INDUSTRIAL AND ENGINEERING CHEMISTRY

ANALYTICAL EDITION

HARRISON E. HOWE, EDITOR ● ISSUED JUNE 15, 1940 ● VOL. 12, NO. 6 ● CONSECUTIVE NO. 12

Microchemistry:

Modern Laboratories:

Publication Office: Easton, Penna.

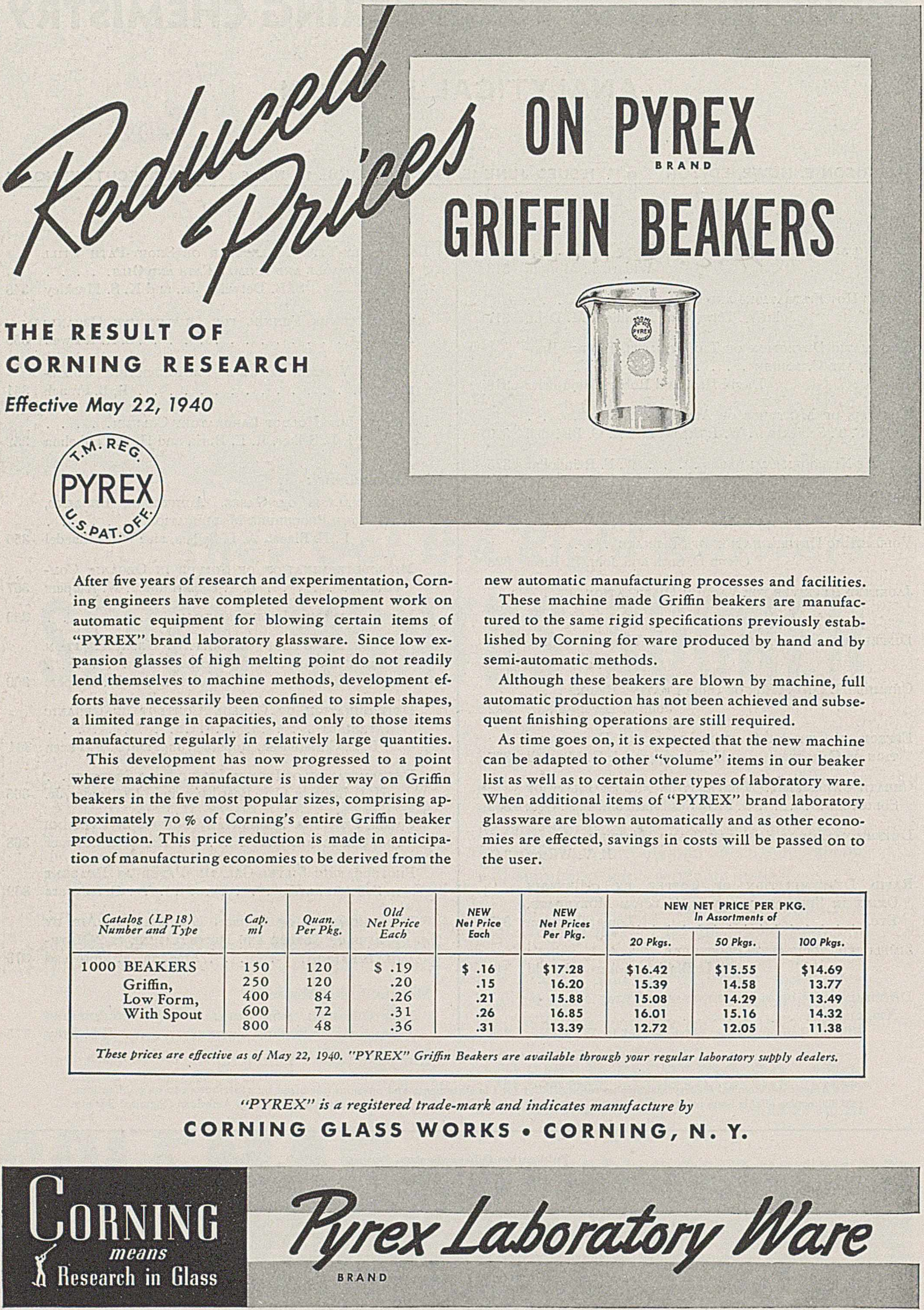
Editorial Office: Room 706, Mills Building, Washington, D. C.
Telephone: National 0848. **Cable:** Jiechem (Washington)

Advertising Department: 332 West 42nd Street, New York, N. Y.
Telephone: Bryant 9-4430

Published by the American Chemical Society, Publication Office, 20th & Northampton Sts., Easton, Penna. Entered as second-class matter at the Post Office at Easton, Penna., under the Act of March 3, 1879, as 24 times a year. Industrial Edition monthly on the 1st; Analytical Edition monthly on the 15th. Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918.

Annual subscription rate, Industrial Edition and Analytical Edition sold only as a unit, $4.00. Foreign postage to countries not in the Pan American Union, $2.25; Canadian postage, $0.75. Single copies: Industrial Edition, $0.75; Analytical Edition, $0.50. Special rates to members.

No claims can be allowed for copies of journals lost in the mails unless such claims are received within 60 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. (Ten days' advance notice required.) "Missing from files" cannot be accepted as the reason for honoring a claim. Charles L. Parsons, Business Manager, Mills Building, Washington, D. C., U. S. A.



Reduced Prices ON PYREX BRAND GRIFFIN BEAKERS

THE RESULT OF CORNING RESEARCH

Effective May 22, 1940

T.M. REG.
PYREX
U.S. PAT. OFF.

After five years of research and experimentation, Corning engineers have completed development work on automatic equipment for blowing certain items of "PYREX" brand laboratory glassware. Since low expansion glasses of high melting point do not readily lend themselves to machine methods, development efforts have necessarily been confined to simple shapes, a limited range in capacities, and only to those items manufactured regularly in relatively large quantities.

This development has now progressed to a point where machine manufacture is under way on Griffin beakers in the five most popular sizes, comprising approximately 70 % of Corning's entire Griffin beaker production. This price reduction is made in anticipation of manufacturing economies to be derived from the new automatic manufacturing processes and facilities.

These machine made Griffin beakers are manufactured to the same rigid specifications previously established by Corning for ware produced by hand and by semi-automatic methods.

Although these beakers are blown by machine, full automatic production has not been achieved and subsequent finishing operations are still required.

As time goes on, it is expected that the new machine can be adapted to other "volume" items in our beaker list as well as to certain other types of laboratory ware. When additional items of "PYREX" brand laboratory glassware are blown automatically and as other economies are effected, savings in costs will be passed on to the user.

Catalog (LP 18) Number and Type	*Cap. ml*	*Quan. Per Pkg.*	*Old Net Price Each*	**NEW** Net Price Each	**NEW** Net Prices Per Pkg.	**NEW NET PRICE PER PKG.** In Assortments of		
						20 Pkgs.	50 Pkgs.	100 Pkgs.
1000 BEAKERS Griffin, Low Form, With Spout	150	120	$ .19	**$ .16**	**$17.28**	**$16.42**	**$15.55**	**$14.69**
	250	120	.20	**.15**	**16.20**	**15.39**	**14.58**	**13.77**
	400	84	.26	**.21**	**15.88**	**15.08**	**14.29**	**13.49**
	600	72	.31	**.26**	**16.85**	**16.01**	**15.16**	**14.32**
	800	48	.36	**.31**	**13.39**	**12.72**	**12.05**	**11.38**

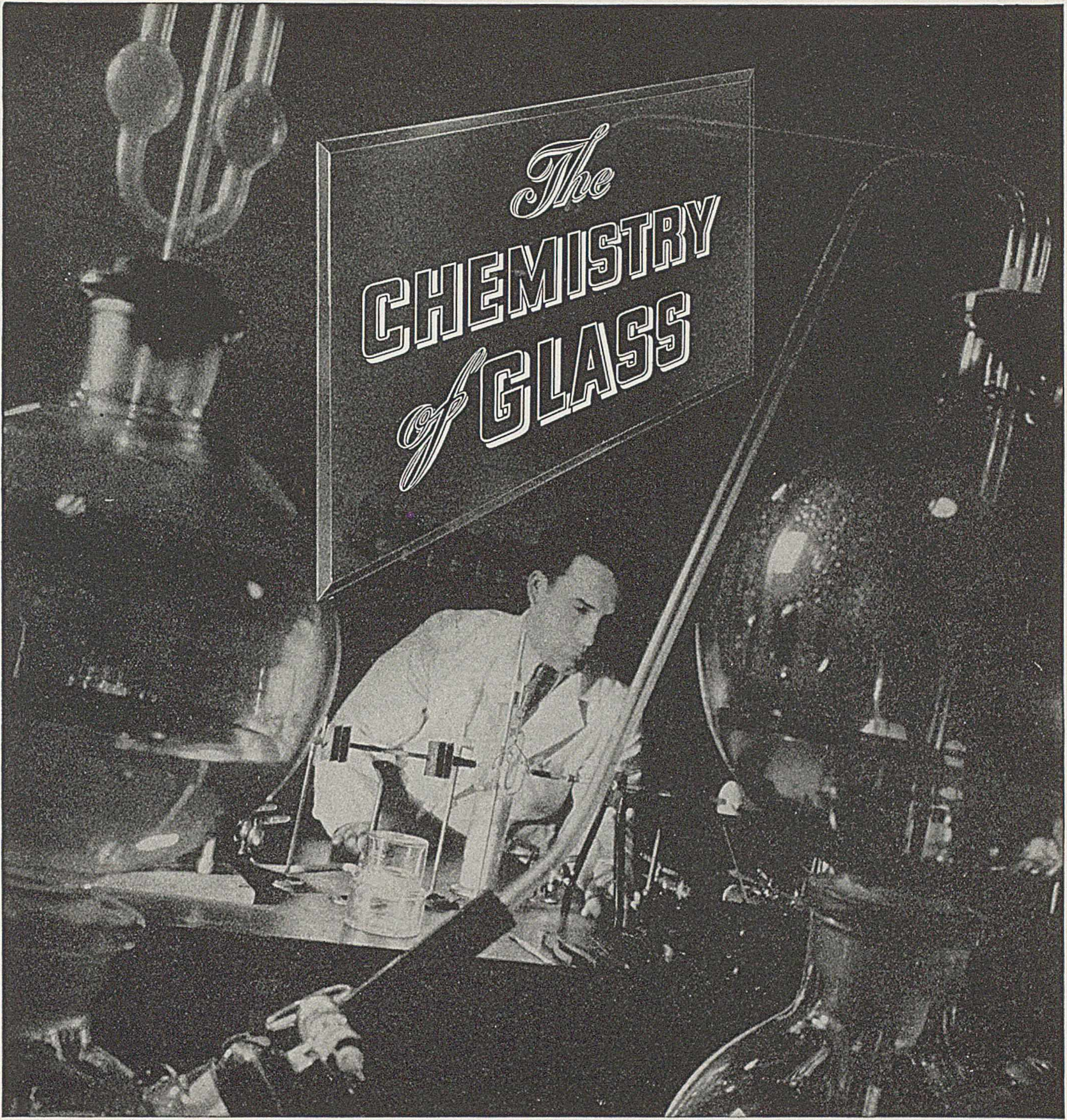
These prices are effective as of May 22, 1940. "PYREX" Griffin Beakers are available through your regular laboratory supply dealers.

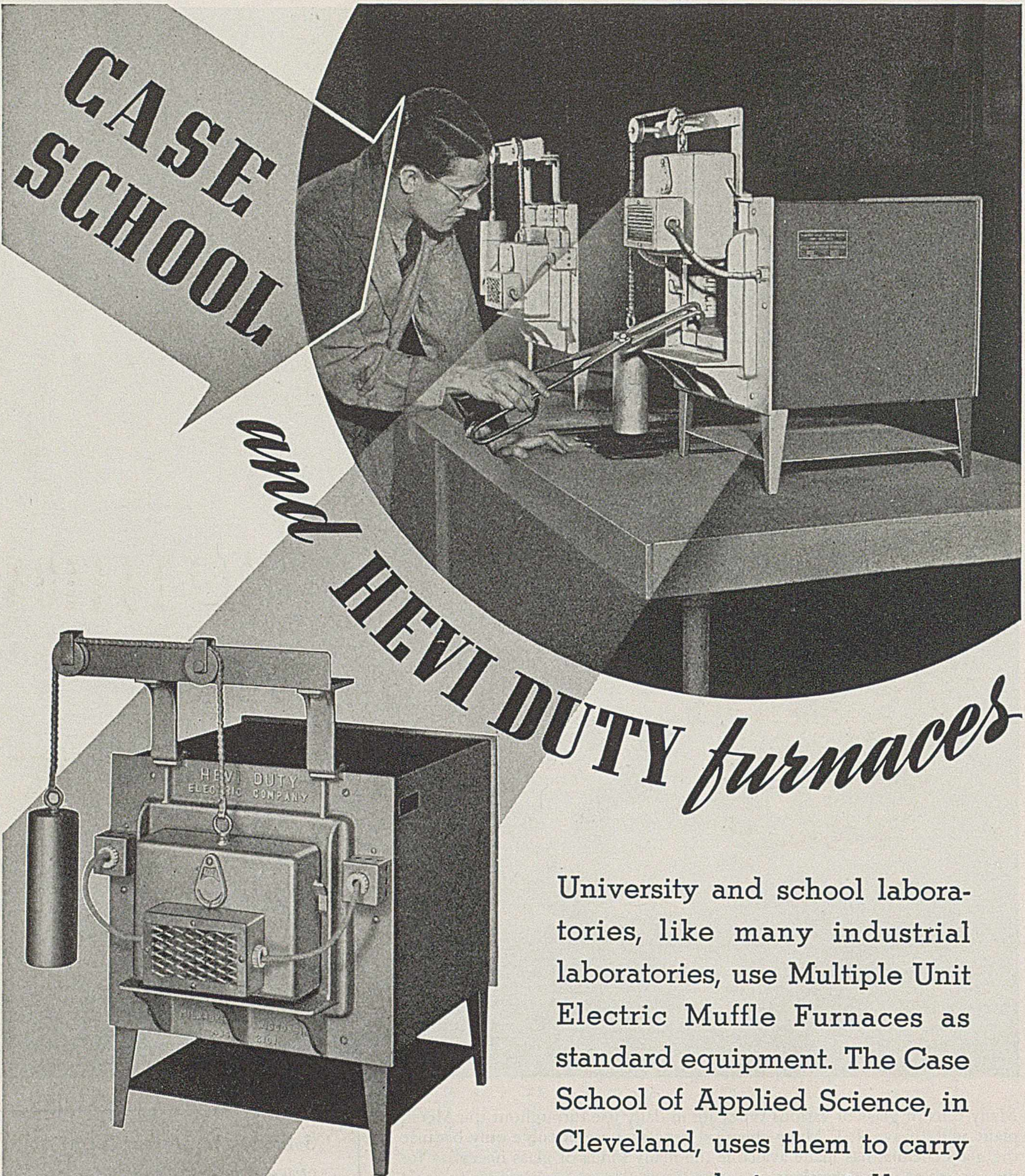
"PYREX" is a registered trade-mark and indicates manufacture by

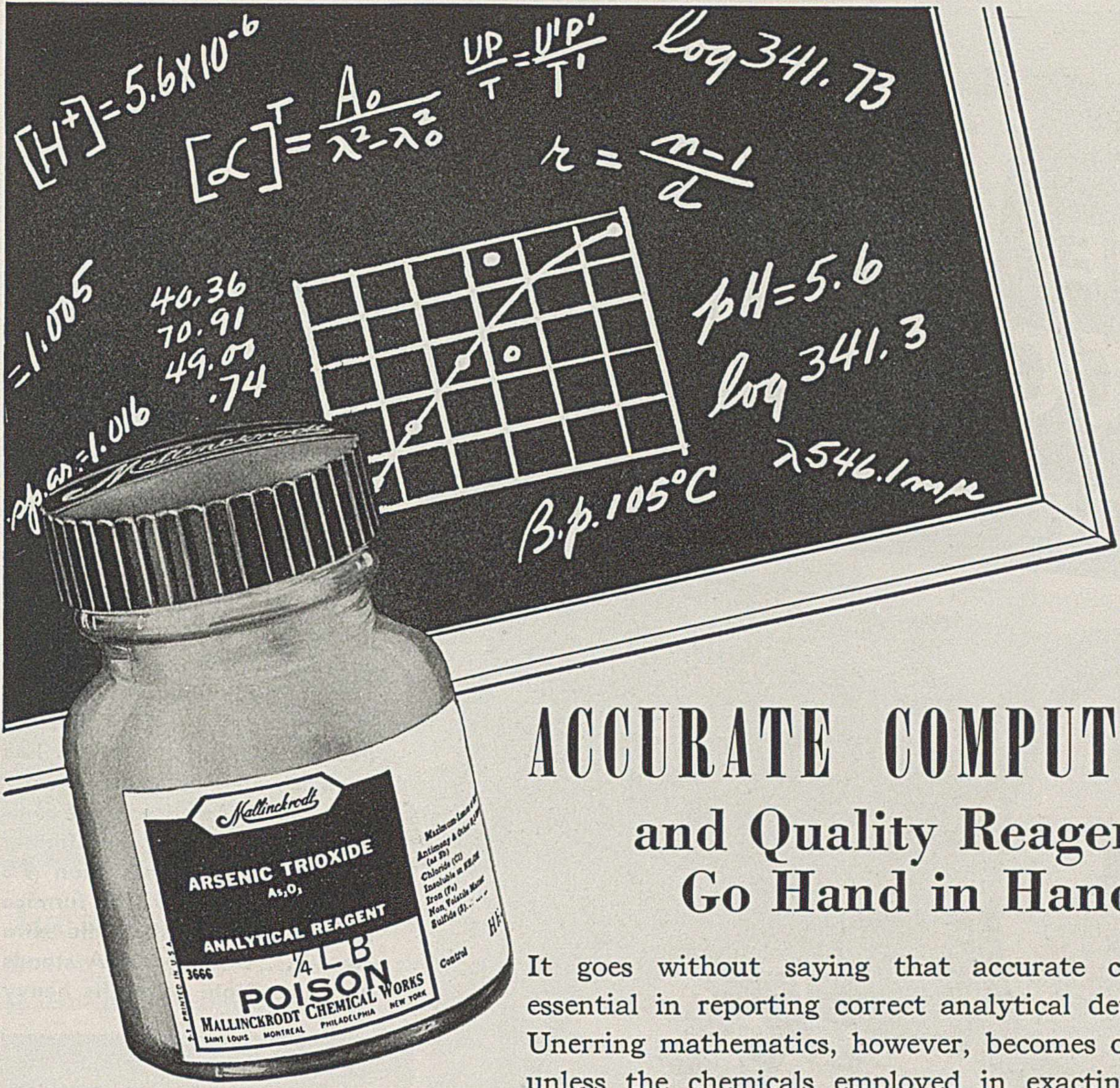
CORNING GLASS WORKS • CORNING, N. Y.

CORNING
means
Research in Glass

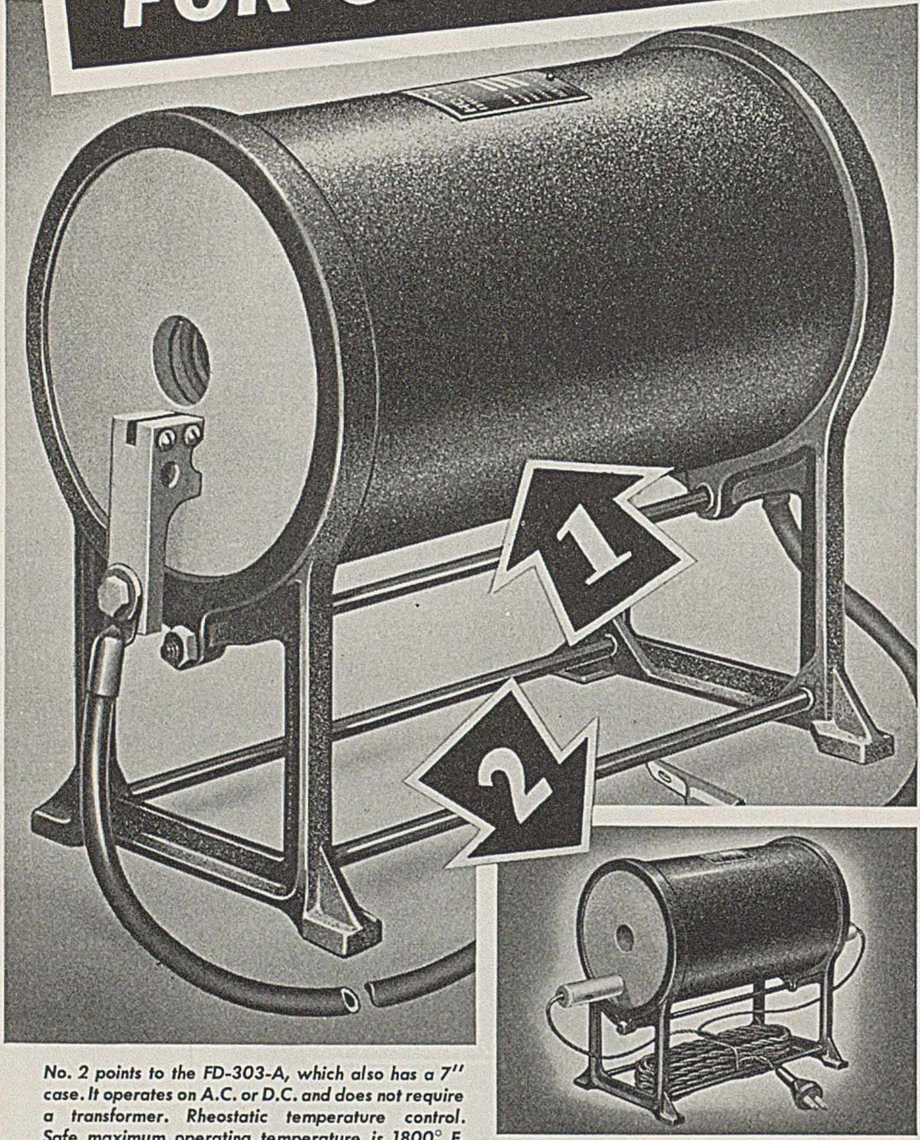
Pyrex Laboratory Ware
BRAND


The
CHEMISTRY
of GLASS


CASE SCHOOL
and
HEVI DUTY furnaces
HEVI DUTY
ELECTRIC COMPANY

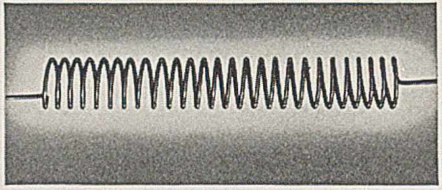

[H+]=5.6X10-6
[α]T= A0 / λ2-λ02
UP/T = U'P'/T'
log 341.73
r = n-1 / d
=1.005
40.36
70.91
49.00
.74
sp.gr.=1.016
pH=5.6
log 341.3
B.p. 105°C
λ546.1 mμ
Mallinckrodt
ARSENIC TRIOXIDE
As2O3
ANALYTICAL REAGENT
3666
¼ LB
POISON
MALLINCKRODT CHEMICAL WORKS
SAINT LOUIS MONTREAL PHILADELPHIA NEW YORK

THE TWO MOST WIDELY ACCEPTED FURNACES FOR CARBON COMBUSTION



No. 2 points to the FD-303-A, which also has a 7" case. It operates on A.C. or D.C. and does not require a transformer. Rheostatic temperature control. Safe maximum operating temperature is 1800° F.

The No. 1 arrow points to our FH-303-A whose case diameter used to be 5" and is now 7". The increased insulation results in a case temperature that is 120° F. cooler. The holding wattage has been reduced 18%. The time to heat from 80° to 2000° F. has been lowered 50% and is now 63 minutes. The price for the complete job, including transformer and rheostat, is less than 9% more than formerly. The furnace is certainly worth that little extra cost. . . . This FH-303-A stands hard use. Note below its heavy heating unit, made of 7 Gauge Chromel A—very hard to wear out, and very easy to renew. The furnace operates only on A.C. through a small transformer. The top safe temperature is 2000° F. and is controlled by a rheostat. If you need a combustion furnace that must stand really hard service, you need this Hoskins FH-303-A. Write to us or your dealer for quotation. . . . Hoskins Manufacturing Company, Detroit, Mich.

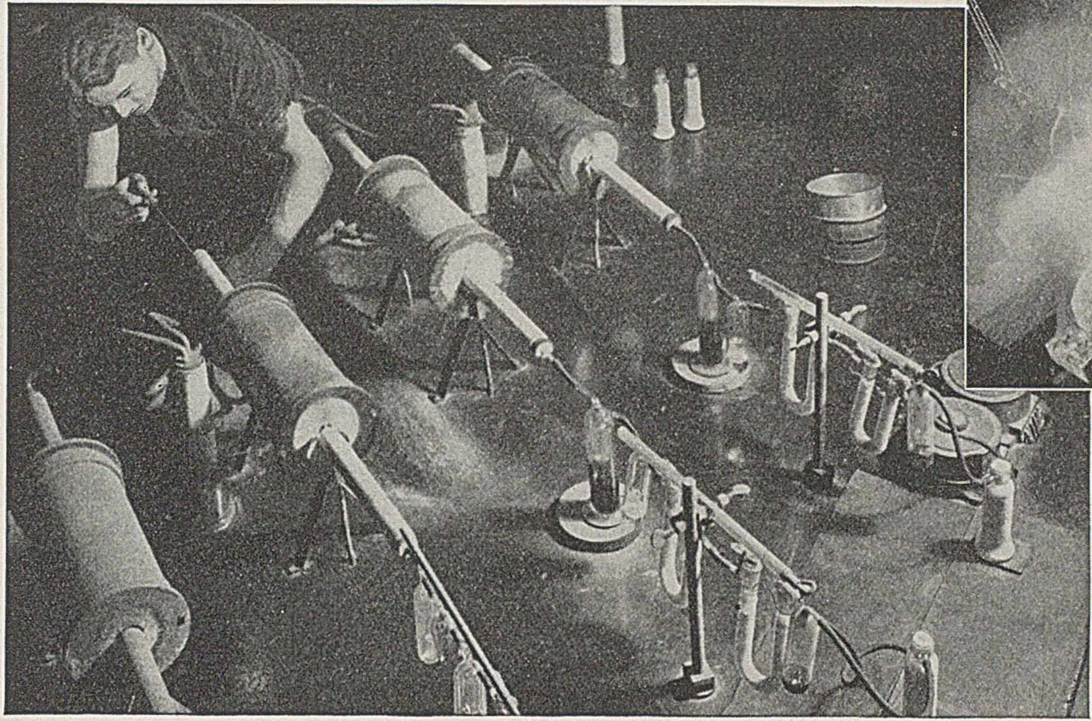


HOSKINS PRODUCTS

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

HEATING ELEMENT WIRE
Chromel
NICKEL-CHROMIUM

FOR *ACCURATE* ANALYSES OF STEELS...



"Rush that analysis of melt 2139!" . . . "Can't hold Furnace 4 much longer—what's the Carbon?" . . . "Does Sample 471 meet specifications?"

TODAY, with the pressure of high speed production forcing demands like these upon the analytical laboratories of steel companies, it is more than ever important that the chemists in these laboratories be backed by reagents of uniform high purity and strength.

Baker and Adamson Reagent Chemicals fill this need. They are manufactured by an organization having nearly 60 years of experience in the manufacture of highest quality analytical chemicals—by men who make certain that Baker and Adamson Reagents meet the high standards of purity set up for them.

The following are a few of the Baker and Adamson Reagents most frequently used in steel analyses:

Code No.	CARBON
1630	Cupric Ammonium Chloride, *Reagent, Crystal, A.C.S.*
2220	Sodium Calcium Hydrate, *Dry, No. 8 Mesh*
	MANGANESE
1308	Ammonium Persulfate, *Crystal, Reagent, A.C.S.*
2199	Sodium Arsenite, *Reagent*
2207	Sodium Bismuthate, *Powder, Reagent, A.C.S.*
	SULFUR
1090	Acid Hydrochloric, *C.P., Specific Gravity 1.18, A.C.S.*
1121	Acid Nitric, Fuming, *Reagent, Specific Gravity 1.49-1.50*
1408	Barium Chloride, *Crystal, Reagent, A.C.S.*
	PHOSPHOROUS
1114	Acid Molybdic, *85%, Reagent*
1300	Ammonium Molybdate, *Crystal, Reagent*
1909	Magnesium Chloride, *Crystal, Reagent, A.C.S.*
	SILICON
1100	Acid Hydrofluoric, *48%, Reagent, A.C.S.*
1144	Acid Perchloric, *70-72%, Reagent, A.C.S.*
1180	Acid Sulfuric, *C.P., Specific Gravity 1.84, A.C.S., Low N*
	ALSO
1120	Acid Nitric, *C.P., Specific Gravity 1.42, A.C.S.*
1760	Ferrous Ammonium Sulfate, *Crystal, Reagent, A.C.S.*
2120	Potassium Iodide, *Crystal, Reagent, A.C.S.*
2341	Stannous Chloride, *Crystal, Reagent, A.C.S.*

No matter what industry you are connected with, your analytical laboratories can benefit by the use of Baker and Adamson Reagents. They complement precise laboratory technique and aid in getting more accurate results.

BAKER & ADAMSON STANDARD OF PURITY B&A QUALITY
FINE CHEMICALS AND LABORATORY REAGENTS
REG. U.S. PAT. OFF.

SETTING THE PACE IN CHEMICAL PURITY SINCE 1882

BAKER & ADAMSON

Reagent Chemicals AND *C.P. Acids*

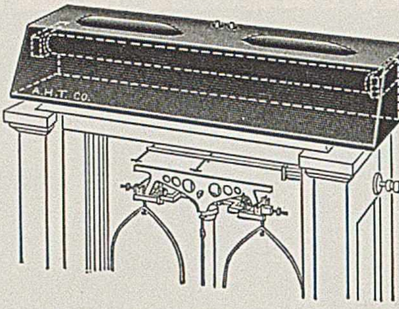
Division of GENERAL CHEMICAL COMPANY, 40 Rector St., New York

Atlanta • Baltimore • Boston • Buffalo • Charlotte (N.C.) • Chicago • Cleveland • Denver • Houston • Kansas City • Los Angeles
Milwaukee • Minneapolis • Montezuma (Ga.) • Philadelphia • Pittsburgh • Providence (R.I.) • San Francisco • St. Louis • Utica (N.Y.)
Wenatchee (Wash.) • Yakima (Wash.) • In Canada: The Nichols Chemical Company, Limited • Montreal • Toronto • Vancouver

THREE NEW, A.H.T. CO. SPECIFICATION

FLUORESCENT DAYLIGHT LAMPS

DESIGNED FOR SPECIFIC LABORATORY PURPOSES



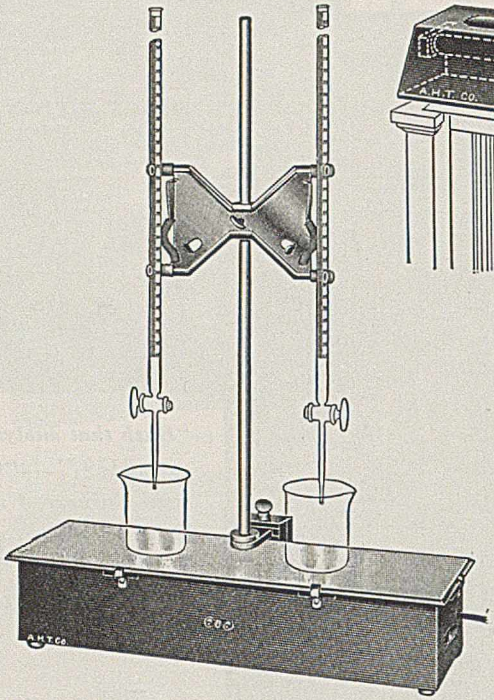
2072-F.

Based on new 15-watt fluorescent daylight bulb, 18 inches long

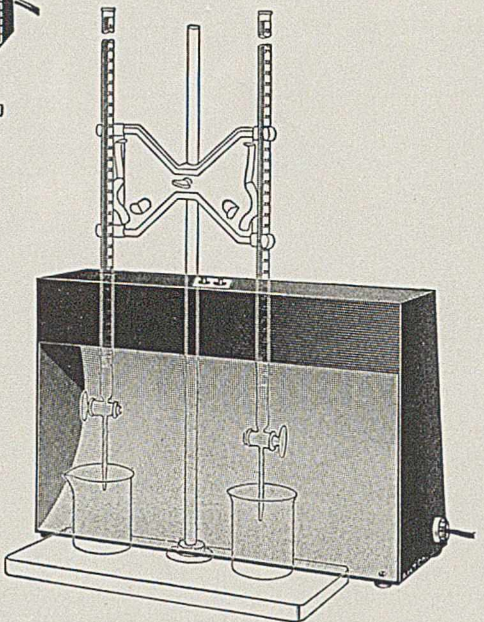
Cold, diffused, glareless light similar to natural daylight

Estimated life of bulb, approx. 2500 hours

Not to be confused with commercial fixtures



2528.



6323.

LABORATORY LAMPS, Fluorescent Daylight. Based on new 15-watt fluorescent bulb, 18 inches long, giving a cold, diffused, glareless light with characteristics similar to natural daylight. Estimated life of the bulb is approximately 2500 hours. Bulb is of the electric discharge type and employs mercury vapor to sustain the arc. A large amount of fairly short wave ultraviolet invisible radiation is produced, which is transformed into longer wave visible radiation by means of a fluorescent powder applied to the inner surface of the glass.

Each lamp is furnished with ballast, i.e. a special choke-coil with arc starting device, as required for operation on 110 volts. Starting is accomplished by means of a push-button switch which insures positive operation. Pressure on the red button closes the circuit and heats the cathode at each end of the bulb. When pressure is released, the circuit is broken and the discharge goes directly through the bulb without any time lag. Pressure on the black button breaks the circuit and extinguishes the lamp.

2072-F. Balance Illuminator, Fluorescent Daylight, A.H.T.Co. Specification. For use directly on top of an analytical balance case. Reflector insures maximum light on the *front* of the balance beam and pointer index. Temperature rise inside the balance case at beam level, due to heat radiation from the bulb, is negligible. Finished with high reflecting white on inside and dull black on outside. Overall dimensions, 18⅛ inches long × 6 inches wide × 3⅜ inches high; mounted on felt feet; fits balance cases 14½ inches or more in length. Complete with 15-watt fluorescent daylight bulb, ballast, push-button starting switch, cord and plug. For 110 volts, 60 cycles, a.c. only........ 14.75
10% discount in lots of 6

2528. Burette Support with Illuminated Base, A.H.T.Co. Specification. For colorimetric titrations or color comparisons by transmitted light under standardized conditions. Consisting of louvered sheet metal base, with flashed opal glass top 19½ inches long × 7 inches wide, aluminum rod in adjustable holder and clamp for two burettes. Base contains two 15-watt, 18-inch fluorescent bulbs with ballasts. The combination of the glareless daylight bulbs and the glass with high transmission value forms an excellent background, free from reflections, directly under the titration vessel. When desired, the rod and clamp holder can be removed to provide an unobstructed lighted surface for color comparison work. Complete with two 15-watt fluorescent daylight bulbs, ballast, push-button starting switch, cord and plug. For 110 volts, 60 cycles, a.c. only........ 27.50

2528-G. Ditto, but without burette clamp........ 26.25

6323. Titration Lamp, Fluorescent Daylight, A.H.T.Co. Specification. With curved white reflector so designed that intensity of illumination over the entire surface does not vary more than 25% and no direct light reaches the eye. The illuminated window, 18½ inches long × 9 inches high, forms an excellent background for titrations, color matching, colorimetric pH determinations, turbidity rings, flocculation and precipitation tests, etc. In the latter work, a sheet of black paper is laid over the central part to obtain dark field effect. Complete with 15-watt fluorescent daylight bulb ballast, push-button starting switch, two sheets of black paper with holders, cord and plug. For 110 volts, 60 cycles, a.c........ 15.00

6323-A. Ditto, but for 110 volts, d.c........ 17.50

ARTHUR H. THOMAS COMPANY

RETAIL—WHOLESALE—EXPORT

LABORATORY APPARATUS AND REAGENTS

WEST WASHINGTON SQUARE, PHILADELPHIA, U.S.A.
Cable Address, "Balance," Philadelphia

INDUSTRIAL AND ENGINEERING CHEMISTRY

ANALYTICAL EDITION

PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY ● HARRISON E. HOWE, EDITOR

Pasting and Identification of Starches

WILLARD L. MORGAN, Arnold, Hoffman & Co., Providence, R. I.

When starches are heated with water, the cloudy suspensions gradually become translucent as pasting occurs. A photoelectric method is used to follow this change at various temperatures, and characteristic curves for each type of starch are secured. Besides indicating the nature of the starch, the curves show progress and completion of pasting. Modified starches show progressive alterations in the curves. By simple mathematical relations the curves may be applied to analysis of mixtures of starches.

