WIRE		
0.3224	11.7	0.0363	8.88	
	11.9	0.0369	8.74	
	11.8	0.0366	8.81	
	11.8	0.0366	8.81	
			Av. 8.81	
0.2733	9.8	0.0304	8.99	
	10.0	0.0310	8.82	
	10.0	0.0310	8.82	
	9.9	0.0307	8.90	
			Av. 8.88	8.89

Table IV—Rapid Estimation of Densities of Various Substances Using Unusually Small Samples

Sample Taken	Difference between Scale Readings	Displaced Volume	Density Found	Density by Pycnometer
Gram		*Cc.*		
		PURE POTASSIUM CHLORIDE		
0.0656	10.5	0.0326	2.01	
0.0606	9.7	0.0301	2.01	
0.0326	5.3	0.0164	1.99	
0.0279	4.5	0.0140	1.99	
			Av. 2.00	1.99
		PURE SODIUM CHLORIDE		
0.0584	8.9	0.0276	2.12	
0.0572	8.6	0.0267	2.14	
0.0413	6.1	0.0189	2.19	
0.0276	4.1	0.0127	2.17	
			Av. 2.16	2.17
		ICELAND SPAR		
0.0516	6.3	0.0185	2.79	
0.0405	4.8	0.0149	2.72	
0.0310	3.8	0.0118	2.63	
0.0202	2.4	0.0074	2.73	
			Av. 2.72	2.72
		PURE ALUMINUM WIRE		
0.0385	4.7	0.0146	2.64	
	4.7	0.0146	2.64	
0.0279	3.4	0.0105	2.66	
	3.5	0.0109	2.56	
			Av. 2.63	2.70

Results

The results obtained on various substances by the above procedure are shown in Tables II to IV. These are all of the values obtained in series of determinations and are not selected results. The values found by the pycnometer method were determined at 20° C. on large samples of the same material as used for the other determinations in each case. Each division of the particular microdensimeter used for this series of determinations represented a volume of 0.0031 ml. at 20° C. The actual determinations by the rapid method were made at room temperatures that ranged from 20° to 25° C.

The best results were obtained when the difference between the two readings amounted to more than ten scale divisions. This is due to the fact that the effect of any error in reading the displaced volume is then a smaller percentage of the total volume than would be the case where a smaller volume is displaced. If possible, therefore, samples large enough to displace a volume of liquid corresponding to at least ten divisions of the scale should be taken. Useful results, however, can be obtained with much smaller samples, as the values in Table IV show. In these cases the results of individual determinations are seen to vary more from the true value than do those where a larger volume of liquid is displaced, but the average value of a series of such determinations is, in general, quite satisfactory.

Aside from the small amount of sample required for density determinations by this method, another advantage lies in the rapidity by which the results may be obtained. A single determination may be made in from 5 to 10 minutes including all operations, and a series of determinations can be made with similar rapidity.

Relay for Use in Regulatory Circuits[1]

L. G. Wesson

Department of Pharmacology, Vanderbilt University, School of Medicine, Nashville, Tenn.

An electromagnetic relay, in which the operating circuit is automatically interrupted and in which undesirable sparking is prevented, has been developed and used in thermoregulation in this laboratory for the past year. Two dry cells only are necessary for operating the relay and will last for months without attention, since current is drawn from the cells only during the time that the relay arm moves from one position to the other. The sparking that occurs at the break of the circuit in thermoregulators, etc., which may be used in connection with this and certain other forms of relays, is the cause of much difficulty in operation because of the corrosion or sticking of the metal tips or oxidation of the mercury surface of the thermoregulator. In the relay to be described this difficulty is avoided, since the actual break of the circuit takes place at an insensitive junction in the relay, instead of at a sensitive junction in the thermoregulator.

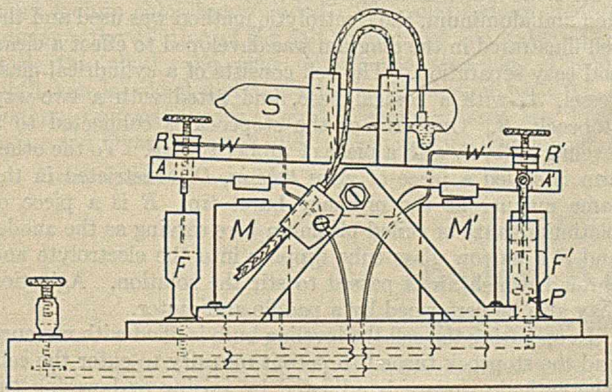


Figure 1—Electromagnetic Relay

The relatively heavy currents that often are switched on and off by a relay are a troublesome feature of regulatory circuits because of sparking. This difficulty is avoided, as in certain other types of regulatory circuits brought out in the past few years, by the use of a mercury switch[2] in connection with this relay. By means of this switch currents as high as 10 amperes may be turned on and off by the extremely small wattage used in the relay.

Description of Relay

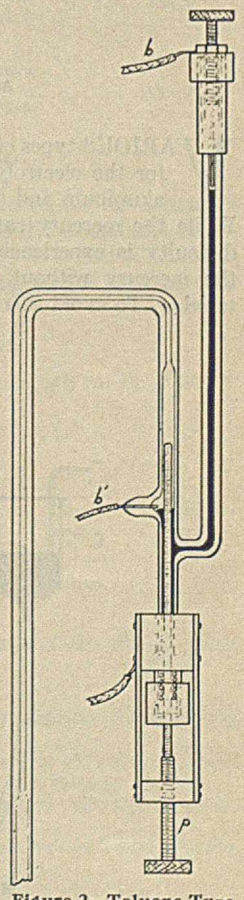


Figure 2—Toluene Type of Thermoregulator

The relay (Figure 1) consists essentially of two electromagnets,[3] *M*, *M'*, each acting on one end of an approximately balanced arm, *A*, *A'*, carrying a mercury switch, *S*. Two wires, *W*, *W'*, which are insulated from the arm and which are provided with platinum tips, are so arranged that they can be lowered by means of thumb screws, *R*, *R'*, into cups of mercury,[3] *F*, *F'*, one of which is below each end of the arm. (A layer of liquid petrolatum protects the mercury from corrosion.) Adjustment of the wires is made so that while the wire at one end of the arm dips well into the mercury when the corresponding end of the arm is down, it just clears the surface of the mercury when that end of the arm is in the raised position. The current from the dry cells passes through the wire which is in contact with the mercury as soon as the circuit is closed at the sensitive junction of the thermoregulator, and passes thence through an electromagnet, *M'*, at the other end of the arm. The magnet pulls down that end of the arm, *A'*, and while doing so lifts the wire from the mercury at the end *A* of the arm, and thus breaks the circuit. As the relay stands now, the circuit is closed through the wire, *W'*, and the corresponding electromagnet, *M*, except for the open junction in the thermoregulator. When this open junction of the thermoregulator is closed by change of tem-

---

[1] Received October 21, 1929.

[2] This switch consists of a closed glass tube into which are sealed contacts of special material. It contains a quantity of mercury which, when the tube is tilted, will make or break the circuit. With the mercury switch there is no open arcing, oxidation, or corrosion. The switch contains inert gases hermetically sealed within the tube which stifle the arc. Different types of mercury switches are available, and are designed to carry loads from 1 to 10 amperes at 110 volts or 1 to 5 amperes at 220 volts. Mercury switches are sold by the Mercoid Corp., 564 West Adams St., Chicago, Ill.

[3] Sounder magnets, rubber-covered, 4 ohms, Catalog 30, No. 6203, J. H. Bunnell & Co., 32 Park Place, New York, N. Y.

perature, the current passes through the electromagnet, *M*, and pulls down the other end of the arm, *A*, and in doing so tilts the mercury switch to the opposite position. The arm stays in the position to which it is drawn by the electromagnets by reason of the fact that the shaft on which the arm pivots is placed slightly below the center of gravity of the arm. The position of the arm changes only when the electromagnet at the other end of the arm becomes activated. The arm moves through an angle of 10 to 12 degrees in passing from one position to the other.

A small, loose-fitting plunger, *P*, surrounded by heavy machine oil, acts as a brake to the motion of the arm, and thus prevents undesirable oscillation.

Thermoregulators Used

Various types of thermoregulators, such as the bimetallic type[4] or the toluene or mercury expansion type, may be adapted for use with this relay, the only requisite being that two contacts are provided, one for the maximum and one for the minimum limit of the desired range of temperature. The same is true of the possible use of the relay in maintaining constant pressure, depth of liquid, hydrostatic head, volume, etc. Other factors being the same, the accuracy of the control attained with the relay is limited only by the sensitiveness of the regulator used in conjunction with it.

Figure 2 illustrates a toluene type of regulator that has been used in this laboratory with satisfactory results. Toluene, by contracting or expanding, forces mercury to make alternate contacts with wires *b*, *b'* that lead to one or the other electromagnet of the relay. The regulator is set by screwing inwards or outwards the metallic plunger, *p*, which extends into the toluene, thus changing the effective volume of the toluene.

---

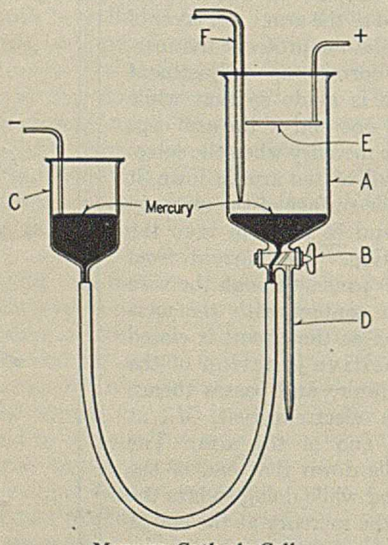
[4] Room thermostats, Type Q-10 or Type 4010, Minneapolis-Honeywell Heat Regulating Co., Minneapolis, Minn., are a readily available form of bimetallic thermoregulators that are adapted for use with this relay for thermo control of rooms or air baths where extreme accuracy is not essential.

Electrolytic Cell for Use with the Mercury Cathode[1]

Arthur D. Melaven

Aluminum Research Laboratories, Aluminum Company of America, New Kensington, Pa.

VARIOUS types of mercury cathode cells have been used for the electrolytic separation of metals, particularly aluminum and magnesium from other common metals. While the mercury cathode method has many advantages, difficulty is experienced in separating the electrolyte from the mercury without resolution of the amalgamated materials. To avoid this the circuit must be closed at all times during the separation. Separation is made in the Smith-Howard (*4*) cell by repeated additions of water prior to the interruption of the current, but this has the disadvantage that the volume of solution is greatly increased. The cells of Frary (*3*) and of Alders and Stähler (*1*) have the same drawback. Cain (*2*) has devised a cell from which the electrolyte can be drawn off with a minimum amount of wash water, but in this case a subsequent filtration is necessary and there is danger of decomposition of some of the less stable amalgams in the process.



Mercury Cathode Cell

In some work demanding the quantitative separation of iron and aluminum, the electrolytic method was used and the cell illustrated in the diagram was developed to effect a clean and easy separation. The cell consists of a cylindrical glass vessel, *A*, with a conical base, and fitted with a two-way stopcock, *B*. One arm of the stopcock is connected to a leveling bulb, *C*, with a piece of rubber tubing. To the other arm is sealed a piece of glass tubing, *D*, constricted in the same manner as the ordinary buret tip. *E* is a piece of platinum gauze or coiled platinum wire serving as the anode, and *F* a narrow glass tube dipping into the electrolyte and through which air is passed to stir the solution. Agitation may also be performed by a paddle and motor.

In operating the cell the leveling bulb is filled with mercury and the stopcock turned to permit mercury to enter the cell. The cathode surface is adjusted by raising or lowering the leveling bulb to the desired height. Contact to the source of current is made by a piece of copper wire dipping into the mercury in the leveling bulb. The solution to be electrolyzed is introduced into the cell and the circuit closed. When the electrolysis is completed, the leveling bulb is lowered until the mercury reaches the upper end of the stopcock bore. The stopcock is then turned through 180 degrees to permit the electrolyte to drain into a suitable vessel. A closed circuit is maintained at all times during removal of the mercury, either by having sufficient electrolyte present to cover the anode when the mercury is at the lowest point or by lowering the anode as the mercury is being removed.

The cell lends itself to easy washing with a minimum amount of wash water.

Literature Cited

(1) Alders and Stähler, *Ber.*, **42**, 2685 (1909).
(2) Cain, J. Ind. Eng. Chem., **3**, 476 (1911).
(3) Frary, *Z. Elektrochem.*, **13**, 308 (1907).
(4) Smith, *J. Am. Chem. Soc.*, **25**, 883 (1903).

---

[1] Received February 15, 1930.

Acid Numbers of Dark-Colored Resins[1]

Hayward H. Coburn

Experimental Station, Hercules Powder Company, Kenvil, N. J.

IN THE paint, varnish, and lacquer industries and in other industries where natural or artificial resins are used, the chemist is frequently called upon to determine the acid number of these resins. Normally this is accomplished by titration of an alcohol or benzene-alcohol solution of the resin with standard alkali, phenolphthalein being used as the indicator. However, when the alcohol or benzene-alcohol solution is dark-colored, as is frequently the case, the phenolphthalein end point is so masked that accurate titration becomes very difficult.

This inexactitude of the ordinary method and the inherent difficulties of the well-known electrometric titration led the writer to investigate the Albert method (*1*, *2*). This method consists in titrating in a two-phase medium a benzene-alcohol layer and an aqueous layer. In order to improve the sharpness of the separation, the lower layer is saturated with sodium chloride. The color bodies which would mask the end point remain in the upper layer, while the indicator color appears in the aqueous layer, and its change is consequently clear and sharp.

The procedure used by the writer contains no change in the principle of the method, but some improvements have been made in the operating technic.

Approximately 1 to 1.5 grams of rosin are dissolved in 25 cc. of a neutral mixture of 2 parts benzene and 1 part alcohol. When solution has taken place, 25 cc. of a neutral saturated sodium chloride solution and several grams of solid sodium chloride are added. The solid sodium chloride prevents the dilution of the salt solution by the water added with the alkali and acid during the titration. Phenolphthalein is added and the solution is titrated with 0.5 *N* sodium hydroxide with vigorous shaking until the lower (aqueous) layer turns red and further shaking does not cause this color to disappear. A considerable excess of reagent will cause no inconvenience. The solution is now titrated with 0.5 *N* sulfuric acid until the red color of the lower layer just disappears. In this titration, since the excess sodium hydroxide in the aqueous layer is being titrated, the flask should be given a rotary swirling motion, but it is not necessary to shake so vigorously as to break up the two layers. If, after the addition of the sodium hydroxide, the separation into two layers is not sharp, neutral alcohol may be added to the solution.

Results

The acid numbers obtained by this method on a number of different grades of rosin and those obtained from determinations made on the same samples by direct titration with alkali are given below.

SAMPLE A	SAMPLE B	SAMPLE C	SAMPLE D
	DIRECT TITRATION		
149.1	118.7	112.8	184.0
150.1	106.4	112.5	
	118.5		
	106.6		
	MODIFIED ALBERT METHOD		
149.0	103.6	115.7	183.7
149.0	103.6	115.5	
	103.0		

Acknowledgment

The writer is indebted to Jean Piccard for his assistance in the preparation of the article, and to the Chemische Fabriken Dr. Kurt Albert, G. m. b. H., Wiesbaden-Biebrich, Germany, for their kindness in sending him a copy of their *Albertschrift* Nr. 15.

Literature Cited

(1) Chemische Fabriken Dr. Kurt Albert, *Albertschrift*, Nr. 15, p. 55.
(2) Stock, *Farben-Ztg.*, **34**, 1727 (1929).

---

[1] Received November 16, 1929.

Duplex Weighing Tube[1]

W. E. Eskew and Frank C. Vilbrandt

University of North Carolina, Chapel Hill, N. C.

LOSS of sample with subsequent inaccuracy of analytical data is likely to occur when samples must be transferred from a watch glass or weighing bottle into a beaker or narrow-neck receptacle. Flicking of sample may also occur when the material must be brushed out of the weighing bottle or off the watch glass with a camel's-hair brush.

In order to avoid such losses and to obviate the necessity of double transference, a weighing tube has been designed to incorporate the principle of a watch glass or weighing bottle provided with an accessible and easily discharging delivery end. The device consists of a wide-mouthed glass tube with a flattened bottom side and a tapering delivery end turning up and away from the flattened side, as shown in the accompanying drawing. Details of size are given, but proportionally larger or smaller sizes are just as applicable. The use of inside or outside ground joints and caps on both ends enables the application of this weighing tube or bottle for all purposes of weighing.

The advantages in the specific details of the design given are as follows:

(1) The large mouth provides for easy addition of or taking portions of the sample from the tube.

(2) The designed slopes permit easy access of brush or stream of water into and against all parts of the interior.

(3) The flattened side permits proper upright position during weighing and standing.

(4) Distribution of the mass of glass assists in preventing the tube from easily toppling over.

(5) Narrow end or stricture at delivery end permits easy transfer of solids or liquids into narrow-neck receptacle.

(6) Variation of size for weighing larger or smaller samples does not involve proportional bulkiness.

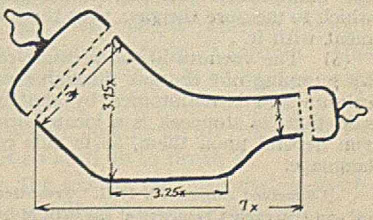


Figure 1—Duplex Weighing Tube
Side view

---

[1] Received February 25, 1930.

The Baro-Buret—A New Accurate Gas Buret[1]

Harold Simmons Booth

Morley Chemical Laboratory, Western Reserve University, Cleveland, Ohio

There is described the construction and use of a new gas buret, the baro-buret, in which the buret becomes the well of a barometer, thus enabling the experimenter to read both pressure and volume simultaneously with greatly increased accuracy and speed. Since with this instrument the volume may be measured at any desired pressure, the accuracy of reading small volumes is especially increased.

The errors and limitations are discussed, including the maximum error possible under the most favorable conditions for minimum error.

The combination of the measurement of pressure and volume in one instrument opens up many applications, some of which are given.

THERE have been attempts to improve the gas buret since its inception. The chief improvements have been the development of devices of one sort or another to compensate for temperature and pressure errors, of which that developed by White (*11*) is one of the best.