STARCH, aside from its chemical conversion to sugars, is primarily used because of its thickening value. Thus, in the pasted or cooked condition it is used in such foods as mayonnaise, pie fillings, soups, and candies, as adhesives, as paper and laundry sizes, as yarn sizes and cloth finishes, and as the carrier in textile printing pastes. For all these uses troubles are avoided and maximum thickening value is secured only by complete pasting.

The starches used in these applications are frequently mixtures of several raw or modified starches, such compounding resulting from the desirable close adjustment of the properties of the starch pastes to the requirements of the work to be done. Determining the types and amounts of starches present in such starch mixtures is consequently difficult. Microscopic examination of the size and shape of the grain, preferably slightly stained with iodine, has been the usual first step in such analyses. The microphotographs of Sjostrom (*4*) and Lane and Eynon (*3*) are very helpful, but differentiation is at best difficult and requires considerable experience and care, as can be seen by studying Figure 1 which shows a mixture of equal parts of corn and tapioca starches.

Having determined the kinds of starches present, viscosity measurements on the cooked pastes will give an idea as to whether the starches used were raw or modified by dextrinizing or other treatment. Deciding on the extent of modification has generally been difficult and uncertain.

Pasting of Raw Starches

When starches are heated in water, the suspensions gradually become translucent as pasting occurs. In 1937 Cook and Axtmayer (*2*) used a photoelectric cell to measure the changes occurring with some tropical starches. The author has found this method highly useful in studying the cooking characteristics of starches and as an analytical tool. By means of apparatus which gradually raises the temperature at the rate of 2.5° C. per minute, the change in transparency is followed with a photoelectric cell and microammeter, as shown in Figure 2.

The meter circuit is shunted by a resistance sufficient to make the readings over the 50-microammeter scale a linear function of the foot-candles of illumination. The light source is a 100-watt projection bulb, used with a collimating lens, so that an approximately parallel beam of light passes through the screen and pasting tube and onto the photocell. The current for the light source is brought in through a constant voltage regulator in order to secure a constant light intensity. The illumination is initially adjusted, just before a determination by use of slide-wire resistor, to a standard value of 250 microamperes or 500 foot-candles. A filter just in front of the cell, capable of cutting the light down to 10 per cent, is used at this time and the test tube is filled with water.

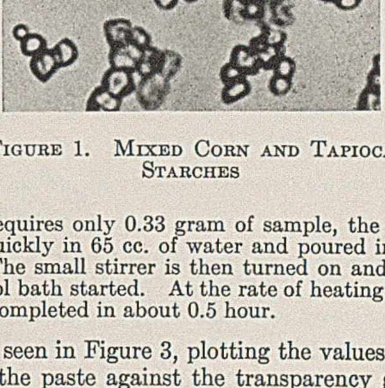


FIGURE 1. MIXED CORN AND TAPIOCA STARCHES

The test requires only 0.33 gram of sample, the starch being rubbed up quickly in 65 cc. of water and poured into the large test tube. The small stirrer is then turned on and the heating of the glycerol bath started. At the rate of heating given, a test is generally completed in about 0.5 hour.

As can be seen in Figure 3, plotting the values of the temperature of the paste against the transparency gives curves which are characteristically different for the various raw starches.

Positive identification of single raw starches becomes easy and certain, inasmuch as the initial pasting temperatures and location and nature of the curve vary considerably with the

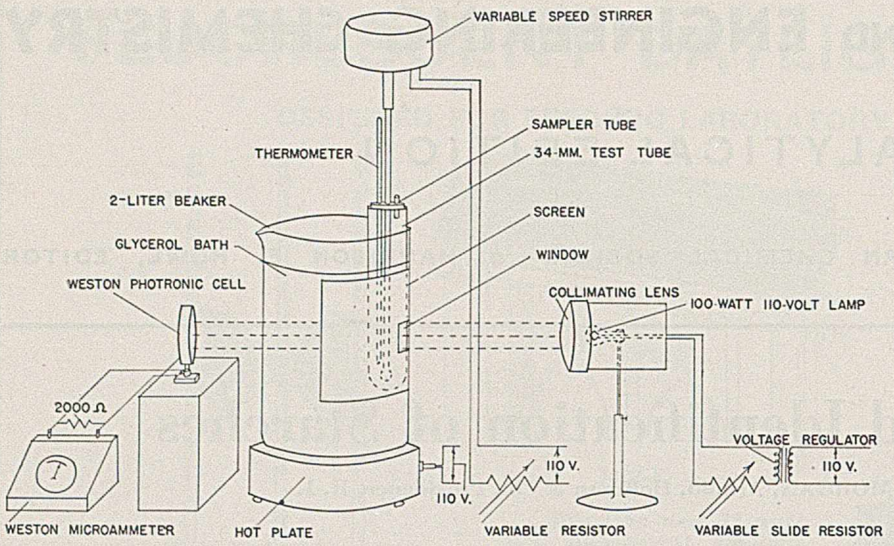


FIGURE 2. PHOTOPASTING APPARATUS

different starches. The initial pasting temperatures, as shown by the point at which the curve rises, correspond to the first appearances of pasting as shown by decrease in number of granules showing polarization under the microscope. However, detection of the start of pasting directly under the microscope, which has been used to some extent to characterize starches, is subject to several errors which lead to discordant results, as shown by Alsberg and Rask (*1*).

The initial suspensions of the larger grained starches at the low dilution of 0.5 per cent are less opaque than the smaller grained cereal starches (Figure 3). The breaking apart of small granules of sago and arrowroot as the individual grains gives a preliminary increase in opacity just prior to the beginning of pasting. This is characteristic of these and other sticky types of starches. The tuber type of starch shows steeper pasting curves than the grain starches—that is, they become pasted over a shorter temperature range. The curves clearly show the greater transparency characteristic of tapioca, potato, and other tuber-starch pastes. The need for high-temperature cooking for complete pasting in making paper or textile sizes or pastes is apparent in these curves. Too low cooking temperature in the industrial pasting of starches is the source of considerable trouble.

Microscopically wheat starch in polarized light shows two types of grains, this evidently being the explanation for the two sections of its pasting curve. In general, as samples of a starch are withdrawn at various stages of the pasting operation and examined microscopically, the smaller grains are the last to paste. The general location of the curves indicates such a relation.

On Figure 4 the difference in the two curves shown for raw rice starches appears to be connected with the grain size distribution.

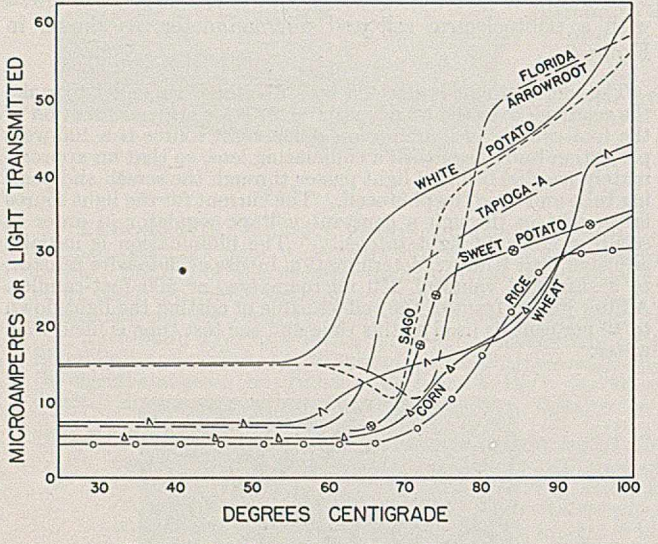


FIGURE 3. PASTING OF RAW STARCHES

Pasting begins at: white potato, 55°; wheat, 56°; tapioca A, 61°; rice, 63–70°; corn, 64°; sweet potato, 64–67°; sago, 69.5–70°; Florida arrowroot, 72° C.

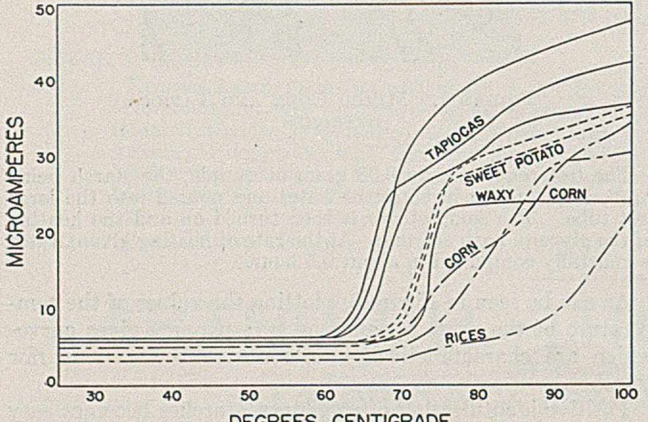


FIGURE 4. VARIATIONS IN RAW STARCHES

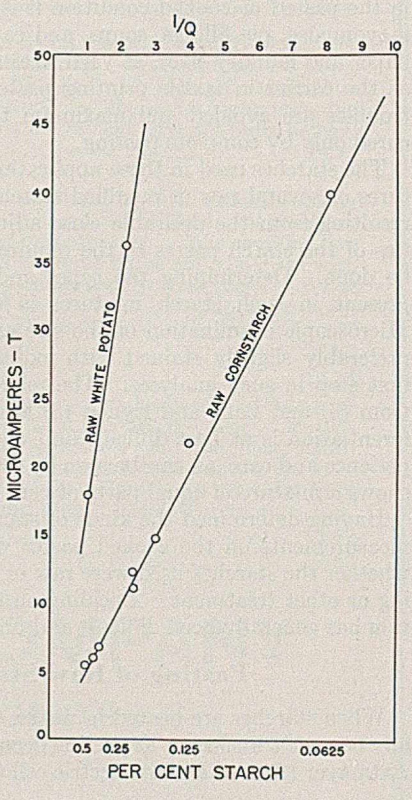


FIGURE 5. OPACITY OF UNPASTED STARCHES

$$T \times Q = K$$

$$T = \frac{K}{Q}$$

$$Q = \frac{K}{T}$$

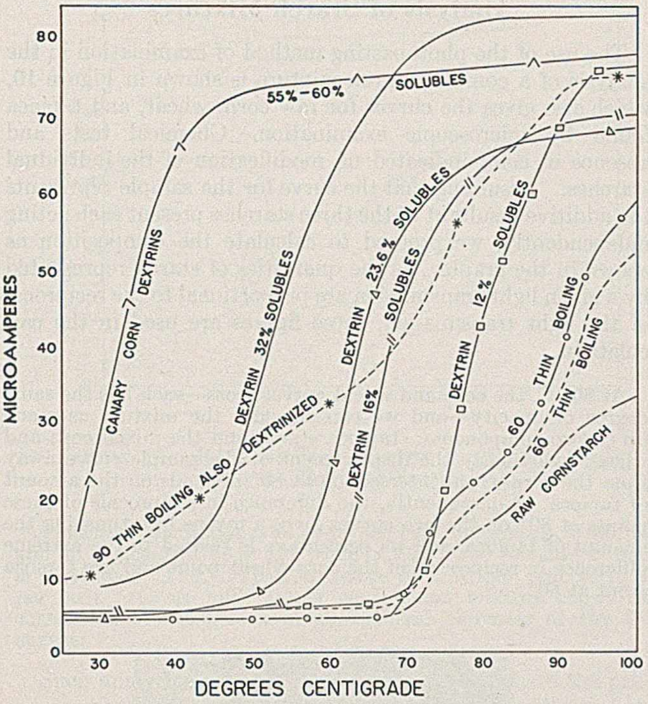


Figure 6. Pasting of Corn Dextrins and Thin-Boiling Starches

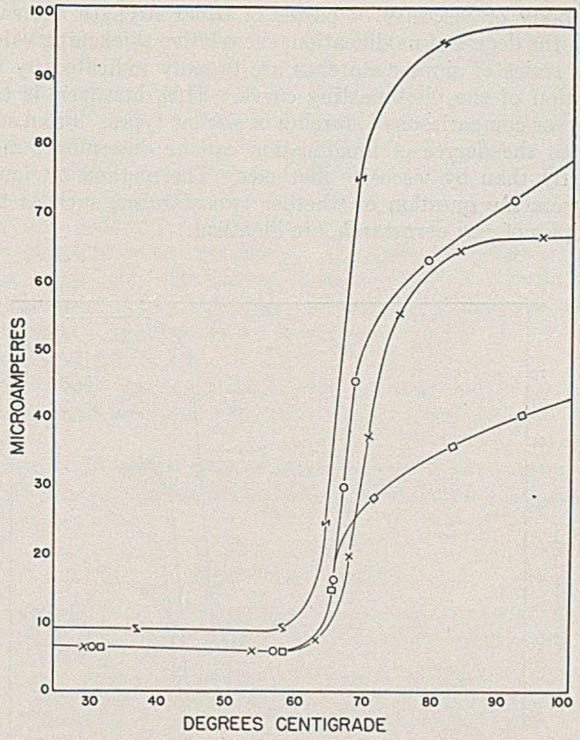


Figure 7. Pasting of Tapioca Dextrins

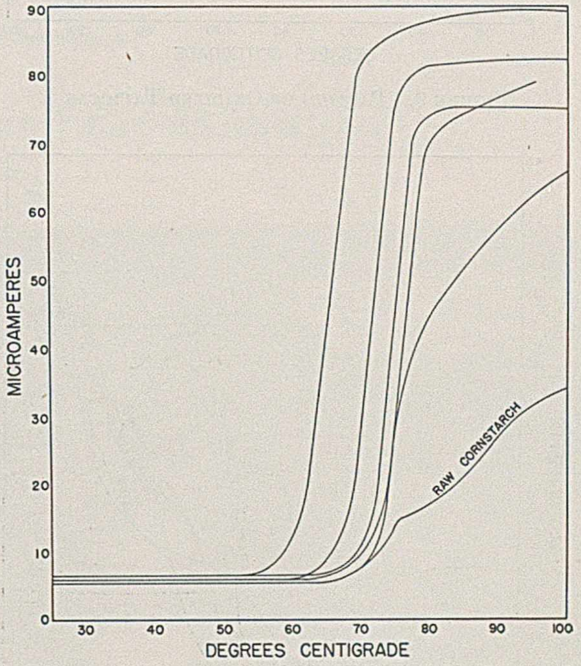


Figure 8. Pasting of Oxidized Cornstarches

Duplicate tests on a single starch generally give very closely checking curves. Various samples of raw cornstarch show the same pasting curve. A new type of cornstarch termed "waxy corn", isolated from a new breed of corn, is shown through the courtesy of one of the large starch companies; this starch pastes completely over a very narrow temperature range below 80° C., making it desirable. Furthermore, as the curve indicates, it is like the sweet potato and tapioca starches in paste characteristics. The two samples of sweet potato from the Laurel, Miss., plant were secured a year apart. Raw tapiocas are available in several grades and, as starch users are aware, vary somewhat in their characteristics. The pasting curves, while of the same type, also show variations.

Pasting of Modified Starches

In considering the graphs here presented, particularly those for modified starches, it is best to keep in mind when attempting to place quantitative values that these curves represent less and less starch as the light transmitted increases.

Thus in Figure 5 the relationship of transparency to amount of starch in suspensions of unpasted starch is shown to be a hyperbolic or inverse ratio function. For the simpler pasted starches this type of relationship also appears to be true.

In Figure 6 the form of the raw starch curve is still found in the acid thin-boiling starch curves, samples of two manufacturers being shown. The initial pasting temperature and the general location of the curve have, however, shifted upwards. Dextrinization has a greater effect, the curves showing decided shifts to lower initial pasting temperatures and greater final clarities, and the shifts being progressive with the increasing degree of dextrinization as shown by the figures for solubles. The 90 thin-boiling starch which had also been dextrinized shows an interesting curve indicating both types of treatments.

Similar shifts in the curves are found as tapioca is progressively dextrinized to higher degrees (Figure 7). Modification of starch by oxidative treatments likewise gives curves with progressive shifting locations (Figure 8). With tapioca starch, increasing degree of oxidative treatment also shifts the starch to earlier pasting and greater paste clarity (Figure 9).

It is apparent in Figures 6 to 9 that such modification leads to easier pasting and to completion of pasting at relatively low temperatures offering advantages for some types of commercial applications. Thus only the least modified oxidized cornstarch needs to be cooked beyond 80° C. As the body or viscosity of pastes of equal strength decreases with the degree of modification, the relative thickening values of a series of similar starches are broadly indicated by the location of the photopasting curve. This, however, is true only for comparisons of starches of similar types. From such curves the degree of modification can be determined more exactly than by viscosity methods. The method obviously answers the question of whether two starches, such as two samples of raw cornstarch, are identical.

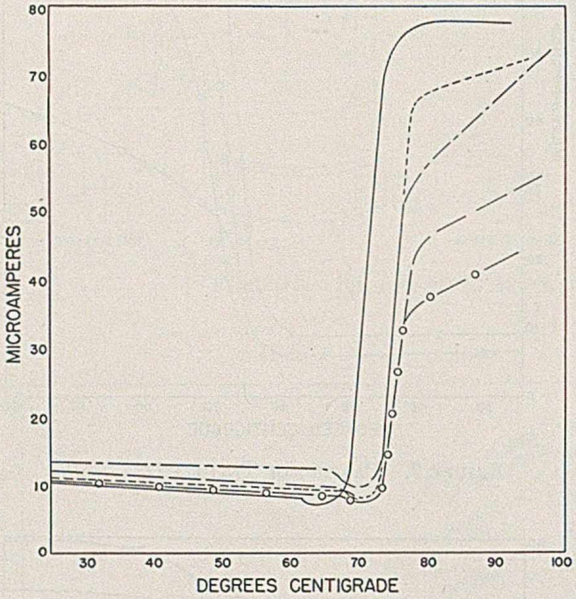


Figure 9. Pasting of Oxidized Tapiocas

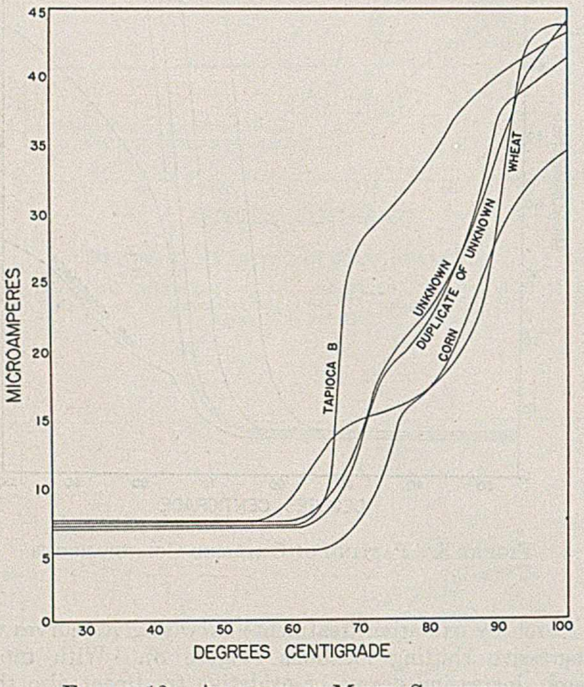


Figure 10. Analysis of Mixed Starches

At 80° C.	T	$1/T$	
Raw wheat Raw corn	17.0 ma.	0.0588	0.0588
Raw tapioca	33.0	0.0303	
Extreme difference		0.0285	
Unknown sample	21.5	0.0465	0.0465
Lower difference			0.0123

$$\% \text{ tapioca} = \frac{0.0123}{0.0285} = 43\%$$

Duplicate of unknown: 20 raw wheat, 40 raw corn, 40 raw tapioca

Analysis of Starch Mixtures

The use of the photopasting method of examination in the analysis of a complex starch mixture is shown in Figure 10, which also gives the curves for raw corn, wheat, and tapioca found by microscopic examination. Chemical tests and absence of color indicated no modification of the individual starches. Assuming that the curve for the sample represents the additive resultant of the three starches present each acting independently, we proceed to calculate the composition as shown in the graph. As the quantities of starch represented by a given light transmission are proportional to the reciprocal of the light transmission, these figures are used in the calculations.

At 80° C. the corn and wheat curves cross—each has the same degree of opacity—and we can consider the mixture as made up of two components: tapioca starch and the mixed corn and wheat. Obviously the displacement of the sample curve away from the corn-wheat intersection at 80° depends on the amount of tapioca. Consequently, the difference in reciprocals of these points at 80° on the two curves gives a means of estimating the amount of tapioca, and its percentage is related to the extreme difference in reciprocals of the corn-wheat point and the tapioca point at 80°.

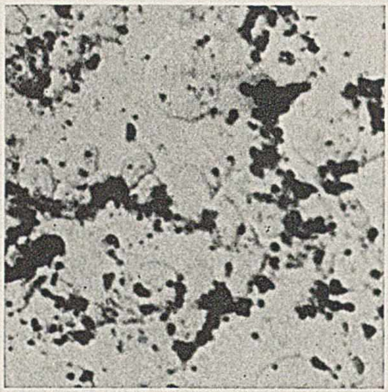


Figure 11. Textile Printing Paste

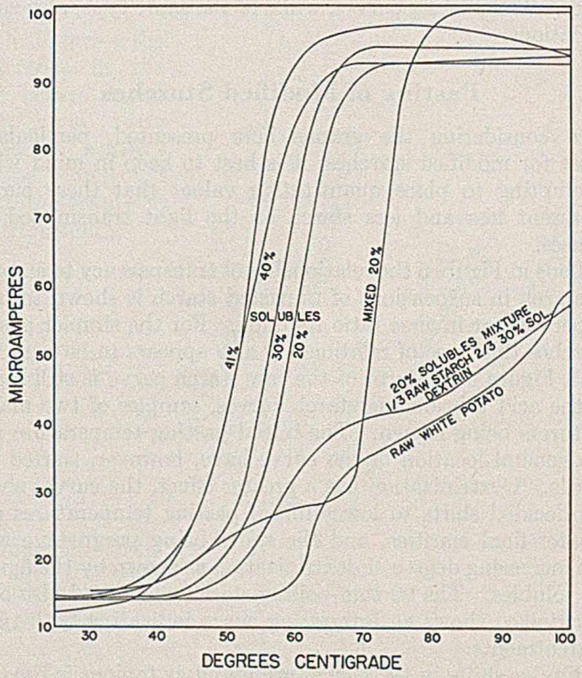


Figure 12. White Potato Dextrins

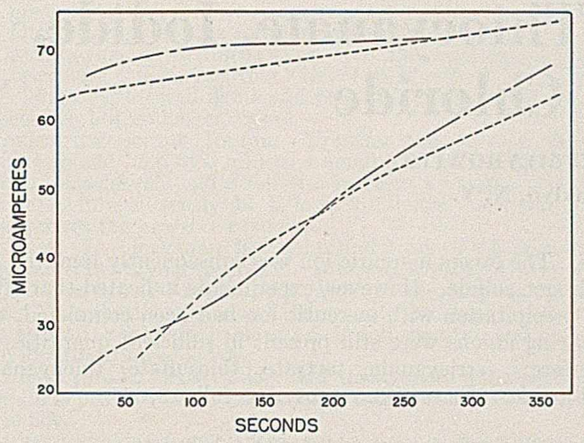


Figure 13. Rate of Solution of Prepasted Cold Water–Soluble Starch

Thus the calculation yields 43 per cent of tapioca at 80° C. and 45 per cent at 89.5° C., while at 66° C. 40 per cent of corn is indicated. The comparison curve of a 40 per cent corn, 40 per cent tapioca, and 20 per cent wheat mixture shows the correctness of conclusions in the general closeness of the two curves.

Such analysis, however, may be used only where the pasting, as shown in Figure 11, results in general swelling of the starch grains. The picture is of a textile printing paste showing swollen pasted starch, which is used as the thickening agent for carrying the dark particles of dyes.

Where the pasting involves fragmentation of the starch particle, as with dextrins which split off ringlike fragments, the relationship of solids to light transmission is evidently different from that shown by unpasted starch suspensions. Thus in Figure 12, which shows the effects of progressive dextrinization of white potato starch, three starches of 20 per cent solubles are shown. The true dextrin of 20 per cent solubles is easily located. The starch made by mixing a 30 per cent solubles with raw starch shows the presence of the raw starch in its curve location. However, it is apparent that this curve could not be used satisfactorily to calculate the composition. The third 20 per cent solubles dextrin was evidently a mixture of at least two dextrins and a small amount of raw starch.

Obviously gums, proteins, oils, or other admixtures not giving clear solutions affect the curves and show their presence.

Figure 13 offers rate of solution curves for a prepasted cold water–soluble starch and for a starch which was evidently the same.

Literature Cited

(1) Alsberg, C. L., and Rask, O. S., *Cereal Chem.*, 1, 107–15 (1924).
(2) Cook, D. H., and Axtmayer, J. H., Ind. Eng. Chem., Anal. Ed., 9, 226–8 (1937).
(3) Lane, J. H., and Eynon, L., "Starch Chemistry", pp. 92–3, Cambridge, England, W. Heffer & Sons, Ltd., 1924.
(4) Sjostrom, R. L., Ind. Eng. Chem., 28, 63 (1936).

Presented before the Division of Sugar Chemistry and Technology at the 98th Meeting of the American Chemical Society, Boston, Mass.

Simple Hot Filtrations and Crystallizations

JOHN W. DAWSON and WILLIAM M. DEHN
University of Washington, Seattle, Wash.

A GREAT inconvenience in filtering hot saturated solutions is crystallization in the paper and in the stem of the funnel. Hot-water funnels are not always available or may be fire hazards.

The depicted forms, built from stock apparatus, employ truncated funnels and filter papers pending therethrough. The beakers are ordinary or are indented to support the funnels. The funnel in the large beaker rests on an inverted cutoff wide-mouthed bottle. The evaporating dish may contain water or ice. The glass cooling bulb is a modification of Conant's apparatus (*1*), carrying warty lumps on its bottom to distribute the condensed solvent over the solid contained in the funnel.

Some of the solvent is placed in the beaker and heated to boiling for the time necessary to heat the entire apparatus. The boiling solution, contained in another beaker, is then poured in and heating is continued until filtering is complete or until the boiling solvent has supplied sufficient vapor to dissolve all material in the filter paper. The large beaker is especially useful when water is the solvent. The bulb condenser is useful with difficultly soluble solids, since it is practically automatic.

This apparatus has a decided advantage over that of Tanner (*2*, *3*), in that fresh solvent is continually in contact with the material being filtered.

Literature Cited

(1) Conant, J. B., "Organic Synthesis", Vol. II, p. 49, New York, John Wiley & Sons, 1922.
(2) Stoltenberg, *Chem.-Ztg.*, 33, 759 (1909).
(3) Tanner, H. G., Ind. Eng. Chem., Anal. Ed., 4, 397 (1932).

Systematic Detection of Thiocyanate, Iodide, Bromide, and Chloride

DAVID HART AND ROBERT MEYROWITZ
Brooklyn College, Brooklyn, N. Y.

SILVER ion (usually as silver nitrate) is used as a group reagent in the majority of methods (*2–7*) that have been proposed for the systematic detection of thiocyanate, iodide, bromide, and chloride.

Since these anions are again brought into solution for identification, the attempt was made to develop a method for the systematic detection of thiocyanate, iodide, bromide, and chloride, wherein a separate portion of the aqueous solution of alkali salts is used for the detection of each anion without the use of silver ion as a group reagent, and provision is made for the interferences that might be present. The work described is based on Curtman's systematic detection of acids (*1*).

In developing the new procedure, the following standard methods were selected for the identification of the halides: ferric ion for thiocyanate; hydrogen peroxide to liberate the iodine, which is then extracted with carbon tetrachloride; potassium permanganate to liberate bromine, which is also extracted with carbon tetrachloride; and silver ion to detect chloride. Using these identification tests, the common interfering anions were found to be ferricyanide, ferrocyanide, cyanide, sulfide, arsenite, thiosulfate, sulfite, oxalate, and tartrate.

DETECTION OF THIOCYANATE. In the systematic detection of the halides, the most serious interference is caused by thiocyanate. Therefore, it is desirable to determine whether or not this anion is present before proceeding with the detection of the halides.

Large amounts of iodide interfere with the detection of thiocyanate by means of ferric ion. Preliminary experiments showed that in the absence of thiocyanate, 100 mg. of iodide, which is the maximum amount likely to be present, would yield a test indistinguishable from a positive test for thiocyanate; but when lead ion was used to precipitate the iodide an insufficient amount remained in solution to give a positive test, while as much as 20 mg. of thiocyanate remained in 5 ml. of solution unprecipitated by the lead ion.

DETECTION OF IODIDE. When 3 per cent hydrogen peroxide and carbon tetrachloride were used to detect iodide, experiments indicated that ferricyanide, ferrocyanide, sulfide, cyanide, arsenite, thiocyanate, and thiosulfate interfered. The following methods were found to be effective in removing these interferences:

Ferricyanide, ferrocyanide, sulfide, and cyanide were precipitated by cobalt acetate from a solution made just acid with dilute sulfuric acid.

Sulfide and cyanide, in the absence of ferricyanide and ferrocyanide, were removed by boiling the solution after acidifying with dilute sulfuric acid.

Arsenite, when treated with hydrogen sulfide in dilute sulfuric acid solution, was converted to insoluble arsenious sulfide.

Thiocyanate was destroyed by boiling with concentrated sulfuric acid.

Thiosulfate was decomposed by boiling the solution which had been acidified with dilute sulfuric acid.

TEST FOR BROMIDES. To avoid the use of a large volume of potassium permanganate solution with the possible formation of manganese dioxide, when testing for bromide, it was necessary to remove as much as possible of other reducing acids that might be present. To accomplish this without removing the bromide, mercuric acetate was found to be effective. The excess mercuric ion was subsequently removed by hydrogen sulfide. However, experiments indicated that after the precipitation with mercuric ion had been completed, the following anions were still present in sufficient quantities to interfere: ferricyanide, tartrate, thiosulfate, thiocyanate, and iodide. These were removed as follows:

Ferricyanide was precipitated with cobalt acetate.

Tartrate was precipitated with lead acetate.

Thiosulfate was destroyed by boiling the solution before filtering off the mercury-reducing acid precipitate.

Thiocyanate was decomposed by boiling with concentrated sulfuric acid.

Iodide was removed by boiling with sodium nitrite in a dilute sulfuric acid solution.

The formation of manganese dioxide has been a disadvantage in the use of potassium permanganate for the detection of bromide. It was found that this could be avoided by making the solution strongly acid with sulfuric acid.

TEST FOR CHLORIDES. In the detection of chloride with silver ion, the interfering anions are ferricyanide, ferrocyanide, sulfide, thiocyanate, cyanide, iodide, bromide, and thiosulfate, which were removed in the following manner:

Ferricyanide, ferrocyanide, sulfide, and cyanide were precipitated with cobalt acetate.

Sulfide and cyanide in the absence of ferricyanide, ferrocyanide, iodide, bromide, and thiosulfate were removed by boiling the solution which had been previously acidified with dilute sulfuric acid.

Iodide, bromide, thiocyanate, and thiosulfate were removed by steam-distillation from a solution containing 30 per cent concentrated nitric acid. A small amount of bromide remained, but this was removed by potassium permanganate and carbon tetrachloride. The color of the excess potassium permanganate was subsequently destroyed by sodium nitrite. An attempt was made to remove the iodide and the bromide from solution merely by boiling instead of steam-distillation. However, under certain conditions, in the presence of iodide, chloride was lost (Table I).

The colloidal sulfur resulting from the decomposition of thiosulfate was removed by shaking with black mercuric sulfide and filtering the mixture.

Systematic Detection of Thiocyanate

Treat 3 ml. of the solution with 3 *M* nitric acid until no more carbon dioxide bubbles are given off (about 3 ml.) and add 1 ml. in excess. Now add 3 ml. of 1 *M* lead nitrate, and if ferricyanide is present add also 2 ml. of 1 *M* cobalt nitrate. Filter or centrifuge. To the filtrate add 1 ml. of 0.3 *M* ferric nitrate. A blood-red solution shows the presence of thiocyanate.

Systematic Detection of Iodide

REMOVAL OF FERRICYANIDE AND FERROCYANIDE. Acidify 3 ml. of the solution with 1.5 *M* sulfuric acid. Add dropwise with constant stirring 2 ml. of 1 *M* cobalt acetate and 3 ml. of water saturated with hydrogen sulfide. Heat to boiling and boil for 30 seconds with constant stirring. Centrifuge or filter into a small test tube, using suction.

The filtration should proceed slowly, at the rate of one drop per second, to prevent the precipitate from passing through the filter. Rinse the container with 2 ml. of water and heat to boiling. Wash the precipitate with the rinsings and combine the washings with the filtrate. The filtrate must be clear.

REMOVAL OF ARSENITE. To the acidified solution add 2 ml. of 1.5 *M* sulfuric acid and pass hydrogen sulfide through the solution until all the arsenic has been precipitated. Filter, wash the precipitate with 5 ml. water, and combine the washings with the filtrate, evaporate the solution to 4 to 5 ml., and cool.

Destruction of Thiocyanate. To the acid solution add dropwise with constant stirring 2 ml. of 18 *M* sulfuric acid. Heat to boiling over a small flame and boil with constant stirring for 30 seconds, but no longer. Cool.

Identification of Iodide. Transfer the solution (whose volume should be 4 to 5 ml.) to a small test tube, add 2 ml. of carbon tetrachloride and 3 ml. of 3 per cent hydrogen peroxide, and shake intermittently for at least 2 minutes. A violet lower layer proves the presence of iodide.

Notes. If thiocyanate is absent, add 1 ml. of 1.5 *M* sulfuric acid before identifying the iodide. If arsenate is absent, evaporate the solution to 4 to 5 ml. and cool, before destroying the thiocyanate. When both arsenite and thiocyanate are absent, evaporate to 4 to 5 ml., cool, add 1 ml. of 1.5 *M* sulfuric acid, and proceed with identification of iodide.

If ferricyanide, ferrocyanide, and thiocyanate are absent and arsenite is present, add 1 ml. of 1.5 *M* sulfuric acid before testing for iodide.

If ferricyanide, ferrocyanide, and arsenite are absent and thiocyanate is present along with either sulfide or cyanide, acidify 3 ml. of the solution with 1.5 *M* sulfuric acid, add 2 ml. in excess, dilute to 12 ml., and evaporate to 4 to 5 ml. Cool. Then proceed with destruction of thiocyanate.

If ferricyanide, ferrocyanide, arsenite, and thiocyanate are absent and sulfide or cyanide is present, acidify 3 ml. of the solution with 1.5 *M* sulfuric acid, add 2 ml. in excess, dilute to 12 ml., and evaporate to 4 to 5 ml. Cool, add 1 ml. of 1.5 *M* sulfuric acid to the solution, and then proceed with identification of iodide.

If ferricyanide, ferrocyanide, arsenite, sulfide, and cyanide are absent and thiocyanate is present, dilute 3 ml. of the solution with 1 ml. of water and proceed with destruction of thiocyanate.

If ferricyanide, ferrocyanide, arsenite, sulfide, cyanide, and thiocyanate are all absent, acidify 3 ml. of the solution with 1.5 *M* sulfuric acid, add 2 ml. in excess, and evaporate to 4 to 5 ml. Cool and proceed with identification of iodide.

Systematic Detection of Bromide

Precipitation of Interfering Acids with Mercuric Acetate. Acidify 3 ml. of the solution with 1.5 *M* sulfuric acid. If ferricyanide is present, add 2 ml. of 1 *M* cobalt acetate dropwise and with constant stirring. Then add 2 ml. of 0.75 *M* mercuric acetate (this solution should contain 5 ml. of glacial acetic acid in 100 ml. of solution) dropwise and with constant stirring. If tartrate is present, add 2 ml. of 1 *M* lead acetate. Stir vigorously for at least 3 minutes. If thiosulfate is present, heat to boiling, boil for 1 minute, and cool. Filter, using suction, into a small test tube. Rinse beaker with 2 ml. of water and wash the precipitate with the rinsings. Combine the washings with the filtrate, transfer the solution to a large test tube, and add 2 ml. of 1.5 *M* sulfuric acid. Pass hydrogen sulfide through the solution until all the mercury has been precipitated. Filter into a small test tube using suction, rinse the large test tube with 5 ml. of water, and wash the precipitate with the rinsings. Combine the washings with the filtrate, transfer to a 100-ml. beaker, and evaporate to 4 to 5 ml. Cool.

Destruction of Thiocyanate. To the solution add dropwise with constant stirring 2 ml. of 18 *M* sulfuric acid. Heat to boiling over a small flame and boil with constant stirring for 30 seconds, but no longer. Cool.

Removal of Iodide. To the solution add dropwise with constant stirring 13 ml. of 3 *M* sodium hydroxide. Under a hood add, with constant stirring, 1.5 ml. of 6 *M* sodium nitrite. Heat to boiling while stirring, evaporate to 4 to 5 ml., and cool. To the solution add with constant stirring 1 ml. of 18 *M* sulfuric acid. Cool.