The sources of errors in the gas buret are fairly obvious:

(1) The measurement of pressure by balancing the mercury column against the atmosphere and by reading the pressure of the atmosphere separately on the barometer increases enormously the errors in pressure reading.

(2) Accurate adjustment of the mercury levels in reading the volume is fraught with difficulty.

(3) Accurate temperature control is impractical.

(4) Leaks in the rubber connections and leaking of gas into the buret through the rubber tubing connecting the buret to the level tube is a hidden source of error.

(5) The experimenter is limited to the measurement of the gases at atmospheric pressure or else may expect serious errors due to leaks.

(6) The use of a compensator introduces errors due to the volume of gas imprisoned in the compensator. In the White buret, however, this error is minimized.

Of these difficulties the first two are probably the most serious.

Several years ago it occurred to the writer that these difficulties might be eliminated by an arrangement whereby the pressure of the gas in the buret was balanced by the pressure of a column of mercury only, rather than by the pressure of the atmosphere. In other words, the gas buret could be made the well of a barometer. There have been several efforts to accomplish this, but they have all resulted in clumsy, complicated apparatus, difficult to make and to maintain. One of the earliest of these was devised by Frankland and Ward (*6*). More recently Bone and Wheeler (*2*, *3*) modified Frankland's buret but limited its usefulness. Bone and Wheeler's buret is of the constant-volume type and suffers from the following defects:

(1) On account of set volume marks the buret has a use limited to ordinary gas analysis.

(2) There is no provision for preventing chance bubbles from the rubber tubing used to connect the level bulb from rising into the buret.

(3) The diameter of the buret and pressure column is too small and may easily vitiate the measurements on account of the capillary-depression effect.

(4) On account of the short length of the pressure column, the manipulator has practically little choice of pressures at which to measure the gas; thus there is no flexibility of measurement with it.

(5) The vacuum in the pressure-reading column is produced by pumping out the gas through a stopcock at the top of the column and is maintained by shutting the stopcock. Morley said that "a stopcock is a located leak," and frequently, when you depend upon them, as in this case, they deserve stronger language.

The baro-buret to be described eliminates all these difficulties.

Obviously the chief difficulty lies in the establishment and maintenance of the Toricellian vacuum in the barometric column. The combination of the overflow method first applied in the Toepler pump, and later to the barometer devised by Germann (*7*), with the gas buret offered possibilities. The practical development of this idea resulted in the "baro-buret," which has been found to be, not only accurate, but also rapid and capable of wide application. It has been thoroughly tested in this laboratory for seven years and has been applied to numerous problems successfully.

Design

The baro-buret consists essentially of two limbs, the 100-cc. calibrated gas buret, *K*, and the barometric column, *B*, made of glass tubing of the same bore as the buret, so that the depression of the mercury due to surface tension shall be the same in both tubes. (Figures 1 and 3) These two parts are connected by the stopcocks *M* and *N* by fused-glass connections, and through pressure rubber tubing to the mercury reservoir, *R*. The tube composing the trap, *L*, should slope slightly towards the buret so that gas bubbles leaking through the rubber tubing will collect in the trap rather than go up the side tubes.

At first it was feared that there would be sufficient strain to break fused connections between the parts of the buret, and connections of rubber tubing were used between stopcocks *M* and *N* and the trap *L*. It was soon found that air leaked in through the best of tubing and that an all-glass apparatus, firmly supported and then fused together in position, would not break. *M* and *N* are large hollow-blown stopcocks with a 6-mm. bore. *L* is an ordinary stopcock. These stopcocks should be carefully greased, so that no grease is left in the bore, and then held in place with clamps (*1*) to prevent loosening and consequent leakage. The overflow capillary tube for establishing and maintaining the vacuum in *B* should have a uniform bore of not more than 1 mm. to prevent breaking of the mercury thread with consequent "lying down" of the gas in the capillary during evacuation of the barometer. The length of this capillary tube should be such that the difference between the surface of the mercury in *D* and the top of the buret is at least 760 mm. The capillary should be bent at the top of the barometer as shortly as possible to prevent the mercury from siphoning back. Where it is planned to use the buret at pressures above 1 atmosphere, the length of column *B* must be proportionately greater.

In Figure 3 is shown a more recent design, especially intended for uses where it is necessary to measure the gas at low pressures or where it is desirable to be able to measure the vapor pressure in the adjoining system. Here the barometric column is a straight tube parallel to the gas buret and is

---

[1] Received August 27, 1927. Presented before the Division of Physical and Inorganic Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924. Revised paper received March 11, 1930. Abstracted in *Science*, **59**, 563 (1924).

supported at the bottom of the case in the same fashion as the buret. With this design it is possible to measure very small gas volumes much more accurately by operating at low pressures. It is the design of most universal application, and is much easier to make than the original. It requires a wide scale and even more careful leveling. If one is limited to a narrow scale, the original design is required.

Buret Case

Figure 2 shows in detail the buret case. The sides are made of $^7/_8$-inch (2.2-cm.) pine and the front and back each of four pieces of glass. The 150-cm. scale in the more accurate types was engraved on white celluloid fastened to a $^5/_8$-inch (1.6-cm.) thick wooden strip, screwed to the metal braces. For less accurate work selected wooden 2-meter sticks mounted on wooden strips have been found satisfactory. In the small types of baro-buret it has been found convenient to support the mercury reservoir in a sliding bracket, *O*, mounted on the slide, *S*, fastened to the case. When the buret is used as part of a large set-up, it is more convenient to support the mercury reservoir on a ring clamp on a vertical steel rod fastened to the whole apparatus. The upper barometric column, *B*, in the type of buret shown in Figures 1 and 2 is supported on the bracket, *R* (Figure 2), fastened by brass plates to the scale.

Assembling

In making the baro-buret the column *B*, the capillary, and the side well *D* are fused together in a straight line and then bent, thus avoiding joints in the capillary in which gas might "lie down." The lower part of the barometer leading to stopcock *N* is then fused on and the whole set in position in the case. Stopcock *M* is fused on to the gas buret and the buret is carefully cleaned, dried, and calibrated with distilled mercury (*4*). The buret is then placed in the case and supported by the slot in the base. Both the barometric column and the buret are then wired permanently in place. Stopcocks *M* and *N* are then fused on to the trap, *L*, which has been previously blown in the blast lamp. Calibrated thermometers are suspended in the case alongside the buret. The slots in the base and the side of the case are stopped with cotton to prevent air currents. A piece of plate glass covers the top of the case. The rubber tubing to the reservoir is wired in place. It is also advisable to wire the rubber tubing near the trap permanently to the buret case, so that the trap may not be inadvertently broken. To prevent smutting of the mercury by dust it is well to stopper the reservoir *R* with a bulb tube filled with glass wool or cotton.

Operation

The stopcocks are greased and clamped and the whole baro-buret is thoroughly dried by applying suction to the mouth of the reservoir *R* and thus drawing air, dried by passage over potassium hydroxide and phosphorus pentoxide or barium oxide (*5*), in through stopcocks *C*, *F*, and *L* for a week. The buret should then be carefully leveled. Before filling with mercury the reservoir *R* is lowered below the level of *N* and the mercury slowly poured in; the entrapped air is removed by manipulating the rubber tubing. Stopcock *L* is clamped in a closed position and stopcocks *M* and *N* are opened. The buret is evacuated through *C* and *F*, the mercury reservoir being kept at a level sufficiently below *N* so that the mercury does not rise into *N*. When evacuation is practically complete, stopcock *F* is closed and clamped and reservoir *R* is slowly raised, allowing the mercury to rise in both *K* and *B*. The reservoir is raised further until the mercury overflows down the capillary and forms a pool about 1 cm. deep in *D;* the reservoir is then quickly lowered and the mercury column breaks, thus leaving a fair vacuum in column *B*. The reservoir should then be lowered well below the base of the buret, so that the mercury in the barometric column is down to stopcock *N*, thus permitting gases adsorbed on the walls to evolve. After a few minutes the reservoir *R* is again raised and the gases are driven out as before. Great care should be taken to decrease the rate at which the mercury rises as it approaches the top of the barometer, or the mercury will strike the constriction with such force as to demolish it. A tiny bubble of air, on being forced down the capillary against atmospheric pressure, tends to "lie down" in it, whereas it is expanded so much if *D* is evacuated that it has to carry along with the mercury into *D*. This evacuating process should be repeated several times after allowing the buret to stand with the mercury level at *N* for several hours to remove adsorbed gases completely.

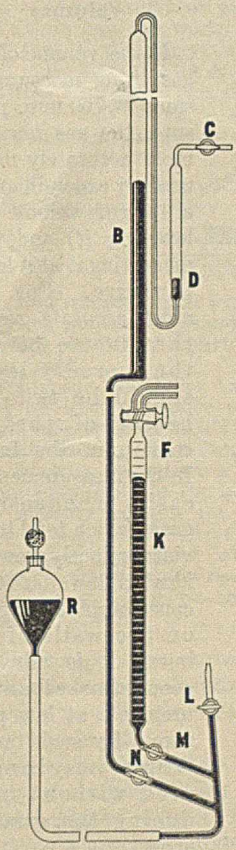


Figure 1—Baro-Buret

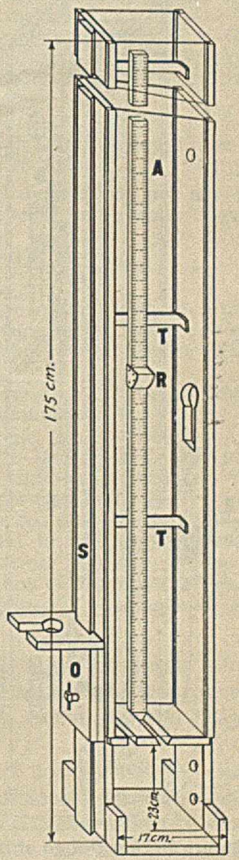


Figure 2—Buret Case

Each day before using the buret it is also advisable to test the vacuum in *B* by driving the mercury over into *D*. If too much mercury collects in *D*, it can be forced back into the buret by admitting dry air through *C*, whereupon the mercury will be forced back into *B* until the difference in level in *D* and the top of *B* is equal to the atmospheric pressure. If at any time it becomes desirable to remove the mercury from the buret, air under slight pressure through *C* will force the mercury completely from *D* into *B*. This process should always be used since, if air is allowed to enter through *N* and thus rise in the barometer column, it will form a mercury hammer, which, lacking an air cushion above it, will strike the top of *B* so hard as to break it.

To use the baro-buret the gas to be measured is introduced through one of the capillary tubes of stopcock *F* by lowering *R* slowly, having stopcock *M* open. If desired, stopcock *N* may be closed during this operation, thus avoiding moving the mercury in the barometric column. If it is desired to flush out the buret with the gas, it may be forced out again by raising reservoir *R*. Care must be taken, however, to raise *R* very slowly as the mercury approaches stopcock *F* to avoid having the impact of the mercury break the stopcock. When a suitable sample of the gas has been introduced into the buret, *F* is closed and *N* opened slowly. When the mercury levels in *B* and *K* have come to equilibrium, the volume of the gas is read on the buret. The pressure on this gas is equal to the difference in height of the mercury columns in *B* and *K* as read on the scale directly behind them. Should it be desirable to measure the gas at a particular pressure, *R* may be raised or lowered until the difference in height of the mercury in *B* and *K* equals the desired pressure, whereupon the volume of gas may be read on the buret.

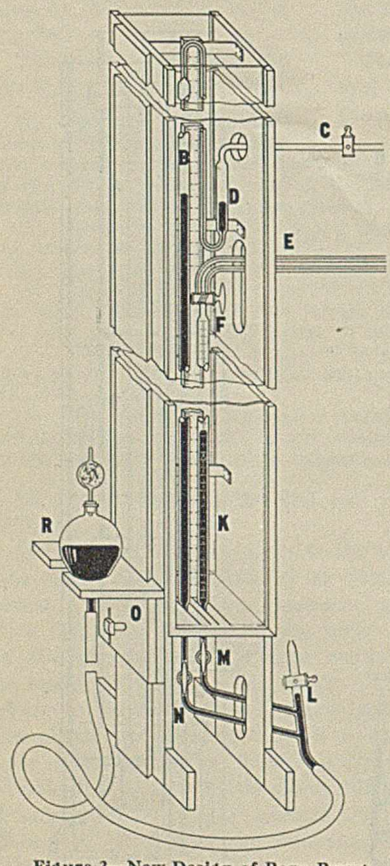


Figure 3—New Design of Baro-Buret

Measuring Small Volumes

If the volume of the gas being measured is small at 760 mm. pressure, the gas may be more accurately measured by expanding it to a larger volume (by lowering *R*) and thus measuring it at a lower pressure. For the most accurate results the distance between the mercury levels should be twice the height of the gas column in the buret. In the measurement of easily condensable gases which tend to deviate seriously from the ideal gas laws and suffer considerable adsorption on the walls of the buret, it is advantageous to make the measurements at low pressure. By such tactics "vapors" may be measured without introducing too great an error.

To Remove a Gas from the Baro-Buret

To remove a gas completely from a buret—as, for example, before introducing another gas—close *N*, open *F*, and raise *R* slowly until the mercury reaches *F*. Close this stopcock and lower *R* until the mercury in *K* is below the previous volume mark. This procedure will free gases that have "lain down" between the buret wall and the mercury when the latter was raised in the first operation. If *R* is raised slowly now, the gases will collect above the mercury in *K* as a small bubble, which can be easily forced through stopcock *F*. This procedure is particularly advisable when measuring high-boiling-point gases and gases which are highly adsorbed by glass.

Corrections

The pressure reading for accurate work should be corrected for the difference in gravity constant at the laboratory where the readings are being made and at sea level. In this laboratory the correct pressure reading (*8*) may be obtained by multiplying the observed pressure by 1.000384. Neglect of this correction introduces an error of −0.04 per cent. Since the temperature of the mercury in the baro-buret is greater than 0° C., the true pressure at 0° C. is less than the observed pressure. The corrected pressure may therefore be obtained by multiplying the observed pressure by a factor which is the ratio of the density of the mercury at the temperature of the buret case to that at 0° C. (*9*).

For extremely accurate measurements the temperature correction for the scale should be known or determined, or else a scale engraved on glass should be used. The ideal scale would be one engraved on glass silvered on the back. This mirror would greatly reduce the error due to parallax.

In calculating V_0 it is well to include a correction for deviation from the gas laws, especially in the case of such an easily condensable gas as sulfur dioxide.

Errors and Limitations of Accuracy

It has been found in this laboratory that the volume of a 100-cc. gas buret graduated to 0.2 cc. can be easily read to an accuracy of 0.05 cc., and by using a mirror or a mirror scale behind the buret to lessen the error due to parallax, the buret, with care, may be read to 0.02 cc.—that is, with an accuracy of 1 part in 5000. By using a White bulbed buret (*12*) doubtless this accuracy can be greatly increased. The pressure can easily be read to 0.2 mm., thus giving an accuracy of approximately 1 part in 4000 when reading 1 atmosphere. According to the International Critical Tables (*10*) on the basis of six thousand observations, one ought to be able to read a linear distance to 0.05 mm. This would represent an accuracy in reading a pressure of 1 atmosphere of 1 part in 15,000. With a cathetometer the pressure might be read to 1 part in 26,000, which would be particularly applicable in the measurement of vapor pressures, though it is doubtful if the temperature could be so controlled as to make such accuracy significant. We find no difficulty in maintaining the temperature in the buret case within 0.1° C., that is, an accuracy of 1 part in 3000. However, it is probable that some of these errors are positive and some negative for any given experiment, so that they may be considered to be to a certain extent self-compensating.

Maximum Possible Error under Most Favorable Conditions for Minimum Error

John A. Maurer, of this laboratory, has calculated as follows the maximum error possible under the most favorable conditions for minimum error in a single reading:

> Perhaps the most important point which we encounter in attempting a comparison between the accuracy of measurements with the baro-buret and that of measurements with the ordinary gas buret is that the principle upon which the baro-buret is constructed makes it necessary for the user to choose a particular one of an unlimited number of pressure-volume combinations at which he might make his readings on a given sample of gas. It is clear that of all the choices possible there will be some one which makes the final error of the measurement a minimum. The present purpose is to discuss this question in connection with an attempt to find a definite expression for the accuracy.
>
> It is easy to show that whenever we have three quantities, *A*, *B*, and *C*, connected by a relation of the form
>
> $$A = kBC \qquad (1)$$
>
> and we wish to determine *A* by measuring *B* and *C*, we obtain the maximum precision consistent with our experimental methods if we can vary the ratio of *B* to *C* so as to make the experimental error in measuring *B* the same fraction of *B* as that in measuring *C* is of *C*.
>
> For, if we represent the error, or perhaps it is better to say the

uncertainty, in the different quantities by E_a, E_b, and E_c, we have, remembering that E_b and E_c are constants but E_a is not,

$$A + E_a = k\,(B + E_b)\,(C + E_c) \qquad (2)$$

and

$$E_a = k\,(BE_c + CE_b + E_bE_c) \qquad (3)$$

The per cent uncertainty in A is

$$100\,\frac{E_a}{A} = 100\left(\frac{E_c}{C} + \frac{E_b}{B} + \frac{E_bE_c}{BC}\right) \qquad (4)$$

The last term on the right-hand side of (4) is negligibly small, so that we may say that in general the per cent uncertainty in A is equal to the sum of the per cent uncertainties in B and C.

To find the condition for making E_a a minimum, we write (3) in the form:

$$E_a = k\,(BE_c + \frac{A}{kB}\,E_b + E_bE_c) \qquad (5)$$

and differentiate with respect to B, and then equate the right-hand side to zero. This gives

$$k(E_c - \frac{A}{kB^2}\,E_b) = 0 \qquad (6)$$

Writing $A = kBC$, we obtain

$$\frac{E_b}{B} = \frac{E_c}{C} \qquad (7)$$

which is the result stated in the first paragraph.

Applied to the case of the gas buret, where we make use of the relation

$$V_0 = \frac{1}{P_0}\,PV \qquad (8)$$

Equation 8 means that we should make our measurements under a pressure such that

$$\frac{E_p}{P} = \frac{E_v}{V}$$

With the ordinary gas buret it is difficult to do this without complicating our procedure in such a way as to introduce greater experimental errors, and measurements are usually made at atmospheric pressure. Suppose we have only 1 cc. of gas. We can easily measure a pressure in the neighborhood of 760 mm. with an accuracy greater than 0.1 per cent, but we must have very highly refined apparatus indeed if we are to measure the volume to within 1 per cent. Thus the accuracy of the pressure reading is of little value because of the large uncertainty in the volume reading.

With the baro-buret, however, we can take our readings at any desired pressure, so that it is a simple matter to fulfil the condition for maximum accuracy in the final result.

Just what the best pressure-volume combination will be for any given baro-buret depends upon how it is set up, calibrated, and used. As an example, let us consider the conditions which apply to those in use at the Morley Laboratory.

These baro-burets are made with the barometer tube the same size as the buret tube. The manner of reading the mercury level is the same for both tubes. Thus there is no need to correct for capillary depression, and the uncertainty of the reading may be assumed to be the same in either tube. The calibration of the instruments is done with the aid of a cathetometer, but the readings are taken by eye and mirror scale. Thus the errors of calibration are negligible in comparison with those of regular use.

Suppose the uncertainty in reading the mercury level is h and the area of cross section of the buret tube, A. If L_1 is the length of the tube occupied by the gas, $V = AL_1$, $E_v = Ah$, and $E_v/V = h/L_1$. The relative uncertainty of E_p/P in the pressure reading is $2h/L_2$, where L_2 is the length of the mercury column balanced by the pressure of the gas. The $2h$ appears because two readings are involved in determining the pressure, and it is easily possible for the errors to be made so that they add. Then the condition $E_v/V = E_p/P$ reduces to $h/L_1 = 2h/L_2$, or $L_2 = 2L_1$; that is, we must adjust the leveling bulb so that the top of the mercury column in the barometer tube stands just as far above the upper end of the buret tube as the top of the column in the buret tube is below it. When this is done we have, from (4) and (8), that the per cent uncertainty in our determination of V_0 is 100 $2h/L_1$.

It is not hard to put this in a form that can readily be applied to practical cases.

$$L_1 = \frac{V}{A}.\quad P = L_2 = 2L_1 = \frac{2V}{A}$$

Substituting this value for P in the relation $V = P_0V_0/P$, we obtain

$$V = \sqrt{\frac{P_0V_0A}{2}};\qquad \frac{200h}{L_1}\qquad \text{becomes}$$

$$\frac{200h}{\dfrac{\sqrt{\dfrac{P_0V_0A}{2}}}{A}}, \text{ or finally}$$

$$\text{Per cent uncertainty in } V_0 = \frac{200\sqrt{2}\,\sqrt{A}\,h}{\sqrt{P_0V_0}} \qquad (9)$$

Since $A = {}^1/_4\,\pi\,D^2$, where D is the diameter of the buret tube, this may also be written

$$\text{Per cent uncertainty in } V_0 = \frac{100\sqrt{2}\,\sqrt{\pi}\,Dh}{\sqrt{P_0V_0}} \qquad (10)$$

Thus the per cent uncertainty of a measurement varies directly as the diameter of the buret tube and inversely as the square root of the quantity of gas being measured.

To show how this works out in practice, suppose $V_0 = 50$ cc. and that h, the uncertainty in reading the mercury level, is 0.02 cm. The area of cross section of the buret tube is not far from 2 sq. cm. This gives, by (9),

$$\text{Per cent uncertainty in } V_0 = \frac{200\sqrt{2}\,\sqrt{2}\,(0.02)}{\sqrt{76 \times 50}} \text{ or } 0.13 \text{ per cent.}$$

But if we are dealing with a small quantity of gas, say 1 cc. under standard pressure, the per cent uncertainty becomes

$$2\,\frac{\sqrt{2}\,\sqrt{2}\,(0.02)}{\sqrt{76}} = 0.92 \text{ per cent}$$

The uncertainty is still less than 1 per cent, whereas with the ordinary gas buret, assuming the same method of reading the mercury levels, the uncertainty in the volume reading alone is 4 per cent.

The above calculation has been carried out on the assumption that we wish to reduce to a minimum the uncertainty in a single measurement on a sample of gas. In carrying out a long investigation in which results are to be averaged, it is probably desirable to adopt a slightly different procedure. If, as seems reasonable to the writer, the worker is as likely to read the mercury column too high as too low, the probability is 1 to 2 that the two errors involved in the pressure reading will cancel instead of add. Therefore, on the average the error of the pressure reading is not of the order of $2h$, but of h. On this basis we should adjust the leveling bulb so as to make $L_1 = L_2$.

The temperature correction has not been taken into account in the above discussion, because as far as it is concerned there is no difference between the baro-buret and the ordinary gas buret.

Experience has shown that it is not difficult to obtain a series of readings which are consistent with each other to a much higher degree of accuracy. Nevertheless it is worth while to know how large the errors may become under the conditions of ordinary use.

Applications

Measurement of External Volumes—The determination of the volume of connecting tubing, or of an apparatus itself connected to the buret, is ordinarily a difficult matter, but is very easily accomplished by means of the baro-buret. To accomplish this, the buret K and the connecting tubing, whose volume is to be measured, are thoroughly evacuated and then filled with a dry, permanent gas, such that the volume V_1 in the buret K shall be about 50 cc. at a pressure, P_1, of about 760 mm. Both pressure and volume are accurately observed with the stopcock F opened to the tubing or apparatus whose volume is to be measured. With stopcock F open, reservoir R is lowered so that the new volume, V_2, is approximately the full capacity of the buret, and the new pressure, P_2, and the volume, V_2, are accurately measured. Then it is easily seen that $P_1\,(V_1 + C) = P_2(V_2 + C)$, where

C equals the constant volume to be determined. Solving this

$$C = \frac{P_2V_2 - P_1V_1}{P_1 - P_2}$$

Obviously, the accuracy of such a measurement is inversely proportional to the volume to be measured, and of course it is assumed that the buret K has been accurately calibrated.

ILLUSTRATION OF DEVIATIONS FROM GAS LAWS—The baro-buret can readily be made the basis of an excellent experiment to demonstrate with such gases as carbon dioxide, sulfur dioxide, etc., the deviation from the gas laws. Of course, the deviation with the so-called permanent gases is too small to be readily measured.

DETERMINATION OF VAPOR PRESSURE—To determine the vapor pressure of a solid or liquid, the substance is placed in a bulb sealed to one of the capillaries connected to F using a baro-buret of the design shown in Figure 3. The buret is then used as the bulb of a Toepler pump, gas being pumped from the bulb into the buret, and by rotating the stopcock F 180 degrees and raising the buret the gas and vapor are driven out. Five or six pumpings are generally sufficient to give a constant pressure. The vapor tension is then equal to the difference in the levels of the mercury in B and K.

The last application illustrates how the buret may be used as a Toepler pump to pump out a small space. This idea has been applied in a number of ways which will be discussed in separate papers, notably to a new method for gas evolution analysis; to the accurate analysis of gases with dry reagents; to a new apparatus for the determination of adsorption by the static method; to an apparatus for the study of gas-solid equilibria in which pressure, volume, and concentration are measured; to the rapid determination of the density of gases; to the measurement of gases evolved from reactions at high temperatures; to the determination of the solubility of gases in liquids; as a laboratory demonstration of Boyle's law; to a method of obtaining accurate gas mixtures for the study of the critical phenomena of gas mixtures; to the measurement of gases at higher pressures, etc.

Literature Cited

(1) Baume and Perrot, *J. chim. phys.*, **11**, 57 (1913).
(2) Bone, *Proc. Chem. Soc.*, **14**, 154 (1898).
(3) Bone and Wheeler, *J. Soc. Chem. Ind.*, **27**, 10 (1908).
(4) Booth and Jones, IND. ENG. CHEM., **19**, 104 (1927).
(5) Booth and McIntyre, *Ibid.*, Anal. Ed., **2**, 12 (1930).
(6) Frankland and Ward, *J. Chem. Soc.*, **6**, 197 (1854).
(7) Germann, *J. Am. Chem. Soc.*, **36**, 2456 (1914).
(8) Germann and Booth, *J. Phys. Chem.*, **21**, 87 (1917).
(9) International Critical Tables, Vol. I, p. 68.
(10) *Ibid.*, p. 94.
(11) White, *J. Am. Chem. Soc.*, **22**, 343 (1900).
(12) White, "Gas and Fuel Analysis," p. 79, McGraw-Hill.

Corrections for Standard Solutions of Inconvenient Strengths[1]

Selma Gottlieb

DIVISION OF SANITATION, KANSAS STATE BOARD OF HEALTH, AND UNIVERSITY OF KANSAS, LAWRENCE, KANS.

IN MAKING a large number of volumetric analyses using the same standard solution, it is of course very convenient to adjust the solution to such a strength that the calculation of results is simplified as much as possible. However, it seems scarcely worth while to make careful adjustments of those solutions which change strength rapidly, when the process will have to be repeated in a short time. The following suggestion is therefore offered to simplify the correction of buret readings for such solutions to those corresponding to the strength desired.

This method was originally applied to a sodium thiosulfate solution used in the dissolved-oxygen determinations required in biochemical oxygen demand tests on sewage, and intended to be 0.025 normal. When a solution of this exact strength is used, the number of cubic centimeters of it required in titrating a 200-cc. portion of the treated liquid is directly equal to the parts per million of dissolved oxygen present. Because of dehydration of the sodium thiosulfate crystals used, the solution as made in one case was 0.02531 normal, or 1.0124 times the intended strength, and because of the instability of sodium thiosulfate solutions it was thought desirable to work out a simple method of applying the necessary correction, rather than to adjust it to the desired titer.

If r is the ratio of the strength of the solution used to that of the solution desired, x the buret reading, and c the correction needed to bring the buret reading to that corresponding to the strength desired, the following relation will be obvious:

$$rx = x \pm c$$

and $$x = \frac{\pm c}{r - 1}$$

The sign of c will be positive when r is greater than one and negative when r is less than one.

By substituting into the equation successive values of c and the value of r as obtained from the standardization of the solution in question, the corresponding values of x can be calculated. The value of x obtained when c is 0.005 represents the lowest buret reading to which it is necessary to add 0.01 cc. as a correction. The next calculated value of x, when c is 0.0149, marks the end of the range for which a correction of 0.01 cc. is sufficient. Similarly, when c is 0.0249, x represents the end of the range to which a correction of 0.02 cc. is applicable, etc.

The corrected volume can then be readily found from the table prepared for the solution used, more rapidly than with a slide rule, and more accurately.

RANGE OF CORRECTION	CORRECTION (c)
Values of x	Add
0.40 − 1.20	0.01
1.21 − 2.00	0.02
2.01 − 2.81	0.03
...	..
6.85 − 7.65	0.09
7.66 − 8.46	0.10
8.47 − 9.27	0.11

Although the application of this equation is limited, it is a marked time saver in the cases in which it can be used. It is useful, for instance, when Kjeldahl determinations are made with acid and alkali solutions that are not exactly equivalent, and in many other routine volumetric determinations.

---

[1] Received January 16, 1930.

Convenient Reflux Regulator for Laboratory Stills[1]

Johannes H. Bruun[2]

Bureau of Standards, Washington, D. C.

For a continuous distillation it has been shown (*2*) theoretically that the reflux ratio (mols of vapor returned as refluxed liquid to the column per unit time divided by the mols of final product obtained per unit time) must always be maintained above a certain minimum value, in order to obtain a certain degree of fractionation. The theoretical calculation is a more difficult one for the ordinary laboratory rectifying still (batch still) in which the composition of the liquid in the different parts of the system is continually changing during the distillation. However, it is generally agreed that a high efficiency of separation is obtained by using a large reflux ratio and a small rate of distillation (*3*).

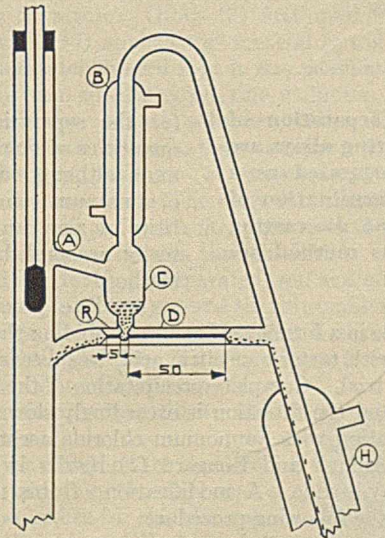


Figure 1—Reflux Regulator for Maintaining a Definite and Constant Reflux Ratio

For the purpose of controlling the reflux ratio and indicating the rate of distillation, the following reflux regulators have been found very convenient. They are modifications of a type which is used on industrial stills and they give a reflux ratio that is independent of the rate of distillation.

For Constant Reflux Ratio

Figure 1 shows a reflux regulator for use on stills for which a definite and constant reflux ratio is desired. The vapor leaves the rectifying column at *A*. By means of a reflux condenser, *B*, it is completely condensed into the bulb *C*. From the bottom of this bulb a certain part of the condensate is returned to the column through the capillary tube, *R*. Another part of the condensate passes through the capillary tube, *D*, into the cooler, *H*, and to the receiver.

In order to obtain a definite and constant reflux ratio, the capillary tubes *R* and *D* are made of the same bore but their lengths are made indirectly proportional to the amounts of liquid they should carry. For instance, if $R = 5$ and $D = 50$, the volume of reflux returned to the column divided by the volume of distillate will be 10. Instead of making the capillary tubes *R* and *D* of the same bore but of different lengths, it may be preferred to have capillaries of different bores but of nearly the same lengths. In order to obtain the right lengths of the two different sizes of capillary tubes, these are sealed horizontally to a vertical glass tube. Liquid is then allowed to run through the T-tube and the flow per unit time is measured for both capillaries. The capillary tubes are then gradually shortened until the desired amount of liquid per unit time will run through each of them. The T-tube is then sealed into the system and recalibrated.

This regulator will maintain a definite and constant reflux ratio at any rate of distillation. However, flexibility in the reflux ratio during a distillation can be accomplished by placing an electric heating coil around the capillary tube, *D*, thus increasing the flow through *D* by decreasing the viscosity of the liquid.

This device is also a convenient indicator of the rate of distillation, since this rate is directly proportional to the height of the liquid in the bulb *C*. This bulb may therefore be provided with a vertical scale on which each mark corresponds to a definite rate of distillation.

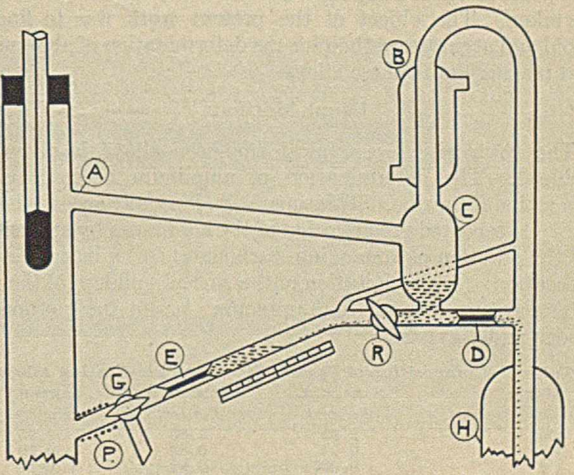


Figure 2—Reflux Regulator for a Measurable and Variable Reflux Ratio

For Variable Reflux Ratio

Figure 2 shows a reflux regulator for measuring and maintaining any desired constant reflux ratio. It is conveniently used where liquids of varied character are to be distilled, and also for determining the most practical reflux ratio in problems involving extensive distillation. The vapor leaves the rectifying column at *A* and is condensed into the bulb *C*. A certain amount of the condensate is returned to the column through a stopcock, *R*, and a capillary flowmeter, *E*, whereas another part is carried through the capillary tube, *D*, to the condenser, *H*, and to the receiver.

The proportion of reflux to distillate may be regulated by adjustment of *R*, and a quantitative measure of the reflux

---

[1] Received December 30, 1929. Publication approved by the Director of the Bureau of Standards. This paper describes a device which has been developed in connection with an investigation on "The Separation, Identification, and Determination of the Chemical Constituents of Commercial Petroleum Fractions," listed as Project No. 6 of the American Petroleum Institute. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] American Petroleum Institute Research Associate.

may be obtained at any time by observing the position of the liquid meniscus above *E*. This flowmeter is easily calibrated for any liquid by turning the 3-way stopcock, *G*, and collecting and measuring the liquid obtained during a short interval of time. With a given setting of *R* the position of the liquid meniscus above *E* is also a sensitive index of the rate of distillation.

The tube which carries the refluxed liquid back into the rectifying column should be surrounded by an electric heating coil, *P*, in order to raise the liquid to its boiling point. If desired, the capillary tube *D* may be replaced by a stopcock in order to give somewhat greater flexibility in reflux ratios, but this introduces the disadvantage of contamination of the distillate by the stopcock lubricant.

In both devices there is a free and unconstricted passage between the vapor outlet, *A*, and the condenser, *H*. Thus these regulators may be used for vacuum distillations as well as for distillations at atmospheric pressure. They have been used successfully with bubbling-cap-plate columns (*1*) as well as with iron jack-chain columns.

Acknowledgment

Acknowledgment is made to B. J. Mair for his helpful suggestions in developing this device.

Literature Cited

(1) Bruun, Ind. Eng. Chem., Anal. Ed., **1**, 212 (1929).
(2) Lewis, J. Ind. Eng. Chem., **14**, 492 (1922), and literature cited there.
(3) Shirk and Montanna, *Ibid.*, **19**, 907 (1927), and literature cited there

---

Determination of Aluminum and Magnesium in Zinc-Base Die-Casting Alloys[1]

Charles M. Craighead

Pennsylvania State College, State College, Pa.

Various methods applicable to the separation of aluminum and zinc in zinc-base die-casting alloys are discussed. The mercury cathode is suggested as a rapid and accurate method for the determination of aluminum and magnesium in zinc-base die-casting alloys, and the results obtained by this method are recorded.

In the course of some work on zinc-base die-casting alloys in the laboratory of the Aluminum Company of America, an investigation of various methods of separation and determination of aluminum and magnesium in the presence of preponderant amounts of zinc and various other alloying elements and impurities was undertaken. The object of the present work was to find a rapid and accurate method for the determination of aluminum and magnesium in these alloys.