Identification of Bromide. Transfer the solution to a small test tube. Add 1 ml. of carbon tetrachloride and then 0.02 *M* potassium permanganate in 1-ml. portions (shaking after the addition of each portion) until the aqueous layer remains pink. A yellow or brown carbon tetrachloride layer shows the presence of bromide.

Notes. If thiocyanate is absent, add 7 ml. of 1.5 *M* sulfuric acid instead of 13 ml. of 3 *M* sodium hydroxide in the removal of iodide. If both thiocyanate and iodide are absent, add 1 ml. of 18 *M* sulfuric acid to the solution and cool before testing for bromide.

Systematic Detection of Chloride

Removal of Ferricyanide and Ferrocyanide. Proceed as in the detection of iodide.

Removal of Thiocyanate, Iodide, Bromide, and Thiosulfate. Transfer the solution to a 100-ml. beaker and dilute to 20 ml. Add with constant stirring 10 ml. of 16 *M* nitric acid, transfer to a 125-ml. Erlenmeyer flask, and steam-distill until 10 ml. of distillate have been collected. The source of the steam is distilled water in a 125-ml. flask.

Removal of the Small Amount of Remaining Bromide. If bromide is present, add 0.1 *M* potassium permanganate in 1-ml. portions until the solution remains pink for at least 4 minutes. Transfer to a 60-ml. separatory or dropping funnel, add 2 ml. of carbon tetrachloride, and shake. Separate the two layers and discard the lower layer. Continue extracting the solution with 2-ml. portions of tetrachloride until the lower layer is colorless. Add to the solution 6 *M* sodium nitrite, one drop at a time, shaking after the addition of each drop, until the color due to the permanganate has been removed.

Identification of Chloride. If the solution is cloudy, owing to colloidal sulfur resulting from the decomposition of thiosulfate, shake it with 0.5 gram of black mercuric sulfide (Ethiops mineral, powder) and filter until a clear solution is obtained. Transfer the solution to a large test tube, add 3 ml. of 0.5 *M* silver nitrate, and stir. Let stand for at least 5 minutes. A white precipitate indicates the presence of chloride. Compare with a 1-mg. chloride control which has been obtained by using the same procedure. If the precipitate obtained is less than the 1-mg. chloride control and iodide was present, compare the precipitate with a control of 100 mg. of iodide and 1 mg. of chloride which has undergone the same procedure. If the original precipitate is similar in size to that obtained in the control, chloride is present; if it is much less than this control, chloride is absent.

Notes. If ferricyanide or ferrocyanide is present and thiosulfate, iodide, bromide, and thiocyanate are all absent, add 1 ml. of 16 *M* nitric acid before proceeding to identification of chloride.

If ferricyanide and ferrocyanide are absent, and cyanide or sulfide is present together with iodide, bromide, thiocyanate, or thiosulfate, acidify 3 ml. of the solution with 1.5 *M* sulfuric acid, add 2 ml. in excess, dilute to 12 ml., evaporate to 4 to 5 ml., and proceed to removal of bromide, iodide, thiocyanate, and thiosulfate.

If thiosulfate, bromide, iodide, thiocyanate, ferricyanide, and ferrocyanide are all absent and cyanide or sulfide is present, treat 3 ml. of the solution with 1.5 *M* sulfuric acid until it is acid to litmus, add 2 ml. in excess, dilute to 12 ml., and evaporate to 4 to 5 ml. Add 1 ml. of 16 *M* nitric acid and then proceed with identification of chloride.

If all interfering acids are absent, acidify 3 ml. of the solution with 16 *M* nitric acid, add 1 ml. in excess, and proceed with identification of chloride.

Table I. Test Analyses for Chloride

(When bromide and iodide are removed by boiling with nitric acid)

Expt. No.	Cl^- *Mg.*	Br^- *Mg.*	I^- *Mg.*	Results
1	1	0	100	No precipitate
2	2	0	100	No precipitate
3	5	0	100	White precipitate approximately same as 1-mg. Cl^- control
4	5	0	50	White precipitate approximately same as 1-mg. Cl^- control
5	1	50	50	No precipitate
6	1	0	25	Faint opalescence
7	1	75	25	Faint precipitate
8	0	75	25	Very faint opalescence[a]

[a] Very faint opalescence is due to a trace of chloride present as impurity in bromide. This chloride is also lost when large amounts of iodide are present (expt. 5).

Test Analyses

To test the efficiency of the above procedures, over 200 test analyses were performed. The results were as follows:

One milligram of thiocyanate was successfully detected in the presence of 100 mg. of iodide, thiosulfate, sulfite, tartrate, oxalate, arsenite, ferricyanide, ferrocyanide, sulfide, and cyanide.

Positive tests were obtained for 1 mg. of thiocyanate in the presence of 100 mg. each of the colored cations of nickel, manganese, cobalt, copper, and chromium.

One milligram of iodide was successfully detected in the presence of interfering anions.

In the presence of 100 mg. of interfering anions, 2 mg. of bromide were successfully detected.

Positive tests were obtained for 1 mg. of chloride in the presence of 100 mg. of interfering anions.

Losses in chloride occur when bromide and iodide are removed by merely boiling with nitric acid (see Table I). Hence, it was found necessary to remove bromides and iodides by steam-distillation.

Summary

A new procedure for the systematic detection of thiocyanate, iodide, bromide, and chloride has been developed which does not involve the use of silver ion as a group reagent. This method is capable of detecting 1 mg. each of thiocyanate, iodide, and chloride, and 2 mg. of bromide in 3 ml. of solution.

In addition to the usual interfering acids, ferrocyanide, ferricyanide, cyanide, and sulfide, it was found that thiosulfate, arsenite, and tartrate interfered in the new procedure. Hence, methods were devised for the removal of all interferences.

Acknowledgment

The authors wish to thank L. J. Curtman for the aid he has given them in the investigation of this problem which originated in the laboratory of the City College, College of the City of New York.

Literature Cited

(1) Curtman, L. J., "Qualitative Chemical Analysis", p. 421, New York, Macmillan Co., 1938.
(2) *Ibid.*, p. 473 (1933 edition).
(3) Curtman and Schneiderman, *Rec. trav. chim.*, 54, 158 (1935).
(4) Heisig and Heisig, Ind. Eng. Chem., Anal. Ed., 7, 249 (1935).
(5) MacAlpin, Soule, Prescott, and Johnson, "Qualitative Chemical Analysis", p. 572, New York, D. Van Nostrand Co., 1933.
(6) Noyes, A. A., "Qualitative Chemical Analysis", 9th ed., New York, Macmillan Co., 1922.
(7) Swift, E. H., "System of Chemical Analysis", New York, Prentice-Hall, 1939.

Analysis of Mixtures of Aliphatic Acids

Simultaneous Qualitative and Approximate Quantitative Determination

S. T. SCHICKTANZ[1], W. I. STEELE, AND A. C. BLAISDELL
U. S. Treasury Department Laboratory, Washington, D. C.

SMALL amounts of mixtures of volatile acids have usually been reported in the literature as calculated as acetic or formic acids, etc. Much more vital information would be obtained if these mixtures could be conveniently separated and reported as a quantitative measure of the amount of the individual acids present.

Much work has been done on the Duclaux (*1*, *2*, *11*) method for separating and identifying quantitatively the acids in a mixture. The method, however, is open to serious objections (*3*) and may give misleading and erroneous results when the mixtures contain more than two acids. This appears to be especially true when the acidic components have not been previously identified.

Klein and Wenzl (*4*) suggest a method for identifying the various acids from formic to caprylic by their precipitation characteristics with inorganic salts. Osburn, Wood, and Werkman (*7*) suggest a method for the quantitative analysis of mixtures, of acids by a combination of simple distillation with partition between water and ethyl ether. McNair (*5*) determines propionic acid in mixtures by an oxidation procedure. Sukhonanskiĭ and Roginskaya (*10*) identify propionic acid by the use of lead oxide and acetic acid by subsequent fusion with potassium hydroxide and copper oxide. Venogrado and Oshoumova (*12*) separate butyric and propionic acids in mixtures by conversion to soaps, then hydrolyzing and estimating butyric acid by the yellow precipitate formed with ferric chloride.

Since practically all methods previously described are applicable only in special instances where the mixtures of acids are relatively simple and the qualitative aspects of the sample are known, it appeared desirable to develop a method which would be quantitative as well as qualitative, require no special apparatus or technique, and be capable of operating on small amounts of material.

The present paper describes a process or method of analysis for the simultaneous qualitative and quantitative analysis of formic, acetic, propionic, isobutyric, and *n*-butyric acids in complex acidic mixtures by azeotropic distillation with benzene and toluene.

Since the homologous series of aliphatic acids belongs to that group of compounds which exhibits molecular association, they tend consequently to form abnormal solutions among themselves. This makes almost impossible a separation of a mixture of the acids by straight distillation alone. Also, small amounts of mixtures of acids would require special distillation units capable of distilling efficiently volumes as small as 1 ml. of liquid. However, because of molecular association the acids are azeotropically active and form minimum boiling azeotropes with hydrocarbons. Molecular association and azeotropic activity of the acids decrease as the series ascends from formic to *n*-butyric, and the acids separate when distilled with selected hydrocarbons. Benzene and toluene appear to be the hydrocarbons best suited for the separation of these acids.

Since the binary azeotropic systems of acid and hydrocarbon are very sensitive to water and to organic solvents, it is necessary to work with anhydrous concentrates of acidic materials which are free of all solvent material.

The method can also be applied successfully to a mixture of the sodium salts of the acids. This makes possible the separation of the acids from all other organic solvents which might interfere with the determination. Furthermore, the salts can be obtained easily in an anhydrous state by refluxing them in a dehydrating apparatus (Youtz type of receiver for moisture determinations, *9*) with toluene or benzene. The dry salts thus obtained are refluxed with anhydrous toluene sulfonic acid dissolved in benzene or toluene, which liberates for analysis the unknown acids. The excess toluene sulfonic acid is stable at the temperatures used and does not appear in the distillate.

Formic and acetic acids, which have low boiling points, form azeotropes with benzene. Propionic, isobutyric, and *n*-butyric acids, which boil so much higher than benzene, are azeotropically inactive with it. Consequently in the distillation of an acid mixture, the formic and acetic acids are removed quantitatively as a mixture. However, because of the lower boiling point and greater azeotropic activity, formic acid is the first to be removed during the distillation. Thus during the benzene distillation the formic acid is removed first, followed by distillation of the acetic, leaving the other acids behind in the still pot.

---

[1] Present address, U. S. Department of Agriculture, Southern Regional Research Laboratory, New Orleans, La.

Toluene forms azeotropes with all the acids from formic to and including *n*-butyric acid. However, since in this procedure the formic and acetic acids are removed by benzene distillation, prior to the addition of toluene, the acidic solution contains only propionic, isobutyric, and butyric acids. The latter three acids form azeotropes with toluene which have boiling points relative to that of the acid itself. Consequently, in the distillation, propionic acid forms the azeotrope having the lowest boiling point and is removed first, followed subsequently by the isobutyric acid azeotrope and then the *n*-butyric acid azeotrope.

Because of the relatively small amount of acids necessary to form the azeotropes, it is possible to work with small volumes of acid mixtures utilizing relatively large-sized equipment for the distillation. In column 3 of Table I are given the moles of the acids contained in 1 ml. of distillate as recovered during a systematic distillation. In column 4 are given the volumes of azeotrope produced by 0.1 mole of the acids.

Advantages of the azeotropic method of distillation are: (1) no high temperatures are encountered; (2) no complicated chemical reactions are involved; (3) all of each acidic constituent is utilized, since during the distillation an excess of hydrocarbon is introduced into the still pot to ensure the removal of the highest boiling acidic constituent at low temperatures and under conditions where no decomposition occurs; (4) the major portion of the azeotrope consists of hydrocarbon, which makes possible the utilization of ordinary laboratory distillation equipment for the analysis of small amounts of acidic material; (5) separation of the azeotropes (hydrocarbon-acid) by distillation is more easily performed than separation of the acids themselves by distillation; and (6) the acid constituents are not destroyed but may be recovered as the sodium salts for further investigation.

TABLE I. AZEOTROPE PRODUCED

Acid	Hydrocarbon	Acid Recovered	Azeotrope Produced by 0.1 Mole of Acid
		Moles/Ml.	*Ml.*
Formic	Benzene	0.00150	66
Acetic	Benzene	0.00027	370
Propionic	Toluene	0.00027	370
Isobutyric	Toluene	0.000049	2040
n-Butyric	Toluene	0.000020	5000

Reagents

Ninety per cent formic acid, reagent grade, and glacial acetic acid, reagent grade, were used without further purification. Eastman Kodak Company's propionic and *n*-butyric acids were redistilled prior to use. Eastman Kodak Company's isobutyric acid contained by analysis 98.7 per cent acid and was not further purified. The benzene and toluene used were from large middle cuts of a simple distillation of technical grades of benzene and toluene. The hydrocarbons were dried by storage over sodium. Toluenesulfonic acid was prepared according to the method of Meyer (*6*); 40 ml. of concentrated sulfuric acid plus 200 ml. of toluene were refluxed for 4 hours in the dehydrating apparatus. After cooling, the mixture plus an excess of toluene was placed in a modified Palkin's (*8*) extractor and extracted for 2 hours. The extract, which amounted to almost 400 ml., contained approximately 0.0014 mole of acid per ml. The solution was stored in a glass-stoppered bottle.

A benzene solution of toluenesulfonic acid was also employed. This solution was prepared by removing the water from toluenesulfonic acid monohydrate obtained from the Eastman Kodak Company, by dissolving the acid in benzene and refluxing for 3 hours in the dehydrating apparatus.

Analytical Procedure

In the event that the mixture of acids is obtained pure and anhydrous, the technique of the method is simplified.

To the acid mixture placed in a distillation flask is added dry benzene (200 to 300 ml.) and the distillation is performed in an ordinary packed-column still (the distillations in this laboratory were all made in a still having a 90-cm., 3-foot, column, 1.25 cm., 0.5 inch, in diameter, and packed with small glass helices). The contents of the still are allowed to reflux 10 minutes before removing the distillate in 10-ml. fractions at a rate of 1 ml. per minute.

Any acid appearing in the benzene distillate will be formic or acetic or both. If they are not present the distillate will be practically neutral, since the higher boiling acids are not azeotropically active with benzene.

If it is found during the distillation that the volume of benzene added originally is insufficient, the distillation may be interrupted and an additional volume of benzene added without harm to the results of the analysis.

After the formic and acetic acids have been removed the distillation is continued to remove most of the excess of benzene before adding 200 to 300 ml. of dry toluene. The small amount (25 to 50 ml.) of benzene remaining distills off first and does not interfere with the azeotropic distillation of the higher boiling acid substances. The toluene distillation is continued until the 10-ml. fractions of distillate contain less than 0.04×10^{-3} mole of acid. At this point practically all of the acid constituents have been removed from the pot liquor.

As the fractions are removed from the still they are mixed with about 20 ml. of water in an Erlenmeyer flask, shaken vigorously for 15 seconds, and titrated with 0.1 sodium hydroxide, using phenolphthalein as the indicator. As the end point is approached, it is necessary to shake the Erlenmeyer flask vigorously to be sure that all of the acid in the hydrocarbon layer has been titrated.

In case the unknown acid mixture is obtained as the sodium salts, the following procedure is recommended:

The salts are evaporated to dryness in an evaporating dish on the steam bath, finely powdered, and placed in a 500-ml. round-bottomed flask equipped with a standard taper joint which fits the distillation column and also the dehydrating unit. To the flask are added benzene and some boiling stones (Carborundum chips) to prevent excessive bumping, and the flask is then attached to the dehydrating apparatus. The contents are allowed to reflux until no moisture is evident in the condensate forming in the condenser. To the cooled contents is now added an excess of the dry solution of toluenesulfonic acid in benzene or toluene, and the flask is attached to the distillation unit and allowed to reflux 0.5 hour before beginning the removal of distillate. During the reflux period the aliphatic acids are liberated from the salts by the stronger toluenesulfonic acid, and thus are available to form the respective azeotropes with the hydrocarbons. The distillation and the titration of the acids in the distillates are carried out as described above.

Discussion

In Table II is given a summary of the results of the distillations of the various acids by themselves and in binary mixtures with benzene and toluene, respectively.

The high content of acid in the first fraction for formic acid and when in combination with acetic acid (columns 2 and 4, respectively) was due to the presence of water in the formic acid that was used. Normally the value for the first fraction for anhydrous formic acid is 15×10^{-3} mole, as evident from the values in Table V.

When the individual acids are distilled alone with the hydrocarbon, a definite reduction in concentration of acid per fraction occurs when the acid is almost completely removed from the still pot (columns 2, 3, 5, 6, and 7). Likewise the mixtures containing only two acids, especially the mixtures formic-acetic and propionic-isobutyric, show a definite decrease in concentration of the acid in the fractions as the lowest boiling acid is completely removed from the mixture. The demarcations are underscored in columns 4, 8, 9, and 10. In columns 9 and 10, however, the end of the distillation of one acid and the beginning of the distillation of the other acid are not very evident. Careful analysis of these data and those for the individual acids themselves (columns 5, 6, and 7) makes it appear that the boiling point difference and azeotropic activity are not great enough to make it possible completely to separate these acids by distillation with toluene. However, since the composition of the complex azeotrope formed with the acids and toluene is very constant, it was possible by di-

Table II. Azeotropic Distillation of Aliphatic Acids and Their Mixtures with Benzene and Toluene

(Volume of hydrocarbon fraction, 10 ml.)

	Benzene			Toluene					
Fraction	1.0 ml. formic	1.0 ml. acetic	1.0 ml. formic, 1.0 ml. acetic	1.0 ml. propionic	0.5 ml. isobutyric	0.25 ml. *n*-butyric	1.0 ml. propionic, 0.5 ml. isobutyric	1.0 ml. propionic, 0.25 ml. *n*-butyric	0.5 ml. isobutyric, 0.25 ml. *n*-butyric
				Moles of acid $\times 10^{-3}$					
1	24.1	2.62	22.47	2.43	0.49	0.23	2.55	2.65	0.45
2	7.9	2.50	3.77	2.60	0.47	0.20	2.66	2.53	0.41
3	1.6	2.43	1.77	2.72	0.46	0.20	2.39	2.17	0.39
4	0.35	2.41	2.14	2.65	0.45	0.20	1.84	1.44	0.37
5	0.19	2.40	1.84	1.58	0.45	0.19	1.49	1.21	0.36
6	0.11	2.34	1.74	0.52	0.45	0.19	1.20	0.89	0.34
7	0.02	1.41	0.99	0.24	0.45	0.18	0.93	0.63	0.32
8	..	0.88	0.72	0.09	0.45	0.18	0.93	0.45	0.31
9	..	0.62	0.62	0.04	0.44	0.17	0.49	0.32	0.29
10	..	0.15	0.50	..	0.42	0.17	0.46	0.26	0.27
11	..	0.08	0.43	..	0.40	0.17	0.45	0.18	0.26
12	..	..	0.33	..	0.34	0.17	0.44	0.17	0.23
13	..	..	0.20	..	0.20	0.17	0.43	0.16	0.20
14	..	..	0.15	..	0.08	0.17	0.43	0.15	0.19
15	..	..	0.12	..	0.02	0.17	0.42	0.14	0.18
16	..	..	0.10	..	..	0.15	0.40	0.13	0.17
17	..	..	0.09	..	..	0.13	0.34	0.12	0.15
18	..	..	0.08	..	..	0.12	0.25	0.12	0.12
19	..	..	0.06	..	..	0.10	0.16	0.12	0.10
20	..	..	0.05	..	..	0.08	0.09	..	0.08
21	..	..	0.05	..	..	0.06	..	..	0.06
22	..	..	0.04	..	..	0.04	..	..	0.04
Total acid used, ml.	1.0	1.0	2.0	1.0	0.5	0.25	1.5	1.25	0.75

rect experimentation to assign a comparatively true demarcation point.

Analysis of the data given in Table II, columns 4, 8, 9, and 10, with regard to the variations of the decrease in concentration of acid per fraction, illustrates the method used to obtain qualitative results on binary mixtures of acids. In column 4, the distillation of a mixture of formic and acetic acids with benzene indicates that formic acid must have been present because of the high acid content of fraction 1 (compare with fraction 1 of column 2). If formic had been the only acid present, a large decrease in acid concentration would have been evident after the removal of fraction 3. However, the variation in the decrease in acid concentration subsequent to fraction 3 indicates the presence of another acid which is acetic, since no other acid distills with benzene, and also since the decrease in acid concentration with an increase in the number of fractions is analogous to the data obtained with pure acetic acid (column 3). Similar analyses are made to obtain qualitative results for the other acid mixtures (columns 8, 9, and 10).

In Figure 1 are shown the curves obtained by plotting moles of acid in the distillate against volume of distillate for the distillation of propionic, isobutyric, and *n*-butyric acids, respectively, with toluene.

In Figure 2 are shown the curves obtained by the distillation of mixtures of acids with toluene. Curve 1 shows the toluene distillation of a binary mixture containing 1 ml. of propionic and 0.5 ml. of isobutyric acids; curve 2, 1 ml. of propionic and 0.25 ml. of *n*-butyric acids; curve 3, 0.5 ml. of isobutyric and 0.25 ml. of *n*-butyric acids.

By comparing the curves of Figure 1 with those of Figure 2, the effect of the presence of an additional acid component on the shape of the propionic acid curve is readily noted. Similarly, the effect of *n*-butyric acid on the distillation behavior of isobutyric acid is also evident.

The quantitative evaluation of the individual acids of a mixture is more difficult and can only be approximate by virtue of inability to separate the acid azeotropes completely from each other. The demarcation lines in columns 4, 8, 9, and 10 of Table II are placed at the points at which it is assumed, from analysis of the distillation behavior of the binary mixtures with that of the individual acids of columns 2, 3, 5, and 6, that the low-boiling acid in the mixture is completely removed from the still. The acid appearing in the distillate from then on is assumed to be the next higher boiling acid.

The volumes of acids and acid mixtures used in the determination indicate the very small volumes of acids and acid

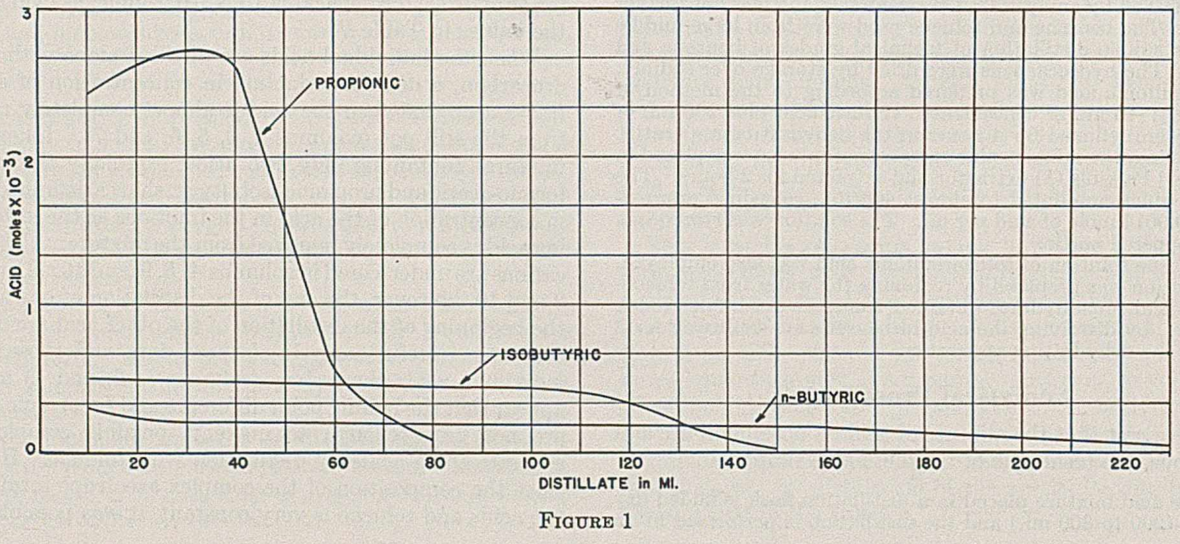


Figure 1

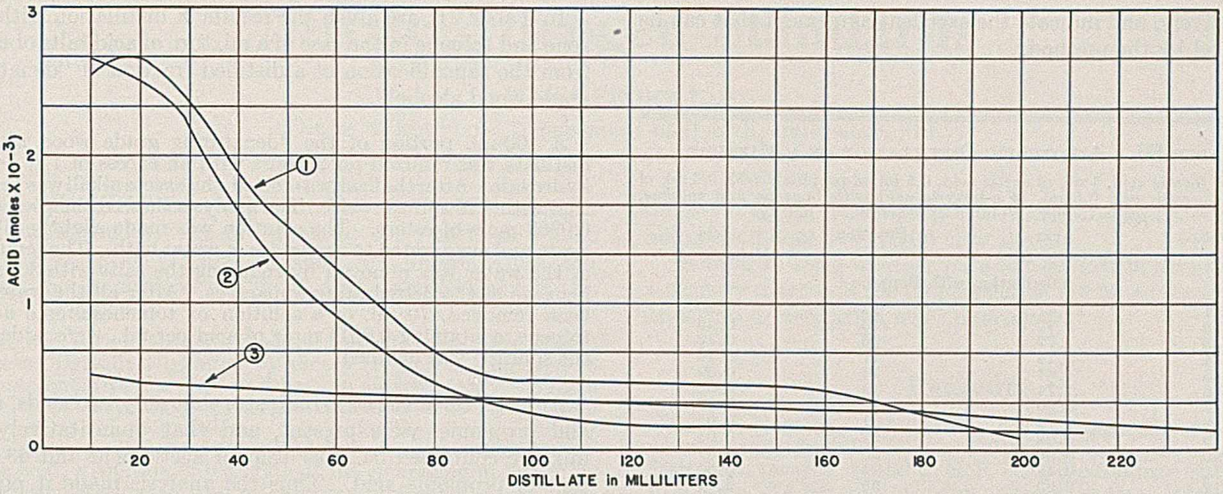


FIGURE 2

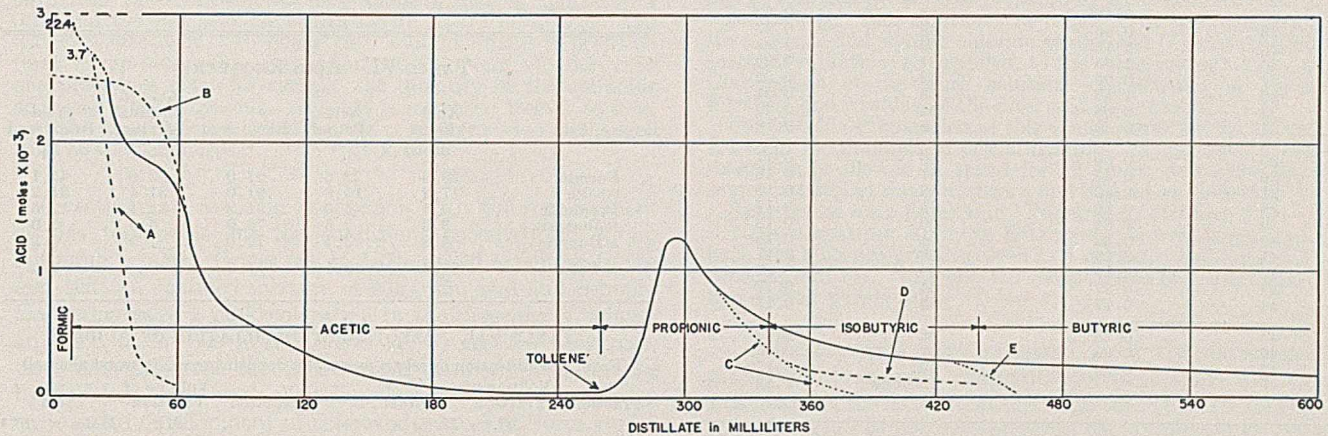


FIGURE 3

mixtures which can be analyzed readily without recourse to micro- or semimicroapparatus.

In Table III are given the results of the analysis of a synthetic mixture of acids containing 1.0 ml. of formic, 1.0 ml. of acetic, 0.5 ml. of propionic, 0.3 ml. of isobutyric, and 0.5 ml. of *n*-butyric acids. The data indicate that most of the formic acid was removed in the first fraction and about 1.18×10^{-3} mole appeared in fraction 2. The acetic acid was all removed at the end of fraction 26, at which time most of the benzene had been removed and toluene added. Propionic acid was present in fractions 27 to 34; isobutyric, in fractions 35 to 44; and the remainder of the fractions plus the still residue contained the *n*-butyric acid.

In Figure 3 is shown the smoothed and approximate curve obtained by plotting the data given in Table III.

If only formic acid had been present, the curve starting at 22.4×10^{-3} mole would not have indicated the plateau for acetic acid and would have followed dotted line *A*. Had acetic been the only acid present, the curve would have started at approximately 2.5×10^{-3} mole of acid instead of 22.4×10^{-3} and would have been similar to the curve indicated by *B*.

After distilling off about 260 ml., most of the acetic acid had been removed. To the still pot, containing the other acids and about 40 ml. of benzene, dry toluene was added and the distillation was continued. The presence of propionic acid was indicated by the peak appearing at the beginning of the toluene distillation. The absence of a peak at this point would indicate that propionic acid was not present in the acid mixture. If neither isobutyric nor butyric acid had been present, the propionic curve would have followed dotted curve *C*.

If *n*-butyric acid had been present and isobutyric acid absent, the curve for propionic acid would have followed *C*, branching off into portion *D*. The curve lying between 340 and 440 ml. of distillate is due to isobutyric acid. If *n*-butyric acid had not been present, the curve would have followed the dotted line at *E*.

In Table IV is given a comparison of the moles of acids originally present in the mixture, and the values obtained from the analysis of the data in Table III. In column 4 is shown the percentage recovery of each acid, also that about 4 per cent of the total acid content is lost during the analysis. In columns 5 and 6 are given the percentage of each acid present in the original synthetic mixture and the percentage found by analysis. The largest error is that for acetic acid, which amounts to only 2.7 per cent.

In Table V are given the results of an analysis of a mixture of sodium salts containing 1 ml. of formic, 1 ml. of acetic, 0.5 ml. of propionic, 0.3 ml. of isobutyric, and 0.4 ml. of *n*-butyric acid, a total of 3.2 ml. or 0.0547 mole of acids. The salts were first dried on a water bath, then dehydrated in the dehydrating apparatus, and finally the acids were liberated by distillation with toluenesulfonic acid.

In Table VI is given a comparison of the moles of acids originally present in the mixture and the values obtained from the analysis of the data in Table V.

Although approximately 9 per cent of the acid mixture is lost during the analysis, it is assumed from the values listed in column 4 of Table VI that the loss in total acids occurring during the analysis is not due to the loss of an individual acid, but is distributed among the respective acids present. Columns 5 and 6 give the percentage amounts of the individual acids present in the original mixture and those recovered, respectively, and indicate the excellent agreement that can be obtained by the method.

TABLE III. AZEOTROPIC DISTILLATION OF A MIXTURE

(1 ml. of formic acid, 1 ml. of acetic acid, 0.5 ml. of propionic acid, 0.3 ml. of isobutyric acid, and 0.5 ml. of *n*-butyric acid with benzene and toluene, respectively. Volume of fraction, 10 ml.)

Fraction	Acid	Fraction	Acid
	Moles × *10*$^{-3}$		*Moles* × *10*$^{-3}$
	Distillation with Benzene		
1	22.47	14	0.20
2	3.77	15	0.15
3	1.77	16	0.12
4	2.14	17	0.10
5	1.84	18	0.09
6	1.74	19	0.08
7	0.99	20	0.06
8	0.72	21	0.05
9	0.62	22	0.05
10	0.50	23	0.04
11	0.43	24	0.04
12	0.33	25	0.04
13	0.61	26	0.03
	Distillation with Toluene		
27	0.10	48	0.23
28	0.46	49	0.23
29	1.18	50	0.23
30	1.25	51	0.22
31	0.90	52	0.22
32	1.16	53	0.21
33	0.68	54	0.20
34	0.58	55	0.18
35	0.50	56	0.17
36	0.45	57	0.18
37	0.40	58	0.18
38	0.36	59	0.17
39	0.34	60	0.18
40	0.32	61	0.18
41	0.29	62	0.17
42	0.29	63	0.17
43	0.27	64	0.17
44	0.27	65	0.17
45	0.25	66	0.17
46	0.25	67	0.17
47	0.24	68	0.17
		Residue	1.52

TABLE IV. ACID RECOVERY

Acid	Acid Present	Acid Found	Recovered	Acid in Original Mixture	Acid Recovered
	Moles × *10*$^{-3}$		%	%	%
Formic	23.30	23.80	102	41.0	43.4
Acetic	17.20	15.1	88	30.3	27.6
Propionic	6.58	6.31	96	11.6	11.5
Isobutyric	3.29	3.49	106	5.8	6.4
n-Butyric	6.42	6.06	95	11.3	11.1
Total	56.79	54.76	96	..	..

TABLE V. AZEOTROPIC DISTILLATION OF ACIDS

(From mixture of sodium salts by liberation with toluenesulfonic acid)

Fraction	Volume of Fraction	Acids	Fraction	Volume of Fraction	Acids
	Ml.	*Moles* × *10*$^{-3}$		*Ml.*	*Moles* × *10*$^{-3}$
	Benzene			Toluene	
1	10	15.1	23	10	0.24
2	10	6.33	24	10	0.93
3	10	3.97	25	10	1.54
4	10	2.77	26	10	1.35
5	10	2.10	27	10	0.90
6	10	1.66	28	10	0.80
7	10	0.91	29	10	0.52
8	10	0.90	30	10	0.61
9	10	0.69	31	10	0.46
10	10	0.58	32	10	0.37
11	10	0.50	33	10	0.33
12	10	0.45	34	10	0.32
13	10	0.49	35	10	0.28
14	10	0.36	36	10	0.27
15	10	0.30	37	10	0.26
16	10	0.23	38	10	0.25
17	10	0.19	39	55	1.26
18	10	0.15	40	71	1.04
19	10	0.12	41	17	0.28
20	10	0.15			
21	10	0.07			
22	50	0.22			

In Table VII are given the results of distillation with benzene and toluene in the case of a mixture of acid salts obtained from the saponification of a distilled fraction of "denaturing grade wood alcohol".

A 100-ml. portion of the "denaturing grade wood alcohol" distillate was refluxed for 2 hours with an excess of 1 *N* sodium hydroxide. After the flask was cooled, the excess alkali was neutralized with 1 *N* sulfuric acid. The analysis showed the presence of 0.0963 mole of esters. The solution was made slightly alkaline again and evaporated to dryness on a water bath. The remainder of the water was removed by refluxing the salts with 300 ml. of benzene in the dehydrating apparatus. After all the water had been removed, 70 ml. of a solution of toluenesulfonic acid in toluene, containing 0.0014 mole of acid per ml., were added and the solution was distilled.

An analysis of the data indicates that only two acids, acetic and propionic, were present, and that quantitatively, the mixture contained 54.7 per cent of acetic acid and 43.3 per cent of propionic acid. Thus the analysis made it possible to estimate rather accurately the amount of each ester originally present in the "denaturing grade wood alcohol".

TABLE VI. ACID RECOVERY

Acid	Acid Present	Acid Found	Recovered	Acid in Original Mixture	Acid Recovered
	Moles × *10*$^{-3}$		%	%	%
Formic	23.3	22.6	97.0	42.6	45.1
Acetic	17.2	15.6	91.0	31.4	31.2
Propionic	6.6	6.3	95.3	12.1	12.6
Isobutyric	3.3	2.5	76.0	6.0	5.0
n-Butyric	4.3	3.1	72.0	7.9	6.2
Total	54.7	50.1	91.5		.

TABLE VII. AZEOTROPIC DISTILLATION OF ACIDS

(From saponification of esters present in denaturing grade wood alcohol)

Fraction	Volume of Fraction	Acid	Fraction	Volume of Fraction	Acid
	Ml.	*Moles* × *10*$^{-3}$		*Ml.*	*Moles* × *10*$^{-3}$
	Benzene			Toluene	
1	10	2.44	1	10	0.01
2	10	2.62	2	10	1.13
3	10	2.50	3	10	2.32
4	10	2.49	4	10	2.60
5	10	2.43	5	10	2.65
6	10	2.39	6	10	2.72
7	10	2.41	7	10	2.72
8	10	2.39	8	10	2.72
9	10	2.40	9	10	2.76
10	10	2.30	10	10	2.76
11	50	11.69	11	10	2.73
12	50	7.04	12	10	2.72
13	20	1.77	13	10	2.74
14	10	0.85	14	10	2.77
15	10	0.62	15	10	2.73
16	50	0.79	16	10	2.37
17	50	0.41	17	10	1.22
18	35	0.28	18	10	0.50
			19	10	0.21
	Total	48.22	20	5	0.07
				Total	39.95

Literature Cited

(1) Dox and Neidig, Iowa Expt. Sta., *Research Bull.* 7 (1912).
(2) Duclaux, *Ann. chim. phys.*, 2, 289 (1874).
(3) Hart and Wiliams, *J. Am. Chem. Soc.*, 34, 1619 (1912).
(4) Klein and Wenzl, *Mikrochemie*, 5, 73 (1932).
(5) McNair, *J. Am. Chem. Soc.*, 54, 3247 (1932).
(6) Meyer, H., Gatterman, and Wieland, "Laboratory Methods of Organic Chemistry", p. 183, New York, Macmillan Co., 1934.
(7) Osburn, Wood, and Werkman, IND. ENG. CHEM., Anal. Ed., 8, 270 (1936).
(8) Palkin, *J. Assoc. Official Agr. Chem.*, 7, 14 (1923).
(9) Sargent & Co., E. H., "Scientific Laboratory Apparatus", p. 437, Catalog No. 50.
(10) Sukhonanskiĭ, and Roginskaya, *Lesokhimicbeskaya Prom.*, 3, Nos. 5–6, 26 (1934).
(11) Upson, Plum, and Schott, *J. Am. Chem., Soc.*, 39, 731 (1917).
(12) Venogrado, and Oshoumova, *J. Applied Chem.* (U. S. S. R.), 8, 378 (1935).

Nitrite Nitrogen Standards

W. F. REINDOLLAR
State of Maryland Department of Health, Baltimore, Md.

PROCEDURES for the determination of nitrite nitrogen in water and sewage are given by the American Public Health Association (*1*), and in cereals, and waters, brines, and salt by the Association of Official Agricultural Chemists (*2*).

Although each of these methods is based upon the diazotization reaction originally suggested by Griess (*4*) and is employed to estimate quantities of nitrite nitrogen in approximately the same range of concentration, the reagents differ both in composition and in mode of preparation. This sulfanilic acid is variously described as an 0.8 per cent weight by volume solution in 5 *N* acetic acid, a solution of 0.5 gram of the compound in 150 cc. of 20 per cent acetic acid, and a 1 per cent aqueous solution. The α-naphthylamine reagent is prepared in one case by dissolving 0.5 gram of the base in 100 cc. of 5 *N* acetic acid; in the other two cases the hydrochloride is employed, making solutions of 0.13 and 0.5 per cent concentration in dilute acetic acid and water, respectively. In every case sodium nitrite is prepared from silver nitrite by interaction with sodium chloride. In one procedure (that for cereals) the quantity of the sulfanilic acid and α-naphthylamine reagents is increased from 1 to 2 cc. and the time period allowed for the color to develop is changed from 30 to 60 minutes.

Investigations made in connection with the development of this test point out the conditions necessary to obtain optimum results. Griess (*3*), in 1879, called attention to the fact that an acidified mixture of sulfanilic acid and α-naphthylamine gave a pink coloration in the presence of minute amounts of nitrous acid. Ilosva (*5*, *6*) studied this reaction and suggested the substitution of acetic acid for the hydrochloric acid used, claiming that the former induced a more rapid development of color and a more uniform gradation of tint. Weston (*9*) in a comprehensive review of the subject concluded, in part, that an excess of hydrochloric acid interferes with the delicacy of the reaction whereas an excess of acetic acid does not, and that the procedure as modified by Ilosva is more rapid than the original method. He recommended also that the reagents be made more concentrated to avoid inconvenient dilution of the sample. Although numerous articles have since appeared suggesting further modifications, the procedure of Weston is essentially the standard today.

Mason (*7*) explains the use of silver nitrite rather than sodium nitrite as primary standard on the basis of the questionable purity and deliquescent nature of the latter salt. Appropriate inquiry has shown that the first objection no longer obtains; sodium nitrite of high quality may be readily secured. This is fortunate, as the employment of the silver salt to prepare nitrite standards entails certain difficulties which are likely to impair accuracy. Silver nitrite is somewhat photosensitive, deteriorates slightly with age, and may become unreliable as a standard. It dissolves slowly and with difficulty. When sodium chloride is added to effect decomposition, the silver chloride, owing to the necessary absence of acid, does not precipitate in its characteristic clotted form but occurs as a colloidal dispersion. The standard method (*1*) specifies that a definite quantity of solution from this mixture be used in preparing the more dilute reagents, leaving the choice of methods of clarification to the operator. If filtration is employed for this purpose, it is necessary to return the liquid to the filter repeatedly and to wash thoroughly to ensure complete removal of sodium nitrite. If a clear liquid is to be obtained by settling and decantation, as suggested by Mason (*7*), 2 to 3 days must elapse before the diluted reagents can be prepared. Centrifuging for a reasonable period does not yield a clear liquid.

In order to learn whether pure sodium nitrite may serve as a primary reagent in the preparation of nitrite nitrogen standards, this investigation was undertaken.

Reagents

SODIUM NITRITE. *Solution A*. A small quantity of Merck's reagent grade granular sodium nitrite was dried overnight in a desiccator, assayed by the U. S. P. XI (*8*) procedure, and found to contain 99.4 per cent of sodium nitrite. A stock solution was prepared making due allowance for the slight amount of impurity present, and from this liquid a standard solution containing 0.0005 mg. of nitrogen per cc. was prepared by successive dilution.

Solution B. This solution was prepared by the interaction of silver nitrite and sodium chloride as directed (*1*) and reduced by successive dilution, as specified, to the same concentration as *A*. Clarification of the stock solution was effected by repeated filtration and washing of the filter and its contents.

Solution C. Preparation of this solution was similar to that of *B* except for the method of clarification. In this case the stock reagent was allowed to stand for 52 hours, and although still somewhat turbid was withdrawn and diluted as specified.

SULFANILIC ACID SOLUTION. Prepared as directed (*1*).

NAPHTHYLAMINE ACETATE SOLUTION. A fresh supply of the base was obtained and dissolved in 5 *N* acetic acid following the procedure of (*1*). The finished reagent was perfectly clear and had a weak purple tint.

Color standards were prepared from the three sodium nitrite solutions and a comparison of their respective values was made at the concentrations suggested (*1*). In every case slightly higher values were obtained for *A* than for *B*, indicating that with the latter solution some nitrite had been lost, probably in the process of clarification. Values obtained when *A* and *C* were compared were in good agreement. In view of this fact it appears that sodium nitrite solution may be substituted for the silver nitrite–sodium chloride solution and that where the latter is employed, decantation should be specified as the method of clarification.

Summary

Sodium nitrite of a sufficiently high degree of purity to serve as a primary standard in the nitrite nitrogen determination is readily obtainable. Its use obviates the delay attendant upon the use of silver nitrite and permits the preparation of all three dilutions of the reagent in a short period. As sodium nitrite is relatively inexpensive and the solution is readily prepared, it may be made fresh when needed, thus eliminating any question of deterioration arising from the use of an old solution.

Literature Cited

(1) Am. Pub. Health Assoc., "Standard Methods of Water Analysis", 8th ed., pp. 46, 133, New York, 1936.
(2) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, 4th ed., pp. 216, 506, 1935.
(3) Griess, Peter, *Ber.*, 12, 426 (1879).
(4) Griess, Peter, *Proc. Roy. Soc.*, 9, 494 (1858).
(5) Ilosva, M. L. I. de N., *Bull. soc. chim.*, (3) 2, 347 (1889).
(6) *Ibid.*, p. 388.
(7) Mason, W. P., and Buswell, A. M., "Examination of Water", 6th ed., p. 51, New York, John Wiley & Sons, 1931.
(8) United States Pharmacopœia XI, p. 344, 1936.
(9) Weston, R. S., *J. Am. Chem. Soc.*, 27, 281 (1905).

Rapid Determination of Quartz in Feldspar

G. H. McINTYRE AND M. BOZSIN, Ferro Enamel Corporation, Cleveland, Ohio

IN THE chemical analysis of feldspar, all of the silica is determined as such, but no determination is made of the amount of quartz. As quartz and feldspar are major ingredients in vitreous enamels, and the ratio between the combined silica and quartz in feldspar is variable, it is important to determine the quantity of quartz present in feldspar in order to ensure uniformity of enamel composition.

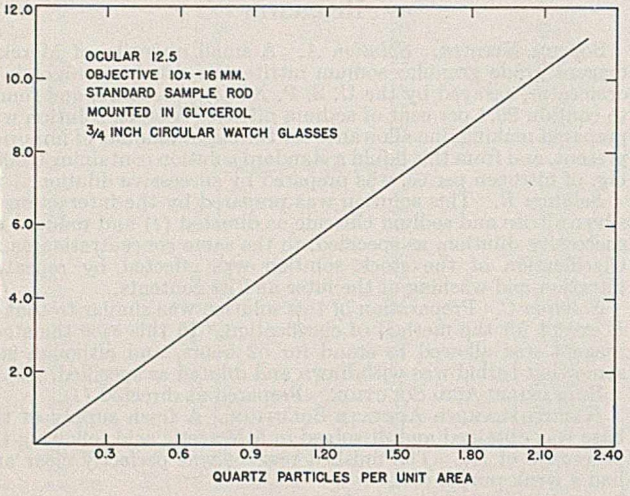


FIGURE 1. TYPICAL STANDARD CHART FOR TRANSLATING QUARTZ GRAIN COUNT TO PERCENTAGE COMPOSITION IN FUSED FELDSPAR

Watkins (*8*) has discussed the relation of quartz in feldspar to chipping of enamels, and gives a method for calculating the quartz from a complete chemical analysis of the feldspar. This is a long and difficult method and does not lend itself to rapid control of raw materials in glass and enamel manufacturing processes.

Method

The method described for the determination of quartz in feldspars is rapid and requires no special apparatus for sample preparation and grain diameter measurements. It has been standard in the analytical laboratories of the Ferro Enamel Corporation for over 10 years and has been proved to be practical. It is based upon the principle that unfused quartz is anisotropic and that when a powdered vitreous mixture is viewed under a polarizing microscope with crossed Nicols, the number of quartz grains in a definite area may be counted. These will appear light or colored, whereas the glass will be dark. Quartz grains which are in the extinction position will remain dark when so examined, but as the standards are examined in the same manner, the error is nullified.

Chamot and Mason (*3*) referred briefly to the method as being fundamentally based on the technique of detecting rice starch adulteration with potato starch.

Booze and Klein (*2*) developed a method basically similar to this one, but differing in technique. Their description does not cover the preparation of standards and the exact technique used in preparation of the slide.

Thompson (*7*) determined free silica in feldspars by the linear intercept method, from these calculating the weight of quartz present. Insley (*4*) also used the linear intercept method on thin sections prepared from fusions of the feldspar. Parmelee and McVay (*6*) used an adaptation of this same method.

McCaughey (*5*) determined quartz in crude feldspar by indices of refraction methods and the proportions determined by counting the grains.

STANDARDS. Before routine determinations can be made, a set of standards must be prepared in order to establish points on a graph which can be used in all subsequent determinations. It is best to select a feldspar that is known to have a low quartz content, for making up the working standards.

Five samples containing feldspar with quartz added in different percentages usually make up the standards. All materials used must be ground so that at least 95 per cent passes a 200-mesh sieve. Feldspar and quartz must be clean and free from impurities such as iron and excessive mica. Quartz of at least 99.70 per cent silica grade should be used. The standard mixes are made in the following proportions:

Sample No.	Quartz	Feldspar	Quartz
	%	*Grams*	*Grams*
1	5	950	50
2	10	900	100
3	15	850	150
4	20	800	200
5	25	750	250

Each combination must be tumbled thoroughly (preferably in a ball mill) for at least an hour, to provide a homogeneous mixture.

FUSION BUTTONS. To about 100 grams of each mixture contained in a casserole, add 10 ml. of 1 per cent gum arabic, gum tragacanth, or gelatin solution. Mix the gum thoroughly with the sample by means of a spatula. The gum acts as a binder which serves to hold the mixture together in a mold. Pack the resulting mixture into a 15-ml. porcelain crucible until level, scrape off even with the top, and invert on a small porcelain plate. Tap the crucible gently to release the fusion button from the crucible mold.

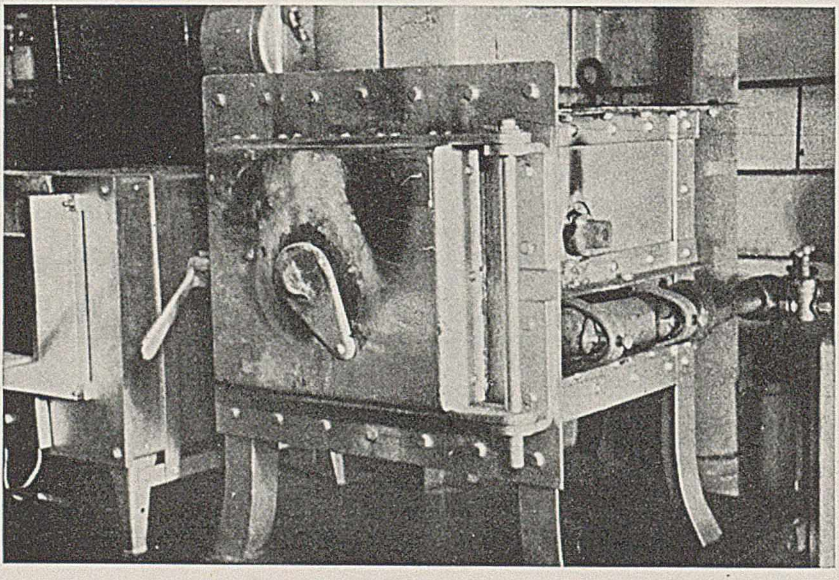


FIGURE 2. PALO MYERS GAS-FIRED FURNACE

Table I. Determination of Quartz

Feldspar	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	Quartz Determined by Count Method	$Na_2O.Al_2O_3.6SiO_2$ $K_2O.Al_2O_3.6SiO_2$	Mineral Composition		
								$CaO.Al_2O_3.6SiO_2$	Kaolinite	Quartz (Calcd.)
	%	%	%	%	%	%	%	%	%	%
Feldspar mill 2282	68.11	17.75	0.25	2.52	11.00	8.7	88.65	2.10	2.90	6.32
Feldspar mill 2513	69.03	19.40	0.22	2.38	10.41	6.4	82.65	1.82	8.78	6.68
Virginia 8922 (high quartz)	68.98	18.81	0.15	4.13	8.07	9.0	83.42	1.23	6.74	8.51
								Dolomite	Magnesite	
Virginia soda spar, 3979	68.58	18.10	0.25	10.00	2.36	2.0	97.00	1.17	0.69	1.14
			MgO 0.82							
Derry spar (Canada)	65.85	18.82	0.32	2.46	12.50	Few particles	95.00	2.72	1.37	0.69
Carolina spar	68.87	17.76	0.032	3.02	9.31	9.2	82.20	2.82	5.10	10.20

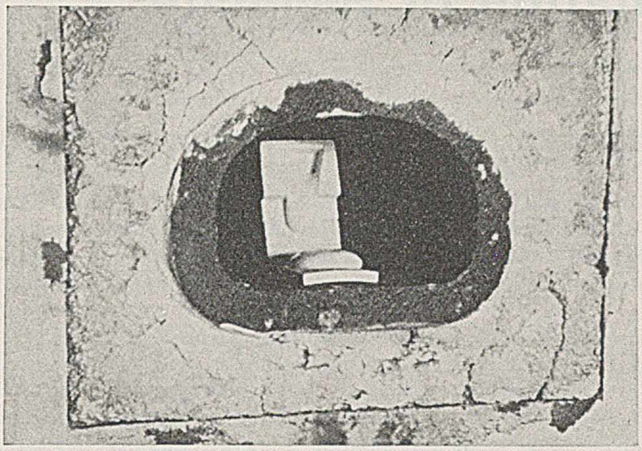


Figure 3. Feldspar Fusion and Button

Prepare a fusion button of each of the five mixtures. Place the buttons in an oven for an hour at 110° C. to allow all free moisture to escape.

After the initial drying, all five samples must be fused. For this purpose a Globar element furnace or a Palo gas furnace may be used. Heat the samples uniformly, gradually increasing the temperature until 1370° C. (2500° F.) is reached, and maintain this temperature for 15 minutes.

Heat Treatment. The following schedule is followed during the heat treatment:

Min.	° *F.*	*Min.*	° *F.*
0	1500	75	2380
15	1700	90	2500
30	1900	95	2500
45	2100	100	2500
60	2240	105	2500

During this heat treatment all of the feldspar fuses to a translucent glass, while the quartz remains unaffected.

When cold, chip the fusion buttons off the porcelain plates and grind off all adhering porcelain on an emery wheel. Pulverize each button by means of a hardened steel mortar and pestle until all the powder passes a 200-mesh sieve. The samples are then ready for microscopical examination.

The sampling rod consists of an eightpenny box nail from which the point has been cut off and in its place a depression about 1 mm. in depth has been drilled.

Preparation of Slide for Microscopical Examination. Spread each sample in approximately a 0.6-cm. (0.25-inch) layer and press the standard sample rod into this sample. Level off the powder which fills the small indentation in the end of the rod and then place it on a slide. Place two of these samples on each slide, making five groups of two each. Next apply a drop of glycerol to each from a stirring rod, which consists of a piece of 5-mm. glass rod drawn to a point 1 mm. in diameter. Drops of uniform size will be obtained if the last drop coming off the rod is used for mounting the sample. Then mix the small sample for 2 or 3 minutes with the glycerol, using a small platinum wire spatula. Place an 18-mm. cover glass over the sample, taking care not to trap air bubbles and to spread the sample completely under the cover glass.

Microscopical Examination. By means of a polarizing microscope equipped with a mechanical stage, bring the sample to focus, using a 12.5-mm. ocular (equipped with a Whipple, *1*, eyepiece micrometer) and a 16-mm. objective. The field is viewed with the Nicols crossed and the quartz can be seen as bright spots, which may be colored if the quartz grains are large.

Count the number of particles of quartz in an area of 9 squares, the small cross-sectioned square being the center of the group. Move the sample to another graduation as shown by the vernier on the mechanical stage, and take another count. Move the sample in a regular manner so as to include the entire area and take counts until a hundred areas are counted. Repeat the operation with a check sample. From the average counts calculate the number of quartz particles per unit area corresponding to the per cent quartz added to the sample. After counts and checks have been made on all five standard samples, plot a graph for particles per unit area in relation to percentage of free quartz. This graph will serve as a standard for all subsequent determinations of quartz in feldspar, providing conditions are kept standard.

On all unknown samples, it is necessary only to mix about 25 to 30 grams of the finely divided feldspar with sufficient gum for bonding, and then fuse to a button in the manner described for the preparation of the standard sample. After fusion the same standard procedure is followed for pulverizing, preparing the slide, and counting. By averaging the counts and calculating particles per unit area, the percentage of quartz can be read from the standard graph.

Once the standards have been made and the graph has been plotted, the determination is not lengthy, the preparation of the buttons and the fusion taking the most time. After the buttons have been fused, the determination takes about an hour.

Results

A series of complete chemical analyses was made on different types of feldspar. The mineral composition was then calculated and compared with results by the above method. These data are shown in Table I.

The chief advantage in using this method is that it is time-

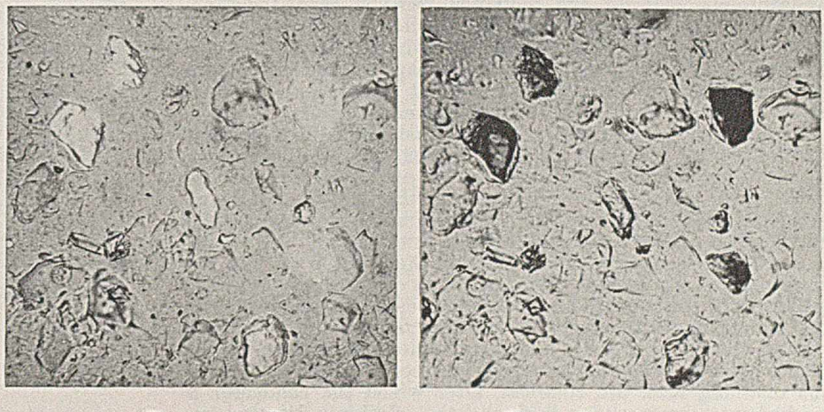


Figure 4. Photomicrographs of Fused Feldspar

Left. Taken with crossed Nicols. Note bright particles of quartz
Right. Taken without crossed Nicols

saving once standards have been set up. It is also not necessary to make the usual tedious determination of the alkalies, which must be made if the quartz is to be determined by calculation from the mineral composition of the spar.

Literature Cited

(1) Bausch & Lomb Optical Co., Rochester, N. Y., *Catalog* 1859-C, 1930.

(2) Booze and Klein, *J. Am. Ceram. Soc.*, 6, 698 (1923).

(3) Chamot and Mason, "Handbook of Chemical Microscopy", Vol. 1, p. 441, New York, John Wiley & Sons, 1931.

(4) Insley, H., *J. Am. Ceram. Soc.*, 10 (9), 651 (1927).

(5) McCaughey, W. J., *Trans. Am. Ceram. Soc.*, 15, 381 (1913).

(6) Parmelee, C. W., and McVay, T. N., Univ. Illinois Eng. Expt. Sta., *Bull.* 233, 1931.

(7) Thompson, C. L., *J. Am. Ceram. Soc.*, 17 (8), 257 (1934).

(8) Watkins, *Enamelist*, 3, No. 2, 11 (November, 1925).

Volumetric Determination of Selenate

GLENN C. SOTH AND JOHN E. RICCI, New York University, New York, N. Y.

IN CONNECTION with certain phase rule studies requiring numerous and readily duplicated accurate determinations of dissolved selenate, some simplifications in the volumetric method first suggested by Pettersson (*9*) were effected, which it seems worth while to describe.

This direct method, studied in detail by Gooch and coworkers (*3*, *4*, *6*), seemed, especially when compared with the gravimetric methods available (determination as lead selenate or as elementary selenium), the best suited for rapid and accurate analysis. The reactions involved are: reduction of the selenate to selenite by means of some halogen acid, distillation of the liberated halogen into potassium iodide solution and titration of the equivalent iodine with standard thiosulfate solution. As described by Gooch and co-workers, however, and also as studied by Moser and Prinz (*8*), the analysis requires a cumbersome apparatus and has several sources of error, so that it seemed desirable to modify and simplify the procedure further. The chief difficulties are the necessity of passing a current of carbon dioxide through the apparatus during the distillation of the bromine to ensure its complete removal, the need of two or more traps of potassium iodide solution to absorb the bromine completely, and the uncertainty of controlling the treatment with hydrochloric or hydrobromic acid without causing either further reduction of the selenite to elementary selenium or the formation of volatile selenium bromide. In the procedure described by Gooch the distillation is continued until the volume in the distilling flask is reduced by one third or until color begins to reappear in the residual liquid. Gooch and Pierce (*5*) in fact recommended indirect titration, not of the liberated bromine but of the selenite formed.

The necessary operations for the direct determination, using hydrobromic acid for the reduction, can be carried out accurately and rapidly by means of the all-glass apparatus shown in Figure 1, consisting of a 200-ml. round-bottomed flask with a sealed-in dropping funnel, a Kjeldahl trap, a condenser, and a receiving flask. In use, a small amount of stopcock grease is applied to the ground-glass joints to prevent sticking.

The sample is placed in the distilling flask and diluted to about 125 ml., and a few glass beads are added to prevent bumping. The solution is heated to boiling and the air driven from the apparatus. When no more bubbles pass through the potassium iodide solution in the receiving flask, the water in the condenser is turned off for a few seconds. After a few more bubbles escape, the water is turned on again, drawing the solution up into the condenser to a height of 5 or 7.5 cm. (2 or 3 inches). Twenty milliliters of concentrated hydrobromic acid are added slowly to the boiling liquid through the dropping funnel, and from time to time thereafter water is added to maintain the volume in the distilling flask. The distillation is continued until the contents of the distilling flask are colorless, after which the condenser is washed into the receiving flask and the solution is titrated immediately. In place of hydrobromic acid (which must be free of bromine), sulfuric acid may be mixed with the sample in the distilling flask at the start, and potassium bromide solution added through the dropping funnel.

Discussion

The distillation as described requires about 20 minutes and the entire analysis about 30 minutes. Although the disappear-

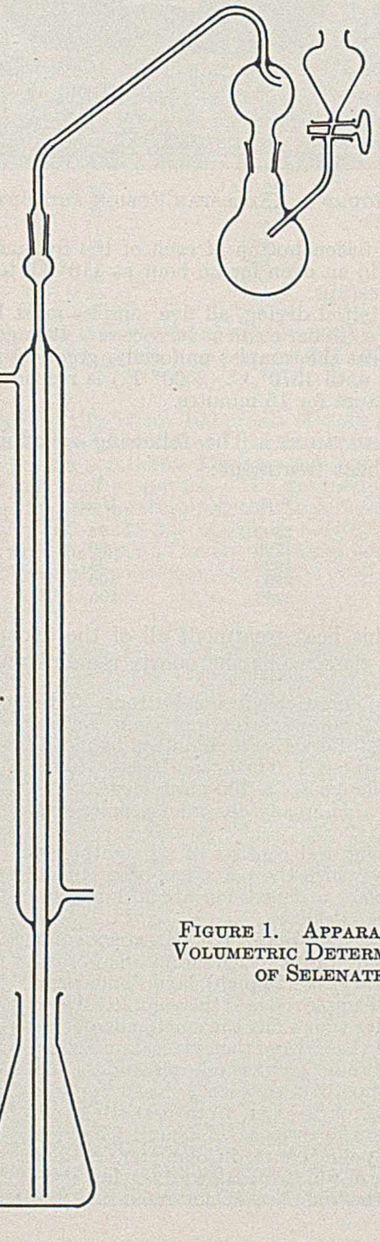


Figure 1. Apparatus for Volumetric Determination of Selenate

TABLE I. DETERMINATION OF SELENATE

Method	Sample	$MgSeO_4$ Found	$MgSeO_4$ Theoretical
	Grams	%	%
Analysis of $MgSeO_4.6H_2O$			
Mg-8-hydroxyquinolate	0.2504	60.65	60.75
	0.2737	60.78	...
	0.2662	60.77	...
Lead selenate	0.2020	60.70	...
	0.2011	60.78	...
	0.1996	60.86	...
Distillation method			
Using HBr	0.8161	60.74	...
	0.8254	60.74	...
	0.8098	60.79	...
Using H_2SO_4 and KBr	0.6675	60.68	...
	0.8189	60.71	...
	0.8175	60.81	...
Analysis of Solution of $MgSeO_4.6H_2O$			
Distillation method, using HBr	2.8192	35.73	35.75[a]
	1.7397	35.56	...

[a] Known from determination of Mg by quinolate method, 35.74 and 35.76 %.

ance of the bromine color in the residual liquid is the best indicator for the completion of the reaction and of the distillation of the bromine, the distillation can also be followed by observing the color of the vapor in the condenser, so that the analysis may be used for colored solutions.

The current of carbon dioxide employed by Gooch has been found unnecessary, inasmuch as the steam from the distilling flask is sufficient to carry over all the liberated bromine. In addition to permitting a simpler setup, this Kjeldahl type of procedure eliminates several possible sources of error. The absorption of bromine by potassium iodide solution is not instantaneous, so that even with the two traps employed by Gooch the current of carbon dioxide passing through the potassium iodide solution may carry with it some bromine. The present method of operation forms a liquid seal to the apparatus, so that no vapor can escape and all the bromine must dissolve in the receiving solution. With only one trap, furthermore, both time and possible loss in transfer are saved, because the contents of several traps need not be combined for the final titration.

When excess of hydrobromic acid is mixed directly with the sample in the distilling flask before boiling, as in the original procedure of Gooch, there is an initial rapid evolution of bromine which is difficult to control. By adding the hydrobromic acid through the dropping funnel the evolution of the bromine is regulated so that none escapes before it can react with the potassium iodide solution. Finally, since the volume of residual liquid is not used as an indication of completion of the reaction, the initial volume being maintained throughout, and since the addition of bromide can be so regulated as to avoid great excess of halogen acid in the boiling solution, there is no danger either of the formation of elementary selenium as stated by Gooch or of the distillation of selenium tetrabromide from concentrated solution.

The procedure described should be useful for the detection and determination of selenate in the presence of selenite and for the determination of purity of salts. Sulfate ion, which must be absent in the lead selenate gravimetric method, does not interfere. The chief limitation, however, is the interference by oxidizing agents other than selenate itself; no other oxidizing agent (including nitrate ion) capable of liberating bromine from hydrogen bromide in boiling solution may be present.

Test of Procedure

MATERIALS. Magnesium selenate hexahydrate, $MgSeO_4.6H_2O$, prepared by recrystallization from magnesium oxide and selenic acid, was used for all analyses. The selenic acid was prepared from elementary selenium according to the method of Gilbertson and King (*2*). Two analyses are included on solutions of pure magnesium selenate whose composition was known from determination of magnesium by the method described below.

Hydrobromic acid was a Merck 40 to 42 per cent solution, free of bromine.

The potassium iodide solution in the receiving flask was made up just before use and contained 8 grams of C. P. salt and 30 ml. of 4 *N* sulfuric acid in 150 ml. of solution.

The liberated iodine was titrated in the usual manner, using starch indicator and 0.15 *N* thiosulfate previously standardized against potassium dichromate.

The purity of the magnesium selenate was checked by precipitation of lead selenate according to the method of Ripan-Tilici (*10, 11*) and by precipitation of magnesium as the *o*-hydroxyquinolate and subsequent titration with standard potassium bromate (Berg's method, *1*), using the procedure of Kolthoff and Furman (*7*), with indigo as indicator.

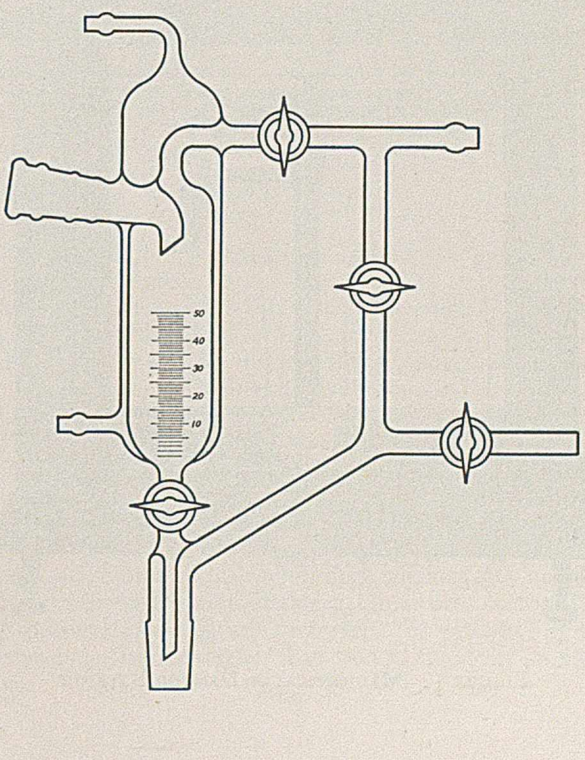
Literature Cited

(1) Berg, *Z. anal. Chem.*, 71, 23 (1927).
(2) Gilbertson and King, *J. Am. Chem. Soc.*, 58, 180 (1936).
(3) Gooch, "Quantitative Analysis", p. 197, New York, John Wiley & Sons, 1916.
(4) Gooch and Evans, *Z. anorg. Chem.*, 10, 253 (1895).
(5) Gooch and Pierce, *Ibid.*, 11, 249 (1896).
(6) Gooch and Scoville, *Ibid.*, 10, 256 (1895).
(7) Kolthoff and Furman, "Volumetric Analysis", Vol. II, p. 483, New York, John Wiley & Sons, 1929.
(8) Moser and Prinz, *Z. anal. Chem.*, 57, 277 (1918).
(9) Pettersson, *Ibid.*, 12, 287 (1873).
(10) Ripan-Tilici, *Ibid.*, 102, 343 (1935).
(11) Spacu, *Bull. soc. chim.*, (5) 3, 159 (1936).

Jacketed Receiver for Vacuum Distillation

J. B. CLOKE, Rensselaer Polytechnic Institute, Troy, N. Y.

THE accompanying figure represents a well-known receiver for distillation under diminished pressure, which has been provided with a jacket for the circulation of ice water or other cooling medium. This all-glass receiver (made by the Ace Glass Co.) is especially useful for handling low-boiling compounds which must be distilled under diminished pressure. The joints are ₮ 24/40.



Differential Temperature Error in Weighing

ELLIS BLADE
Columbia University, New York, N. Y.

Weighings of a specially prepared steel plummet and a standard porcelain crucible, on a magnetically damped balance, indicate that a temperature difference between object and balance causes a weighing error proportional to the magnitude of the difference, which may persist a half hour, and which dissipates logarithmically with time. The 17-gram plummet exhibited a constant maximum error of 0.05 mg. per degree, and the 17-gram crucible, 0.19 mg. per degree.

IT IS recognized that prior to weighing, objects should be brought to balance temperature. But in quantitative terms, what is the penalty for disregarding the old axiom? On the freely swinging balance, the problem was difficult, if not impossible, to study properly because of the transient nature of the temperature difference. The following investigation was carried out on a magnetically damped balance (Figure 1), using the counterpoise method of weighing. The object was a highly polished alloy steel plummet, which was brought to temperature in a specially constructed thermostat, and then transferred to the balance pan. Observations of the pointer were begun at the end of the first minute and continued at regular intervals.

In the first group of observations, the plummet was merely weighed, with temperature differences ranging from 1° to 15°. Table I shows the maximum errors observed for each weighing. The duration of the phenomenon and its time rate of variation are shown by the curves of Figure 2.

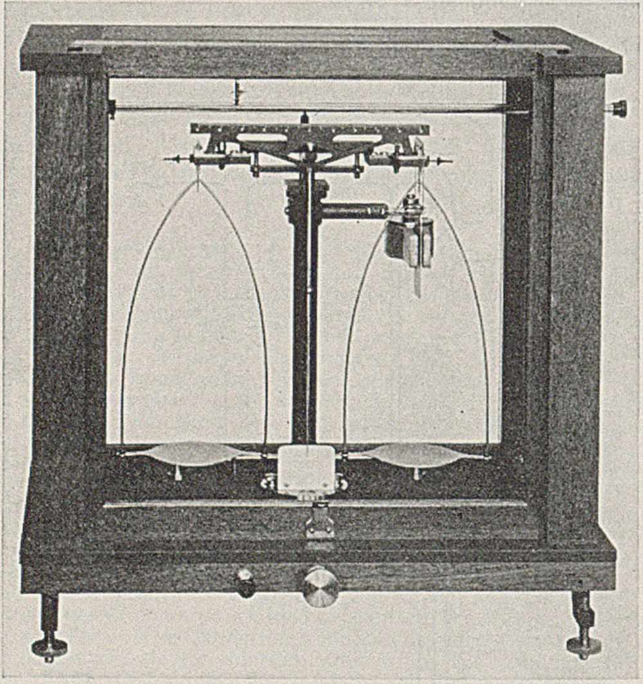


Figure 1. Magnetically Damped Balance

In the second group of observations an attempt was made to stifle convection currents in the vicinity of the right-hand pan. To limit air currents from below, a cardboard platform 12.5 cm. (5 inches) square was placed within about 0.5 mm. of the lowest part of the pan. Currents from the sides were prevented by curved vertical cardboards several inches high, resting on the platform close to the pan on each side. The maximum errors under this arrangement are shown by items 11, 12, and 13 of Table I.

In the third group the plummet was not placed on the pan at all, but on an asbestos pad directly beneath the right pan, and no load was on the balance pan. The response of the pointer under these conditions indicated the existence of air currents from the plummet.

Following these experiments a standard glazed porcelain crucible was weighed under conditions similar to the first group above. Four runs were made, and as shown in Table II and Figure 3 the maximum error was nearly three times that for the plummet, but the phenomenon was of shorter duration.

Table I. Maximum Errors with Plummet

No.	Mg.	° C.[a]	Mg./° C.	Remarks
1	0.16	3.0 C	0.0533	Polished Ni-Cr steel plummet (17.376 grams) resting directly on balance pan (normal weighing)
2	0.12	2.7 W	0.0444	
3	0.18	4.1 C	0.0439	
4	0.14	2.1 C	0.0667	
5	0.18	2.8 W	0.0643	
6	0.04	0.9 W	0.0444	
7	0.44	8.4 C	0.0524	
8	0.36	6.7 W	0.0537	
9	0.48	10.4 W	0.0461	
10	0.74	14.4 C	0.0514	
		Mean	0.0521, average deviation 0.0019	
11	0.20	7.8 W	0.0256	Same as above, except cardboard shielding used to diminish convection currents
12	0.28	9.6 W	0.0292	
13	0.16	8.1 W	0.0197	
		Mean	0.0248, average deviation 0.0020	
14	0.30	6.8 W	0.0441	Normal weighing of plummet
15	0.30	10.4 W	0.0288 W	Polished plummet on asbestos pad, directly beneath balance pan, hence affecting it by convection only
16	0.02	9.5 C	0.0021 C	
17	0.00	9.1 C	....	
18	0.36	11.6 W	0.0310 W	
19	0.04	14.8 C	0.0028 C	
		Mean	0.0300 W, 0.0025 C	
20	0.54	11.0 C	0.0491	Normal weighing of plummet

[a] W, plummet warmer than balance.
C, plummet colder than balance.