Usual Methods

The composition of typical zinc-base alloys is given in Table I. The determination of aluminum necessitates a separation from zinc. This separation is usually accomplished by: (1) repeated precipitation of the aluminum by ammonia; (2) the addition of ammonium carbonate; (3) a basic acetate separation; (4) precipitation of the zinc as sulfide; (5) the use of ammonium chloride and ammonia; or (6) the method of Gooch and Havens.

Table I—Composition of Typical Zinc-Base Die-Casting Alloys

Metal	Sample A	Sample B	Sample C
	Per cent	*Per cent*	*Per cent*
Cu	2.82	2.86	2.95
Pb	0.03	0.32	0.60
Cd	0.007	0.29	0.10
Al	4.04	4.04	0.58
Mg	0.11	0.10	0.00
Fe	0.050	0.080	0.028
Sn	0.00	0.00	5.95
Zn (diff.)	92.943	92.31	89.792

(1) The separation of aluminum and zinc by means of ammonia is unsatisfactory, since the alkalinity required would cause the solution of an appreciable quantity of aluminum hydroxide (*9*).

(2) Separations based upon ammonium carbonate (*5*) are not satisfactory.

(3) The basic acetate method, with its tedious neutralization, the sometimes uncertain precipitation of aluminum, and the adsorptive nature of the colloidal precipitate, is not suited for the separation of large quantities of zinc from aluminum, although a separation of aluminum from small quantities of zinc can be satisfactorily accomplished by this method.

(4) The precipitation of zinc as sulfide in a formic acid solution, holding the aluminum in solution with tartaric or citric acid, was discarded after a preliminary trial. Complete precipitation of the zinc is time-consuming and the filtration is exceedingly slow.

(5) Separation with ammonium chloride according to the method of Ardagh and Bongard (*1*) results in the loss of aluminum hydroxide. A modification of this method was tried, using the following procedure:

> Twenty grams of alloy were dissolved in 100 cc. of water and 70 cc. of concentrated nitric acid, the nitric acid being added in small portions. The solution was evaporated to a sirup, diluted to 200 cc. and boiled until solution of the salts was complete, allowed to stand several hours, and the precipitate of metastannic acid filtered off and washed with 1:9 nitric acid.
>
> The filtrate was electrolyzed overnight for copper and lead. The electrolyte was saturated with hydrogen sulfide and the precipitate of sulfur and sulfides filtered and washed with acid hydrogen sulfide wash. The filtrate was boiled to remove hydrogen sulfide, a small quantity of bromine water added if necessary, cooled, and made up to a volume of 500 cc. in a graduated flask. A 50-cc. aliquot of this solution was taken for the determination of aluminum and magnesium. To the aliquot of this solution 10 cc. of concentrated hydrochloric acid and 20 grams of solid ammonium chloride were added, the solution diluted to 200 cc., brought to a boil, and the aluminum hydroxide precipitated with ammonia according to the method of Blum (*2*). The precipitate was transferred to the original beaker, and dissolved in 10 cc. of concentrated hydrochloric acid and 100 cc. of hot water. The solution was heated to boiling and neutralized as before. A third precipitation was made in the same manner and the hydroxide precipitate filtered, dried, and burned off at 500° C., and then ignited for 1 hour at 1100° C., cooled, and weighed. The combined filtrates were evaporated in acid solution to 200 cc. and the magnesium was determined as phosphate by a double precipitation.

The results of this procedure on a series of nine alloys were invariably high and zinc was present in sufficient amount to account for the errors in the determination of aluminum. Several samples were precipitated as before, 5 cc. excess am-

---

[1] Received February 28, 1930. A thesis submitted in partial fulfilment of the requirements for the degree of master of science in physical chemistry from the Graduate School of the Pennsylvania State College.

monia over neutrality being added each time. The dissolved aluminum hydroxide was recovered in the filtrate by a double precipitation. The combined precipitates were dried, ignited, and weighed. These determinations were high and zinc was again found in sufficient quantity to account for the error. Additional precipitations using 10 grams of solid ammonium chloride upon the second precipitation gave results little better than the preceding determinations.

(6) The method of Gooch and Havens (*8*), although applicable to some separations, need hardly be considered. It is not only tedious, but with the various inaccuracies of the method and the necessity for small volume and consequently a small sample the value of the result would be questionable.

The unsatisfactory nature of these methods made it seem desirable to investigate any method which gave promise of being more convenient and more accurate. For this reason a study was made of an electrolytic method, using mercury as a cathode.

Review of Literature on Mercury Cathode

Numerous references to the use of the mercury cathode are found in the literature. Gibbs (*7*) first used the mercury cathode. Smith (*15*) applied this method to the determination of zinc and later showed that it was possible to separate quantitatively iron, cobalt, nickel, zinc, cadmium, and copper from the respective sulfate solutions (*14*). Kimley (*10*) showed that accurate determinations of copper and zinc could be made in this way, but Price (*13*) stated that the results obtained with zinc were low. The early investigators weighed the amalgam formed and made no application of the possible separation of various cations in the solution.

Drown and McKenna (*6*) separated iron and aluminum by this method and Smith (*16*) showed that chromium would also form an amalgam. Meyers (*12*) separated chromium from aluminum and molybdenum from vanadium, and Smith (*15*) quantitatively removed iron from titanium, uranium, zirconium, and thorium solutions.

Cain (*4*) gives a method for the determination of vanadium in steel and a sketch of a special cell for this electrolysis. Lundell, Bright, and Hoffman (*11*) apply the same method with slight modification to the determination of vanadium in steel. Brophy (*3*) used the mercury cathode to separate iron in the determination of aluminum in special steels.

Hillebrand and Lundell (*9*) state that by means of the mercury cathode titanium, zirconium, phosphorus, arsenic, vanadium, uranium, and aluminum can be quickly and quantitatively separated from elements such as iron, chromium, zinc, nickel, cobalt, tin, molybdenum, copper, bismuth, and silver.

From a consideration of the various separations which are recorded in the literature it seemed very probable that a complete separation of aluminum from zinc, copper, cadmium, lead, tin, and iron could be obtained by using a mercury cathode and working with sulfate solutions of low acid concentration. The magnesium, because of its high decomposition potential, would be found in the solution after electrolysis with the aluminum. Under these conditions it would be unnecessary to remove any element from a zinc-base alloy before electrolysis. The rapidity and ease with which such a separation could be effected would give a very desirable method for the analysis of these alloys.

An investigation was made therefore of the conditions under which such separation is possible, and the completeness of separation and accuracy of determination.

Experimental Work

A standard solution having the approximate composition of sample A, Table I, was made from metals of known purity. The analysis of the materials used is given in Table II.

Table II—Analysis of Metal Used in Standard Solutions

	ZINC[a]		ALUMINUM[b]		COPPER (ELECTROLYTIC)		MAGNESIUM (DISTILLED)
	Per cent		*Per cent*		*Per cent*		*Per cent*
Cd	0.002	Si	0.003	Cu	99.921	Si	0.005
Fe	0.002	Fe	0.012	Pb	0.013	Fe	0.004
Pb	0.0029	Cu	0.014			Al	0.006
As	0.000008	Al	99.971 (diff.)			Mg	99.985 (diff.)
Zn	99.993						

[a] New Jersey Zinc Company.
[b] Aluminum Company of America.

The standard solution was made by dissolving 0.5703 gram of copper, 0.8078 gram of aluminum, 0.0249 gram of magnesium, and 18.5970 grams of zinc in 60 cc. of 1:1 sulfuric acid, 30 cc. of concentrated hydrochloric acid, 20 cc. of concentrated nitric acid, and 200 cc. of water. When solution was complete the volume was made up to 500 cc. in a calibrated flask and 50-cc. aliquots were evaporated and fumed for one-half hour to insure the complete removal of nitric and hydrochloric acids. The samples were cooled and 5 cc. of 1:1 sulfuric acid and 100 cc. of water were added. The solution was boiled to complete the solution of the salts and then cooled and transferred to a 200-cc. electrolytic beaker containing approximately 200 grams of mercury. A current strength of 1 ampere per 6.25 sq. cm. was found to be most satisfactory. Constant agitation of the solution was maintained by means of compressed air. Figure 1 shows a diagram of the apparatus.

After 7 hours the electrolysis was complete and the solution was siphoned off, the beaker and electrode being washed three times before the circuit was broken. The current was then turned off and the mercury shaken with 25 cc. of water to remove the last of the electrolyte. To this solution 10 cc. of concentrated hydrochloric acid were added and the aluminum was precipitated by the method of Blum (*2*), by a double precipitation. The magnesium was determined in the filtrate by a single precipitation as phosphate.

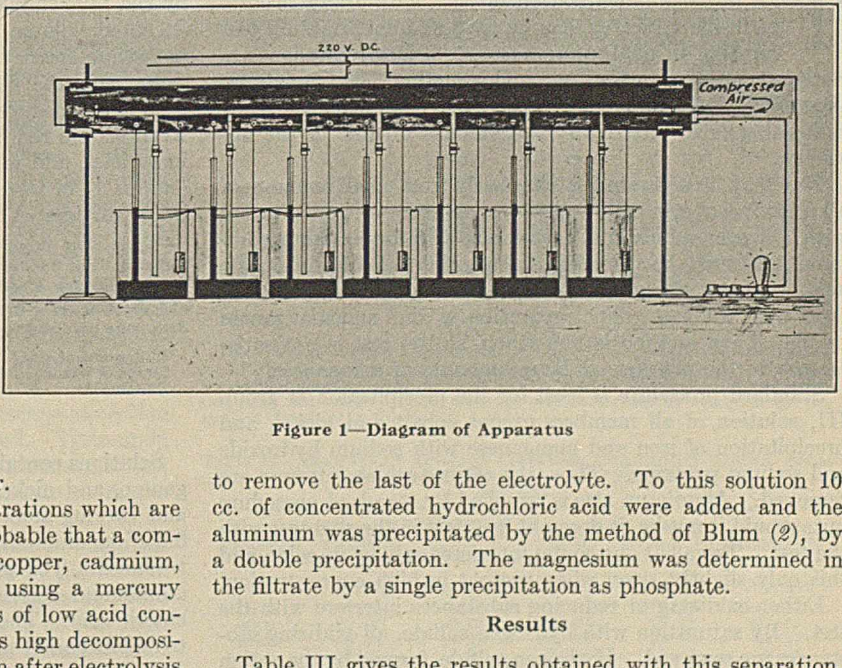


Figure 1—Diagram of Apparatus

Results

Table III gives the results obtained with this separation. The average deviation of the aluminum determination is 1 part in 320, and no deviation is found in the magnesium determination. It is concluded from these results that a rapid and accurate method for the separation and determination of aluminum and magnesium in zinc-base alloys is possible by using the mercury cathode.

Table III—Results Obtained with Mercury Cathode Using a Standard Solution

Taken *Gram*	Found *Gram*	Error *Gram*	Free H_2SO_4 *Gram per cc.*
		ALUMINUM	
0.0808	0.0809	+0.0001	0.044
0.0808	0.0802	−0.0006	0.044
0.0808	0.0807	−0.0001	0.044
0.0808	0.0806	−0.0002	0.044
		MAGNESIUM	
0.0025	0.0025	0.0000	0.044
0.0025	0.0025	0.0000	0.044
0.0025	0.0025	0.0000	0.044
0.0025	0.0025	0.0000	0.044

The results obtained with Bureau of Standards zinc-base die-casting alloys are recorded in Table IV. Equally concordant results have been found in the case of other zinc-base alloys (about sixty in number) of known composition obtained from other sources.

Table IV—Results Obtained with Bureau of Standards Zinc-Base Die-Casting Alloys

	Bureau of Standards			Hg Cathode Method		
	A	B	C	A	B	C
Al	4.04	4.04	0.58	4.03	4.00	0.56
Mg	0.11	0.10	Not detected	0.12	0.11	0.00

Recommended Procedure

The following method was adopted for the separation of aluminum and magnesium in zinc-base alloys:

Dissolve a 2-gram sample of alloy with 20 cc. of 1:1 sulfuric acid and 100 cc. of water. When all action has ceased, transfer this solution containing the undissolved copper to the electrolytic beaker. The copper will alloy with the mercury. Electrolyze the solution for 5 hours and complete the analysis as described under Experimental Work.

Acknowledgment

The author wishes to thank H. V. Churchill, chief chemist, Aluminum Company of America, for permission to use the data, R. W. Bridges for valuable suggestions and criticism during the course of the work, and the New Jersey Zinc Company for a sample of high-purity zinc.

Literature Cited

(1) Ardagh and Bongard, Ind. Eng. Chem., **16**, 297 (1924).
(2) Blum, *J. Am. Chem. Soc.*, **38**, 1282 (1916).
(3) Brophy, Ind. Eng. Chem., **16**, 963 (1924).
(4) Cain, *Ibid.*, **3**, 476 (1911).
(5) Demorest, *Ibid.*, **5**, 302 (1913).
(6) Drown and McKenna, *J. Anal. Chem.*, **5**, 627 (1891).
(7) Gibbs, *Am. Chem. J.*, **13**, 571 (1891); *Chem. News*, **42**, 291 (1880).
(8) Gooch and Havens, *Am. J. Science*, [4] **2**, 416 (1896).
(9) Hillebrand and Lundell, "Applied Inorganic Analysis," p. 390, Wiley 1929.
(10) Kimley, *J. Am. Chem. Soc.*, **32**, 637 (1910).
(11) Lundell, Bright, and Hoffman, Ind. Eng. Chem., **15**, 1064 (1923).
(12) Meyers, *J. Am. Chem. Soc.*, **26**, 1124 (1904).
(13) Price, *J. Soc. Chem. Ind.*, **26**, 345 (1907).
(14) Smith, "Electro-Chemical Analysis," p. 55, Blakiston's, 1907.
(15) Smith, *J. Am. Chem. Soc.*, **25**, 883 (1903).
(16) Smith, *Ibid.*, **27**, 1255 (1905).

Confirmatory Test for Zinc[1]

J. Stanton Pierce and Ethyl D. Nave

Transylvania College, Lexington, Ky.

THE ferrocyanide titration of zinc, with uranyl acetate as inside indicator, can be used as a confirmatory test for zinc in qualitative analysis, if interfering ions are removed previous to the test. This method has the advantage over most confirmatory tests that it affords a means of estimating fairly accurately the amount of zinc in the unknown.

Zinc may be separated satisfactorily from small amounts of all members of group III cations except iron, by precipitation with hydrogen sulfide in 1 *N* acetic acid solution containing ammonium acetate, by filtration, and solution in 1 *N* hydrochloric acid. A trace of iron, particularly if in the ferric state, interferes with the test. The separation of zinc and manganese by the above method is not sharp, so the test is not satisfactory in the presence of large amounts of manganese.

Standard procedure is used for the precipitation of group III, solution of all members except cobalt and nickel, and precipitation of iron and manganese with sodium hydroxide and sodium peroxide. Thus, the cations which interfere are removed. Aluminum also is removed by standard procedure but, should it not be, it does not interfere in the slightest with the test. Trivalent chromium interferes only by its color, and this only slightly, even when present in high concentration.

Either oxidizing or reducing substances interfere with the test. By saturation with hydrogen sulfide, all oxidizing substances are removed. Hydrogen sulfide, formed by the action of hydrochloric acid on zinc sulfide, is removed by evaporation to dryness. The residue is dissolved in a small volume of 1 *N* acetic acid.

The titration may be carried out with sufficient accuracy by the following method: To the acetic acid solution add an equal volume of 0.01 *N* uranyl acetate and add 0.5 *N* potassium ferrocyanide from a medicine dropper (15 to 17 drops per cubic centimeter), noting the number of drops required to produce a distinct reddish brown color. If over 15 drops are required, or if the precipitate is colored due to impurities, add more uranyl acetate. The number of drops (minus 1) of ferrocyanide represents the approximate number of milligrams of zinc in the unknown.

Note—The dropper used gave 17 drops per cc. Actually, 1 drop corresponds to 0.96 mg. of zinc, but the method is not accurate enough to warrant making a correction for this. By using a standard zinc solution and titrating directly (without precipitating as sulfide, etc.), the following data were obtained:

Milligrams of zinc	0	2.5	5	10	25	50
Drops of ferrocyanide	1	4	6	12	28	54

Test of Method

Solutions containing 5 mg. each of aluminum, cobalt, manganese, and nickel, and 100 mg. of chromium as chromate, and varying amounts of zinc, were made 1 *N* in acetic acid, 0.2 *N* in ammonium acetate, and hydrogen sulfide was introduced. The precipitate was filtered, washed with dilute ammonium chloride solution, and dissolved in 1 *N* hydrochloric acid. The hydrochloric acid solution was evaporated to dryness and the residue was dissolved in 2 cc. of 1 *N* acetic acid. Titration was carried out as indicated above.

Zinc, mg.	0	2.5	5	10	25	50
Ferrocyanide, drops	1	2	5	8	23	50

As is evident from the amount of ferrocyanide used for the lower concentrations of zinc, a little zinc is lost, probably as the sulfide.

---

[1] Received September 16, 1929. Revised paper received January 4, 1930.

Determination of Total Nitrogen of Plant Extracts in Presence of Nitrates[1]

George W. Pucher, Charles S. Leavenworth, and Hubert Bradford Vickery

Biochemical Laboratory, Connecticut Agricultural Experiment Station, New Haven, Conn.

The observation of Ranker that the salicylic acid–zinc method does not give quantitative results when applied to aqueous extracts of plant tissue that contain nitrates has been confirmed. An error due to the loss of from 40 to 95 per cent of the nitrate nitrogen may occur. The total nitrogen of such extracts may, however, be quantitatively determined if a preliminary reduction of the nitrates with reduced iron powder and dilute sulfuric acid is carried out, followed by Kjeldahl digestion with sulfuric acid in the customary way. This method was originally suggested by Olsen for use in determining the nitrogen content of soils and its application to plant extracts is herein described.