Table II. Maximum Errors with Crucible

No.	Mg.	° C.[a]	Mg./° C.	Remarks
1	0.86	4.7 W	0.183	Porcelain crucible, of approximately same weight as plummet (16.486 grams), placed directly on balance pan (normal weighing)
2	0.92	5.3 C	0.174	
3	0.54	3.0 W	0.180	
4	0.94	4.6 C	0.204	
		Mean	0.185, average deviation 0.005	

[a] W, crucible warmer than balance.
C, crucible colder than balance.

Discussion

The temperature difference can produce a weighing error either through expansion or by deflection of the moving system by air currents. Expansion of the pan and bows is trivial, while the beam is, thermally speaking, only indirectly connected with the object on the pan and hence is not noticeably affected. On the other hand, an updraft of air produced by a warm object would tend to lift the pan, thereby making the object appear too light. Such convection may arise directly from the object, or indirectly through conduction from the pan. The time variation of the error depends in part upon the manner in which the heat divides between the two paths, and is therefore a complex function of heat capacity, conductivity, emissivity, and geometry.

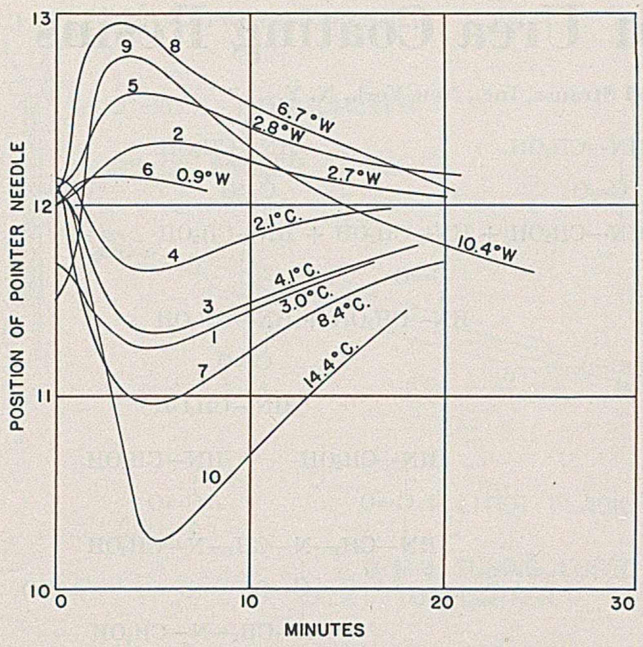


FIGURE 2. ERROR IN SCALE DIVISIONS DUE TO WARM OR COOL PLUMMET

10, middle of scale
1 division = 0.4 mg.

The effect of cutting down the convection was shown by the second group of experiments, in which shields were used about the pan, and by the third group, in which conduction to the pan was eliminated by keeping the object out of contact with the pan. It is assumed that perfect shielding would have eliminated the error entirely in the former case, and it seems reasonable to suppose the full error would have been produced in the latter case, if the full force of the convection had been felt by the pan.

Apparatus

The plummet was ground down from a 0.9-cm. (0.375-inch) alloy steel rod, and buffed to a high polish. A large eye in one end enabled it to be hooked from the bottom of the thermostat by means of a bent wire. The plummet's weight was 17.376 grams. The thermostat was a 1.25-cm. (0.5-inch) copper tube, 17.5 cm. (7 inches) long, with a soldered-in closed bottom. The copper tube and a thermometer were immersed in a water bath contained in a Fisher outer tube (Figure 4). A bent wire was used for agitation of the bath. The whole assembly was arranged so that a beaker of warm or cold water could be brought up around the Fisher tube for adjusting and controlling the temperature. Temperatures were obtained by the bath thermometer and a balance-case thermometer, previously compared.

The crucible, which was of a common type, weighed 16.486 grams or slightly less than the plummet. A second thermostat, made for the crucible, was similar in every respect to the first, except that it was larger. A wire cradle with a long stem was used to place and remove the crucible, the cradle being so constructed that the crucible was allowed to rest directly on the bottom of the thermostat.

Summary

When a temperature differential exists between object and balance, a weighing error occurs which is linear with the magnitude of the differential and of opposite sign, referred to the balance temperature as standard. A highly polished plummet weighing 17.376 grams gave a maximum error of 0.05 mg. per degree C., for differences up to 15° in either direction. Thus in analytical work, where calibrations of brass weights are depended upon to the nearest 0.1 mg., a difference of only a few degrees is very objectionable. For the larger differences, the error may persist up to a half hour, while small ones may last 10 minutes.

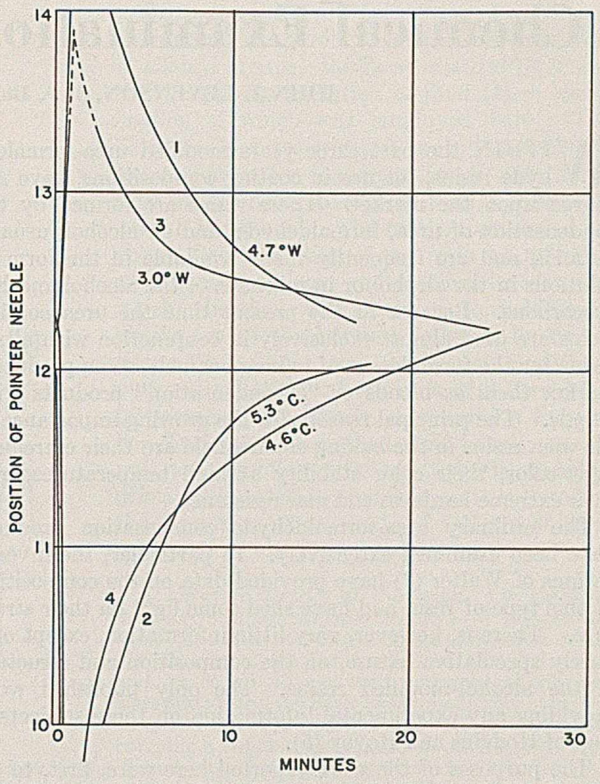


FIGURE 3. ERROR IN SCALE DIVISIONS DUE TO WARM OR COOL CRUCIBLE

10, middle of scale
1 division = 0.4 mg.

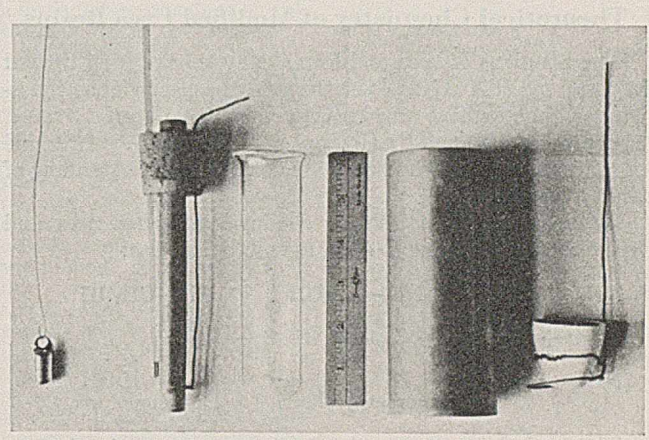


FIGURE 4. APPARATUS

A common glazed porcelain crucible weighing 16.486 grams gave a maximum error of 0.19 mg. per degree C. For a temperature difference of 5°, this amounts to 1 mg. Fortunately, the effect vanishes much more rapidly than in the case of the plummet, and will usually be gone in 15 minutes.

The zero point of a balance shifts temporarily when a warm or cold object is weighed, thereby subjecting subsequent weighings to error.

The magnetically damped balance, operating on a null principle, is especially suitable for analyzing weighing problems in which time is an element, since readings may be taken as frequently as desired. If external influences such as temperature and vibration are controlled, the precision of this balance is potentially higher than that of the freely swinging type.

Chemical Examination of Urea Coating Resins

JOHN J. LEVENSON, JR.[1], Barsky and Strauss, Inc., New York, N. Y.

WITHIN the past three years modified urea-formaldehyde resins, for use in coating compositions, have appeared upon the market. These resins are formed by the condensation of urea, formaldehyde, and an alcohol, usually butanol, and are frequently made available in the form of solutions in the alcohol or in mixtures of the alcohol and hydrocarbons. Because at the present time the urea coating resins are used almost exclusively in conjunction with alkyd resins for the formulation of baking enamels, some producers market them as blends or "cocondensation" products with alkyds. The principal reasons for the growing importance of the urea resins in the baking enamel field are their extremely light color, their color stability at high temperatures, and their extreme hardness and mar resistance.

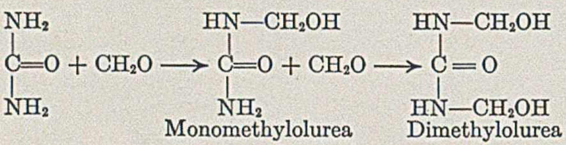
The ordinary urea-formaldehyde condensation products have been examined extensively. In particular, the investigations of Walter (*7*) have provided data on the composition of this type of resin and have shed some light on their structure. There is, however, very little information, except of a purely speculative nature, on the composition and structure of the alcohol-modified resins. The only published work providing any experimental information on these subjects is that of Hodgins and Hovey (*5*).

The purposes of the work reported here were, first, to establish suitable methods of analysis; and secondly, to investigate the composition of the modified resins and to determine the effect of curing on their composition.

Theoretical Chemistry of Modified Urea Resins

The reactions of urea and formaldehyde have been treated in detail by Ellis (*4*), and the theoretical aspects of the chemistry of the modified urea coating resins have been discussed by Cheetham (*3*) and by Hodgins and Hovey (*5*). A résumé of the reactions is given here to facilitate an understanding of what follows.

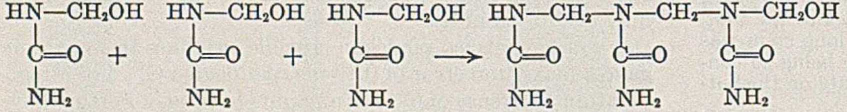
In the presence of alkaline condensing agents, urea and formaldehyde combine to form the methylolureas:



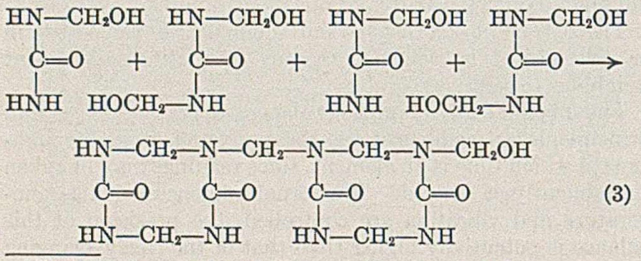
$$\begin{array}{c}NH_2\\|\\C{=}O\\|\\NH_2\end{array} + CH_2O \longrightarrow \begin{array}{c}HN{-}CH_2OH\\|\\C{=}O\\|\\NH_2\end{array} + CH_2O \longrightarrow \begin{array}{c}HN{-}CH_2OH\\|\\C{=}O\\|\\HN{-}CH_2OH\end{array} \quad (1)$$

Monomethylolurea Dimethylolurea

The methylolureas may then undergo condensation to form substances of higher molecular weight. Several types of reaction are possible according to theory:

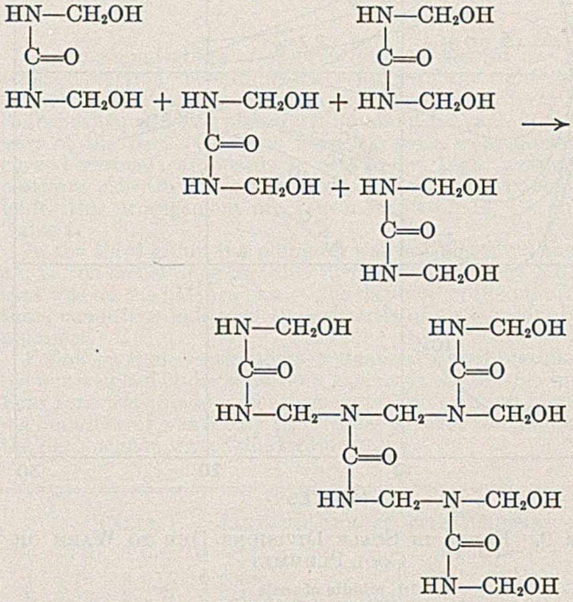


$$\begin{array}{c}HN{-}CH_2OH\\|\\C{=}O\\|\\NH_2\end{array} + \begin{array}{c}HN{-}CH_2OH\\|\\C{=}O\\|\\NH_2\end{array} + \begin{array}{c}HN{-}CH_2OH\\|\\C{=}O\\|\\NH_2\end{array} \longrightarrow \begin{array}{ccccc}HN{-}CH_2{-}&N{-}CH_2{-}&N{-}CH_2OH\\|&|&|\\C{=}O&C{=}O&C{=}O\\|&|&|\\NH_2&NH_2&NH_2\end{array} \quad (2)$$



$$\begin{array}{c}HN{-}CH_2OH\\|\\C{=}O\\|\\HNH\end{array} + \begin{array}{c}HN{-}CH_2OH\\|\\C{=}O\\|\\HOCH_2{-}NH\end{array} + \begin{array}{c}HN{-}CH_2OH\\|\\C{=}O\\|\\HNH\end{array} + \begin{array}{c}HN{-}CH_2OH\\|\\C{=}O\\|\\HOCH_2{-}NH\end{array} \longrightarrow$$

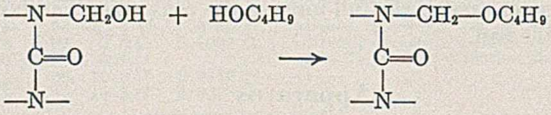
$$\begin{array}{cccc}HN{-}CH_2{-}&N{-}CH_2{-}&N{-}CH_2{-}&N{-}CH_2OH\\|&|&|&|\\C{=}O&C{=}O&C{=}O&C{=}O\\|&|&|&|\\HN{-}CH_2&{-}NH&HN{-}CH_2&{-}NH\end{array} \quad (3)$$



$$\begin{array}{c}HN{-}CH_2OH\\|\\C{=}O\\|\\HN{-}CH_2OH\end{array} + \begin{array}{c}HN{-}CH_2OH\\|\\C{=}O\\|\\HN{-}CH_2OH\end{array} + \begin{array}{c}HN{-}CH_2OH\\|\\C{=}O\\|\\HN{-}CH_2OH\end{array} + \begin{array}{c}HN{-}CH_2OH\\|\\C{=}O\\|\\HN{-}CH_2OH\end{array} \longrightarrow$$

$$\begin{array}{lll}HN{-}CH_2OH & & HN{-}CH_2OH\\|&&|\\C{=}O&&C{=}O\\|&&|\\HN{-}CH_2{-}&N{-}CH_2{-}&N{-}CH_2OH\\&|&\\&C{=}O&\\&|&\\&HN{-}CH_2{-}&N{-}CH_2OH\\&&|\\&&C{=}O\\&&|\\&&HN{-}CH_2OH\end{array} \quad (4)$$

The alcoholic modifying agent may be added at various stages in the process. In any event, there is strong evidence pointing to the occurrence of a chemical reaction between the urea-formaldehyde condensation product and the modifying agent. There are various ways in which such a reaction might occur. One of these, which has frequently been suggested, is the etherification reaction shown in Equation 5.



$$\begin{array}{c}{-}N{-}CH_2OH\\|\\C{=}O\\|\\{-}N{-}\end{array} + HOC_4H_9 \longrightarrow \begin{array}{c}{-}N{-}CH_2{-}OC_4H_9\\|\\C{=}O\\|\\{-}N{-}\end{array} \quad (5)$$

Methods of Examination

Hodgins and Hovey (*5*) made their examinations by the method of ultimate analysis. In the present work nitrogen was determined by the Kjeldahl method and from this the urea content of the resin was calculated. The aldehydic and alkoxyl residues were determined as groups and were calculated as formaldehyde and butanol. The method of group analysis has the advantage of giving more information regarding the composition and structure of the resin than does the method of ultimate analysis.

DETERMINATION OF NITROGEN. Little need be said about the Kjeldahl method for nitrogen. The Gunning modification as given in the methods of the Association of Official Agricultural Chemists (*1*) was used. Probably any of the common modifications can be used successfully. In some cases sulfuric acid alone gives sufficiently rapid digestion; in most cases, however, small amounts of copper and potassium sulfates, as specified in the Gunning modification, materially hasten the digestion.

DETERMINATION OF FORMALDEHYDE. The method employed involved decomposition of the resin with phosphoric acid and distillation of the liberated formaldehyde into alkaline hydrogen peroxide which oxidized each mole of formaldehyde to one mole of formic acid. The excess alkali was

---

[1] Present address, Reichhold Chemicals, Inc., Elizabeth, N. J.

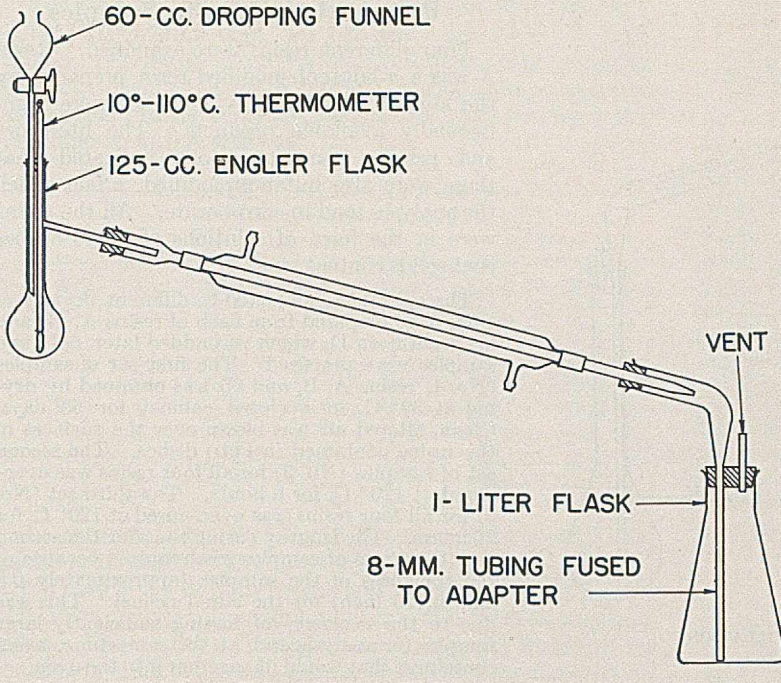


Figure 1. Diagram of Apparatus

then back-titrated. The apparatus employed in the distillation is shown in Figure 1.

A 1.0-gram sample of the resin was placed in the bottom of the distilling flask, a piece of porous tile was added, and the flask was closed by the stopper bearing the dropping funnel and the thermometer. Exactly 50.0 cc. of 0.5 *N* sodium hydroxide were run into the Erlenmeyer receiving flask from a buret and 60 cc. of 3 per cent hydrogen peroxide were added by pipet. The Erlenmeyer receiving flask was then connected to the condenser as shown in Figure 1. Approximately 25 cc. of 85 per cent orthophosphoric acid and 25 cc. of distilled water were run into the distilling flask through the dropping funnel. The flask was then carefully heated to the boiling point (about 110° C.), at which temperature the resin dissolved rapidly and formaldehyde, water, and butanol began to distill over. During the course of the distillation the volume in the distilling flask was kept constant by adding distilled water continuously from the dropping funnel at such a rate as to maintain the temperature at about 110° C. Two hundred cubic centimeters of distillate were collected.

When the distillation had been completed the condenser and adapter were carefully washed down into the receiver with distilled water, a piece of porous tile was added, and the receiver was connected to a 30-cm. (12-inch) spiral reflux condenser. The solution was then refluxed for 0.5 hour in order to decompose the small quantities of acetals present and to oxidize the formaldehyde thus liberated. Following this, the solution was cooled to room temperature, the reflux condenser carefully washed down, and the excess sodium hydroxide titrated with 0.5 *N* hydrochloric acid using methyl red indicator. A blank titration was made on a mixture of 50.0 cc. of the standard alkali and 60 cc. of the 3 per cent hydrogen peroxide. The difference between the titration of the experiment and that of the blank was taken as the standard acid equivalent of the formaldehyde from the resin.

Several precautions must be observed in making this determination. The early stages of the heating, prior to distillation, should be conducted cautiously, as frothing is liable to occur when distillation begins. For a 1.0-gram resin sample at least 150 cc., and preferably 200 cc., of distillate should be taken, as otherwise the recovery may be low. Unless decomposed by refluxing, acetals, formed by combination of formaldehyde and butanol, will reduce the formaldehyde recovery by 3 to 4 per cent. Carbon dioxide liberated by partial hydrolysis of the urea will produce a titration error unless methyl red or an indicator of the same pH end point is used.

Determination of Butanol. Two principal methods are available for the determination of alkoxyl groups—the Zeisel method (*6*, *8*) and the dichromate oxidation method (*2*), a modification of which was employed here. The Zeisel method was rejected, as it did not appear to be suitable for the quantitative determination of alcohols having as high a molecular weight as butanol. The method employed involved decomposition of the resin by refluxing with phosphoric acid and *m*-phenylenediamine which absorbed the liberated formaldehyde; distillation of the butanol, followed by oxidation with sulfuric acid and potassium dichromate; distillation and titration of the resulting fatty acids; and, finally, a correction for carbon dioxide. This method should apply equally well to any other primary aliphatic monohydric alcohols used as modifiers, as it is based on the formation of one mole of fatty acid from each mole of alcohol.

A 1.0-gram sample of the resin, 1.0 gram of *m*-phenylenediamine, and a piece of porous tile were placed in a 500-cc. round-bottomed flask. Twenty-five cubic centimeters of distilled water and 25 cc. of 85 per cent orthophosphoric acid were added, and the flask was immediately attached to a 30-cm. (12-inch) spiral reflux condenser carrying a vapor trap (Figure 2) at its top. The mixture was refluxed on a boiling water bath for 1 hour, after which it was cooled to room temperature. The water trap and condenser were carefully washed down into the flask, the solution was diluted to 350 cc. with distilled water, and the flask was connected for distillation as shown in Figure 3. The end of the adapter was sealed by placing a few cubic centimeters of distilled water in the bottom of the Kjeldahl flask.

The solution was heated slowly to the boiling point and 200 cc. of dilute butanol distillate were collected. When the distillation had been completed the condenser and adapter were carefully washed down into the Kjeldahl receiver, a piece of porous tile was added, and the Kjeldahl flask was connected to the spiral reflux condenser by a stopper which also carried a dropping funnel. The top of the condenser was fitted with a vapor trap. About 100 cc. of dichromate oxidizing solution were added through the dropping funnel to the solution in the Kjeldahl flask. The oxidizing solution was prepared by dissolving 100 grams of potassium dichromate in 900 cc. of distilled water and adding 100 cc. of concentrated sulfuric acid. The Kjeldahl flask was then heated on a water bath, the bath being brought to the boiling point in 0.5 hour and kept at the boiling point for an additional 0.75 hour. Following this, the solution was cooled to room temperature and the apparatus was washed down.

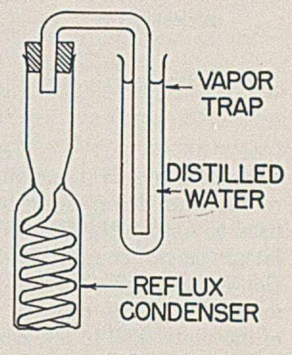


Figure 2

The Kjeldahl flask was then fitted with a stopper bearing a gooseneck and a dropping funnel and was connected for distillation, the condensing and receiving apparatus being the same as that shown in Figure 1. The end of the adapter was sealed with a few cubic centimeters of distilled water and the distillation started. The solution was concentrated to about 400 cc., after which its volume was kept constant by continuous addition of distilled water through the dropping funnel. Between 850 and 900 cc. of distillate were collected. The condenser and adapter were carefully washed down into the Erlenmeyer receiver and the distilled fatty acids were titrated with 0.5 *N* sodium hydroxide, using phenolphthalein as indicator.

Carbon dioxide present in the distillate produces an error in the titration which was corrected for by a determination of the carbonate present. The determination was made by adding excess 0.5 *N* sodium hydroxide to the titrated distillate, precipitat-

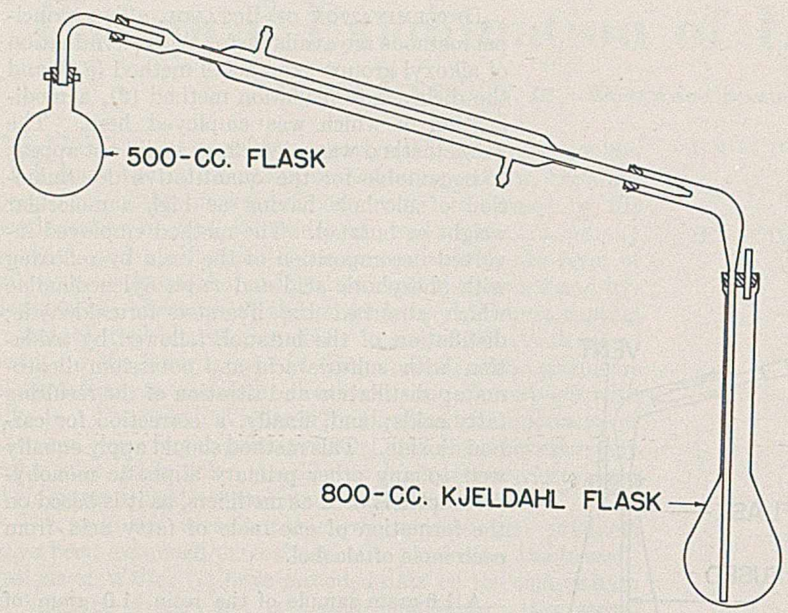


Figure 3. Flask Connected for Distillation

ing with barium chloride, filtering and washing in a Gooch crucible, dissolving in excess 0.5 *N* hydrochloric acid, boiling off the carbon dioxide, and titrating back the excess hydrochloric acid.

Table I. Precision of Formaldehyde and Butanol Determinations

Substance Determined	Sample	Determined	Recovery
	Gram	*Gram*	%
Formaldehyde	0.3399	0.3421	100.7
	0.4375	0.4311	98.5
	0.5350	0.5403	101.0
Butanol	0.3080	0.3157	102.5
	0.3257	0.3248	99.7
	0.3239	0.3237	99.9

Several observations may be made with regard to this method for determining butanol. *m*-Phenylenediamine was used to absorb the formaldehyde after it was found that the latter was not completely oxidized to carbon dioxide, the portion appearing in the final distillate as formic acid producing an indeterminate error in the titration. The large quantity of distillate (850 to 900 cc.) taken in the final distillation appears to be necessary for maximum recovery. The ratio of the quantity of distillate to the size of the sample appears to have a considerable bearing on the efficiency of recovery. Thus, for 850 cc. of distillate the normal size of sample is 1.0 to 1.1 grams. A 50 per cent increase in the size of the sample (1.5 grams) produced a 2 per cent drop in recovery. Failure to correct for carbon dioxide may result in an error of as much as 15 per cent.

Precision of the Methods

Before the methods for determining formaldehyde and butanol were employed for analysis of resins their precision was determined by running control tests. These tests were made on U. S. P. formaldehyde solution (36.07 per cent by weight) and technical *n*-butanol (99.87 per cent by weight). In each of these control tests urea, formaldehyde, and butanol were present in approximately the same proportions as they occurred in the resins. The substance being determined (formaldehyde or butanol) was measured out accurately from a weight pipet. The results of the control tests are shown in Table I.

Preparation of Resin Samples

Four different resins were examined. Resin A was a *n*-butanol–modified resin prepared by the author. Resins B, C, and D were commercially available products. The literature and private communications indicated that these were also butanol-modified, a fact which the analyses tend to corroborate. All the resins were in the form of solutions of 50 to 60 per cent solids content.

Three samples, subjected to different degrees of cure, were prepared from each of resins A, B, and C; from resin D, which was added later, only two samples were prepared. The first set of samples (No. 1, resins A, B, and C) was obtained by drying at 30° C. in a closed cabinet for 53 days. Clean, filtered air was blown over the surfaces of the resins contained in Petri dishes. The second set of samples (No. 2) for all four resins was oven-cured at 120° C. for 6 hours. The third set (No. 3) for all four resins was oven-cured at 120° C. for 26 hours. The lengthy curing time for the second and third sets of samples was required because of the thickness of the samples [approximately 0.3 cm. (0.125 inch) for the cured resins]. This was due to the necessity of having sufficiently large samples for analysis and, at the same time, using containers that would fit together into the oven.

In Table II the residual weights of the samples, after drying, are expressed as per cent by weight of the original resin solutions. Standard films, having about the same thickness and degree of cure as ordinary lacquer or varnish films, were prepared from each resin for the purpose of showing comparatively the extent of cure of the analytical samples. The standard films were obtained by diluting 10 grams of resin solution with 5 grams of butanol, weighing 2.5 grams into a 8.75-cm. (3.5-inch) flat-bottomed container, and curing for 1 hour at 120° C.

Table II. Residual Weights of Analytical Samples and Standards

Resin	Sample No.	Residual[a] Weight	
		Sample	Standard film
A	1	61.8	59.0
	2	58.1	
	3	55.4	
B	1	62.5	62.1
	2	63.7	
	3	57.8	
C	1	52.2	52.7
	2	49.8	
	3	46.3	
D	2	63.0	63.8
	3	61.7	

[a] Per cent by weight of original resin solutions.

It was originally intended that No. 1 samples should be dried with as little curing as possible, but this objective was not realized. No. 1 samples were dried for over 50 days before they approached closely to a constant weight. When they were removed for analysis it was found that they had cured to the point where they were permanently insoluble in butanol. The prolonged drying was occasioned by the fact that the drying curves gave no indication of the point at which the free solvent had been removed. In the case of resin B, No. 1 was actually cured further than No. 2.

Analytical Results

The resin samples after curing were analyzed by the methods previously described. The results are shown in Table III.

The sum of the percentages of urea, formaldehyde, and butanol is greater than 100 per cent, the difference (last column, referred to as the water of reaction) being the water split out during the formation and curing of the resin and added again to the separate components when the resin was decomposed during analysis.

TABLE III. ANALYTICAL RESULTS
(Per cent by weight of sample)

Resin	Sample No.	Urea	Formaldehyde	Butanol	Total	Water of Reaction
A	1	37.3	39.4	37.0	113.7	13.7
	2	40.2	41.4	37.6	119.2	19.2
	3	42.5	41.7	32.8	117.0	17.0
B	1	39.5	42.8	32.9	115.2	15.2
	2	38.8	42.4	37.2	118.4	18.4
	3	42.7	41.1	31.2	115.0	15.0
C	1	43.5	43.6	27.3	114.4	14.4
	2	45.4	45.4	27.9	118.7	18.7
	3	49.2	44.2	25.2	118.6	18.6
D	2	42.3	44.7	32.6	119.6	19.6
	3	43.6	45.5	31.6	120.7	20.7

In order to show the effects of curing more clearly, the ratios of formaldehyde to urea (F/U) and of butanol to urea (B/U) are given as both weight and mole ratios in Table IV. The ratio of water of reaction to urea is also given as a weight ratio. The results for each resin are arranged from top to bottom in order of increasing cure, as indicated by decreases in the F/U and B/U ratios.

TABLE IV. RATIO OF COMPONENTS TO UREA

Resin	Sample No.	Weight Ratio			Mole Ratio	
		F/U	B/U	W/U	F/U	B/U
A	1	1.06	0.99	0.37	2.12	0.80
	2	1.03	0.94	0.48	2.06	0.76
	3	0.98	0.77	0.40	1.96	0.62
B	2	1.09	0.96	0.47	2.18	0.78
	1	1.08	0.83	0.38	2.16	0.67
	3	0.96	0.73	0.35	1.92	0.59
C	1	1.00	0.63	0.33	2.00	0.51
	2	1.00	0.62	0.41	2.00	0.50
	3	0.90	0.51	0.38	1.80	0.41
D	2	1.06	0.77	0.46	2.12	0.62
	3	1.04	0.72	0.47	2.08	0.58

For resin B the figures show that No. 1 was more highly cured than No. 2, corroborating the residual weight data given for these samples in Table II. In the case of resin C the data of Tables II and IV appear to be conflicting. Table II indicates that No. 2 was more highly cured than No. 1, while the F/U and B/U ratios are nearly identical. This is accounted for, apparently, by the fact that the loss consisted almost entirely of water.

TABLE V. PER CENT LOSS OF FORMALDEHYDE AND BUTANOL ON CURING

Resin	Sample No.	Formaldehyde Loss	Butanol Loss
A[a]	1–2	2.8	5.1
	1–3	7.6	22.2
B[b]	2–1	0.9	13.5
	2–3	11.9	24.0
C[a]	1–2	0.0	1.6
	1–3	10.0	19.1
D[b]	2–3	1.9	6.5

[a] Per cent of content of No. 1.
[b] Per cent of content of No. 2.

The losses of formaldehyde and butanol, expressed as percentages of the formaldehyde or butanol content of the sample having the lowest degree of cure, show the effect of curing even more markedly than does Table IV. Thus, the loss when resin A was cured from the stage represented by No. 1 to that represented by No. 2 was:

$$\text{Formaldehyde } \frac{1.06 - 1.03}{1.06} \times 100 = 2.83\%$$

$$\text{Butanol } \frac{0.99 - 0.94}{0.99} \times 100 = 5.05\%$$

Losses expressed in this manner are given in Table V.

Examination of Data

Despite the possible effect of accumulative errors, it was possible to get a reasonable correlation between the loss in weight on curing as calculated from the residual weight data of Table II and the loss as calculated from the analytical data of Table IV. The decrease in residual weight between two successive samples divided by the per cent of urea in the original resin solution gives the loss of weight per gram of urea. The weight losses thus determined are shown in Table VI (last column). The algebraic sum of the differences in the F/U, B/U, and W/U ratios for two successive samples also gives the curing loss per gram of urea. The total net losses calculated by this latter method are shown in Table VI (sixth column). The losses obtained by the two methods are in fair agreement.

TABLE VI. CHANGE IN LOSSES ON CURING
Grams per gram of urea

Resin	Sample No.	Δ(F/U)	Δ(B/U)	Δ(W/U)	Total Net Loss	Loss Calcd. from Residual Weight
A	1-2	0.03	0.05	0.11	0.19	0.16
	2-3	0.05	0.17	−0.08	0.14	0.12
B	2-1	0.01	0.13	−0.09	0.05	0.05
	1-3	0.12	0.10	−0.03	0.19	0.19
C	1-2	0.00	0.01	0.08	0.09	0.11
	2-3	0.10	0.11	−0.03	0.18	0.15
D	2-3	0.02	0.05	0.01	0.08	0.05

The negative values for the changes in the W/U ratios are difficult to account for. As previously explained, the W/U ratio for any sample represents the total amount of water split out while the sample was being formed from its individual components. A negative value of Δ (W/U) indicates one of three possibilities—that water was taken up during the curing process; that the curing process took place in an essentially different manner for the two samples involved; or that negative values are due to the effect of accumulative errors.

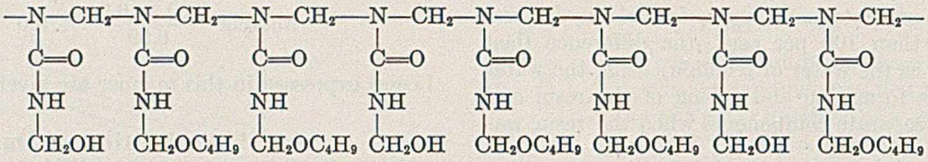
Examination of the data in Table VI shows that the formaldehyde and butanol losses increase as curing proceeds. The occurrence of negative values makes it impossible to say anything definite about the loss of water. However, in the case of resins A and C, the data suggest a decrease in water loss as curing progresses. In general, the data suggest that water comprises a large part, if not a major part, of the loss during the early stages of the curing; while during the latter stages losses of formaldehyde and butanol predominate.

Any attempt to examine into the structure of the resins on the basis of the knowledge available here is handicapped by three factors: (1) The possibility that the resins are not characterized by any particular type of structure, but are mixtures of two or more types. In such a case the analyses would give only the average composition, which consequently might not be characteristic of any of the structures present. (2) Lack of knowledge of the relative number of methylene and methylol groups makes it difficult to select the most probable from the various possible structures. (3) The tremendous possibilities of isomerism introduce further complications.

The average molar composition of the resins as given by the data of Table IV is:

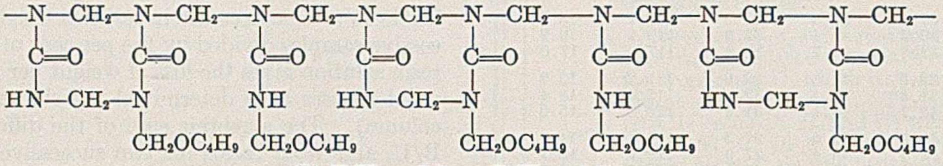
$$F/U = 2.0 \qquad B/U = 0.62$$

These figures do not impose any limitations as to the types of structure which are possible. Thus it is possible to have simple chains as indicated on the following page.