Extracts of green tobacco leaves grown under different conditions have been found to contain widely variable proportions of the total nitrogen as nitrate (*6*). More than 30 per cent of the water-soluble nitrogen is sometimes present in this form, although smaller proportions are perhaps more usual. The presence of nitrate nitrogen necessitates the use of special methods for the determination of the total nitrogen in such extracts, and the writers' attempts to employ the salicylic acid–zinc method (*1*) have substantiated the results of Ranker (*5*), who found that this method cannot be successfully used to determine nitrogen in aqueous solutions although it is perfectly satisfactory when applied to properly dried material. The writers have therefore developed a method for the determination of nitrogen in the presence of nitrates that can be applied directly to aqueous solutions. A description of this method and data illustrating the errors that may arise when the salicylic acid–zinc method is improperly used are herein presented.

Analyses by Salicylic Acid–Zinc Method

Table I gives the results of analyses by the salicylic acid–zinc method of 10- and 20-cc. portions of a series of tobacco-leaf extracts. Although duplicate analyses agree moderately well with each other, it is clear that material losses of nitrogen occur during the digestion of the larger samples. Furthermore, a serious error even in the analysis of the smaller samples becomes evident when the amount of nitrogen found by this method is compared with the nitrogen content of the extract calculated from the difference in the amounts of nitrogen in the leaf material before and after extraction. These results are in accord with Ranker's view that water, present during the treatment of the sample with the acid reagent, gives rise to side reactions which involve loss of nitrogen. The insidious nature of this difficulty is apparent when it is recalled that such losses may escape detection entirely if nitrogen balances are not calculated. Tests upon extracts which contain a high proportion of nitrate nitrogen emphasize this error, but it is of equal importance in the analysis of extracts of low nitrate content.

In Table II are presented data secured from the analysis of mixtures of the products of acid hydrolysis of the protein edestin with known amounts of potassium nitrate in ratios of nitrate to total nitrogen varying from 8 to 50 per cent. The losses of total nitrogen shown in column 5 varied from 7 to 22 per cent. On the assumption that the entire error is due to loss of nitrate nitrogen, the figures in column 6 show that this varied from 43 to 96 per cent. These data are especially significant since the solution analyzed simulates in many respects the composition of a plant extract. It is clear that the analysis by the salicylic acid–zinc method of samples of plant extracts that contain water cannot be conducted without the danger of loss of much of the nitrate nitrogen.

Development of New Method

Attention was therefore directed to the development of a procedure that might be conveniently applied to aqueous solutions containing nitrates. Methods involving the reduction of the nitrate in the solution by means of Dvarda's alloy were not considered because of the close attention required to the details of the procedure. Ranker's method of drying the samples at exact neutrality in the Kjeldahl flasks before digestion with salicylic acid–thiosulfate mixture calls for a considerable expenditure of time. The present writers therefore turned to the use of reduced iron powder in dilute acid as a means for the reduction of the nitrate to ammonia before the application of the Kjeldahl digestion process.

Table I—Analyses of Tobacco Extracts by Salicylic Acid–Zinc Method

Sample	N in 8 Liters of Extract[a]	N Found in 8 Liters of Extract from Analysis of: 20-cc. aliquot	10-cc. aliquot	Error Due to Loss of N: 20-cc. aliquot	10-cc. aliquot
	Grams	*Grams*	*Grams*	*Per cent*	*Per cent*
E	110	68.7 69.3	81.8 81.8	37.2	25.7
A	178	132.9 134.0	152.3 152.3	25.0	14.7
B	177	127.8 128.4	143.1 142.0	27.6	19.5
C	168	128.9 129.5	139.7 138.6	22.9	17.1

[a] The figures for the total nitrogen in these extracts were calculated from the difference in the nitrogen in the dry leaf before and after extraction with hot water. Their accuracy was confirmed by analyses by the method described in this paper.

Table II—Analyses of Aqueous Solutions Containing Amino Acids and Potassium Nitrate by the Salicylic Acid–Zinc Method

Volume Analyzed	Total N Present	Nitrate N / Total N	Total N Found	Loss of Total N	Loss of Nitrate N[a]
Cc.	*Grams*	*Per cent*	*Grams*	*Per cent*	*Per cent*
15.0	19.13	51.75	14.91	22.06	42.63
30.0	32.97	30.03	25.28	23.31	77.67
27.0	26.98	14.49	23.29	13.68	94.37
26.0	25.05	7.81	23.15	7.57	95.96

[a] Calculated on the assumption that the entire loss falls upon the nitrate nitrogen.

A method for the determination of the total nitrogen of soils, which involved reduction of the nitrates with iron powder, has been described by Olsen (*4*), but no data on the application of this procedure to the analysis of plant

---

[1] Received December 19, 1929. The expenses of this investigation were shared by the Connecticut Agricultural Experiment Station and the Carnegie Institution of Washington, D. C.

extracts were given by him. The reaction of dilute sulfuric acid on reduced iron powder has been widely used for the quantitative reduction of nitrate to ammonia in analytical procedures. Jones (*2*) has reported quantitative recoveries of nitrate by this method, as have Vickery and Pucher (*6*). McCandless and Burton (*3*) have reported incomplete recoveries by this method. The analyses in Table III were therefore conducted in order to furnish an additional check upon Olsen's statement that the amount of reduced iron employed influences the completeness of the reduction. In columns 2 and 3 are given results of the analyses of different amounts of potassium nitrate using 2 grams of reduced iron. The low recoveries indicate that this is insufficient. When 3 grams of reduced iron were used, however, the average recovery was 99.46 per cent, which agrees with the results of Olsen, who used 5 grams and obtained a recovery of 99.5 per cent. It is highly probable that different lots of reduced iron powder differ in quality, and before use each lot should therefore be tested in this respect as well as for its content of nitrogen. The fact that the results are almost invariably slightly low suggests that a small but ordinarily negligible loss of nitrate nitrogen occurs.

Table III—Determinations of Nitrogen in Potassium Nitrate Solution Using Reduced Iron Powder Method

NITRATE N PRESENT	2 GRAMS REDUCED IRON		3 GRAMS REDUCED IRON	
	Nitrate N found	Recovered	Nitrate N found	Recovered
Mg.	*Mg.*	*Per cent*	*Mg.*	*Per cent*
9.90	9.78	98.79	9.80	98.99
9.90	9.37	94.64	9.80	98.99
19.80	18.03	91.05	19.74	99.70
19.80	18.74	94.62	19.60	98.99
19.80	...	...	19.60	98.99
29.71	26.84	90.36	29.54	99.43
29.71	27.12	91.31	29.54	99.43
29.71	...	...	29.54	99.43
39.60	37.06	93.57	39.90	100.7
39.60	35.50	89.64	39.48	99.70
39.60	...	...	39.48	99.70
Average		92.99		99.46

It is clear, therefore, that, when properly used, reduced iron may be depended upon to effect practically complete reduction of the nitrates present in a plant extract and since these, in general, form only a small proportion of the total nitrogen, the small error may in most cases be safely disregarded.

Reduced Iron-Powder Method

The sample is delivered from a pipet into a Kjeldahl flask (700 cc.) and diluted to 30–40 cc. with distilled water; 10 cc. of 1:1 sulfuric acid and 3 grams (±0.3) of reduced iron powder are added. A funnel is placed in the neck of the flask, which is shaken at room temperature for 10 minutes and then slowly heated and the contents boiled for 5 minutes. The flask is cooled and 30 cc. of concentrated sulfuric acid, a drop of mercury (0.5 gram), a few angular quartz pebbles, and 5 grams of anhydrous sodium sulfate are added. The flask is heated slowly to evaporate the water and the contents are digested in the usual way until the acid layer is clear and the precipitate assumes a yellow color. Heating is then continued for 1 to 2 hours more. A few crystals of potassium permanganate are dropped into the hot acid, which is then cooled and diluted with 300 cc. of water; 3 to 5 grams of sodium thiosulfate and a small piece of paraffin are added. An excess of sodium hydroxide and a little zinc are then introduced and the ammonia is distilled into standard acid in the usual way.

It is important that the reduction of the nitrate be carried out with careful attention to the prescribed volumes of water and acid; otherwise loss of nitrogen may occur. The evaporation of the solution before the digestion is sometimes troublesome, since bumping may take place in the early stages and, as the acid concentration increases, a heavy froth may form. After this stage is passed, however, digestion runs smoothly and more rapidly than is usually the case with salicylic acid digestions. The addition of the sodium sulfate and of the mercury is essential to a smooth and rapid digestion. After the dilution of the digest any cake of salt at the bottom of the flask must be dissolved before adding the alkali. The initiation of boiling during the distillation is sometimes accompanied by violent frothing, although this seldom becomes uncontrollable if due care is exercised. The contents of the flask should be black during the distillation; if they are red or brown an insufficient amount of alkali has been added. Blank determinations on the reagents, especially the reduced iron powder, must be conducted.

Accuracy of Method

Table IV gives the results obtained on solutions containing mixtures of the products of hydrolysis of the protein edestin and potassium nitrate. The total nitrogen content of the hydrolysate was established by ordinary Kjeldahl determinations and four mixtures with different ratios of nitrate nitrogen to total nitrogen were prepared. The recovery of nitrogen from these mixtures was extremely good and indicates that the method gives satisfactory results.

Table IV—Analyses of Mixtures of a Solution of Amino Acids with Potassium Nitrate by the Reduced Iron-Powder Method

TOTAL N PRESENT	NITRATE N PRESENT	$\frac{\text{NITRATE N}}{\text{TOTAL N}}$	TOTAL N FOUND	RECOVERY OF TOTAL N
Mg.	*Mg.*	*Per cent*	*Mg.*	*Per cent*
19.13	9.90	51.75	19.31	100.9
			19.45	101.6
			19.45	101.6
			19.03	99.59[a]
			19.17	100.2
Average				100.78
32.97	9.90	30.03	32.94	99.91
			32.94	99.91
			32.90	99.79
Average				99.87
26.98	3.91	14.49	27.12	100.5
			26.84	99.47
			27.12	100.5
			26.99	100.0
Average				100.01
25.05	1.98	7.81	24.99	99.75
			24.99	99.75
			24.85	99.45
Average				99.65
Grand average				100.08

[a] 0.5 gram sucrose added before reduction.

Table V—Total Nitrogen in Samples of Dry Tobacco by Reduced Iron-Powder Method and by Salicylic Acid–Zinc Method

SAMPLE	IRON REDUCTION METHOD		SALICYLIC ACID–ZINC METHOD	
	Per cent		*Per cent*	
1	4.58 4.49	4.54	4.60 4.42	4.51
2	4.38 4.47	4.43	4.54 4.48	4.51
3	4.82 4.86	4.84	4.84 4.86	4.85
4	5.01 5.03	5.02	4.83 4.91	4.87
5	3.27 3.41	3.34	3.38 3.30	3.34

As a final check upon the accuracy of the method a series of dry samples of tobacco was analyzed by the new method and by the standard salicylic acid–zinc method. The samples contained approximately 20 per cent of the total nitrogen in the form of nitrate. The data (Table V) show that the two methods lead to practically identical results; they further demonstrate that the new method can be safely employed for the determination of the total nitrogen in solutions of the complex mixture of substances found in leaf tissue.

Literature Cited

(1) Assocn. Official Agr. Chem., Methods, 1925, p. 9.
(2) Jones, IND. ENG. CHEM., **19**, 269 (1927).
(3) McCandless and Burton, *J. Assocn. Official Agr. Chem.*, **10**, 216 (1927).
(4) Olsen, *Compt. rend. trav. lab. Carlsberg*, **17** [3], 1 (1927).
(5) Ranker, *J. Assocn. Official Agr. Chem.*, **10**, 230 (1927).
(6) Vickery and Pucher, IND. ENG. CHEM., Anal. Ed., **1**, 121 (1929).

Titrometric Determination of Magnesium[1]

J. Stanton Pierce and M. B. Geiger

GEORGETOWN COLLEGE, GEORGETOWN, KY.

MAGNESIUM has been determined titrometrically in the presence of calcium by the use of the hydrogen electrode (*2*, *4*), with trinitrobenzene as indicator (*7*), and in 66 to 75 per cent alcohol solution with thymolphthalein as indicator (*9*). In the absence of calcium, magnesium has been determined by precipitation of the hydroxide with excess alkali, separation of the precipitate and solution, and titration of the excess alkali in an aliquot of the solution (*3*, *8*). However, in the presence of a high concentration of calcium salts this method fails unless some means is used to indicate the completeness of precipitation of magnesium, for on the addition of more alkali calcium also is precipitated.

Since calcium is associated so frequently with magnesium in nature and in manufactured products, and since the determination of magnesium in such mixtures often is very important, there is need for a practical, rapid, convenient, and fairly accurate laboratory method for the determination of magnesium in the presence of calcium. Direct titration of a neutral solution with alkali, using trinitrobenzene as indicator (*7*), gives results accurate enough for most control work, but requires a matching of colors. The method worked out in this laboratory for the determination of magnesium in cement (*6*) gives fair results, but the filtration and washing of the gelatinous precipitate of magnesium hydroxide is tedious if this precipitate is large. Also, if the time required for this operation is long, there is danger of adsorption of carbon dioxide from the air and precipitation of calcium carbonate with the magnesium hydroxide.

Since the time factor determines the value of analytical procedures in industrial laboratories, the work on magnesium was continued so that the tedious filtration could be avoided and the method made more universal.

In this work magnesium is precipitated as the hydroxide, with standard carbonate-free alkali. When the end point for trinitrobenzene (a dark brick red) is obtained, the calcium remains in solution. The solution containing the precipitate is diluted to a definite volume, an aliquot filtered, and the excess alkali titrated.

The accuracy of this method depends, not on the sharpness of the break of the neutralization curve in the titration of magnesium with alkali, but on the completeness of the precipitation of magnesium, with calcium remaining in solution, and the end point when the excess alkali is titrated with acid. This end point is around a pH of 4, and is quite definite. Kolthoff (*4*) states that calcium hydroxide does not precipitate in 0.01 *N* sodium hydroxide and in this work its concentration does not become half so great.

Experimental Procedure

The following procedure for limestone, with slight modification, may be used for many substances containing magnesium. Dissolve sample of 0.500 gram in about 50 cc. of 0.25 *N* hydrochloric acid, boil out carbon dioxide, add 5 or 6 drops of 0.04 per cent alcohol solution of bromothymol blue, and add alkali until a blue color, indicating neutrality, is obtained. Filter and wash the precipitate, catching the washings in the same beaker as the original filtrate. To the filtrate add 5 drops of 0.1 per cent alcohol solution of dimethylaminoazobenzene and 0.25 *N* hydrochloric acid to the appearance of a faint pink. Add 10 cc. of a saturated alcoholic solution of trinitrobenzene and titrate with 0.25 *N* carbonate-free sodium hydroxide (B_1) to the appearance of a deep red color. Transfer the solution to a 100-cc. volumetric flask and continue titration, if necessary, to hold the deep red color. Dilute to 100 cc., mix, and filter through a dry filter paper into a dry beaker, keeping the funnel covered with a watch glass as much as possible. Pipet 50 cc. of the filtrate and add an indicator which at a pH of about 4.0 has a color change easily recognizable in a reddish solution. Titrate with 0.25 *N* hydrochloric acid (A_1) to the color change of the indicator.

A sufficiently close approximation of the per cent magnesium oxide is as follows:

$$B_1 - 2A_1 = \text{per cent MgO}$$

Solutions of samples containing no cation whose hydroxide is insoluble at neutrality are treated as is the neutral filtrate mentioned above.

LIMESTONES

Sample	MgO present	MgO found
	%	%
1	1.0	1.0
2	4.0	4.1
3	16.8	16.7

TECHNICAL SALTS OF MAGNESIUM CHLORIDE

Sample	Mg present	Mg found	
	%	%	
4	7.4	7.4	(contains $CaCl_2$)
5	12.2	12.4	
6	23.8	23.5	

With the same samples the magnesium was determined as described in the article on the determination of magnesium in cement (*6*). Satisfactory data were obtained, but the method is much longer than the one given above.

Instead of filtering an aliquot of the solution above, the sample may be centrifuged after precipitation of the magnesium hydroxide and a sample for analysis pipetted. If a large number of samples are to be run in which the magnesium content is not very high, it may be advantageous to place each solution, after dilution to 100 cc., in a tall cylinder to allow the precipitate to settle, and to pipet a sample of the supernatant liquid for titration.

Discussion of Method

Bromophenol blue was used as indicator for obtaining the data given above. This is a satisfactory indicator if an aliquot of the alkaline filtrate is titrated right away. Trinitrobenzene in alkaline alcoholic solution readily changes to some compound which retains a distinct red color after

---

[1] Received March 21, 1930.

Note—Hepp (*1*) obtained a product with properties of a nitrated phenol by allowing an alcoholic solution of trinitrobenzene to stand for a short time with 2 mols of potassium hydroxide. Lobry de Bruyn (*5*) obtained 3,5,3′,5′-tetranitroazobenzene and dinitrophenol by boiling trinitrobenzene with dilute sodium carbonate or by allowing the mixture to stand at room temperature for 3 days. Sodium hydroxide reacted similarly slowly at room temperature.

acidification. In such a solution the color change of bromophenol blue cannot be detected easily. Congo red is a satisfactory indicator in such cases, and good results were obtained by using it, for the change from red to blue-violet is detected with ease in the presence of a high concentration of the product from trinitrobenzene.

Neither Congo red nor bromophenol blue is as satisfactory as dimethylaminobenzene as an indicator for adjusting the acidity before the initial titration. The red color of Congo red in alkaline solution interferes with the end point of trinitrobenzene. If the final titration is made with bromophenol blue as indicator, the end point is located more quickly if one is warned of its approach by the decrease in the depth of the trinitrobenzene color. The presence of bromophenol blue in the solution increases the difficulty of recognizing this point, so this indicator is not added until the solution is about neutral.

A slight error is introduced by using one indicator for the initial adjusting of the acidity of the solution and another for the final titration. The error thus introduced, however, does not exceed 0.1 per cent of MgO.

Acknowledgment

Acknowledgment is made to the Dow Chemical Company for the analyzed samples of magnesium chloride salts used in the determinations.

Literature Cited

(1) Hepp, *Ann.*, **215**, 360 (1882).
(2) Hildebrand and Harned, *8th Intern. Cong. Appl. Chem.*, **1**, 217 (1912).
(3) Kolthoff, *Z. anorg. allgem. Chem.*, **112**, 172 (1920).
(4) Kolthoff, *Rec. trav. chim.*, **41**, 787 (1922).
(5) Lobry de Bruyn, *Ibid.*, **13**, 151 (1894).
(6) Pierce and Setzer, IND. ENG. CHEM., Anal. Ed., **1**, 25 (1929).
(7) Pierce and Setzer, with Peter, IND. ENG. CHEM., **20**, 436 (1928).
(8) Rhodes, *J. Soc. Chem. Ind.*, **46**, 159 (1927).
(9) Willstätter and Waldschmidt-Leitz, *Ber.*, **56**, 488 (1923).

Multiple Standard Colorimeter for pH Determinations[1]

S. L. Leiboff

BIOCHEMICAL LABORATORY, LEBANON HOSPITAL, NEW YORK, N. Y.

THIS colorimeter was especially designed for matching colors of unknown solutions where a single standard cannot be used, particularly in colorimetric hydrogen-ion determinations of wide range.

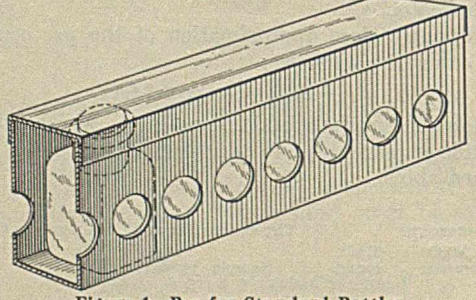


Figure 1—Box for Standard Bottles

Usually such determinations are done in test tubes in a block comparator where the tubes are placed side by side and the color differences observed. In the colorimeter here described all the standards are contained in small, rectangular bottles of uniform size with two opposite parallel plane sides, the distance between which is uniform in all the bottles.[2] This allows the passage of light through equal depths of solution. The standard bottles are placed close together in a a black rectangular box. (Figure 1) This box contains circular fenestræ on two opposite sides parallel to each other. Each bottle fits snugly between a pair of fenestræ, thus allowing the light to pass through a uniform depth of solution with all the standards.

Figure 2 shows the colorimeter with the standards in place. It consists of compartment *A*, which contains two mirrors, *M* and *M′*, placed at an angle of 45 degrees and parallel to each other. Mirror *M′* is half the size of mirror *M*. The cylinder *B* carries a magnifying lens, *L*, and an eyepiece, *E*. To facilitate the reading the reading tube itself may be sloped, with the mirrors tilted at an appropriate angle.

For the determination of pH the following arrangement is used: In compartment *C* are placed the unknown, standards, and compensators. Bottle 1 contains the unknown solution with the appropriate indicator. Bottle 2 contains distilled water. Bottle 3 contains the unknown solution, but without indicator, to compensate for cloudiness and color of the unknown. The box containing the standards is placed at 4 and is moved along the stage *S* horizontally by means of a rack and pinion, *RP*, with the thumb screw *TS*. This box is moved along on the stage while the operator is looking through the eyepiece until the closest match is obtained between the standard and the unknown. The light passing through the fenestræ *F* and *F′* is reflected upward by the mirrors—mirror *M′* covering one-half of mirror *M*, and produces, when viewed through the eyepiece, the effect of a circle, one-half representing the standard and the other half representing the unknown.

Comparisons may be made by artificial light by placing a few sheets of tissue paper between the source of light and the colorimeter in order to diffuse the light.

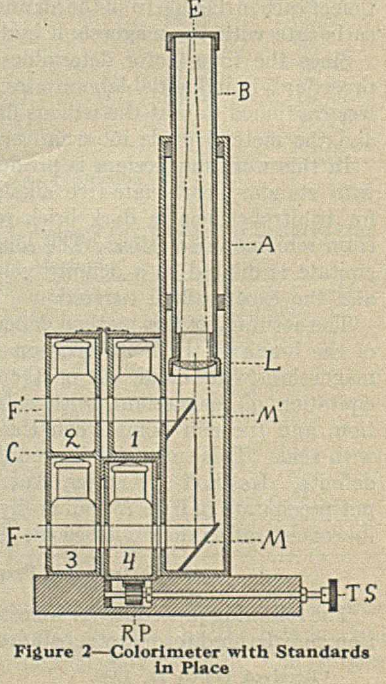


Figure 2—Colorimeter with Standards in Place

---

[1] Received December 13, 1929.

[2] Very suitable bottles are Nos. 31,190 and 31,192, Eimer & Amend Catalog, 1927, p. 705. These bottles are used for spectroscopic work and are inexpensive.

Modified Peterson-Palmquist Apparatus for the Determination of Carbon Dioxide in Air[1]

Edwin P. Jones

Duke University, Durham, N. C.

A REVIEW of the literature dealing with the determination of carbon dioxide in air reveals many methods which seem to have fulfilled the requirements of the various investigators. The Peterson-Palmquist method was best suited for the problem of interest to the writer, and after an unsuccessful attempt to make use of what seemed to be the best apparatus of this type (*1*), the writer designed and constructed an apparatus which seems to possess advantages over its predecessors.

In principle, the decrease in volume at constant temperature and pressure of a known volume of air is measured subsequent to the absorption of the carbon dioxide in a concentrated solution of sodium hydroxide.

The modified apparatus consists essentially of (1) a bulb of known volume terminating in a uniform calibrated glass tube which is connected to a mercury leveling reservoir, (2) an absorption pipet, and (3) a manometer.

Manipulation

Detailed instructions for carrying out a determination follow. It is assumed that the apparatus has been constructed in accordance with the accompanying sketch and that the glass jar, *Q*, is filled with water which is being constantly agitated by means of a stirrer, *R*. The manometer, *M*, is filled to the bottom of the bulb *U* with water. The absorption pipet, *K*, is half filled with concentrated sodium hydroxide solution. The bulb *A* contains a few drops of water and the mercury reservoir, *C*, is partly filled with clean mercury.

With stopcocks *G*, *D*, *E*, and *F* open, increase the pressure in *K* by blowing through *P* until the caustic solution stands at a definite point in *L*, a capillary tube connecting *K* and *A*. Note the position of the water meniscus on the scale back of *M* and close *F*. Thus the air in *L* is at the pressure of the atmosphere. Close *E*. Raise the reservoir *C* until any air in *A* is forced out through *D* via *S*. The sample for analysis is drawn in through *D* via *T* by lowering *C* until the mercury meniscus is at a predetermined zero point in tube *I*. Allow to stand a few minutes (3 or 4 usually suffice) in order for the sample to attain the temperature of the bath and at the same time become saturated with water vapor. Open *D* to the atmosphere for a short time, keeping the mercury level on the zero point. Close *D*, open *E*, *G*, and *F*, and force the sample into *K* by raising *C*. Allow to stand about 2 minutes and lower *C* to bring the sample back into *A*. Close *G* and adjust to their initial positions both the water level in *M* and the absorbing liquid level in *L*. This is done by manipulation of *J* (a device for raising or lowering the mercury in *I* independent of *C*), *N* (a screw clamp to which have been soldered wide strips of heavy galvanized iron), *O* (a regular screw clamp), and *P*. Allow to stand 2 minutes and note the position of the mercury in tube *I*. This tube has been previously calibrated so that the relation between its volume for a given length and the total volume of *A* is known. Fifteen minutes usually suffice for a determination. In order to simplify the drawing the wooden support on which is mounted the stationary part of the apparatus has not been shown.

Calculations

The amount of carbon dioxide as determined represents the quantity present in saturated air at the temperature of the bath and at a given barometric pressure.

If the amount of carbon dioxide present in dry air (X) is desired, it is necessary to increase the value as above determined (A) by a factor which is dependent on the vapor pressure of water at the temperature of the bath.

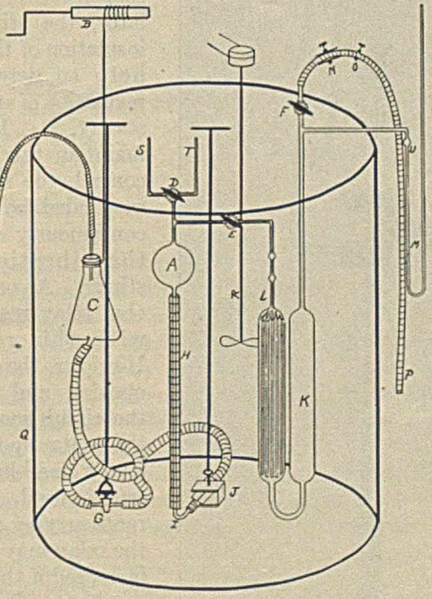
$$X = A + \frac{B - P}{B} A$$

B is the barometer reading and P is the vapor pressure of water at the bath temperature.

The quantity X can be further corrected to standard temperature and pressure by the application of the gas laws.

Advantages of Apparatus

The obvious advantages of this piece of apparatus are twofold. There are no rubber connections in that part of the apparatus that is in contact with the sample; and the number of stopcocks in contact with the sample has been reduced because the manometer is actuated by the movement of the liquid in the absorption pipet. Both of these advantages minimize the leakage of the sample and thus correspondingly increase the accuracy of the determination.



Accuracy of Method

In order to compare the accuracy of this method and a standard one, analyses were made of the same air–carbon dioxide mixture by two methods. The standard method chosen consisted in passing a known volume of an air–carbon dioxide mixture through an absorption train composed of two calcium chloride tubes, two absorption bulbs containing ascarite, and a third calcium chloride tube, in the order named. During the two runs neither the calcium chloride tube nor the second

---

[1] Received January 31, 1930.

ascarite bulb showed a change in weight. On this basis it was assumed that the change in weight of the first ascarite bulb represented the weight of the carbon dioxide contained in the known volume of the mixture. The volume used for these determinations was 2100 ml.

Three analyses of the air-carbon dioxide mixture were then made in the apparatus herein described. A tabulation of the results, expressed as parts of carbon dioxide by volume in 10,000 volumes of the mixture at 28° C. and 760 mm., is given below.

Run	Standard Method	Modified Peterson-Palmquist Method
1	115.3	118.2
2	115.8	117.6
3		119.4
Average	115.5	118.4

If care is exercised in the selection of a uniform capillary for tube *I*, the accuracy of the method may be correspondingly increased.

Literature Cited

(1) Anderson, *J. Am. Chem. Soc.*, **35**, 96 (1916).

Some Improvements in Thermoregulators[1]

Henry J. Wing

Bureau of Standards, Washington, D. C.

In a former paper (*4*) a new type of thermoregulator was described. One of its features was the fact that toluene could be used without danger of fouling the mercury surface.

In the further development of the regulator mentioned above a reservoir shaped as shown in Figure 1 has proved very effective. A thermostat made from an uninsulated 20-liter stoneware crock has been maintained for several hours at 37° C. with a variation, as measured by a Beckmann thermometer, of ±0.002° C. Of course, the type of heater, the relay, the suspension of the regulator, the stirring, and insulation of the bath all help to determine the regulation of any thermostat (*1*, *2*). In order to maintain this degree of control, the regulator is suspended so that it is continuously shaken by the vibration of the stirrer. An ordinary 20-ohm relay may be used with this regulator. However, the frequent opening and closing of the circuit soon wear out the contact points unless a very small heating current is used. The current-carrying capacity of the relay may be greatly increased if the ordinary contact points are removed and flat plates of pure silver, 10 mm. in diameter and 3 mm. thick and fastened by means of countersunk screws, are substituted. If a 0.5-microfarad condenser is used in parallel with these contact points, currents up to 2 amperes at 110 volts can be easily handled.

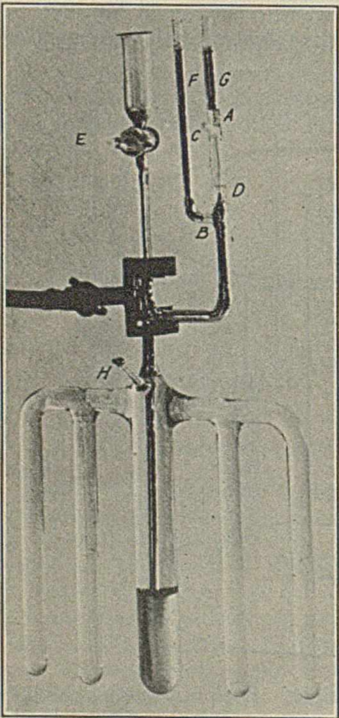


Figure 1—Thermoregulator

The new regulator is made entirely of Pyrex. The regulator head, the other new feature, may be sealed to any form of bulb. The contact leads at *A* and *B* are of tungsten, which can be sealed through the Pyrex. The bulb is filled with mercury and toluene and the whole heated to drive off dissolved air as described in the previous paper, or the toluene may be heated almost to boiling to expel the air and may then before it cools be filled in, through *H*, on top of the mercury. *H* is then sealed off.

The contact chamber is filled with hydrogen. This is accomplished by filling the whole regulator with mercury, the tube *C* being unsealed. A stopcock is then attached to *C* by means of rubber tubing. Hydrogen from a cylinder is allowed to enter, making sure that all connecting tubes are washed free from air, until the mercury is forced some distance below the contact point, *D*. The stopcocks at *C* and *E* are both closed and the hydrogen tube is removed. The stopcock at *C* is opened and *C* is immediately sealed off as shown. The expansion and escape of some of the hydrogen during the sealing process cause the mercury to be forced up above the contact point, *D*. If the height of the mercury above the contact *D* is not too great, the setting of the regulator is accomplished by suction through a tube fitted to the cup at *E* by means of a rubber stopper.

The use of Pyrex makes this new modification much easier to build than the old. In addition, this new design lessens the danger of breakage when making electrical connections. These connections are made through mercury in the cups *F* and *G*.

It has been pointed out (*1*) that iron is a better material for the contact point than platinum because mercury does not wet iron. It has been found that tungsten has this same advantage. Clean mercury in contact with the tungsten wire shows a depression around the wire, indicating no tendency to wet it.

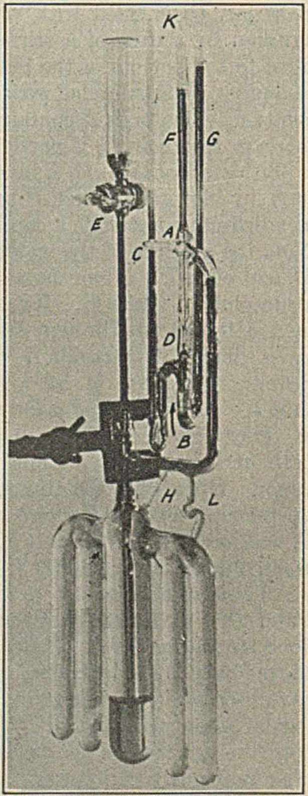


Figure 2—Thermoregulator of Sensitivity to 0.5° C.

The usual formation of oxide at the mercury contact surface

---

[1] Received January 20, 1930. Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

permits the use of only very small relay currents with most other regulators. Since the contact is always made in an atmosphere of hydrogen, the amount of current which may be used in this regulator is limited only by the volatilization of the mercury at the contact point. If too large currents are used, the mercury will spatter away and so cause the bath temperature to vary. Currents up to 0.5 ampere may be used if a small condenser is placed in parallel with the contact. However, better regulation is obtained with small currents.

In operation this regulator is entirely closed. Hence there is no danger of mercury vapors no matter what the temperature of the heated bulb may be, provided the pressure does not become too great for the instrument. Therefore this type of regulator has been used to control furnaces at temperatures even above the boiling point of mercury (*3*). This is accomplished by making the vertical distance from the heated bulb to the stopcock *E* about 30 cm. or more. The pressure of this column of mercury prevents the boiling of the mercury at temperatures well above its normal boiling point. If the heated bulb is horizontal, the mercury in the tube below *E* is not heated by convection. This is important in order that the grease in the stopcock may not be melted. Better regulation is obtained if capillary tubing is used.

The useful range of the mercury thermoregulator is thus extended from the freezing point to above the boiling point of mercury. Low-temperature furnaces may be easily regulated without resort to expensive equipment.

Less-Sensitive Thermoregulator

In many cases it is not necessary to control a constant-temperature bath to 0.001° or 0.01° C. There are bimetallic regulators on the market, for use in a thermostat, which will respond to a change of approximately 1.0° C. The regulator shown in Figure 2 is intermediate in sensitivity between the very sensitive mercury regulator and relay and the bimetallic regulator. It operates differently from the other in that the expansion of the regulator liquid directly opens the heating circuit. It will make and break a current of 0.5 ampere at 110 volts without trouble. It has been used with currents as high as 1.5 ampere at 110 volts. If more than 55 watts energy is required to heat the bath, it is supplied by other heaters so designed that they will not keep the bath at quite the desired temperature. The final heating is accomplished by a 50-watt heater in series with this regulator.

Its sensitivity is ±0.5° C. over a period of several hours. Changes in barometric pressure will have some effect on the temperature of the thermostat.

The entire regulator is made of Pyrex and the electrical lead wires are of tungsten. Varying amounts of hydrogen were tried in the contact chamber. A comparatively small amount, as indicated in the illustration, was most effective.

This regulator is filled with hydrogen in the same way as the one first described, but in the sealing-off process the tube *K*, Figure 2, must be tightly stoppered to prevent too much mercury or even air from being forced in through this side arm.

In Figure 2, *L* is a solid glass support for the side arm.

Literature Cited

(1) Beaver and Beaver, Ind. Eng. Chem., **15**, 359 (1923).
(2) Geer, *J. Phys. Chem.*, **6**, 85 (1902).
(3) Wing, Thesis, University of Iowa, 1929.
(4) Wing and Thompson, Ind. Eng. Chem., **17**, 1242 (1925).

Safety Device to Protect Heating Units[1]

F. H. Fish

Virginia Polytechnic Institute, Blacksburg, Va.