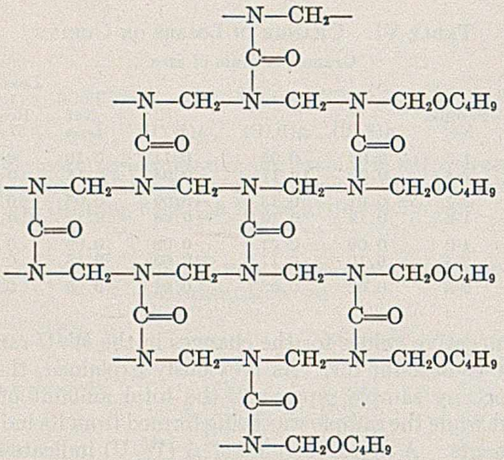
(a) F/U = 2.0 B/U = 0.62

or ring chains



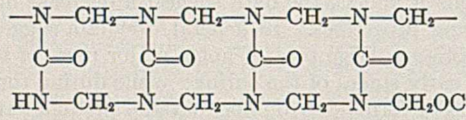
(b) F/U = 2.0 B/U = 0.63

or three-dimensional branched molecules



(c) F/U = 2.0 B/U = 0.63

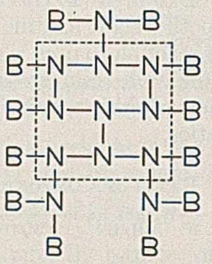
Examination of the foregoing formulas shows that the composition does impose some structural limitations in the case of the ring-chain and branched types. Thus in the ring-chain type, the length of the individual rings is limited by the butanol content. Rings such as



(d) B/U = 0.25

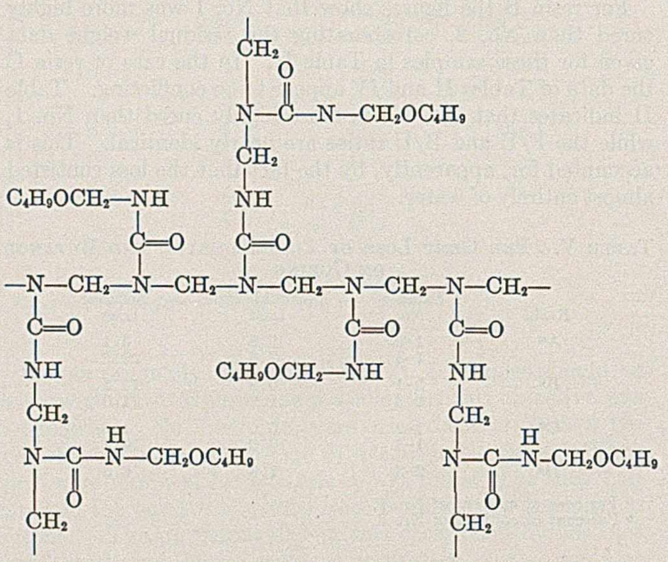
can exist only in small numbers if at all; while rings of more than four urea residues in length are still less probable. Again, it is interesting to note that the molecular weights of closely branched molecules (Formulas *c* and *e*) are dependent upon the B/U ratio, the degree of butanol saturation, and the shape of the molecule. This is due to the fact that the butoxyl groups can be located only at the extremities of the molecule and that, consequently, the B/U ratio decreases as the molecule grows. If the shape of the molecule and the degree of butanol saturation were known, it would be possible to calculate the molecular weight from the B/U ratio. Thus, Formula *e* shows, in skeleton form, a saturated molecule whose projected shape is a square.

For such a molecule a B/U ratio of 0.62 requires a molecular weight of slightly more than 10,000. For other rectangular shapes the molecular weights, which are dependent upon the relative dimensions of the molecule, may also be calculated.



(e)

Other types of three-dimensional molecules, having less frequent branching, are also possible. One of these is illustrated by Formula *f*. Because of the relatively larger number of positions available for butoxyl groups, this type would permit greater variations in molecular weight and structure.



(f) F/U = 2.0 B/U = 0.63

Summary and Conclusions

Existing methods for the determination of formaldehyde and butanol have been modified in order to apply them to the analysis of urea coating resins. Although the methods were used only on resins containing formaldehyde and butanol, they should prove satisfactory for any aldehydes or primary aliphatic monohydric alcohols liable to be used in this type of resin. Control tests indicated a precision of about 1 part per 100.

Several different urea resins were examined. Three samples of each resin, representing different degrees of cure, were analyzed.

The analyses were sufficiently accurate to show losses of formaldehyde and butanol on curing, but not to permit calculation of the water loss or of the number of methylene and methylol groups.

During the earlier stages curing appears to proceed chiefly through loss of water, although formaldehyde and butanol are also lost. In the latter stages of curing, butanol and formaldehyde are the principal losses.

The magnitude of the losses varies considerably for different resins subjected to the same curing conditions. The loss of butanol is generally greater than that of formaldehyde but, otherwise, there appears to be no particular relation between the two losses.

Despite the considerable losses, the butanol content of highly cured resins remains surprisingly large (25 to 32 per cent of the cured resin).

The analytical results provided very little information regarding the structure of the resin molecules. A further knowledge of molecular structure would seem to depend largely on obtaining methods for quantitatively distinguishing methylene from methylol groups.

Acknowledgment

The author is indebted to George Barsky and Frank A. Strauss for their many helpful suggestions and for permission to publish.

Literature Cited

(1) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, 3rd ed., p. 11, 1930.

(2) *Ibid.*, p. 145 (method for fusel oil).

(3) Cheetham, H. C., *Paint, Oil Chem. Rev.*, 99, No. 12, 42, 44 (June 10, 1937).

(4) Ellis, C., "Chemistry of Synthetic Resins", Vol. I, pp. 576–87, New York, Reinhold Publishing Corp., 1935.

(5) Hodgins, T. S., and Hovey, A. G., Ind. Eng. Chem., 30, 1021–9 (1938).

(6) Kamm, O., "Qualitative Organic Analysis", 2nd ed., pp. 206–8, New York, John Wiley & Sons, 1932.

(7) Walter, G., "Phenomena of Polymerization and Condensation", pp. 377–95, London, Gurney and Jackson, 1935 (reprint from *Trans. Faraday Soc.*).

(8) Zeisel, *J. Chem. Soc.*, 81, 318 (1902); **115**, 193 (1919).

Presented before the Division of Paint and Varnish Chemistry at the 98th Meeting of the American Chemical Society, Boston, Mass.

Effect of Certain Carbohydrates on the Determination of Carotene

E. J. LEASE AND J. H. MITCHELL, South Carolina Agricultural Experiment Station, Clemson, S. C.

SOME commonly used methods for the determination of carotene in forages, feeds, foodstuffs, and plant tissue involve the use of alcoholic potassium hydroxide as an extraction medium (*1–4, 7*). Guilbert (*3*) pointed out the obvious advantages of this technique, which has been used with apparent success by many workers. In the course of investigations on the vitamin A value of the sweet potato (*Ipomoea batatas*), attempts were made to determine the carotene content of the Porto Rico variety after cooking, by methods involving initial extraction with alcoholic potassium hydroxide. Practically no carotene was detected in cooked sweet potatoes by these methods, although biological studies with the rat indicated that these sweet potatoes were potent sources of provitamin A, whether raw or cooked.

In many instances the use of potassium hydroxide facilitates disintegration of the tissue and liberates the pigments (*1–5, 7–9*); in some methods not involving the initial use of potassium hydroxide, drastic or tedious measures are needed to free the pigments from the plant tissue (*6, 10–13*). The advantages and disadvantages of some of these methods are summarized by Munsey (*6*). With the sweet potato, however, these difficulties are not encountered nor are other pigments a complication; thus, although alcoholic potassium hydroxide does not remove carotene completely from the cooked sweet potato, the carotene is readily extracted by boiling 95 per cent ethanol. The difficulty which is encountered in removing the carotene of cooked sweet potato and of certain other vegetables seemed to be due to interfering substances formed during the cooking process. The nature of these substances and their possible action are here discussed.

The carotene content of raw Porto Rico sweet potatoes, when analyzed by methods involving the use of alcoholic potassium hydroxide (*2, 3, 7*), was found to average 124 micrograms per gram of dry matter. Portions of these same potatoes, when boiled for 30 minutes or baked at 205° C. for 30 minutes and analyzed by the same methods, yielded practically no carotene (Table I). During the refluxing of the cooked sweet potato with alcoholic potassium hydroxide the solution became light yellow and outward appearance indicated that carotene was being extracted from the sample. The solution darkened as refluxing continued and at the end of the 30-minute refluxing period, some samples were yellow-orange while others were black. These pigments were all found to be water-soluble; no carotene was evident. When this procedure was repeated, omitting the potassium hydroxide, darkening did not occur and carotene was completely extracted from cooked or raw sweet potato (Table I). Readings were made photoelectrically and checked colorimetrically. No appreciable amount of pigments was removed from the petroleum ether solution by 92 per cent methanol, indicating an absence of xanthophylls.

Most of the dry matter of raw sweet potato is starch and cooked sweet potatoes contain large amounts of reducing sugars. It seemed probable that the darkening in color was due to polymerization by the potassium hydroxide with subsequent interference with carotene determination, and experiments to clarify this point were undertaken.

Interfering Substances

After the cooked sweet potato had been thoroughly leached with water to remove soluble carbohydrates, almost all the

Table I. Carotene Extracted by Alcoholic Potassium Hydroxide Procedures

(Calculated to moisture-free basis)

Sample	Carotene Extracted by 95% Ethanol	Carotene Extracted by KOH Procedures	
	Micrograms per gram		%
Raw sweet potato	130	124	95.4
Boiled sweet potato	130	5	3.8
Baked sweet potato	130	2	1.5
Baked sweet potato, refluxed with alcoholic KOH, then water, and extracted	130	130	100
Stored sweet potato			
5° C. for 4 months	127	83	65.3
37° C. for 4 months	124	25	20.1
Water-extracted cooked sweet potato, residue	154	153	99.4
Water-extracted cooked sweet potato after incorporating:			
Glucose	52	25	48.1
Fructose	49	26	53.1
Dextrinized starch	77	0.5	0.6
Maltose	95	50	52.6
Sucrose	35	20	57.1
Cooked carrot	302.5	100.9	33.3
Alfalfa hay	32	32	100
Lespedeza hay	34	33.8	99.4
Fresh mixed grasses	41	40.1	97.8
Squash (summer, yellow), surface layer only			
Raw	15	4	26.6
Cooked	13	4	30.8
Pumpkin (canned)	92.6	77.2	83.4

carotene was readily extracted from the residue with alcoholic potassium hydroxide (Table I). Practically none of the carotene was extractable after thorough incorporation of the evaporated leachings with the residue, accomplished by placing a mixture of the residue and evaporated (sirup stage) leachings under alternate vacuum and pressure, and finally removing the excess moisture by a fan at room temperature.

The residue of the water-extracted cooked sweet potatoes was incorporated with known compounds to see whether they would render the carotene unextractable by alcoholic potassium hydroxide. Equal weights of sweet potato starch and extracted boiled sweet potato residue were mixed, moistened, and autoclaved to dextrinize the starch, and after partial drying the mixture was treated with alcoholic potassium hydroxide. It was found impossible to extract more than a trace of the carotene present in the mixture (Table I). Glucose, maltose, or fructose when incorporated as described above prevented the extraction of more than half of the carotene contained in the mixture (Table I).

Action of Interfering Substances. At first it was thought that some of the polymerized carbohydrates reacted with or adsorbed the carotene from solution. However, when an alcoholic potassium hydroxide solution of crystalline carotene was refluxed with glucose, fructose, maltose, or a water extract of cooked sweet potato, the carotene was found to be readily available for determination. When a solution of carotene in oil was refluxed with a mixture of alcoholic potassium hydroxide and cooked sweet potato, the added carotene was neither removed from the solution nor destroyed. It thus became apparent that the difficulty lay in the initial extraction of carotene from the cooked sweet potato rather than in any subsequent adsorptive or destructive action of the polymers.

When treated with alcoholic potassium hydroxide, the tissue of raw sweet potato disintegrated into shreds in a normal fashion, whereas cooked sweet potato became gummy, lumpy, and resinous. Since the bulk of the dry matter of raw sweet potato is starch, it seemed probable that the hydrolytic products of starch, formed on cooking, reacted with potassium hydroxide to form resins, binding the carotene mechanically. This resinous film held the carotene particles so tightly that it prevented their extraction with cold or boiling 95 per cent ethanol, ethyl ether, petroleum ether, or acetone. This resinous matter could be dissolved, however, by boiling the sweet potato for 5 minutes with three volumes of water. The carotene was then readily extracted by fat solvents and its determination could proceed as usual.

Results with Other Foodstuffs

Some of the carotene of certain other foodstuffs and of raw sweet potatoes stored under certain conditions was also resistant to extraction following treatment with alcoholic potassium hydroxide (Table I). Certain samples of cooked carrot also possessed carotene which was not extracted by alcoholic potassium hydroxide. The carotene of raw or cooked summer squash, although readily extracted with ethanol, was difficult to extract with alcoholic potassium hydroxide, although the xanthophyll was readily extracted. The pigments of canned pumpkin could be extracted fairly well with alcoholic potassium hydroxide, but were much more readily extracted with alcohol.

For many food materials, including fresh raw sweet potato, methods involving extraction with alcoholic potassium hydroxide are satisfactory. However, since there is a tendency to increase the carotene content of feeds by adding concentrated carotene preparations such as dehydrated sweet potato, the importance of a suitable extraction method for all types of tissue is obvious. If alcoholic potassium hydroxide is used, an added precaution is recommended: boiling the residue (which is supposed to be carotene-free after treatment with alcoholic potassium hydroxide) with water, and subsequently extracting with ether and alcohol. This checkup may show that large amounts of carotene remain unextracted.

Summary

Methods involving the use of alcoholic potassium hydroxide were found inapplicable to cooked sweet potatoes, stored raw sweet potatoes, and certain other cooked vegetables because subsequent extraction of carotene was incomplete.

Apparently polymerization of carbohydrate by the alkali, forming a resinous film, rendered the carotene unextractable by cold or boiling 95 per cent ethanol, ether, acetone, or petroleum ether.

In samples containing large amounts of carbohydrate, carotene may be determined by extraction with ethanol; if alcoholic potassium hydroxide is used, the material should be subsequently boiled with water to dissolve the resins before extraction of the carotene by fat solvents.

Acknowledgment

The authors wish to acknowledge the invaluable help of Jane G. Lease and the technical assistance of G. S. Irby.

Literature Cited

(1) Fraps, G. S., Ind. Eng. Chem., Anal. Ed., 10, 525 (1938).
(2) Fraps, G. S., and Kemmerer, A. R., Texas Agr. Expt. Sta., *Bull.* 557 (1937).
(3) Guilbert, H. R., Ind. Eng. Chem., Anal. Ed., 6, 452 (1934).
(4) Hegsted, D. M., Porter, J. W., and Peterson, W. H., *Ibid.*, 11, 256 (1939).
(5) Moon, F. E., *J. Agr. Sci.*, 29, 295 (1939); *Nutrition Abstracts & Revs.*, 9, 286 (1939).
(6) Munsey, V. E., *J. Assoc. Official Agr. Chem.*, 20, 459 (1937).
(7) Peterson, W. J., Hughes, J. S., and Freeman, H. F., Ind. Eng. Chem., Anal. Ed., 9, 71 (1937).
(8) Pyke, M., *J. Soc. Chem. Ind.*, 55, 139T (1936).
(9) Ratchevsky, P., *Bull. soc. chim. biol.*, 17, 1187 (1935).
(10) Reti, L., and Arias da Silva, C., *Anales asoc. quím. argentina*, 24, 20B (1936).
(11) Russell, W. C., Taylor, M. W., and Chichester, D. F., *Plant Physiol.*, 10, 325 (1935).
(12) Schertz, F. M., *Ibid.*, 3, 211 (1928).
(13) Wiseman, H. G., and Kane, E. A., *J. Biol. Chem.*, 114, cviii (1936).

Published by permission of the Director of the Experiment Station as Technical Contribution No. 72.

Cerate Oxidimetry

Preparation and Stability of Solutions

G. FREDERICK SMITH AND C. A. GETZ
University of Illinois, Urbana, Ill.

A DISTINCT advantage in using tetravalent cerium in volumetric analysis, rather than permanganate, with which it compares favorably in the number of practical applications, is the fact that its sulfate solutions are completely stable during long storage and are stable at the boiling temperature for considerable periods of time. Moreover, hydrochloric acid in moderate concentrations is not a complicating factor, as in the case of permanganate. The fact that permanganate serves as its own indicator while the tetravalent cerium does not is no disadvantage, since the high potential indicator, ferroin, has come into wide use.

Cerium in volumetric analysis has one disadvantage as compared to permanganate. The oxidation potential of the system $Ce^{++++} + e = Ce^{+++}$ in molar sulfuric acid is 1.44 volts, whereas that of the couple $MnO_4^- + 5e + 8H^+ = Mn^{++} + 4H_2O$ is 1.52 volts. The former system in hydrochloric acid medium has a potential of 1.28 volts. This fact, which places such reactions on a par only with dichromate reactions as to oxidation potential, is not sufficiently recognized.

The use of tetravalent cerium in nitric and perchloric acid solution provides the potentials 1.61 and 1.70 volts, respectively, for the system $Ce^{++++} + e = Ce^{+++}$. At these potentials such solutions extend the field of possible analytical applications. Standard solutions of tetravalent cerium would be expected to undergo change as a result of the slow formation of oxygen, owing to the reaction of the couple, $O_2 + 4e + 4H^+ = H_2O$, the potential of which is approximately 1.2 volts.

It is the purpose of the present study to determine the magnitude of the last-mentioned effect.

Previous Studies

The most recent summary of published data in the use of tetravalent cerium in volumetric analysis has been given by Furman (*1*), who presents a general review of the subject and an extensive bibliography.

Ceric oxide, CeO_2, anhydrous ceric sulfate, $Ce(SO_4)_2$, and the so-called double sulfate, $Ce(SO_4)_2.2(NH_4)_2SO_4.2H_2O$, originally served as materials for the preparation of solutions for use in analysis. The use of the complex salt hexanitrato ammonium cerate, $(NH_4)_2Ce(NO_3)_6$, was proposed by Smith, Sullivan, and Frank (*6*). The corresponding potassium salt, $K_2Ce(NO_3)_6$, may be similarly employed. The electrolytic oxidation of cerous sulfate, nitrate, and perchlorate to form the complex acids $H_2Ce(SO_4)_3$, $H_2Ce(NO_3)_6$, and $H_2Ce(ClO_4)_6$ by an improved procedure not requiring the use of a diaphragm cell was described by Smith, Frank, and Kott (*3*). The potential relationships of the couple $Ce^{++++} + e = Ce^{+++}$ in hydrochloric, sulfuric, nitric, and perchloric acids were studied by Smith and Getz (*4*), who developed a cerate-ion concept. Improved procedures in the standardization of the nitrato and perchlorato cerate anion, using sodium oxalate and arsenious oxide as reference standards, were described by Smith and Getz (*5*), who used nitro-ferroin for the first time as indicator in this work.

Preparation and Materials

Hexanitrato ammonium cerate, $(NH_4)_2Ce(NO_3)_6$, was prepared as previously described (*5*). Salts of two different types were employed: a pure grade, 98 to 100 per cent, and an impure grade, 90 to 95 per cent. Hexanitrato potassium cerate was similarly prepared, using potassium nitrate in place of ammonium nitrate.

Solutions of perchlorato ceric acid, $H_2Ce(ClO_4)_6$, in perchloric acid were prepared by electrolytic oxidation of pure cerous perchlorate (*2*). The cerous perchlorate was completely oxidized before use.

Solutions of pure cerous nitrate in nitric acid were completely oxidized electrolytically to nitrato ceric acid, $H_2Ce(NO_3)_6$, by the method of Hengstenberger (*2*).

Preparation and Standardization of Solutions

Solutions were all standardized using Bureau of Standards sodium oxalate and arsenious oxide, as well as ferrous sulfate that had been standardized indirectly with sodium oxalate and sulfato cerate solution, using ferroin as indicator in all cases. The methods have been described in detail by Smith and Getz (*5*). The solutions tested for stability in storage are described in Table I.

Variation in Solution Normality with Time of Storage

Data showing the change in normality with time for ten solutions prepared as shown in Table I are given in Table II. Some solutions studied are omitted to conserve space. The solutions omitted, all of which were acidified with perchloric acid from 1 to 8 *N* in strength, were increasingly less stable in the following order: 11, 12, 13, 14, 15, 16, 17, and 18.

Discussion of Results

Of the seven most stable solutions five were stored in the dark, which indicates that decomposition is in part a photochemical reaction. The most stable solution consisted of purified hexanitrato ammonium cerate in 2 *N* perchloric acid. For change in normality of 1 part in 10,000, 10 days' storage time is required.

TABLE I. COMPOSITION AND STANDARDIZATION VALUES OF NITRATO AND PERCHLORATO CERATE SOLUTIONS

(Solutions numbered in the order of their stability)

Solution No.	Starting Material	Acid Concentration	Standard Factor	Purity of Starting Material	Type of Storage	Duration of Test
						Days
1	$(NH_4)_2Ce(NO_3)_6$	2.0 *N* $HClO_4$	0.1008	Purified	Dark	235
2	$(NH_4)_2Ce(NO_3)_6$	3.0 *N* HNO_3	0.05147	Commercial	Dark	183
3	$(NH_4)_2Ce(NO_3)_6$	1.4 *N* HNO_3	0.07082	Purified	Dark	237
4	$(NH_4)_2Ce(NO_3)_6$	1.0 *N* $HClO_4$	0.08406	Commercial	Diffused daylight	246
5	$(NH_4)_2Ce(NO_3)_6$	1.4 *N* HNO_3	0.07020	Commercial	Diffused daylight	237
6	$(NH_4)_2Ce(NO_3)_6$	1.0 *N* HNO_3	0.05333	Purified	Dark	179
7	$H_2Ce(ClO_4)_6$	3.0 *N* $HClO_4$	0.05642	Purified	Dark	167
8	$K_2Ce(NO_3)_6$ + $(NH_4)_2Ce(NO_3)_6$	1.0 *N* $HClO_4$	0.04274	Commercial	Dark	181
9	$(NH_4)_2Ce(NO_3)_6$	1.4 *N* HNO_3	0.007143	Purified	Dark	241
10	$(NH_4)_2Ce(NO_3)_6$	2.0 *N* $HClO_4$	0.01132	Purified	Dark	242
11	$(NH_4)_2Ce(NO_3)_6$	1.4 *N* HNO_3	0.007351	Purified	Diffused daylight	242
12	$H_2Ce(ClO_4)_6$	4.0 *N* $HClO_4$	0.09700	Commercial	Dark	17
13	$H_2Ce(ClO_4)_6$	8.0 *N* $HClO_4$	0.05439	Purified	Dark	183
14	$(NH_4)_2Ce(NO_3)_6$	2.0 *N* $HClO_4$	0.01039	Purified	Diffused daylight	243
15	$H_2Ce(ClO_4)_6$	1.0 *N* $HClO_4$	0.05624	Purified	Dark	171
16	$(NH_4)_2Ce(NO_3)_6$	1.0 *N* $HClO_4$	0.009081	Commercial	Diffused daylight	95
17	$(NH_4)_2Ce(NO_3)_6$	2.0 *N* $HClO_4$	0.09540	Purified	Diffused daylight	236
18	$H_2Ce(ClO_4)_6$	8.0 *N* $HClO_4$	0.04188	Purified	Diffused daylight	115

Table II. Variation in Solution Normality during Storage for Extended Time Periods

Solution No.	Time	Normality	Total Change in Normality	Change	Av. Change per Day
	Days			%	%
1	0	0.10080	.....	..	...
	19	0.10050	0.00030	0.30	0.016
	85	0.09985	0.00095	0.94	0.011
	134	0.09961	0.00119	1.18	0.008
	235	0.09874	0.00206	2.04	0.008
2	0	0.05147	.....	..	...
	30	0.05110	0.00037	0.72	0.024
	78	0.05103	0.00044	0.85	0.011
	183	0.05048	0.00099	1.94	0.011
3	0	0.07082	.....	..	...
	18	0.07050	0.00032	0.45	0.025
	87	0.06974	0.00108	1.56	0.018
	134	0.06958	0.00124	1.75	0.013
	237	0.06850	0.00232	3.26	0.014
4	0	0.08406	.....	..	...
	20	0.08363	0.00043	0.51	0.025
	52	0.08313	0.00093	1.71	0.021
	94	0.08250	0.00156	1.86	0.020
	143	0.08187	0.00219	2.60	0.018
	246	0.07958	0.00448	5.33	0.021
5	0	0.07020	.....	..	...
	18	0.06996	0.00034	0.48	0.027
	87	0.06971	0.00049	0.70	0.008
5 (*cont'd*)	134	0.06946	0.00074	1.05	0.008
	237	0.06903	0.00117	1.69	0.007
6	0	0.05333	.....	..	...
	27	0.05288	0.00045	0.84	0.031
	75	0.05264	0.00069	1.29	0.017
	179	0.05084	0.00249	4.67	0.026
7	0	0.05642	.....	..	...
	15	0.05607	0.00035	0.62	0.041
	63	0.05554	0.00088	1.56	0.025
	167	0.05377	0.00265	4.72	0.028
8	0	0.04274	.....	..	...
	28	0.04225	0.00049	1.14	0.041
	76	0.04208	0.00066	1.52	0.020
	181	0.03938	0.00336	7.86	0.043
9	0	0.007143	.....	..	...
	21	0.007077	0.000066	0.92	0.044
	91	0.006990	0.000253	3.54	0.039
	241	0.006755	0.000388	5.42	0.022
10	0	0.01132	.....	..	...
	22	0.01119	0.00013	1.15	0.052
	92	0.01088	0.00044	3.89	0.042
	242	0.01071	0.00061	5.39	0.022

Hexanitrato ammonium cerate in 1.0 to 3.0 *N* perchloric or nitric acid made up the ten most stable solutions without much preference for one or the other. Solutions of perchlorato ceric acid in perchloric acid were the least stable—obviously a result of their higher potential as compared to solutions containing nitrate. This potential difference amounts to 0.2 volt or more in some cases.

In every case the stability increased with time. This is to be expected, since the potential of each solution falls as cerous ions accumulate.

All of the first ten solutions had a very satisfactory stability. The tenth solution in the order of stability would require restandardization only every 4 days on the average before a difference of 1 part in 10,000 could be detected. Solutions of perchlorato ceric acid in 8 *N* perchloric acid, the least stable solution of Table I, would require standardization each day when freshly prepared and once every 4 days when 4 months old to keep values within a maximum variation of 1 part in 10,000, if stored in diffused daylight. The oxidation potential of perchlorato ceric acid in 8 *N* perchloric acid, when oxidized to as great an extent as possible, is over 2.0 volts. This value rapidly falls as the cerous ion accumulates. Stability increased fourfold when 10 per cent of the perchlorato cerate ions were reduced to cerous ions.

The study shows no advantage in the elimination of the last 5 to 10 per cent of the associated rare earth elements such as lanthanum, neodymium, and praseodymium. Four of the eight most stable solutions were prepared from commercial grades of materials, in which were present a few per cent of the cerous ion. In most of these cases the solutions were stored in diffused daylight and their stability could be enhanced by storage in the dark.

Influence of Nitric and Perchloric Acids

The use of tetravalent cerium in volumetric analysis in the absence of hydrochloric or sulfuric acids, which are ordinarily present, and in the presence of nitric or perchloric acids, improves conditions of analysis. The potentials attainable are from 0.16 to 0.42 volt higher. The determination of iron, arsenic, oxalate (*5*), and many other frequently determined ions is better carried out using the solutions which have been described in this work. If a lower oxidation potential is in demand, the addition of the sulfate ion immediately converts the nitrato and perchlorato cerate ions to the sulfato cerate ion with an abrupt drop in potential (*4*). A greater lowering of the potential results from the addition of hydrochloric acid.

Using hexanitrato ammonium cerate as solute, but a small concentration of nitrate ions results upon acidification with perchloric acid. Consequently, the potential of such solutions is but slightly less than that of the perchlorato cerate ion in perchloric acid. Both the nitric and perchloric acid solutions of the corresponding cerate ions are suitable for oxidation of the oxalate ions (*5*) at room temperature. Ferroin or nitroferroin may be used as indicator, preferably the latter.

All solutions when heated showed marked decrease in stability. Because of the high potential of such solutions this is not important, since all reactions are rapidly completed at ordinary temperatures.

Summary

Eighteen solutions of the nitrato and perchlorato cerate ions in various concentrations of nitric and perchloric acid were prepared and their stability under various conditions and for extended time intervals was determined.

A small but detectable photochemical decomposition was observed in the case of solutions stored in diffused daylight.

Nitric and perchloric acid solutions of hexanitrato ammonium cerate between 1 and 3 molar in nitric and perchloric acids were found to show the highest stability.

Perchloric acid solutions of perchlorato ceric acid required standardization at frequent intervals.

The stability of all solutions increased with time, showing the influence of the accumulation of cerous ions in lowering the oxidation potentials, 5 to 10 per cent increasing the stability two- and threefold.

Five to 10 per cent of other rare earths of the cerium group present as impurities did not affect the stability adversely.

A 0.1 *N* solution of commercial hexanitrato ammonium cerate in 1.0 *N* perchloric acid was sufficiently stable in ordinary light not to require restandardization for a period of 20 days.

Literature Cited

(1) Brennecke, E., Furman, N. H., Stamm, H., Lang, R., and Fajans, K., tr. by Oesper, "Newer Methods of Volumetric Chemical Analysis", pp. 27–52, New York, D. Van Nostrand Co., 1938.

(2) Hengstenberger, "Electrolytic Oxidation of Cerous Salts and Chlorination Experiments in Contact with Cerous Chloride", Munich, Germany, J. Fuller, 1914.

(3) Smith, Frank, and Kott, Ind. Eng. Chem., Anal. Ed., **12**, 268 (1940).

(4) Smith and Getz, *Ibid.*, **10**, 191 (1938).

(5) *Ibid.*, **10**, 304 (1938).

(6) Smith, Sullivan, and Frank, *Ibid.*, **8**, 449 (1936).

Determination of Boron in Plant Material

An Ignition–Electrometric Titration Method

L. V. WILCOX

U. S. Department of Agriculture, Division of Irrigation Agriculture, Rubidoux Laboratory, Riverside, Calif.

RECOGNITION by Kelley and Brown (*4*) in 1928 of the toxic effect of boron, occurring naturally in irrigation waters, upon citrus trees led to an investigation of this problem by the Division of Western Irrigation Agriculture of the United States Department of Agriculture. In connection with this study a method (*7*) for the determination of boron in plant material was worked out. This method is satisfactory for the determination of relatively large quantities of boron but it is not well adapted to the study of low concentrations—e. g., under 50 mg. of boron per kilogram of dry material—because of a rather large blank and the relatively small samples that can be analyzed.

The confirmation by Warington (*6*), that boron is essential to plant growth, and the demonstration of boron deficiency in the field by Brandenburg (*2*) in Germany and later by McMurtrey (*5*) in the United States, led to a very large number of investigations of boron deficiency. An accurate method for the determination of boron in these low concentrations was greatly needed but was not available. To fill this need, a study was made of the possibilities of adapting the electrometric titration method (*1*, *8*) to the determination of boron in plant material, and as a result a satisfactory method has been developed and is presented herein.

The accuracy and reproducibility of the electrometric titration of boric acid were discussed in an earlier paper (*8*). Since that time, the procedure has been used in this laboratory for the determination of boron in approximately 10,000 samples, mostly natural waters.

Reagents Used

Lead nitrate solution, 1 *N;* sodium bicarbonate, powder; calcium oxide, fine powder. Quinhydrone, reagent quality, free from heavy metals. Bromothymol blue indicator solution, 1 per cent. Hydrochloric acid, 6 *N*, 2 *N*, and 0.02 *N*. Sodium hydroxide, 0.5 *N*, carbonate-free. Sodium hydroxide, standard 0.0231 *N*, carbonate-free (1 ml. is equivalent to 0.25 mg. of boron).

Boric acid solution. Dissolve 0.5716 gram of reagent grade, dry H_3BO_3 in carbon dioxide–free distilled water and dilute to 1 liter. One milliliter contains 0.1 mg. of boron. This solution is used in standardizing the 0.0231 *N* sodium hydroxide.

Mannitol (mannite), neutral. The blank titration for 5 grams of mannitol should not exceed 0.1 ml. of the standard 0.0231 *N* sodium hydroxide.

Apparatus

The choice of apparatus for the electrometric titration of boric acid should be determined by the instruments available, the number of analyses to be made, and the frequency of use. The requirements for satisfactory operation are:

Sensitivity. At the end point, in an unbuffered solution, a single drop of 0.0231 *N* sodium hydroxide should deflect the galvanometer 5 to 10 scale divisions. The galvanometer used has a sensitivity of 0.025 microampere per scale division.

Stability. The end point should be stable with little if any more drift than occurs in the potentiometric measurement of pH. In this connection, it has been observed that traces of iron in the quinhydrone cause a slow drift to the acid side.

Rapid equilibrium. Some of the high-resistance glass electrodes would probably be unsatisfactory because of the slowness with which equilibrium is reached.

Three sets of apparatus are described below, any one of which will give satisfactory results.

The first requires a minimum of equipment. The operation depends upon the fact that a 0.7 *N* calomel and a quinhydrone electrode come to a null point (reversal of polarity) at approximately pH 7.

Galvanometer. An enclosed lamp and scale type sensitive to 0.025 microampere per scale division.

Quinhydrone electrode. A piece of platinum wire 7.5 cm. (3 inches) in length, with suitable contact above the surface of the solution, is preferable to an electrode of platinum sealed through glass and connected with mercury, as minute cracks develop in the glass and cause erratic results.

Calomel electrode, 0.7 *N* with respect to potassium chloride. In the determination of boron in natural waters (*1*, *8*), a silver–silver chloride electrode was suggested. This can be used in place of the 0.7 *N* calomel electrode in the method here described, but it is necessary to adjust the chloride concentration to some predetermined value and to standardize the sodium hydroxide in the presence of this concentration of chloride. The calomel electrode is recommended.

Motor stirrer.

Switch, single-pole single-throw.

The electrodes are connected through the switch to the galvanometer. A shunt to protect the galvanometer is desirable but not essential. This circuit diagram was shown in the earlier paper (*1*).

The second apparatus is a simple potentiometer and is illustrated in Figure 1. In addition to the parts listed above, the following are required: resistance wire, 1500 ohms tapped at 60 ohms; a 1.5-volt dry cell: and a calomel electrode, 0.1 *N* with respect to potassium chloride. This is substituted for the 0.7 *N* electrode described above.

The third apparatus makes use of either a potentiometer or "pH meter" as indicating system. The following electrode pairs have been found satisfactory: quinhydrone and 0.1 *N* calomel; quinhydrone and saturated calomel; glass and saturated calomel. There are, no doubt, other combinations that might be used but their suitability should be considered, taking as a criterion the above statements on sensitivity and stability.

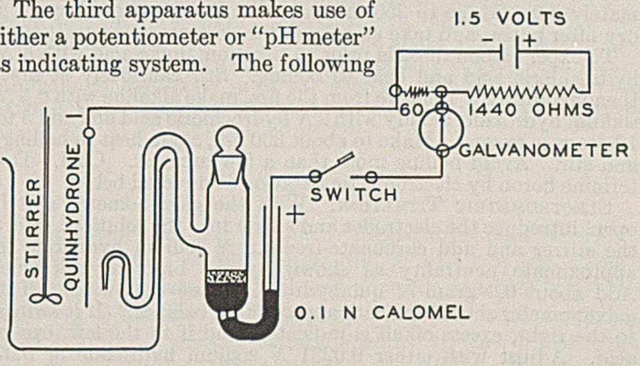


FIGURE 1. CIRCUIT DIAGRAM OF ELECTROMETRIC TITRATION APPARATUS

E. m. f. of two half-cells is balanced against potentiometer.

Procedure

PREPARATION OF SAMPLE. Remove all foreign matter from the green plant material but avoid excessive washing. Dry at 70° C., grind, dry again to constant weight, and store in tightly stoppered bottles. If it is desired to express the results on the green weight basis, weigh the material before and after drying.

Weigh an aliquot part of the dry sample and transfer to a glazed paper. From 5 to 25 grams of the material should be taken, depending on the boron content; there should be not more than the equivalent of 2 mg. of elemental boron in the portion ti-

TABLE I. REPRODUCIBILITY OF IGNITION–ELECTROMETRIC TITRATION METHOD

Sample No.	Replication	Plant Species	Weight of Sample	Boron Found	Notes
			Grams	*Mg./kg.*[a]	
L-701	1	Strawberry fruit, dry	10	19	
	2		10	18	
	3		15	18	
	4		15	19	
	5		25	18	
	6		25	19	
P-430	1	Alfalfa, field grown	15	10	Characteristic boron deficiency
	2		25	10	
P-424	1	Alfalfa, field grown	10	60	Normal
	2		10	60	
P-519	1	Alfalfa, greenhouse culture	4	190	Dwarfing due to boron toxicity
	2		4	191	

[a] Mg. per kg. of dry material.