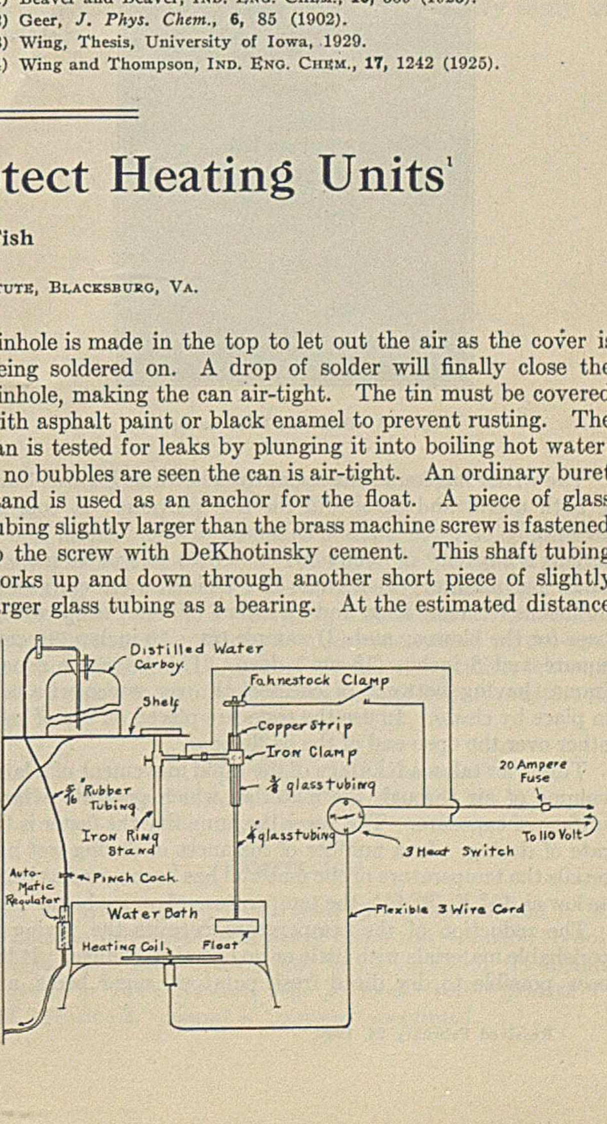
IN MANY laboratories electrically heated hot-water baths must be used, and frequently, especially in limestone regions, either rain or distilled water is necessary in order to prevent scale formation.

In many places the distilled water is made on certain days of the week and distributed in carboys to the smaller laboratories of the plant. If the supply runs out and the water bath becomes empty, the heating coil is ruined. In other laboratories where the city water is used, owing to the shutting off of the supply for some reason, heating units have been burned out no matter how careful the attendant has been.

The simple device described herein makes it impossible to burn out the heating unit, and will be especially appreciated if one has classes to attend while carrying on research or doing analyses requiring long, slow evaporations. A fuse, which costs 5 cents, is blown in the main circuit, thus cutting the heat off from the heating unit. The cost of the heating coil to one of these baths, 15 × 58 × 13 cm. deep, having seven holes, is $30.

Description of Parts

A small tin can 7.5 cm. in diameter and 2.5 cm. high is used as a float. A small No. 6 machine screw 4.5 cm. long is soldered in the center with the threads sticking up and out at the top. The cover is then soldered to the can. A small pinhole is made in the top to let out the air as the cover is being soldered on. A drop of solder will finally close the pinhole, making the can air-tight. The tin must be covered with asphalt paint or black enamel to prevent rusting. The can is tested for leaks by plunging it into boiling hot water; if no bubbles are seen the can is air-tight. An ordinary buret stand is used as an anchor for the float. A piece of glass tubing slightly larger than the brass machine screw is fastened to the screw with DeKhotinsky cement. This shaft tubing works up and down through another short piece of slightly larger glass tubing as a bearing. At the estimated distance



---

[1] Received February 1, 1930.

from the end of the shaft a No. 2 Fahnestock clip such as one finds on radio batteries is slipped on and a flexible wire is fastened to it in the usual way. A piece of thin copper sheet with a hole in it is extended from the clamp jaw up and over the end of the larger glass tubing.

Operation

When the safety device is operating, the single throw switch must be closed. As long as the Fahnestock rides high enough so that it does not touch the copper strip, no current flows through the flexible cord or the single-throw switch but may flow through the three-heat switch and thus heat up the water which is kept at a constant level. If the bottle of distilled water is allowed to become dry for any reason, the float will sink with the level of the water until the Fahnestock touches the copper strip, making a direct short-circuit across the 20-ampere fuse, which burns out immediately, thus cutting off the source of heat to the heating element.

A Rapid Bulk-Sample Drier[1]

T. H. Hopper

North Dakota Agricultural College, Fargo, N. D.

In the preparation of materials of plant or animal origin for chemical analysis it is frequently necessary to dry bulk samples to an air-dry condition. In such cases it is desirable and frequently necessary, in addition to rapid drying, to dry the material at a reduced temperature.

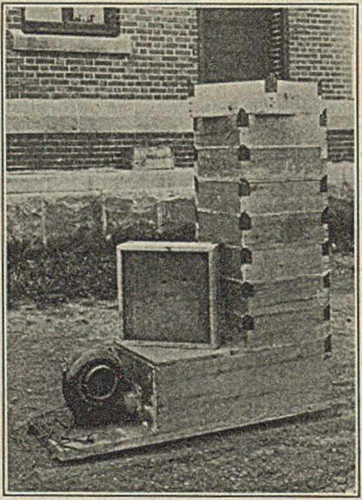


Figure 1—Drier for Bulk Samples

The writer has found the apparatus shown in Figures 1 and 2 both useful and successful for this purpose. It consists essentially of three parts: (1) motor driven volume blower having a capacity of about 300 cubic feet (8.5 cubic meters) of air per minute; (2) a baffle box 18 inches (46 cm.) wide, 36 inches (91 cm.) long, and 12 inches (30 cm.) deep, with a base for the blower; and (3) sample trays 18 inches (46 cm.) square and 6 inches (15 cm.) deep. The trays are square frames having bottoms of cheesecloth over screen wire held in place by cleats. In use the trays are placed on top of each other over the open end of the baffle box.

This drier takes advantage of the rapid movement of a large volume of air through the material, which presents a large surface of exposure. The lower the humidity the faster is the rate of drying. In a number of instances of drying wet materials the temperature of the material has been noted as being as low as 46° F. (8° C.), the temperature of an ice box.

The reduction of the temperature permits the drying of perishable materials with little or no chemical change. It has been possible to dry diced fresh potatoes, sugar beets, and mangel beets with but little if any oxidase reaction, and the dried ground sample was almost white.

That the drying of materials in this apparatus does not allow any appreciable changes in the nitrogen compounds has been observed in the case of bovine feces. No loss of nitrogen was observed, nor was there any change in the true and non-protein nitrogen.

For the drying of very wet, sticky, or pasty substances the cloth-bottom trays are not suitable, and a special box with glass plates, as shown in Figure 2, has been found practical. This box has a bottom of cheesecloth and screen wire as does the trays. One side of the box has a door for the introduction and removal of the glass plates. The glass plates are staggered so that the air must pass over one after the other. After the material has lost its sticky characteristics it is scraped from the plates onto the cloth of the bottom of the box, where it has greater exposure to the air current.

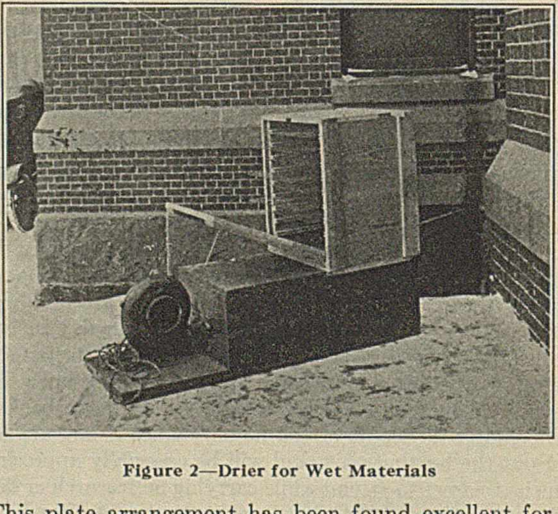


Figure 2—Drier for Wet Materials

This plate arrangement has been found excellent for the drying of ground lean meats for animal-feeding tests. With a room temperature of 72° F. (22° C.) and humidity of 44 per cent it has been possible to dry ground lean meat to a dryness that permitted grinding in a burr mill in less than 20 hours. The temperature of the meats, under these room conditions, during the removal of the major portion of the moisture has been observed to be as low as 48° F. (9° C.), averaging approximately 50° F. (10° C.). The dried meats have had the fresh odor of the raw material.

This drying apparatus has been duplicated by other workers, who have reported favorably regarding it. The writer has had one in use for more than eight years.

---

[1] Received February 24, 1930.

Improved Laboratory Condenser and Its Use in the Construction of Apparatus[1,2]

Edward S. West

Department of Biological Chemistry, Washington University School of Medicine, St. Louis, Mo.

A SIMPLE and efficient laboratory condenser of Pyrex glass was recently described by the writer (*1*). The essential points of construction are: a narrow space between jacket and inner tube, insuring a rapid flow of water; a thin inner tube for rapid heat transfer; and the whole welded into a compact, sturdy unit. Quite satisfactory condensers can be made by using a somewhat heavier wall inner tube and slipping the narrow water jacket on with rubber tubing, although they are not quite so efficient as the all-glass ones with thin wall tubes.

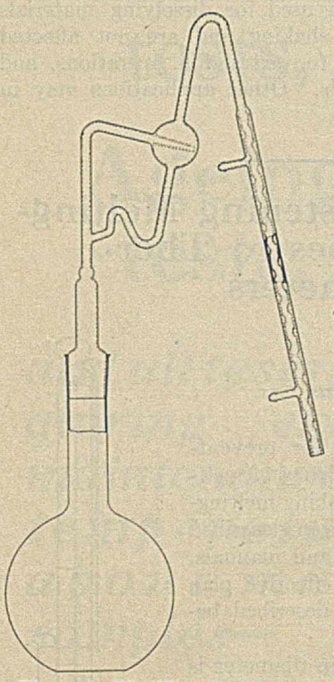


Figure 1—Distilling Apparatus with Trap

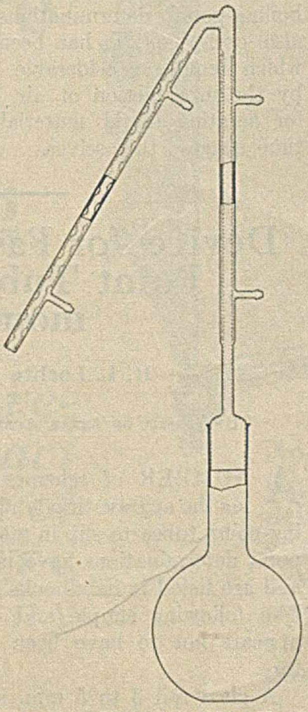


Figure 2—Reflux-Distilling Head with Condenser Attached

The efficiency of the condenser has been greatly increased by indenting the walls of the inner tube. The indentations are best made by plugging one end of the tube, heating small areas, and applying a slight suction. They should extend into the tube a distance equal to its radius or slightly further, and are conveniently arranged in two opposite rows, the indentations alternating. The indented condensers have approximately the efficiency of a Liebig coil condenser of the same length, and for ordinary distillations a condenser with an effective water column of 8 to 10 inches (20 to 25 cm.) is sufficient.

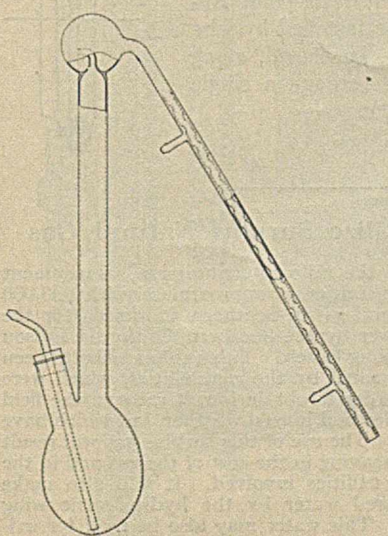


Figure 3—Steam-Distillation Apparatus

These small condensers, both plain and indented, have been found especially adaptable to the construction of pieces of all-glass distillation apparatus of a variety of kinds. Figure 1 shows an all-glass distilling apparatus, with trap, for the preparation of pure water, etc. An all-glass reflux-distilling apparatus is pictured in Figure 2. In using this it is convenient to connect both condensers in parallel with the water supply by means of T-tubes. The water is permitted to flow through both condensers during reflux and, for distillation, is simply cut out of the reflux condenser by a screw clamp. Figure 3 represents an all-glass steam-distillation apparatus with trap and Figure 4 a distilling flask with ground-glass thermometer holder and attached condenser. Simple and combination reflux distilling heads may be very easily assembled.

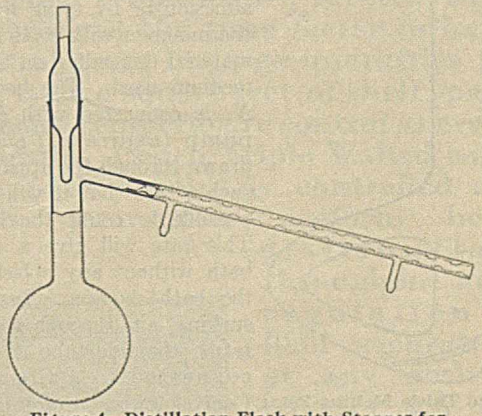


Figure 4—Distillation Flask with Stopper for Thermometer

The usefulness of such pieces of apparatus in the research laboratory well repays the amateur glass blower for the trouble of making them, and, since it is possible to obtain standardized ground-glass joints of Pyrex glass, their assembly is not difficult. Further adaptations of these condensers to the construction of all-glass apparatus is evidently possible where it is not feasible to use the cumbersome and less efficient Liebig type.

Literature Cited

(1) West, Ind. Eng. Chem., **20**, 737 (1928).

---

[1] Received February 17, 1930.

[2] Condensers and apparatus embodying them of the types discussed may be obtained from Arthur H. Thomas Co., Philadelphia, Pa.

Correction

In the article by W. F. Faragher, J. C. Morrell, and I. M. Levine, entitled "Determination of Olefin and Aromatic Hydrocarbons," Ind. Eng. Chem., Anal. Ed., 2, 18 (1930), the column headings in Table XIV on page 23 should read "Benzine 1" and "Benzine 2," instead of "benzene" as printed.

A Modified Thiele Melting-Point Apparatus[1]

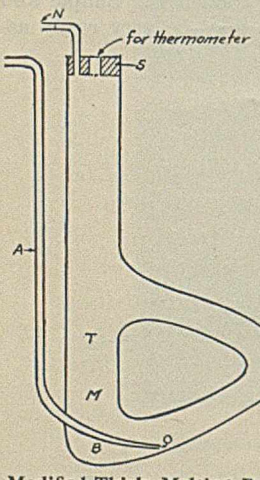
Ernest Conte

The Mallinckrodt Chemical Works, Jersey City Laboratory, 223 to 243 West Side Ave., Jersey City, N. J.

MELTING-POINT determinations made with an ordinary Thiele or Dennis apparatus are not very reliable since the temperature of the bath varies considerably at different parts of the tube. These variations depend on the temperature to which the bath is heated, the method and rate at which the bath is raised, and the length and shape of the thermometer bulb; the human element is also involved. A modified Thiele tube with which it is easy to obtain a bath having a practically uniform temperature without any complicated or expensive mechanical devices is described herein.

The apparatus consists of a regular Thiele tube with a 4-mm. (o. d.) side tube, *A*, having a 0.5-mm. orifice, *O*. It is important that the orifice extend about 12 mm. into the side arm of the Thiele tube; otherwise some of the air bubbles would find their way through the bath proper, thereby reducing the efficiency of the apparatus. The rubber stopper, *S*, has one hole at the center for the thermometer and another hole a little to the side for the bent tube, *N*, through which air is to be drawn.

The substance under test is introduced as usual in a capillary tube and placed on the thermometer. The capillary tube is held in place either by adhesion or by tying it to the thermometer with some suitable material depending on the bath medium used. The bent tube, *N*, is connected with a water pump (aspirator) and air is drawn through the apparatus at such a rate that it will be just possible to count the bubbles. This rate will give a uniform bath without any splashing of the bath medium. Instead of sucking air through the apparatus, the side tube *A* may be connected to a Gramercy or Cenco blower. Compressed air may also be used satisfactorily. The apparatus is now heated as usual with a Bunsen burner or a suitable electric coil.



Modified Thiele Melting-Point Tube

The following table shows the decided advantage of the modified Thiele tube:

	Ordinary Thiele Tube				Modified Thiele Tube			
Temperature at:	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.
T	50	100	150	200	50	100	150	200
M	42	89	138	187	50	99.8	149.5	199.2
B	36	76	122	168	49.9	99.5	148.8	198.0

The above readings were taken simultaneously when the temperature at *T* had been held within 1° C. for 5 minutes. Three standard thermometers were used; one was placed at *T*, a height so that the bath just covered the mercury bulb, one at *M*, the center, and the other at *B*, the bottom of the tube. Stem corrections were given to all these readings.

It will be noticed that the temperature of the bath varies considerably at different parts of the ordinary Thiele tube. This variation makes the position of the capillary tube, containing the material under test, in respect to the mercury bulb of the thermometer very critical. With the modified tube the temperature variation throughout the tube is greatly reduced, thereby accomplishing the much desired need of a uniform temperature bath which is so essential to obtain dependable melting points.

This laboratory has also satisfactorily used the tube for boiling-point determinations, where a uniform bath is also desirable. It has been used for dissolving materials which require considerable shaking and are not affected by the introduction of air, for extraction operations, and for aerating liquid materials. Other applications may in time suggest themselves.

[1] Received January 24, 1930.

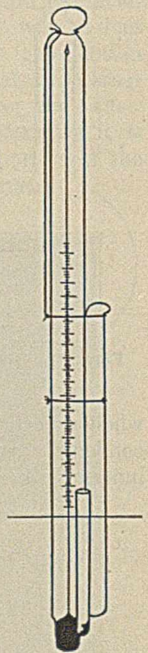
Device for Fastening Melting-Point Tubes to Thermometers[1]

H. L. Lochte

University of Texas, Austin, Tex.

A NUMBER of schemes for preventing the aggravating tendency of melting-point tubes to slip in making melting-point determinations have been described and are listed in handbooks and manuals. The following simple and effective plan appears not to have been described before.

A glass rod 3 to 5 mm. in diameter is fastened to the stem of the thermometer as indicated in the figure. Even the most vigorous stirring will not cause the tube to turn loose when in the position shown in a sulfuric acid bath. If the plan is to be used with the Thiele melting-point apparatus the rod may be fastened by wire as shown or, preferably, be passed, along with the thermometer, through a single elongated hole in the cork.