TABLE II. RECOVERY OF BORON

(Added as crystalline boric acid, to 10 grams of plant material prior to ignition)

Sample No.	Replication	Initial Boron Content		Boron Added	Boron Found	Boron Recovered	
		Mg./kg.[a]	*Mg.*	*Mg.*	*Mg.*	*Mg.*	%
L-701	1	18	0.18	1.10	1.28	1.10	100
	2	18	0.18	1.10	1.28	1.10	100
	3	18	0.18	1.50	1.70	1.52	101
P-424	1	60	0.60	0.94	1.54	0.94	100

[a] From Table I.

trated. For each gram of the sample, add 0.1 gram of calcium oxide and mix well on the paper. Transfer to a porcelain casserole or platinum dish, ignite as completely as possible in a muffle at low red heat, cool, and moisten with water. Cover with a watch glass, introduce 15 to 20 ml. 6 *N* hydrochloric acid, which should make the solution strongly acid, and heat on a steam bath for 30 minutes.

Cool, transfer to a beaker, and add 1 *N* lead nitrate solution, 1 ml. for each gram of plant material in the sample, to remove phosphate from the solution. Add sodium bicarbonate, 1 gram at a time, until a precipitate forms. Heat on a steam bath and continue adding sodium bicarbonate until neutral to bromothymol blue. The color should be blue-green, and the pH approximately 7.0. Make to 250 ml., mix thoroughly, filter through a dry filter paper, and take an aliquot for electrometric titration.

To expel carbon dioxide prior to titration, make acid with 6 *N* hydrochloric acid and heat to boiling. Stir cautiously at first, then vigorously. Remove from the fire, make alkaline with 0.5 *N* sodium hydroxide, acidify with 2 *N* hydrochloric acid and add 5 to 10 drops in excess. Make to about 300 ml., again heat to boiling, and stir. Avoid boiling more than a few minutes. Cool. Determine boron by electrometric titration as directed below.

ELECTROMETRIC TITRATION. With the galvanometer switch open, introduce the electrodes and stirrer into the solution. Start the stirrer and add carbonate-free 0.5 *N* sodium hydroxide to approximate neutrality as shown by the bromothymol blue. Add about 0.2 gram of quinhydrone. Close the switch. The galvanometer should indicate approximate balance. If it swings to the right, excess alkali is indicated, and if to the left, excess acid. Adjust with either 0.0231 *N* sodium hydroxide or 0.02 *N* hydrochloric acid. The galvanometer should be steady, showing at most only a slow drift. This is the initial point of titration. Add 5 ± 0.1 grams of mannitol. If boric acid is present, the indicator will change to the acid color and the galvanometer will swing to the left. Add standard sodium hydroxide until balance is again attained. This is the end point.

Note the number of milliliters of sodium hydroxide required after adding the mannitol at the initial point of titration. The buret should be of such accuracy that the volume of alkali can be estimated to 0.01 ml. A blank is determined by substituting some boron-free organic material, such as ashless filter paper, for the plant sample and proceeding as indicated above. From the gross volume this blank is subtracted. The blank used in the work represented below varied from 0.14 to 0.17 ml. of standard 0.0231 *N* sodium hydroxide. The equivalency of the standard sodium hydroxide with respect to boron is established by titrating an aliquot of the boric acid solution. Report the results as milligrams of boron per kilogram of dry plant material.

Discussion

COMPARABLE SAMPLES. In collecting plant material for boron studies, two facts should be recognized: (1) Boron is not uniformly distributed throughout the plant, as is illustrated in Table III. (2) In the plant parts that normally accumulate boron, the concentration is a function of maturity. Leaf samples from Persian walnuts were collected at intervals of 4 weeks during the growing season. The boron determinations, reported in Table IV, show the relationship between maturity and boron concentration.

It is the practice of this laboratory to collect alfalfa at the early flower stage, citrus leaves when 9 to 15 months old, deciduous leaves at the time of maturity of the fruit, and grasses at the time of flower.

GLASSWARE. Boron-free glassware is not essential for this determination, provided that heating in alkaline solution is not prolonged. Blank determinations completed in Pyrex glassware were not significantly different from those in Kavalier brand boron-free glassware. The time of heating on the steam bath was about 0.75 hour. Table V reports the results of several experiments with Pyrex glassware.

Referring to the second entry in Table V which, in length of time of heating, is similar to the procedure suggested, it is probable that most of the boron found in the solution came from the reagents, as a similar experiment with a Kavalier brand boron-free beaker yielded essentially the same quantity of boron.

INTERFERING SUBSTANCES. Phosphate reacts with mannitol, though not quantitatively, and must be removed prior to titration. This can be done with calcium, barium, or lead in alkaline solution, but if either sodium hydroxide or sodium carbonate is used to make the solution alkaline, a fine, gelatinous precipitate results that adsorbs measurable quantities of boron. In this procedure, lead nitrate and sodium bicarbonate are suggested. It is assumed that the excess lead is precipitated as the normal carbonate rather than as a basic carbonate. In any event, the occlusion of boron by the precipitate is negligible, as reference to Table II will show.

Germanium, as germanic acid, reacts with mannitol to liberate hydrogen ion, but it is not a normal constituent of plant ash in excess of spectroscopic quantities. It has been shown that small quantities are removed from solution by the lead nitrate precipitation.

Iron, aluminum, and probably most of the weak anions, that would tend to buffer the solution, are removed by this process.

Other substances, present in plant ash, appear to be without effect.

REAGENTS. The standard 0.023 *N* sodium hydroxide can be stored in paraffin-lined bottles or in copper tanks, the seams

TABLE III. BORON IN MAMMOTH RUSSIAN SUNFLOWERS

(Grown in a nutrient solution containing 2.5 p. p. m. of boron)

Laboratory No.	Plant Part	Boron
		Mg./kg.
P-487	Leaves, petioles	597
P-488	Stems	27
P-489	Roots	40

TABLE IV. BORON IN PERSIAN WALNUT LEAVES

(Collected at intervals of four weeks during growing season)

Laboratory No.	Date of Collection	Boron
		Mg./kg.
L-199	July 22, 1929	166
L-256	August 19, 1929	257
L-306	September 17, 1929	301
L-312	October 14, 1929	346

TABLE V. BORON DISSOLVED FROM 400-ML. PYREX BEAKERS BY HOT ALKALINE SOLUTIONS

Solution		Treatment		Boron Dissolved
Ml.			*Hours*	*Mg.*
250	Water only	Steam bath	0.5	0
250	Saturated $NaHCO_3$	Steam bath	0.5	0.02
250	Saturated $NaHCO_3$	Steam bath	24	0.69

of which should be brazed rather than soldered. The solution should be protected from carbon dioxide and ammonia by an absorption train, preferably an acid and an alkali in solution, as dry reagents tend to absorb moisture.

LOSS OF BORON DURING IGNITION. The addition of an alkali before ignition appears to be necessary in the case of certain samples, as, for instance, the dry strawberry fruit (Sample L-701). In an experiment similar to that reported in Table II, but in the absence of calcium oxide, the recovery of added boron was only 84 per cent.

Dodd (*3*) reported that boron is lost, even in the presence of alkali, when fatty substances are ignited, and suggested that the fat be extracted with ether or benzene prior to ignition. This procedure was tried in the case of sunflower seeds with results that tend to support Dodd's findings, although the indicated loss was small.

Summary

The electrometric titration method has been adapted to the determination of boron in plant material. It is particularly suited to low concentrations found in boron deficiency studies —e. g., in the range below 50 mg. of boron per kilogram of dry material.

Literature Cited

(1) Am. Pub. Health Assoc., "Standard Methods for Examination of Water and Sewage", 8th ed., pp. 30–3, 1936.
(2) Brandenburg, E., *Phytopath. Z.*, 3, 499–517 (1931).
(3) Dodd, A. S., *Analyst*, 54, 715–25 (1929).
(4) Kelley, W. P., and Brown, S. M., *Hilgardia*, 3, 445–58 (1928).
(5) McMurtrey, J. E., Jr., *J. Am. Soc. Agron.*, 27, 271–3 (1935).
(6) Warington, K., *Ann. Botany*, 37, 630–70 (1923).
(7) Wilcox, L. V., IND. ENG. CHEM., Anal. Ed., 2, 358–61 (1930).
(8) *Ibid.*, 4, 38–9 (1932).

Rapid Determination of Copper

By α-Benzoin Oxime in Ferromolybdenum, Calcium Molybdate, Etc.

LOUIS SILVERMAN, 5559 Hobart St., Pittsburgh, Penna.

FEIGL (*3*) introduced α-benzoin oxime, $C_6H_5.C(NOH).CHOH.C_6H_5$, as a specific reagent for copper in ammoniacal solution. He suggested that the compound formed was one of new structure in which the principal valences of copper are connected through the oxygens of the oxime and hydroxyl groups, respectively, and the coordinate valences are attached to the phenyl groups. Azzalin (*1*), however, found (1) that for direct weighing procedures excess reagent could not easily be washed away; (2) that for ignition procedures only slow and careful ignition would remove all carbon; and (3) that in the presence of other elements the precipitate is contaminated with these elements.

Obviously, then, the final determination of the copper should be made either by electrodeposition or by the short iodide titration (*2*, *5*, *8*). The rapid determination of copper in ferromolybdenum or in molybdenum steels is thus accomplished.

Proposed Procedure

PREPARATION OF SAMPLE. For analyses where silicon is also to be determined (*6*), weigh 1 gram, place in a tall 300-cc. beaker, and treat with 20 cc. of (1 + 2) nitric acid. After rapid action ceases, heat the beaker until solution of the sample is about complete, cool somewhat, and cautiously add 10 cc. of concentrated sulfuric acid. Place the beaker in a bumping beaker, and heat to heavy fumes of sulfuric acid. Cool, add 75 cc. of (1 + 4) hydrochloric acid, heat until soluble salts are dissolved, and filter at once. Wash alternately with cold (1 + 4) hydrochloric acid and water six times, then with hot solutions to remove iron completely. The filtrate is used for copper.

Where silicon is not required, obtain complete solution by the above nitric acid mixture with the aid of some hydrofluoric acid. After cooling, and diluting with water, add 10 cc. of hydrochloric acid.

For molybdenum steels, the nitric acid solution method may be followed by fuming with perchloric acid. After cooling, add water and hydrochloric acid.

For calcium molybdate, use 25 cc. of (2 + 1) hydrochloric acid.

For ferrotungsten, use 10 cc. of (1 + 4) nitric acid, 5 cc. of hydrochloric acid, then hydrofluoric acid dropwise to complete solution.

PRECIPITATION OF COPPER. Dilute the prepared solutions to about 150 to 200 cc., and add a solution of 15 grams of Rochelle salt dissolved in 15 cc. of water. Add a strong solution of sodium hydroxide until the test solution is alkaline to Congo red paper, but still acid to litmus paper. If necessary, allow to cool to room temperature. Add ammonium hydroxide till the solution turns blue (copper above 0.5 per cent), or until distinctly alkaline to litmus, and add about 5 cc. in excess. Add slowly, with stirring, a 2 per cent α-benzoin oxime solution (10 cc. for 0 to 0.5 per cent, 15 cc. for 0.5 to 1.5 per cent copper). Let stand about 15 minutes, filter the green precipitate on an 11-cm. No. 40 Whatman paper, and wash with warm (1 + 99) ammonium hydroxide solution.

DETERMINATION OF COPPER. Return the paper and contents to the beaker and add 15 cc. of nitric acid (specific gravity 1.4) and 10 cc. of perchloric acid (60 or 70 per cent grade). Mix, heat until the nitric acid has been driven out and the perchloric acid condenses on the walls of the beaker, cool, dilute with water, and boil out the chlorine. [If desired, the short iodide titration (*2*, *5*, *8*) for copper may be used instead, starting at this point.] Add ammonium hydroxide until the solution is blue, discharge the color with nitric acid, add 4 cc. of (1 + 1) sulfuric acid, and plate the copper at 3 volts and 0.5 ampere.

Discussion

The reasons for this particular procedure should be noted.

After solution of the sample and addition of the sodium potassium tartrate, the sodium hydroxide is added until the solution is alkaline to Congo red paper but acid to litmus (pH 4 to 6). If enough caustic is added to turn litmus blue, sample No. 26789 (1.00 per cent copper) returns only a portion of the copper (0.60 per cent) even after 3 hours' standing. Evidently the alkaline tartrate has partially removed cupric ion from solution.

Again, precipitation should take place at room temperature. When precipitation was made hot, the results were low and inconsistent. It is conceivable that some of the oxime was hydrolyzed into ketone and hydroxylamine, which might reduce some cupric ions to the cuprous stage and be held in solution by the ammonia and ammonium salts. Feigl stated that there should be no ammonium salts present.

In the final determination of the copper either by electrodeposition or by titration, impurities such as excess reagent, molybdenum, nickel, manganese, iron, etc., do not interfere. In many cases the colorimetric ammonia method could be used.

The usual methods for separation of copper from ferromolybdenum require separation from the molybdenum by use of caustic (or fusion), then separation of the copper from the iron—operations which are slow and undesirable. The pro-

Table I. Copper Determined

Ferromolybdenum	
No. 26789	1.00, 1.01% (low in silicon)
No. 15806	0.73, 0.74% (contractor, 0.67%)
No. 27534	0.78, 0.78% (contractor, 0.74%)
U. S. Bureau of Standards No. 71 calcium molybdate	0.10, 0.10% (*7*)
U. S. Bureau of Standards ferrotungsten (0.039% Cu)	0.03%
U. S. Bureau of Standards No. 5g cast iron (1.44% Cu)	1.44%
U. S. Bureau of Standards No. 107 (Cu 0.074%, Mo 0.687%)	0.07, 0.08%
Calcium molybdate	0.40, 0.41%

posed method performs the separation from other elements in only one step without excess care or labor.

Results on calcium molybdate were included (Table I) to confirm those of Murray and Furman (*7*). There is no change in technique. With ferrotungsten considerable manganese and iron precipitated in the alkaline solution, but aside from making the washing operation slow, no harm was done. For molybdenum steels Kar (*4*) first separated copper and molybdenum from the steel by thiosulfate, ignited the two oxides, dissolved the oxides, and then precipitated the copper by α-benzoin oxime. The proposed procedure makes the separation directly. On the other hand, this laboratory has merely attacked the steel with dilute sulfuric acid, added thiosulfate, filtered off the copper and molybdenum, fumed them in nitric-perchloric acids, and electroplated the copper. The proposed method could claim no superiority over this latter method, aside from the greater solution speed in nitric acid as compared to sulfuric acid. The same may be said for high chrome-nickel (18–8 per cent) steels.

The reaction as described is not hazardous.

Literature Cited

(1) Azzalin, E., *Ann. chim. appl.*, 15, 373 (1925).

(2) Crowell, Ind. Eng. Chem., Anal. Ed., 10, 80 (1938).

(3) Feigl, F., *Ber.*, 56 (B), 2083 (1923).

(4) Kar, H. A., Ind. Eng. Chem., Anal. Ed., 7, 193 (1935).

(5) Lord and Demorest, "Metallurgical Analysis", p. 202, New York, McGraw-Hill Book Co., 1916.

(6) Lundell, Hoffman, and Bright, "Chemical Analysis of Steel", p. 485, New York, John Wiley & Sons, 1931.

(7) Murray and Furman, *J. Am. Chem. Soc.*, 58, 1863 (1936).

(8) Scott, "Standard Methods of Chemical Analysis", p. 193b, New York, D. Van Nostrand Co., 1927.

A Simplified Inoculation Procedure

T. L. BLACK AND AARON ARNOLD

Nopco Laboratories, Harrison, N. J.

Some standard bacteriological procedures (*1, 2, 3*) involve the use of inoculation with an inoculum varying from a drop to 1.0 cc. in size. There are several manipulative difficulties associated with this procedure, particularly where a large number of inoculations are to be made with a suspension of the same organism.

It is possible to circumvent a number of objectionable steps by the use of a syringe as illustrated in the diagram.

The size of the syringe is adjusted to the number of inoculations to be made. The authors have found that a 5-cc. resistant glass syringe has wide application. The syringe may be sterilized in a hot-air oven shortly before use. The size of the needle used may be varied in accordance with the size of the drop desired or rapidity of delivery. The authors have used a 20-gage, 7.5-cm. (3-inch) needle, which allows the operator to drop the inoculum directly into the medium. The needle may be platinum-iridium or other alloy which may be flamed repeatedly without loss of temper before use. The syringe is clamped to a stand at an angle of approximately 30° from the horizontal. At this angle the plunger is easily tapped or pushed to yield a drop at a time or other required amount, such as 0.5 cc. for phenol coefficient tests, but will not move without external pressure.

The needle is attached to the sterile syringe and flamed. The lip of the test tube containing the inoculum is flamed, and brought up to the needle and the inoculum is drawn into the syringe.

For inoculation, the needle is inserted 2.5 to 5 cm. (1 to 2 inches) inside the test tube containing the medium to be inoculated, the plunger is given a slight tap or push to release a drop or more of inoculum, and the test tube is withdrawn and flamed in the usual manner.

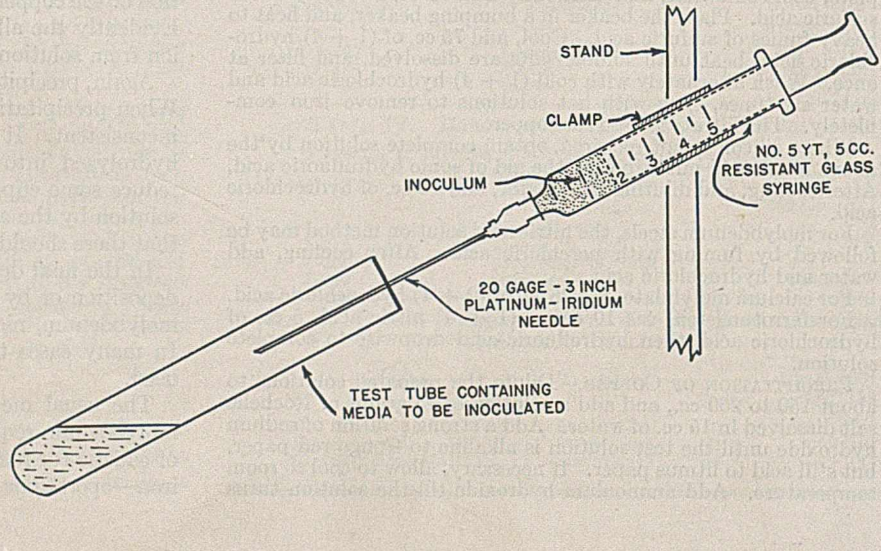
Since the inoculum in the needle is not exposed to air currents except to a very limited extent and is not subjected to the handling required when a pipet is used, the danger of contamination is reduced to a minimum. The operator has free use of both hands throughout and the time of inoculation is decreased to a third or fourth of that required by the pipet technique.

Literature Cited

(1) Ruehle, G. L. A., and Brewer, C. M., U. S. Dept. Agr., *Circ.* 198 (1931).

(2) Snell, E. E., and Strong, F. M., Ind. Eng. Chem., Anal. Ed., 11, 346 (1939).

(3) Woolley, D. W., *J. Biol. Chem.*, 130, 417 (1939).



Determination of *m*-Xylidines and Total *o*- and *p*-Xylidines

WILLIAM SEAMAN, A. R. NORTON, AND R. W. MASON
Calco Chemical Division, American Cyanamid Company, Bound Brook, N. J.

TECHNICAL xylidine, which is obtained by nitrating xylene and then reducing the nitroxylene, has been thought to contain all five of the six theoretically possible isomers except 3,5-dimethylaniline. Cooper (*1*) has pointed out that of the other five isomers, the presence of 2,3-dimethylaniline has never been proved, and that it probably is not present. The determination of the proportions of the remaining four isomers in commercial xylidine assumed importance in connection with the production of the food color F. D. and C. Red No. 32 (also known as Oil Red XO) which is the azo dye prepared by coupling 2-naphthol with diazotized xylidine. The Government has set an upper limit on the proportion of the meta isomers (2,4- and 2,6-dimethylaniline) which may be present. It was necessary, therefore, as has been pointed out (*9*), to have a method which could be applied to the xylidine obtained by reduction of the dyestuff, for the purpose of satisfying the government's requirements concerning the proportion of meta isomers which may be present. From the point of view of manufacture, such a method was needed to control the raw material xylidine entering into the final dyestuff.

Hodgkinson and Limpach's method (*6*, *7*) has been used frequently in the past to determine the isomeric xylidines, but it is now recognized as faulty. The first step consists of the precipitation of the 2,4-dimethylaniline as the acetate by means of glacial acetic acid. Morgan and Hickinbottom found that even with pure 2,4-dimethylaniline only 60 per cent of the calculated amount of acetate is precipitated (*8*). Cooper proved the presence of 2,4-dimethylaniline in the supposed mixture of 2,3- and 3,4-dimethylaniline (*1*). Various other objections have also been made to this method by Vaubel (*10*) and by Fedorow and Spryskow (*4*).

Another approach to the analysis of xylidine may be made through the difference in bromination properties of the isomeric xylidines. The more powerful ortho- and para-directive influence of the amino group over that of the methyl groups results in substitution of bromine only in positions ortho and para to the amino group, so that the meta isomers form monobromoxylidines, whereas the ortho and para isomers form dibromoxylidines. The amount of bromine consumed by the xylidine should, therefore, serve as a measure of the proportion of meta and of combined ortho and para isomers.

Vaubel (*10*) tested this principle but found that bromination with a solution of bromine in sodium hydroxide solution resulted in oxidation of the xylidine with the formation of colored products. Francis and Hill (*5*), working with a number of other oxidizable amines such as *o*- and *m*-toluidine, and phenylenediamine, recommended titrating in an acid medium with bromide-bromate solution at a temperature of 0° C. or lower in order to prevent oxidation.

Fedorow and Spryskow (*2*, *3*, *4*) sought a solvent in which to conduct the bromination of xylidine which would prevent the production of colored oxidation products. They reported that a mixture of alcohol and concentrated hydrochloric acid would give satisfactory results, and that a solution of dry hydrogen chloride in alcohol would give exact results. They recommended a bromination procedure based upon the use of the latter solvent. The solution is titrated in an ice bath with bromide-bromate solution, and back-titrated with sodium thiosulfate solution after the excess bromine has been reacted with potassium iodide. They reported analyses for five mixtures, using dry hydrogen chloride in alcohol as a solvent, which were made up to contain various percentages of 2,4-, 2,6-, 2,5-, and 3,4-dimethylaniline, and stated that they had run fifty others with similar results. With these five mixtures the values which they found differed from the actual values by from 0.1 to 0.3 per cent actual *m*- or *o*- and *p*-xylidine.

Attempts to duplicate this work in this laboratory were not successful. It was found that several mixtures of the isomers all gave high values of ortho and para (from 115 to 159 per cent of the *o*- and *p*-xylidine present), indicating overconsumption of bromine. The conclusion was drawn from this experience that Fedorow and Spryskow had evidently not defined their conditions precisely enough. Additional work emphasized the necessity for strictly defining conditions of temperature, time, and excess of bromine. A mixture of alcohol and concentrated hydrochloric acid was more convenient than dry hydrogen chloride in alcohol. Fedorow and Spryskow state that the former solvent is not so satisfactory as the latter, but some of their own figures do not bear out this conclusion. It was decided, therefore, to use the former solvent in working out the conditions of bromination.

A procedure was developed which involved bromination for a definite length of time in a mixture of five parts by volume of No. 3A denatured alcohol (95 parts of grain alcohol and 5 parts of methyl alcohol) and three parts of concentrated hydrochloric acid, at a bath temperature of from −4° to −8° C., with an excess of bromide-bromate solution which was fixed within definite limits. It was found, as a result of analyses of 48 synthetic mixtures of varied composition, that there was a correction to be applied to the values which were found, and that this correction varied with the percentage of *m*-xylidine in the mixture. It so happens that for the percentages of *m*-xylidine which Fedorow and Spryskow reported, the correction is zero, within the limits of reproducibility of the method, for mixtures which varied widely in isomeric composition. Lower percentages of meta cause high meta values; higher percentages, low meta values. The corrections, as well as the reproducibility of the determinations, have been established for mixtures containing from 0 to 100 per cent of *m*-xylidine.

Preparation of Isomers

3,4-Dimethylaniline (melting point, 48.6–49.2° C., corrected) was prepared from mixed xylidine by the method described by Morgan and Hickinbottom (*8*). 2,4-Dimethylphenylammonium acetate (melting point, 68.0–69.0°, corrected), 2,6-dimethylaniline hydrochloride (melting point, 236.2–237.1°, corrected), and 2,5-dimethylaniline hydrochloride (melting point, 223.9–224.7°, corrected), each recrystallized to a constant melting point, were used in the preparation, respectively, of pure 2,4-, 2,6-, and 2,5-dimethylaniline.

Method of Analysis

The validity of the method of analysis depends upon having a sample of known xylidine content which contains no bromine-consuming substances other than xylidine. The sample is analyzed for total xylidine content by its consumption of standard sodium nitrite solution, and the weight of the sample used is corrected to a 100 per cent xylidine basis.

NITRITE CONSUMPTION. To 6 grams (±0.1 gram) in a 500-ml. iodine flask are added 25 ml. of water, about 50 grams of ice, and

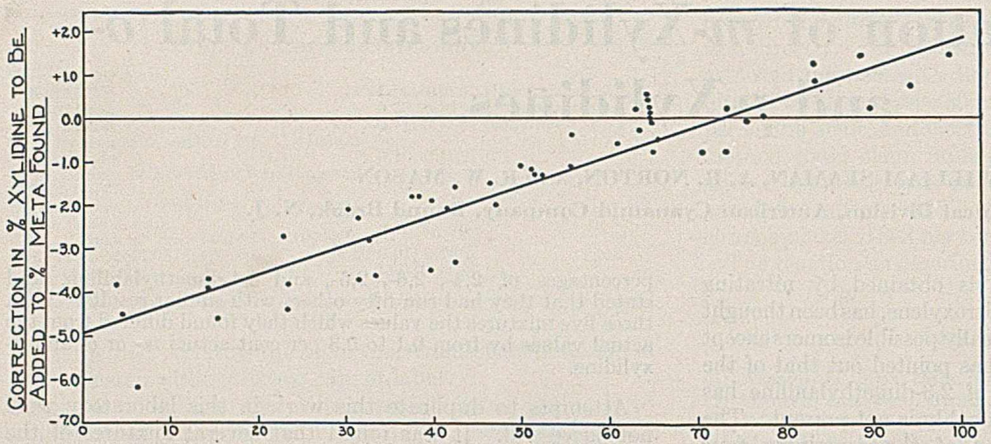


Figure 1. Per Cent of Meta Found

52 ml. of 1 N sodium nitrite solution. Then 25 ml. of concentrated hydrochloric acid are added rapidly, and the flask is stoppered immediately, shaken well, and allowed to stand in an ice bath for 5 minutes. An excess of 0.1 N sodium sulfanilate solution is added rapidly and the flask is stoppered, shaken, and titrated with 1 N sodium nitrite solution until an immediate blue coloration is obtained upon streaking some of the solution on a smear of starch paste containing potassium iodine. At the end point this immediate blue coloration may be obtained repeatedly during a period of 10 minutes without adding additional nitrite.

$$\% \text{ xylidine} = \frac{\text{net ml. of } 1\ N\ \text{NaNO}_2 \times 0.1212}{\text{grams of sample}} \times 100$$

The factor 0.1212 represents the value for one milliequivalent of xylidine.

Bromination Value. An accurately weighed sample of xylidine (between 0.19 and 0.21 gram) is weighed into a 500-ml. iodine flask containing 45 ml. of 3A denatured alcohol (95 per cent grain alcohol and 5 per cent methyl alcohol). From a 50-ml. buret sufficient 0.1611 N bromide-bromate solution is added to furnish an excess of from 2 to 4 ml. (The excess must be within these limits and should be ascertained in a separate determination as described below.) The flask is stoppered and placed in an ice-salt bath, the temperature of which should be from −4° to −8° C. While it is cooling, 30 ml. of concentrated hydrochloric acid are placed in a graduate in the freezing mixture. To increase the rate of cooling, the contents of the graduate and the flask should be swirled in the bath.

At the end of 10 minutes the acid is poured rapidly into the flask, which is stoppered immediately and allowed to stand in the bath for exactly 10 minutes longer. A solution of 0.5 gram of potassium iodide in 20 ml. of water is added in two portions to the well of the iodine flask and allowed to seep in. The flask is shaken well after each addition of iodide solution. The mixture is titrated with standard 0.1 N sodium thiosulfate solution until it is a light yellow color. The flask is filled almost up to the neck with water (in order to avoid the interference of a high alcohol concentration with the starch end point) and the mixture is titrated with thiosulfate solution to the disappearance of the blue color of the internal starch indicator.

Calculations

The formula for calculating the results is derived as follows:

Let X = ml. of 0.1611 N bromate-bromide solution required to brominate the o- and p-xylidines; and let A = net ml. of 0.1611 N bromate-bromide required for the sample; then $A - X$ = ml. of 0.1611 N bromate-bromide solution required for the m-xylidine.

Let C = per cent of xylidine by nitrite consumption × 0.01; and let B = weight of sample × C.

Since 1 ml. of 0.1611 N $\text{Br}^- - \text{BrO}_3^-$ = 0.004880 gram of o- and p-, and 1 ml. of 0.1611 N $\text{Br}^- - \text{BrO}_3^-$ = 0.009761 gram of m-, then, $0.004880\,X + 0.009761\,(A - X) = B$, and $X = 2A - \dfrac{B}{0.004880}$.

The weight of o- and p-xylidine = 0.004880 X, or 0.009761 $A - B$.

The uncorrected percentage of o- and p- =

$$\frac{(0.009761\,A - B)\,100}{\dfrac{B}{C}}$$

The uncorrected percentage of m- = 100 C − the uncorrected percentage of o- and p-.

Excess Bromine

It is necessary to have an excess of not less than 2 ml. nor more than 4 ml. of bromide-bromate solution. To determine the proper volume to use, a trial determination is made and the percentage composition calculated. From this the number of milliliters of bromide-bromate solution theoretically necessary is calculated and the analysis is repeated, using this calculated volume plus 3-ml. excess. Usually the second determination will have the proper 2- to 4-ml. excess.

Corrections

On the basis of the data which are reported in Table I, a curve (Figure 1) has been constructed showing the corrections

Table I. Analysis of Known Mixtures of Xylidines

% 2,4-, Actual	% 2,6-, Actual	Total (2,4- + 2,6-) Actual	% Meta Found	% Meta, Actual, Minus % Meta, Found	% 3,4-, Actual	% 2,5-, Actual	Total % 3,4- and 2,5-, Actual
0.0	0.0	0.0	3.8	−3.8	2.0	98.0	100.0
0.0	0.0	0.0	6.2	−6.2	9.8	90.2	100.0
0.0	0.0	0.0	4.5	−4.5	4.9	95.1	100.0
7.5	3.1	10.6	14.3	−3.7	2.0	87.4	89.4
7.4	3.0	10.4	14.3	−3.9	4.8	84.8	89.6
7.7	2.9	10.6	15.2	−4.6	9.0	80.4	89.4
15.8	3.1	18.9	23.3	−4.4	9.6	71.5	81.1
16.6	2.9	19.5	23.3	−3.8	5.9	74.6	80.5
17.2	3.0	20.2	22.9	−2.7	1.9	77.9	79.8
25.0	3.0	28.0	30.1	−2.1	2.0	70.0	72.0
24.8	2.9	27.7	31.4	−3.7	9.7	62.6	72.3
26.2	2.9	29.1	31.4	−2.3	2.4	68.5	70.9
26.8	3.0	29.8	32.6	−2.8	5.0	65.2	70.2
26.8	2.9	29.7	33.3	−3.6	9.9	60.4	70.3
32.8	3.0	35.8	37.6	−1.8	1.8	62.4	64.2
33.6	2.9	36.5	38.3	−1.8	2.7	60.8	63.5
33.2	3.0	36.2	39.7	−3.5	9.8	54.0	63.8
35.0	3.0	38.0	39.9	−1.9	1.9	60.1	62.0
36.6	2.9	39.5	41.6	−2.1	6.7	53.8	60.5
36.1	3.0	39.1	42.4	−3.3	9.9	51.0	60.9
37.8	3.0	40.8	42.4	−1.6	2.0	57.2	59.2
41.9	3.0	44.9	46.4	−1.5	2.0	53.1	55.1
42.1	3.0	45.1	47.1	−2.0	6.9	48.0	54.9
48.9	0.0	48.9	50.0	−1.1	2.2	48.9	51.1
47.1	2.9	50.0	51.2	−1.2	2.1	47.9	50.0
40.3	10.0	50.3	51.6	−1.3	4.9	44.8	49.7
48.1	3.0	51.1	52.4	−1.3	6.9	42.0	48.9
51.5	3.0	54.5	55.6	−1.1	2.1	43.4	45.5
52.3	3.0	55.3	55.7	−0.4	6.9	37.8	44.7
50.4	10.0	60.4	61.0	−0.6	4.9	34.7	39.6
60.3	2.9	63.2	63.0	+0.2	2.6	34.2	36.8
60.3	3.0	63.3	63.6	−0.3	7.6	29.1	36.7
61.8	2.5	64.3	65.1	−0.8	6.9	28.8	35.7
61.7	3.1	64.8	64.6	+0.2	2.0	33.2	35.2
61.7	3.1	64.8	64.8	0.0	2.0	33.2	35.2
61.7	3.1	64.8	64.9	−0.1	2.0	33.2	35.2
61.7	3.1	64.8	64.3	+0.5	2.0	33.2	35.2
61.7	3.1	64.8	64.4	+0.4	2.0	33.2	35.2
61.7	3.1	64.8	64.7	+0.1	2.0	33.2	35.2
62.1	3.0	65.1	65.6	−0.5	2.0	32.9	34.9
60.0	9.9	69.9	70.7	−0.8	5.0	25.1	30.1
68.8	3.8	72.6	73.4	−0.8	7.2	20.2	27.4
69.8	3.9	73.7	73.5	+0.2	2.0	24.3	26.3
71.5	4.0	75.5	75.6	−0.1	2.3	22.2	24.5
73.7	3.9	77.6	77.6	0.0	5.1	17.3	22.4
79.2	5.3	84.5	83.3	+1.2	2.3	13.2	15.5
79.1	5.2	84.3	83.5	+0.8	2.6	13.1	15.7
85.4	4.7	90.1	88.7	+1.4	3.1	6.8	9.9
84.6	5.5	90.1	89.9	+0.2	1.7	8.2	9.9
89.3	5.6	94.9	94.2	+0.7	1.8	3.3	5.1
89.7	5.5	95.2	94.5	+0.7	2.1	2.7	4.8
94.4	5.6	100.0	98.6	+1.4	0.0	0.0	0.0
94.8	5.2	100.0	98.6	+1.4	0.0	0.0	0.0

which are to be applied to the found meta content. The curve was drawn by the method of least squares to fit best the values which are given in Table I. The corrected percentage of meta is subtracted from the total percentage of xylidine (as determined by the nitrite titration) to get the corrected percentage of ortho and para.

Precision and Accuracy

The precision of the method was calculated by making six determinations upon aliquots from a single alcoholic solution which was made up to contain in 10 ml., 0.2016 gram of xylidine, of which 61.7 per cent was 2,4-, 3.1 per cent 2,6-, 33.2 per cent 2,5-, and 2.0 per cent 3,4-dimethylaniline. The separate uncorrected values and the deviations were as follows:

Determination	1	2	3	4	5	6	Mean
Meta, per cent	64.6	64.8	64.9	64.3	64.4	64.7	64.6
Deviation of meta from mean, per cent	0.0	0.2	0.3	0.3	0.2	0.1	..
Average per cent deviation of meta from mean	±0.2						

Although the average deviation from the mean for the example given is only ±0.2 per cent, yet the variations caused by differences in composition of the sample are more serious. Table I summarizes the values which were obtained with a number of synthetic mixtures in which the percentage of meta was varied from 0 to 100 per cent, with corresponding variations in ortho and para. Obviously it would be impossible to cover all the possible variations in the proportions of the isomers, but it was thought that those chosen gave a selection which was inclusive enough so that the information could be applied to the analysis of the commercial mixtures which might be encountered. In all these synthetic mixtures (with one exception) the 2,4- and 2,5- isomers are each present in higher concentration than the 2,6- and 3,4-, as would be true for actual commercial samples. Neither 3,5- nor 2,3- was included because their presence in commercial xylidine has not been proved. Figure 1 gives the corrections to be applied for various percentages of meta. It is obvious that the method gives decreasingly high values for meta up to about 70 to 75 per cent meta content, above which it gives low values. By applying these corrections, the values for *m*-xylidine (and for total *o*- and *p*-xylidines) will usually vary from the true values within about ±1 per cent of xylidine.