[1] Received December 26, 1929.

California to Utilize Surplus Natural Gas

Through the efforts of the railroad commission, arrangement has been made for the utilization of approximately 500,000,000 cubic feet of surplus natural gas in Southern California for the generation of electric power by the Southern California Edison Company in its plant at Long Beach. This gas has hitherto been blown into the air and wasted by the gas utilities, which were required to purchase in order to obtain lowest rates in the field and to care for the peak demand in cold weather, but which have had no available market. The use of this surplus gas will result in a substantial economic saving in the cost of the gas and in the cost of operation of the utilities involved. It will also make possible a saving of stored water by the hydroelectric wing of the Edison Company. This water may also be used for irrigation purposes in times of need.

LARGE CAPACITY PRECISION

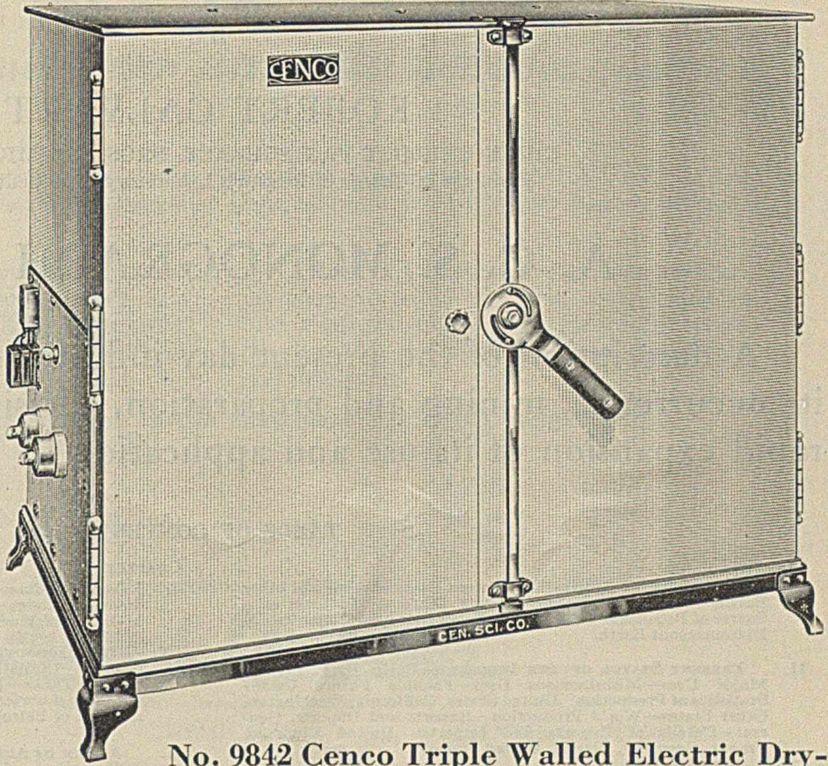
CENCO
OVENS

for routine

Moisture tests,

Ageing tests,

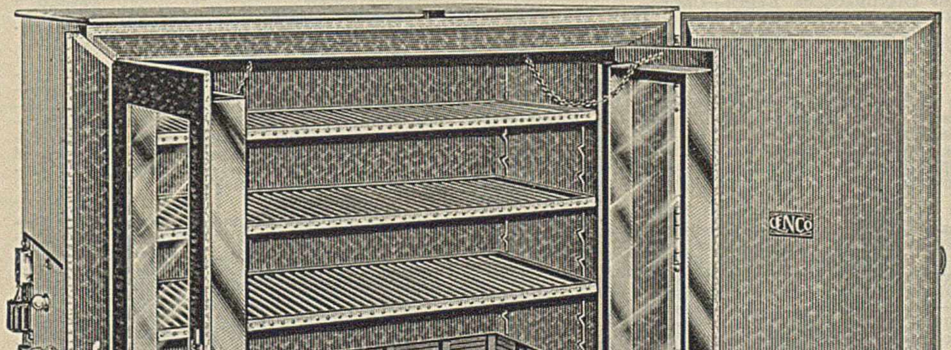
and all tests requiring exact maintenance of temperature about many samples—



No. 9842 Cenco Triple Walled Electric Drying Oven reduces the time factor in handling control tests in large quantities by supplying twelve square feet of shelf space—with precise temperature control at every and all points. Cenco Triple Walled construction, with absolutely controlled air convection, guarantees uniform heat distribution throughout and regulation is held accurately at any desired point up to 200°C. by the well known Cenco DeKhotinsky control.

Price..... $750.00

Ask for our special catalog of Cenco constant temperature equipment, R-26F.



CENTRAL SCIENTIFIC COMPANY
LABORATORY TRADE MARK CENCO REG. U.S. PAT. OFF. SUPPLIES
Apparatus Chemicals
460 E. Ohio St. Chicago U.S.A.

DIATOMACEOUS EARTH

BY

ROBERT CALVERT

CHIEF CHEMIST VAN SCHAACK BROS. CHEMICAL WORKS
Formerly in Charge of Research Laboratory, The Celite Company

A. C. S. MONOGRAPH NO. 52

A description of the present day industry of diatomaceous earth, its occurrence, mining and preparation, physical properties, and the rapid expansion of its use and application to new industries.

TABLE OF CONTENTS

Chapter

I. Introduction—Distinction between Diatomaceous and other Earths—Alternative Names—Living Diatoms—Diatoms as a Source of Petroleum—Varieties of Fossil Diatoms—Impurities in Diatomaceous Earth.

II. Present Status of the Industry—Early Uses—Present Major Uses—Miscellaneous Uses—Possible Future Uses—Statistics of Production: United States, California, Washington, Other States—World Production—Exports and Imports, General—Details of Exports and Imports: United Kingdom, France, Germany, Algeria, United States.

III. Occurrence of Diatomaceous Earth—General—Analyses of Diatomaceous Earths of the United States—Present Producing Areas in the United States—Occurrence in the United States: Lompoc, Pit River, and Miscellaneous Deposits in California; Washington; Oregon; Nevada; Arizona; Eastern States—Canada—Germany—France—United Kingdom—Austria—Australia — Algeria — Italy — Spain — Belgium — Japan — Other Foreign Countries—World Trade in Diatomaceous Earth.

IV. Mining and Preparation of Diatomaceous Earth for the Market—General—Choosing and Testing the Strata—Underground Mining—Removing the Overburden—Quarrying—Drying—Effect of Temperature on Rate of Drying—Milling—Grades of Finished Product—Screening—Settling in Water—Dredging—Ignition of Organic Matter—Removal of Iron.

V. Physical Properties of Diatomaceous Earth—Color—Optical Properties—Specific Gravity—Porosity—Adsorption—Specific Heat—Thermal Conductance—Temperature of Fusion—Latent Heat of Fusion—Thermal Expansion—Colloidal Properties and Size of Particle.

VI. Filtration Medium of Diatomaceous Earth—General—Purpose of Filtration Powder—Effect of Species of Diatoms—Effect of Impurities—Settling in Water—Rate of Settling, Rate of Filtration, and Clarity—Calcination—Calcination with Chemicals—Density of Aqueous Suspensions—Rigid Filters of Diatomaceous Earth—Effect of Conditions of Filtration on Rate of Filtration.

VII. Filtration of Sugar Solutions—General—Corn Products—Beet Sugar Solutions—Molasses—Raw Cane Juice—Raw Cane Sugar—Costs—Recovery of Filter Cake—Results of the Filtration—Sterilization of Sugar Solutions by Filtration—Calcined *vs.* Natural Diatomaceous Earth in Sugar Filtration—Miscellaneous Filter-Aids—Mixed Filter-Aids—Diatomaceous Decolorants—Usual Conditions of Filtration—Effect of Various Factors on the Rate of Filtration: Temperature, Concentration of the Solution, Proportion of Filter-Aid, Length of Filtration Cycle, Pressure of Filtration.

VIII. Miscellaneous Filtrations with Diatomaceous Earth—General—Vegetable Oils — Lard — Linseed Oil — Varnish—Oil and Water Emulsions—Crude Glycerin Solutions—Fruit

Chapter

Juices and Cereal Beverages—Pectin—Citric Acid—Water—Sewage Sludge—Metallurigcal Slimes—Milk—Serums and Materials of Biochemistry.

IX. Diatomaceous Earth in the Petroleum Industry—General—Insulation of Heated Equipment—Insulation of Storage Tanks—Resolution of Oil Water Emulsions—Recovery of Used Lubricating Oil—Drying of Transformer Oil—Adsorption of Petroleum Vapors—Dewaxing of Lubricating Oil.

X. Action of Alkalies upon Diatomaceous Earth—Lime—Sodium Hydroxide and Carbonate—Sodium Nitrate—Sodium Chloride.

XI. Diatomaceous Earth as an Admix in Portland Cement and Plaster—Portland Cement: General, Increase in Water-Proofness, Strength, Specific Gravity, Workability, Method of Mixing Diatomaceous Earth and Portland Cement, Other Siliceous Admixes—Insulation of Rotary Cement Kilns—Miscellaneous Compositions—Plaster.

XII. Diatomaceous Brick—General—Sawed Brick—Calcined Block—Pressed Brick, Usual Type—Artificially Lightened Pressed Brick—Tridymite Brick—Properties of Diatomaceous Brick—Insulating Mortar.

XIII. Miscellaneous Insulating Compositions Containing Diatomaceous Earth—Powder—Granules—Portland Cement Aggregate—Plastic Insulation—Magnesia, Diatomaceous Earth, and Fibre—Lime, Diatomaceous Earth, and Asbestos—Need of an Insulating Non-Inflammable Wall Board—Sound Insulation.

XIV. Thermal Conductance and Loss of Heat through Furnace Walls—Factors Affecting Quantity of Heat Lost—Thermal Conductivity Units—Measurement of Thermal Conductivity: Box Method, Method of Disc with Guard Ring—Results of Thermal Conductivity Measurements—Factors Affecting Thermal Conductivity—Temperature Gradients of Composite Walls—Heat Losses through Insulated and Uninsulated Walls—Economics of Heat Insulation.

XV. Diatomaceous Earth as Absorbent—Porosity of Diatomaceous Earth—Dynamite—Liquid Air Explosives—Solidified Fuels—Disinfectants, Fungicides, and Insecticides—Removal of Oil from Crude Sulfur—Sulfur Compositions—Degreasing Wool—Absorption of Acids—Absorption of Liquid Fertilizers—Acetylene Tank Filler.

XVI. Miscellaneous Uses of Diatomaceous Earth—In Polishing Compositions—In Soaps—In Rubber—In Flooring and Roofing Compositions—In Paints—In the Electrical Industry—In Pharmaceuticals—In Foundry Practice—As Filler for Miscellaneous Materials—As a Source of Reactive Silica—In Catalysis.

Index of Authors, Index of Subjects.

256 Pages Illustrated Price $5.00

The CHEMICAL CATALOG COMPANY, *Inc.*
419 FOURTH AVENUE NEW YORK, U. S. A.

CEMENTYTE

a laboratory cement with unusual adhesive qualities

Stronger, by actual tests, than any similar cement on the market, CEMENTYTE is ideal for setting up or repairing apparatus, sealing vacuum lines, laboratory set-ups and gas connections, for sealing wires in glass, etc.

CEMENTYTE A: For joining glass, porcelain, metal, etc.; sealing wires and metals in glass tubes, repairing apparatus, preventing leaks of gases and liquids in laboratory set-ups, vacuum seals, etc.

CEMENTYTE C: For the same purposes as Cementyte A, where it is desirable to use a softer cement. Also for joining wood, hard rubber, bakelite, etc., and for electrical insulation.

CEMENTYTE is supplied in two convenient size sticks, weighing approximately 1 and 2 ounces each.

	small	large
No. 1909-A CEMENTYTE A.	$0.75	1.40
1909-C CEMENTYTE C.	.75	1.40

Less 10% in cartons of 1 dozen sticks

Schaar & Company

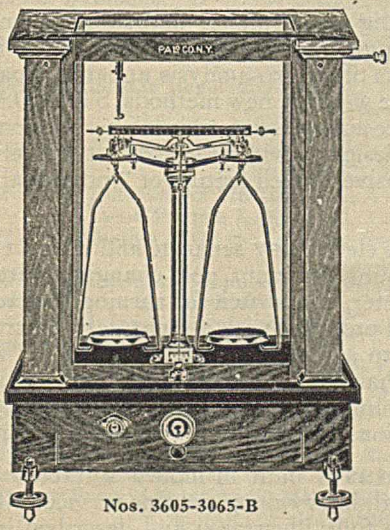
Manufacturers—Importers—Distributors

LABORATORY SUPPLIES - CHEMICALS - SCIENTIFIC APPARATUS

556-558 West Jackson Blvd. **Chicago, Illinois**

ANALYTICAL BALANCES WITH GUARANTEED SENSITIVITIES

equipped with New Rider Carrier



Nos. 3605-3065-B

THERE ARE NO OTHER BALANCES OF EQUAL QUALITY AVAILABLE AT LOWER PRICES

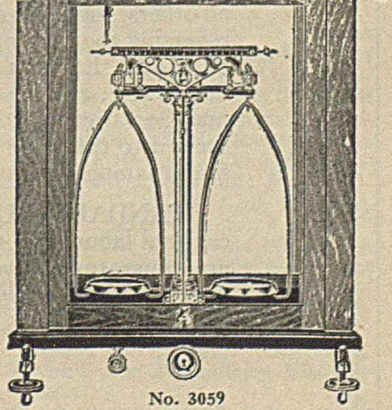
The patented rider carrier on these balances is arranged so that the rider is carried in a small hook which closes as it is raised off the beam making it absolutely impossible to drop the rider. Rider is lifted vertically off beam.

No. 3065

CAPACITY—100 grams in each pan.
SENSITIVITY—1/20 milligram.
KNIFE EDGES—Finest agate.
PLANES—Finest agate.
BEAM—Aluminum alloy, 6¼ inches long, calibrated on both sides.
PANS—2½ inches in diameter.
Complete in mahogany case with rests **$65.00**

No. 3065-B

This balance is same as 3065 but has capacity of 200 grams, sensitive to 1/20 mgm., 3 inch pans, and 6¾ inch beam **$75.00**



No. 3059

No. 3059

CAPACITY—200 grams in each pan.
SENSITIVITY—1/10 milligram.
KNIFE EDGES—Finest agate.
PLANES—Finest agate.
BEAM—Aluminum alloy, 6¼ inches long, calibrated on both sides.
PANS—3 inches in diameter.
BOWS—4¼ inches wide.
Complete in mahogany case with rests **$54.00**

Write for Balance Bulletin BI

PALO COMPANY

APPARATUS FOR INDUSTRIAL AND LABORATORY USE
153 WEST 23RD STREET NEW YORK, N. Y.

A New Idea in Modern Design

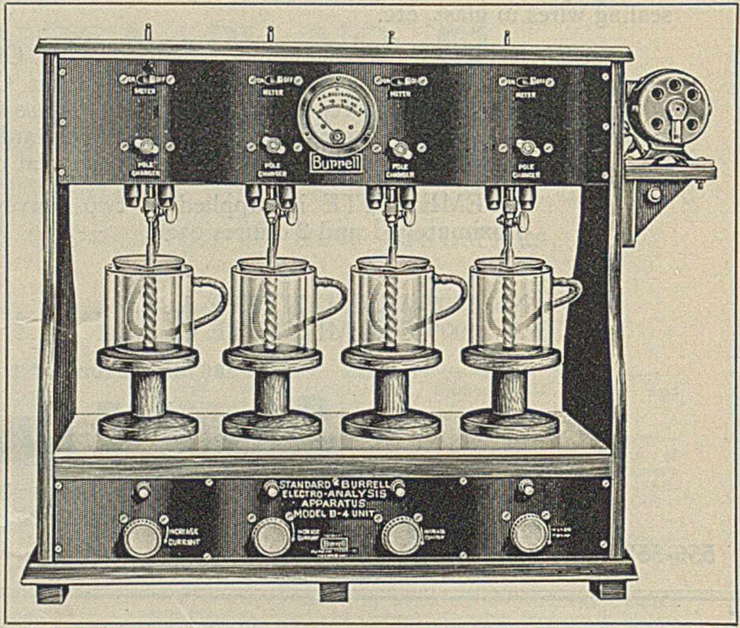
Standard Burrell Electro-Analysis Apparatus

"Individualized"

Unit Control

An Exclusive

Burrell Feature



Ask for Burrell Catalog-77.

New Applications are constantly being found for electro-analysis. These include the new and more rapid determinations of aluminum and copper in steels. Metals regularly determined are copper, lead, antimony, cadmium, nickel, tin, zinc, and others of the non-ferrous group.

Modern Methods require equipment capable of passing much higher amperages than formerly. With the new Burrell apparatus, these higher amperages shorten the time of analysis without sacrificing the accuracy of the result. The types of electro-analysis apparatus passing only 3 or 4 amperes are inadequate for fast work. In line with the new methods, STANDARD-BURRELL Electro-Analysis Apparatus are built to produce accurate determinations when passing any current ***up to 10 amperes.*** In addition, the Burrell design provides the greatest flexibility of electrical and mechanical adjustment, because of the exclusive Burrell feature of "individualized" unit control.

Individualized Unit Control means that each unit is electrically separate and distinct from all others, having its own rheostat for controlling the amount of current, pole-changing switch for reversing the current flow, meter-reading switch for ammeter, and switch for turning the current on or off. Efficient agitation is necessary and each unit is provided with a separately controlled, detachable, turbine-type, high-speed, glass stirrer fused to a tungsten rod, the speed of which may be varied by a simple adjustment of the driving mechanism. The analyst, therefore, is not limited to the same current flow and stirring speed in all units, but he may handle as many different samples, with varying currents and operating conditions, as there are units in the apparatus.

STANDARD-BURRELL Electro-Analysis Apparatus is built in models suitable for occasional laboratory work as well as in designs for continual, heavy-duty, routine service. There are apparatus of two, four and six units, all of which are fully illustrated and described in the new **Burrell Catalog-77** to which you are welcome.

Burrell Technical Supply Co.
CHEMICAL-BIOLOGICAL-METALLURGICAL
LABORATORY APPARATUS AND REAGENT — CHEMICALS
1702-4-6-8 FIFTH AVENUE PITTSBURGH, PA.