Effects of Isomers upon Bromination

This behavior indicates that one or both of the *m*-xylidines consume more than the theoretical amount of bromine, whereas the ortho or para isomers, or both, consume less than the theoretical amount of bromine.

The curves in Figure 2 correlate the positive and negative deviations from the values given in Figure 1 for the corrections to the percentage of meta, with the percentage of 3,4-dimethylaniline for a number of series of values taken to include in each series mixtures which are within a restricted range of meta values. Almost all these curves show a definite trend for increasing 3,4- concentrations to cause increasing negative deviations from Figure 1. In other words, 3,4- causes high meta values, which means that the bromine consumption of 3,4- is low.

The behavior of the individual isomers to bromination tends to confirm these conclusions. 3,4-Dimethylaniline always gave very low bromination values which ranged from about 55 to 85 per cent of the theoretical consumption of bromine, depending upon the conditions of bromination. 2,4-Dimethylaniline, under conditions of bromination even less vigorous than those which gave about 80 per cent bromination for a sample of 3,4-dimethylaniline, brominated to the extent of from about 106 to 113 per cent. Under similar conditions 2,6- brominated to about 103 per cent and 2,5- to about 99 to 100 per cent.

Summary

A method is described for the determination of *m*-xylidine and of total *o*- and *p*-xylidines in mixed xylidines, which depends upon the difference in bromine consumption of the *m*-xylidines on the one hand, and the *o*- and *p*-xylidines on the other. From the analyses of 48 mixtures of pure isomers containing from 0 to 100 per cent of meta, a curve was obtained to correct for the underconsumption of bromine caused by 3,4-dimethylaniline and the overconsumption caused mainly by 2,4-dimethylaniline. With such variations in isomeric composition as may conceivably be obtained in practice, the method should give values for the meta isomers or the ortho

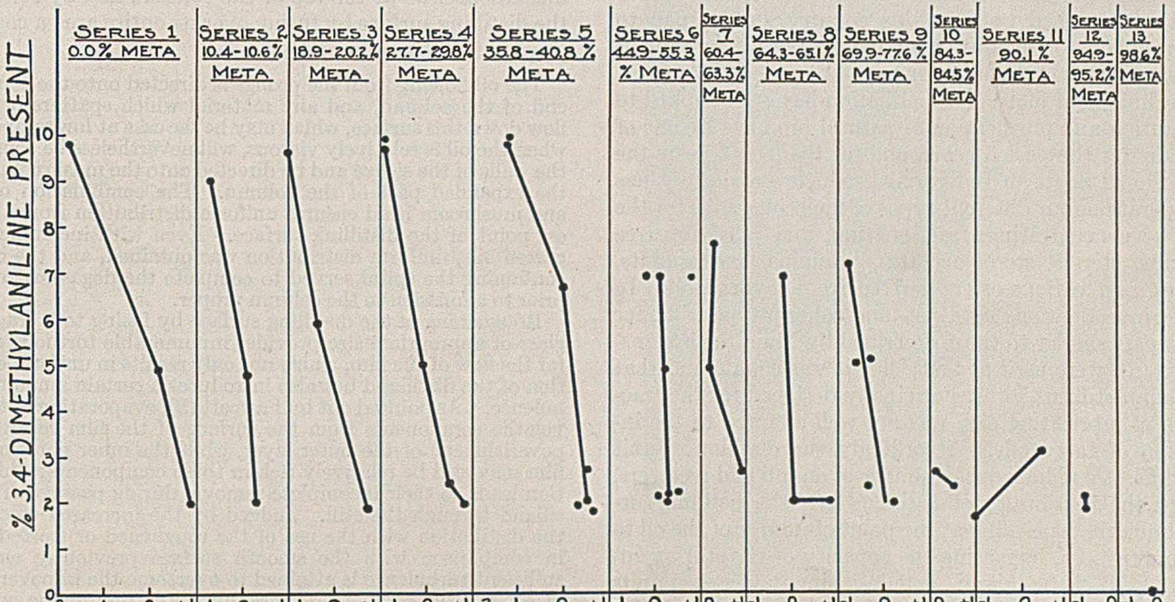


Figure 2. Deviations in Per Cent of Meta from Correction Curve (Figure 1)

(+) Deviation above curve. (−) Deviation below curve and para isomers which will usually be correct to within about ±1 per cent of xylidine. Of the six theoretically possible xylidine isomers, the effect upon the method of the presence of 3,5-dimethylaniline and 2,3-dimethylaniline was not considered because of their probable absence from commercial xylidines.

Acknowledgment

Acknowledgment is made of W. J. Mader's assistance in preparing the pure isomers that were used in this work.

Literature Cited

(1) Cooper, R. C., *J. Soc. Chem. Ind.*, 54, 134T (1935).
(2) Fedorow, B. P., and Spryskow, A. A., *Anilinokrasochnaya Prom.*, 5, 143–6 (1935).
(3) Fedorow, B. P., and Spryskow, A. A., *Org. Chem. Ind.* (U. S. S. R.), 2, 101–2 (1936).
(4) Fedorow, B. P., and Spryskow, A. A., *Z. anal. Chem.*, 105, 412–18 (1936).
(5) Francis, A. W., and Hill, A. J., *J. Am. Chem. Soc.*, 46, 2498–505 (1924).
(6) Hodgkinson, W. R., and Limpach, L., *J. Chem. Soc.*, 77, 65–8 (1900).
(7) Limpach, L., German Patent 39,947 (Sept. 19, 1886).
(8) Morgan, G. T., and Hickinbottom, W. J., *J. Soc. Chem. Ind.*, 45, 221–2T (1936).
(9) Seaman, W., Norton, A. R., and Hugonet, J., "A Method for the Reduction of 2-Naphtholazoxylene" (to be published in IND. ENG. CHEM., Anal. Ed.).
(10) Vaubel, W., *Z. anal. Chem.*, 36, 285–9 (1897).

Laboratory-Type Molecular or Short-Path Still

For Vegetable and Animal Fats and Oils

S. B. DETWILER, JR., AND K. S. MARKLEY
U. S. Regional Soybean Industrial Products Laboratory, Urbana, Ill.

SUSTAINED interest is evident in the application of molecular or short-path distillation to the concentration, separation, and/or purification of a considerable number of organic substances whose extremely low vapor pressures or thermal instabilities render impossible their distillation under ebullient conditions. A partial bibliography on the subject published by the authors (*1*) last year contained more than 100 references to the scientific and patent literature for the period 1922 to 1938. Additions to this bibliography since that time have brought the list of titles to approximately 150, a considerable number of which are concerned with the design and application of stills and accessory equipment. The stills thus described range in size from micro to plant scale having capacities as high as 8 tons of distillate a day and, in design, from simple pot or batch types to wholly automatic, single- and multiple-column types. In addition to the various types and sizes of stills which have been described in the literature, numerous others have been designed and applied both in this country and abroad to specific problems of separation or purification of natural or synthetic products of organic origin.

The technique of molecular distillation has been applied to the separation and purification of natural products by one of the authors for the past 5 years, and for the past 2 years the U. S. Regional Soybean Industrial Products Laboratory has had in operation four different types of molecular stills for the purpose of concentrating, fractionating, and purifying free fatty acids, sterols, sterol acetates, vitamins, antioxidants, glycerides, and various esters derived from soybean oil. In the latter investigations both pot- and column-type stills, for the most part similar to those described by Mair, Schicktanz, and Rose (*6*), were used at first; but it was soon found that their column still, which was originally designed for the fractionation of lubricating oils, was not well adapted to the investigation of fatty oils. Accordingly the distillation unit was modified by reducing the number of annuli and receivers, increasing the distribution of distilland over the distilling surfaces, eliminating splashing at the point of ingress of the oil to the column proper, increasing the capacity of the still by enlarging the size of the column, and designing the receiver units to allow for intermittent withdrawal of fractions without interrupting the distillation. As a consequence the over-all efficiency of the distillation of the fatty oils was increased.

Details of Still Construction

Various methods have been devised in an effort to direct the distilland onto the distilling surface without splashing and to provide even distribution of the film over the distilling surface. Jewell, Mead, and Phipps (*5*) resorted to the use of a serrated distributor at the top of the column and a spirally wound wire over the distilling surface in order to distribute and turn the film. Hickman (*4*) introduced a pair of concentric wire gauze distributors at the point of ingress of the oil to the column and applied a spiral embossing to the surface of the column in order to improve the distribution of the film. Fawcett and Burrows (*3*) surrounded the column at intervals with bands of wire gauze or employed a combination of recesses and baffles at intervals along the surface of the column. In the column still shown in Figure 1 these objectives were accomplished in a simple manner by the use of a tapered sleeve-guide to admit the oil to the still, by the provision of a mushroom head at the top of the column, and by roughening the distilling surface by fusing over its entire area a coating of fragmented glass of proper size.

The oil flowing from the prongs is directed onto the constricted end of the column, and any material which spatters or fails to flow down this surface, which may be the case at low temperatures when the oil is relatively viscous, will nevertheless be confined by the walls of the sleeve and be directed onto the mushroom head at the expanded part of the column. The combination of sleeve and mushroom head ensures uniform distribution from the highest point of the distilling surface. Even with incompletely degassed oils, uniform distribution was obtained, and the chamber containing the spiral served to complete the degassing of the oil prior to admission to the column proper.

Roughening of the distilling surface by fusing to it fragmented glass of appropriate size provides innumerable tortuous channels for the flow of the film, which not only results in uniform distribution of the distilland but also introduces a certain amount of turbulence. As pointed out by Fawcett (*2*), evaporation of the more volatile components from the surface of the film results in impoverishment of the outer layer, while the inner portions of the film may still be relatively rich in these components; this condition leads to their incomplete removal during passage of the distilland through the still. Judged by the increased efficiency of the distillation with the use of the roughened or frosted surface in comparison with the smooth surface previously employed, sufficient turbulence is attained to overcome the impoverishment of the volatile components through distillation at the outer surface of the film.

The particle size of the glass fragments may be varied to suit conditions, and other materials such as quartz, garnet, and silicon

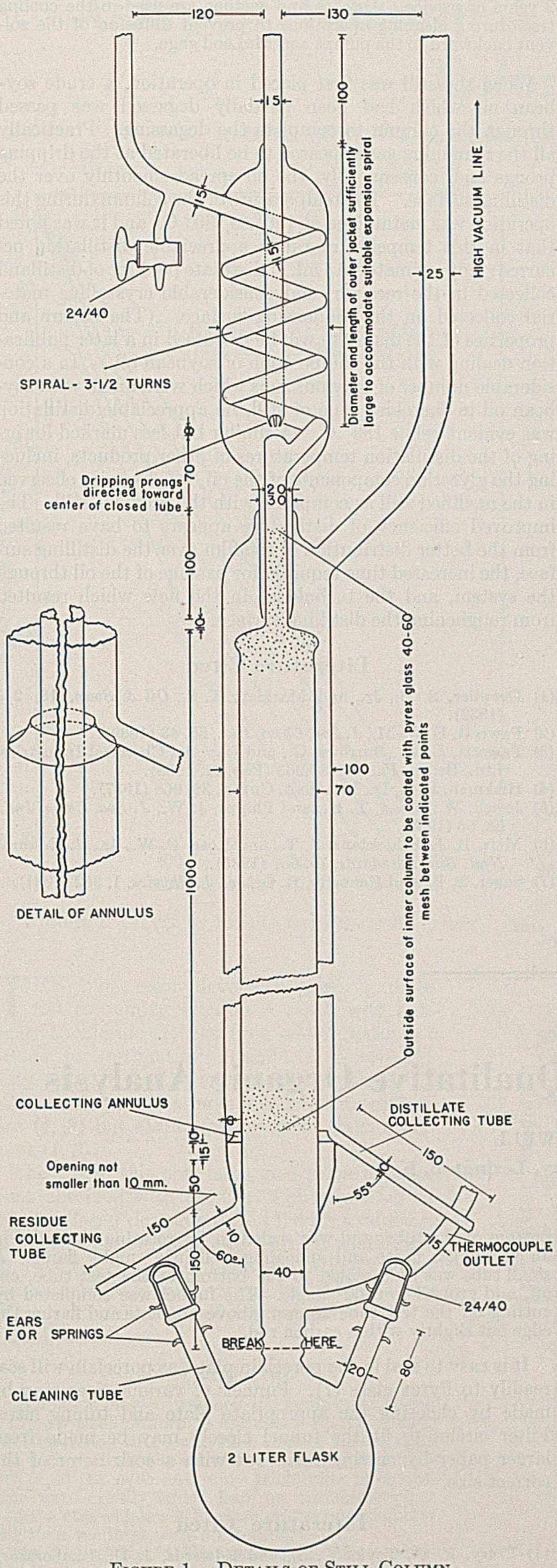


Figure 1. Details of Still Column

All dimensions are given in millimeters and are approximate. Outside diameter given for all tubing

carbide may be used in the place of glass. Because of its sharpness, which it retains even after fusing to the glass, silicon carbide is ideal from certain standpoints, but it presents difficulties in fusing to the glass and tends to become detached during service. Several techniques have been developed for frosting the surface without resultant distortion of the column. This operation is, however, most readily accomplished by selecting a glass of a lower (ca. 100° C.) fusion point than that of the column proper. The glass is crushed in an iron mortar and sifted to provide the required size, which should not be too fine or too uniform, and glass of coarser mesh is preferred to finer sizes. The temperature should be as low, and the time of heating during the application of the frosting as short, as possible commensurate with good adherence, in order to avoid too much fusion and consequent smoothing of the attached fragments. A similar type of surface can be obtained with metal columns, either by the use of rough sand-cast tubes or by sandblasting in the case of turned surfaces.

The multiple collecting annuli and receivers of the original still were replaced in the new design by a single annulus and receiver, the latter arranged to permit removal of fractions without interfering in any way with the continuous distillation (see Figure 2).

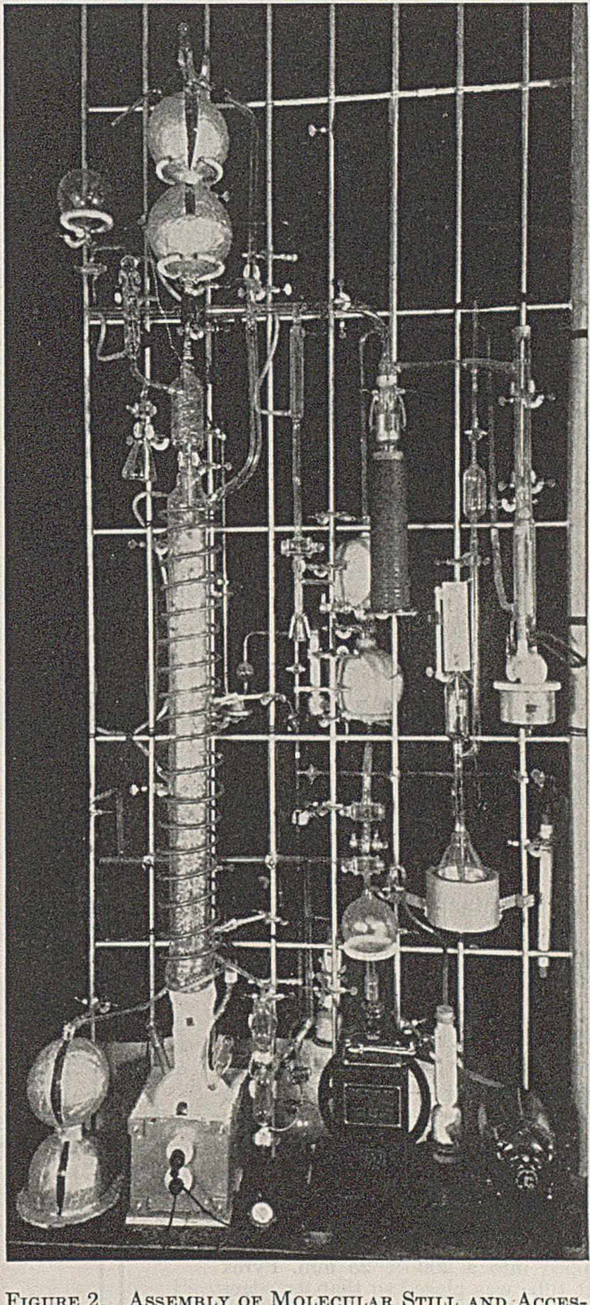


Figure 2. Assembly of Molecular Still and Accessory Equipment

The large internal volume of the still made it impractical to pack the interior with jack chain as was done in the original and much smaller still. Coarse aluminum turnings were found to be ideally suited as a packing material. Temperatures in the packed column are measured by means of a number of thermocouples mounted in thin, small-bore glass tubes bound together by asbestos cord and situated in the axis of the column, and also by red reflecting mercurial thermometers placed in the packing next to the interior front surface. Both thermocouples and thermometers are supported and maintained in their proper positions by the packing material; and, at equilibrium, their readings differ by not more than 2° to 3° C.

As in the case of the original still, the present column is heated internally by refluxing over the packing material a suitable solvent such as kerosene or an Arochlor. The flask containing the reflux liquid is heated on the bottom by a variac-controlled resistance coil and on the sides by a woven basket of resistance wire. An auxiliary mechanical pump, immediately below the one shown in Figure 2, is used for controlling the pressure above the liquid in the reflux boiler, as well as for lowering the mercury in the McLeod gage. A manometer in the reflux line shown just to the upper right-hand side of the column is graduated to correspond to approximate temperatures produced in the still rather than to actual pressure.

The condensing surface of the column is cooled by air jets directed against its surface from a perforated spiral of 1.25-cm. (0.5-inch) copper tubing as shown in Figure 2. The helix was formed on a mandrel and then perforated around the inside with holes drilled at intervals of 2.5 cm. (1 inch). The spiral was fitted with four feed lines for compressed air and the completed coil screwed over the column prior to sealing on the reflux boiler at the point indicated by the dashed line in Figure 1.

The accessory vacuum-producing equipment is of the conventional type and consists essentially of a mechanical pump, mercury diffusion pump, and a cooling trap. The free air pressure is measured by means of a McLeod gage, and total pressure within the still is approximately measured by a thermal conductivity gage. No stopcocks are used in the high vacuum line except in the by-pass to the McLeod gage, the fraction cutter, and the residue receiver. The first-mentioned is of the mercury-sealed type, and the latter two are sealed with glycol phthalate resin (*7*) which is solid except for the interval in which it is heated during the operation of removing fractions. In the low vacuum lines either double 15-mm. bore vacuum-ground, grease-lubricated stopcocks or single mercury-sealed stopcocks are used. Only dry air is admitted to the system, except during charging and cleaning. Consequently, the mercury in the diffusion pump and in the McLeod gage has remained brilliant and free from fouling after more than 2 years of service. Dry ice and acetone are used in the cooling trap during cleaning operations to prevent diffusion of the solvent backward to the pumps and McLeod gage.

When the still was first placed in operation, a crude soybean oil which had been partially degassed was passed through the column to complete the degassing. Practically all the remaining gas appeared to be liberated at the dripping prongs and, consequently, the oil spread smoothly over the distilling surface. The temperature of the column during this operation was maintained at 100° to 130° C., and it was noted that in this temperature range appreciable distillation occurred; approximately 15 ml. of distillate per liter of distilland collected in the receiver, and considerable crystalline material collected on the condensing surface. (The nature and properties of the distillate will be discussed in a later publication dealing with the composition of soybean oil.) In a considerable number of previous runs which were made with soybean oil in the older type of still, no appreciable distillation was evident below 180° C. A similar but less marked lowering of the distillation temperatures of other products, including the glyceride components of the oil, was likewise observed in the modified still as compared with the previous still. The improved efficiency of distillation appears to have resulted from the better distribution of the film over the distilling surface, the increased time required for passage of the oil through the system, and the turbulence in the flow which resulted from roughening the distilling surface.

Literature Cited

(1) Detwiler, S. B., Jr., and Markley, K. S., *Oil & Soap*, 16, 2–5 (1939).

(2) Fawcett, E. W. M., *J. Soc. Chem. Ind.*, 58, 43 (1939).

(3) Fawcett, E. W., Burrows, G., and Imperial Chemical Industries, Ltd., British Patent 480,265 (Feb. 21, 1938).

(4) Hickman, K. C. D., Ind. Eng. Chem., 29, 968 (1937).

(5) Jewell, W., Mead, T. H., and Phipps, J. W., *J. Soc. Chem. Ind.*, 58, 56 (1939).

(6) Mair, B. J., Schicktanz, S. T., and Rose, F. W., Jr., *J. Research Natl. Bur. Standards*, 15, 557 (1935).

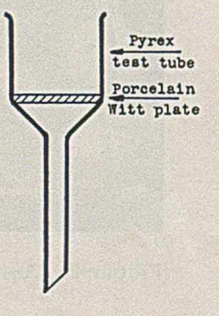
(7) Sager, T. P., and Kennedy, R. G., Jr., *J. Physics*, 1, 352 (1931).

A Small Büchner Funnel for Qualitative Organic Analysis

C. A. ROSWELL

University of Kentucky, Lexington, Ky.

IN THE analysis of organic compounds small amounts of crystalline derivatives must often be filtered with suction. The usual method, employing a small 60° funnel with a loose Witt plate and a side-arm test tube, is not always satisfactory. Considerable trouble may be encountered in obtaining a tight fit between the filter paper and the funnel, and the loose plate invariably tilts to one side or the other, giving an uneven deposit of crystals. The funnel shown in the drawing is a more convenient arrangement.



A Witt plate of a size that just slipped into a 200 × 25 mm. Pyrex test tube was placed so that its edges rested against the curved portion of the bottom of the tube, and was sealed in by rotating the tube in an oxgyen gas flame and annealing well in a smoky flame. A small tube was then sealed to the bottom of the test tube, cut off, and ground to a 60° angle. The funnel was completed by cutting off the test tube 20 mm. above the plate and flaring the edge out slightly with a carbon rod.

It is easy to seal in the porcelain plate, as porcelain will seal readily to Pyrex glass (*1*). Funnels of various sizes may be made by choosing the appropriate plate and tubing sizes. Filter circles to fit the funnel closely may be made from larger paper by cutting them out with a cork borer of the correct size.

Literature Cited

(1) Frary, F. C., Taylor C. S., and Edwards, J. D., "Laboratory Glass Blowing", 2nd ed., p. 91, New York, McGraw-Hill Book Co., 1928.

Assay of Vitamin A with the Photoelectric Colorimeter

R. B. FRENCH, Florida Agricultural Experiment Station, Gainesville, Fla.

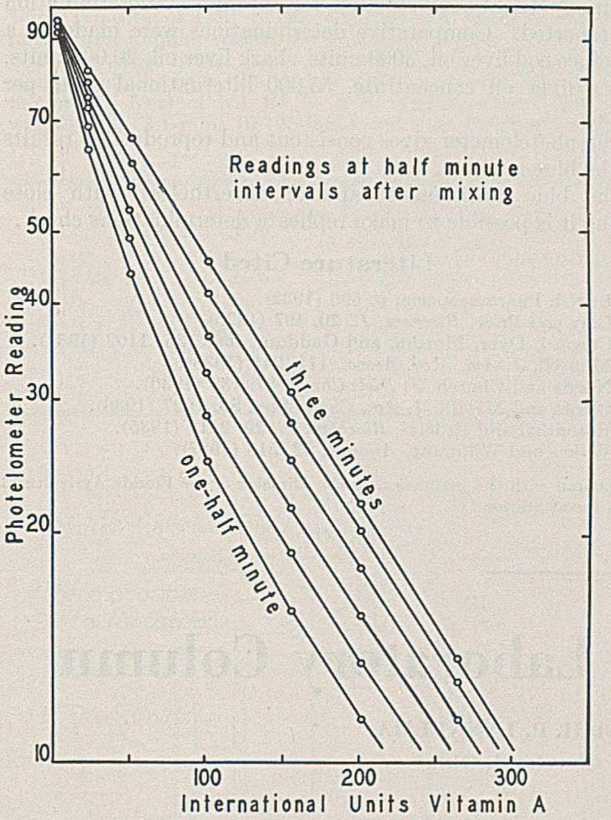


FIGURE 1. RATE OF FADING WITH BLUE REACTION

THE blue color developed when a material containing vitamin A reacts with antimony trichloride (*1*) has been widely used as a means for estimating vitamin A colorimetrically (*4*). It has been recognized that this colorimetric reaction not only presents difficulties (*5, 8*) but also has value under given conditions (*1, 3*).

The aim of this note is to give some observations obtained with the Cenco photelometer using the Carr-Price procedure (*2*) with a reference cod liver oil containing 3000 units, a shark liver oil (Sharkol, Shark Ind.) containing 20,000 units, and a fish liver oil concentrate (Hepicoleum, Lilly) containing 55,000 international units of vitamin A per gram.

Experimental

Samples of oil were weighed and made up to 25-ml. volume with chloroform. Aliquots from this volume were increased to 10 ml., and 1 ml. of this mixture was pipetted into the colorimeter cup. Ten milliliters of 30 per cent antimony trichloride in chloroform were rapidly added from an automatic pipet into the cup which was in place on the photelometer and then readings were started.

The Cenco No. 4 filter was used with the instrument, which is calibrated to read percentage transmission of light directly. The blue color developed after mixing fades rapidly. To exemplify the fading, Figure 1 was constructed. Samples containing different quantities of Hepicoleum were treated according to the outlined procedure and readings were taken at consecutive 30-second intervals after the instant of mixing, as indicated by the stopwatch. The international units noted on the abscissa were obtained from the manufacturer's analysis. Rates of fading for all the samples were similar and the blue color had disappeared from the more dilute samples by the end of 10 minutes, being supplanted by a rose.

Figure 1 shows that the depth of blue color developed is proportional to the quantity of oil taken if the time interval used is a constant. Taking the convenient interval of 30 seconds for measurement, color was developed in different quantities of Hepicoleum, Sharkol, and the standard cod liver oil both before and after saponification. The data resulting are plotted for purposes of comparison in Figure 2. The concentration of vitamin A was computed from the manufacturers' report and an equivalent distance was laid off on the *x*-axis for each sample. Saponification was accomplished by adding to each gram of the oil 1.5 ml. of 77 per cent alcohol saturated with potassium hydroxide and warming until solution occurred (*6*).

The unsaponified material was extracted 5 times with petroleum ether. The petroleum ether was evaporated over nitrogen and the residue taken up in chloroform and treated as outlined above.

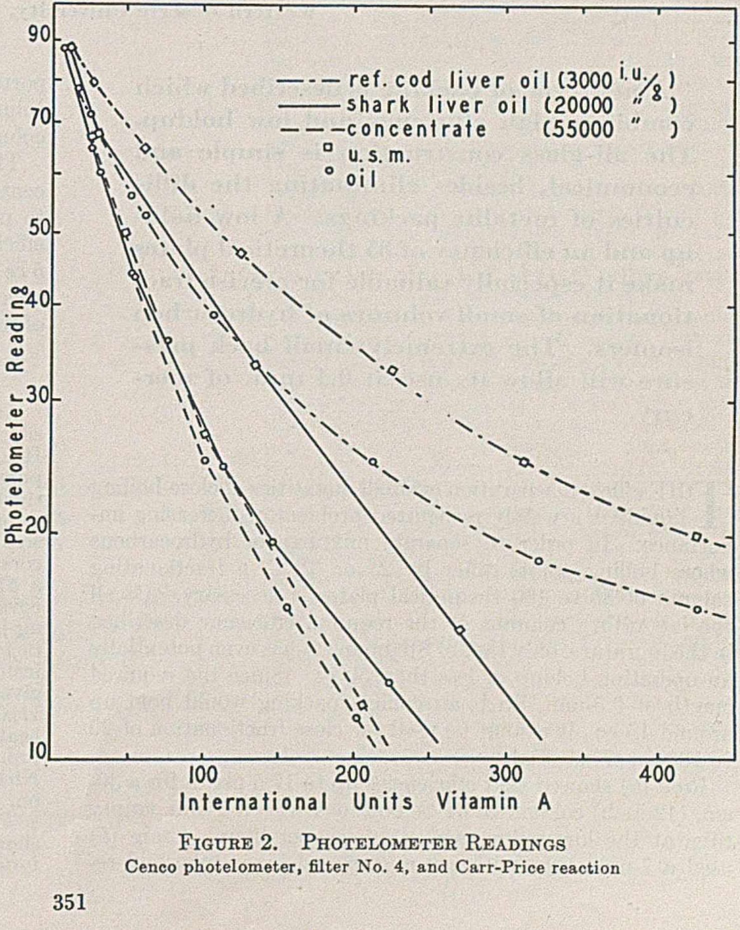


FIGURE 2. PHOTELOMETER READINGS
Cenco photelometer, filter No. 4, and Carr-Price reaction

Discussion

From the graphs presented it is obvious that it is possible to measure the blue color developed with antimony trichloride with accuracy, even though the rate of change in the intensity of color is rapid.

An attempt was made to slow down the rate of fading of the blue color through addition of acids, dehydrating agents, or phenols (*7*). Of the materials tried phosphoric acid seemed the most efficient, but its effect was only apparent, since a slight cloudiness developed in the solution that tended to compensate for the fading of the blue color.

Fading continued progressively beyond the readings given, although at a slower rate, but on the more dilute solution was complete in from 5 to 10 minutes.

The data in Figure 2 indicate that Beer's law is followed by the color development in each sample. The reference cod liver oil developed the least color for a given amount of vitamin A and saponification reduced considerably the quantity of material that formed color with the reagent. The outside limits of losses due to the manipulation of saponification are suggested by a comparison of the two curves for the concentrate. Resaponification of this material caused only a small change in value. A comparison of the curves for cod liver oil and the concentrate shows (if the biological standardizations are accurate) that there are still major quantities of material, other than vitamin A, left after saponification that are capable of either forming the blue color or perhaps inhibiting its formation in the oils. Thus, this colorimetric procedure could be used with confidence only with evidence that various samples of the same kind of oil contained, either before or after saponification, approximately the same ratio of vitamin active to inactive chromogenic materials.

Summary

Results obtained using the Cenco photelometer and the antimony trichloride reaction for vitamin A determination are reported. Comparative determinations were made on a reference cod liver oil, 3000 units, shark liver oil, 20,000 units, and a liver oil concentrate, 55,000 international units per gram.

The photelometer gives consistent and reproducible results on the blue reaction.

The blue color fades rapidly; nevertheless, with close timing it is possible to make replicate determinations check.

Literature Cited

(1) British Pharmacopoeia, p. 596 (1932).
(2) Carr and Price, *Biochem. J.*, 20, 497 (1926).
(3) Coward, Dyer, Morton, and Gaddum, *Ibid.*, 25, 1102 (1931).
(4) Munsell, *J. Am. Med. Assoc.*, 111, 245 (1938).
(5) Norris and Church, *J. Biol. Chem.*, 87, 139 (1930).
(6) Olcott and Mattill, *J. Am. Chem. Soc.*, 58, 1627 (1936).
(7) Rosenthal and Erdélyi, *Biochem. J.*, 29, 2112 (1935).
(8) Wokes and Willimott, *Analyst*, 52, 515 (1927).

PUBLISHED with the permission of the Director of the Florida Agricultural Experiment Station.

An Efficient Low-Holdup Laboratory Column

M. L. SELKER, R. E. BURK, AND H. P. LANKELMA
Western Reserve University, Cleveland, Ohio

A new type of packing is described which combines high efficiency and low holdup. The all-glass construction is simple and economical, besides eliminating the difficulties of metallic packings. A low holdup and an efficiency of 85 theoretical plates make it especially valuable for precise fractionation of small volumes of hydrocarbon isomers. The extremely small back pressure will allow its use at 0.4 mm. of mercury.

THE efficient separation of small quantities of close-boiling liquids is a widely recognized problem of increasing importance. In order to separate mixtures of hydrocarbons whose boiling points differ by 2° or 3° C. a fractionating column of 80 to 100 theoretical plates is necessary. Of all the laboratory columns of the required efficiency described in the literature, only that of Stedman (*2*) has even potentially an operating holdup of less than 50 cc. Since the required length of 9.5-mm. Stedman conical packing would hold up around 15 cc., it cannot be used for close fractionation of 20 to 100 cc. of material.

Rose (*9*) showed that efficiencies up to 17.5 plates for a 30-cm. (12-inch) column could be obtained with a 6-mm. empty tube at the low reflux rate of 11 cc. per hour. Craig (*5*) used a 7-mm. tube with a 4-mm. closed inner tube and reported 17 plates for a 25-cm. (10-inch) air-jacketed microcolumn. Low capacities have limited the utility of such columns.

This article details the use of close-fitting, multiple concentric glass tubes as packing in an efficiently insulated jacket to produce an inexpensive 150-cm. (5-foot) column with an efficiency of about 85 theoretical plates and a holdup of some 5 cc., at the reflux rate of 100 cc. per hour. With this column it is possible to extend precise fractionation to small volumes of material.

Still Construction

An assembly drawing is given in Figure 1. The Pyrex glass, silvered vacuum jacket is made from 16- and 35-mm. tubing. It is evacuated by means of a mercury diffusion pump and Hyvac pump for some time before use and continuously during a distillation. A discharge tube operated from a spark coil serves as a rough vacuum gage. Pyrex neon sign electrodes are inexpensive and excellent for use in discharge tubes. Two tightly fitting cork cylinders carrying thermometers hold the vacuum jacket in a 51-mm. tube which thus provides an air jacket. Asbestos-covered Nichrome wire, B. & S. No. 20, was wound around the air jacket one turn per 2.5 cm. (1 inch). Standard 3.75-cm. (1.5-inch) magnesia pipe lagging for 5-cm. (2-inch) pipe completed the insulation. The heated jacket was not used in the efficiency tests given below, but at temperatures above 100° C. it would be advisable. The air space and pipe lagging are necessary when the heated jacket is used. The column was mounted using two 3-prong clamps which were tightened on the 51-mm. tube after the Nichrome wire was wound and before the pipe lagging was bound on.

The packing consisted of Pyrex glass tubes of the dimensions shown in Table I, carefully selected for straightness and uniformity.

The 16-mm. outside diameter tube was the inner tube of the vacuum jacket. The upper ends of the tubes were ground flat, the lower ends at an angle to the long axis. The tubes were spaced with respect to each other by sealing small glass tips on the outside of each tube every 37.5 cm. (15 inches). Indentations on successive tubes, each supporting the end of the inside one, served to hold them in the jacket and in place. The tubes were made 142.5 cm. (57 inches) long, as was the jacket, because the longest glass available was the standard 150-cm. (5-foot) length. The ratio of volume to surface is the same in each annular space. There is a total of 2450 sq. cm. of surface and 120 cc. of free space in the three annular spaces of the packing.

The external heater used consisted of a flat ring of Transite wound radially from the middle outward to the edge with 4.5 meters (15 feet) of No. 24 B. & S. Nichrome wire previously wound in a 3.1-mm. (0.125-inch) coil. A variable autotransformer controlled by a thermionic relay regulated the current through the heater. For heating volumes over 100 cc. more resistance is needed in the heater. The manometer, which also serves as a manostat, contains redistilled dibutyl phthalate on the still-pot side and 6 per cent sodium chloride solution on the atmosphere side. The salt solution serves as the regulating contact for the thermionic relay. The manometer is read directly in terms of millimeters of dibutyl phthalate, since the densities of the two liquids are the same. At low reflux rates the still-pot heating was set manually because the column was too sensitive to changes in heat input. For the same reason it is good practice to use a voltage-regulating transformer as input to the Variac autotransformer because of line fluctuations on 110-volt alternating current.

For efficiency or test distillations a special 140-cc. flask with an inner-sealed siphon was used, in order that samples might be taken while the still was in operation. The still pot was held in place by means of springs joining the glass hooks on the column and pot.

A calibrated 5-junction copper-constantan couple was inserted 5 cm. (2 inches) into the second annular space at the head of the column and cemented through a hole in the wall of the head with Insalute cement. At low reflux rates the temperature as registered here fluctuates as much as 0.3° C. At moderate reflux rates, however, no variation of temperature occurs. For the distillation of small amounts of material at low reflux rates a modified Craig-type head (*5*) is very convenient, but it is not suited for reflux rates over 125 cc. per hour because it strictly limits the take-off rate. The sample-collecting cup sealed on the condenser tip has a capacity of 0.4 cc. The distribution of the reflux in the head is important, because the reflux ratio in each space must be the same or the efficiency will be limited by the lowest ratio. The outside annular space is supplied with reflux from the walls of the head itself. The innermost space is supplied by the drip from the bottom of the cup. The middle space is not normally supplied with reflux from the vapors effluent from it. To remedy this two silver strips 1 mm. wide extending to the edge of the middle space were fastened to the take-off cup. Reflux is carried by the strips to the walls of the space.

TABLE I. DIMENSIONS OF PYREX TUBE PACKING

Outside Diameter	Inside Diameter	Ratio of Volume to Surface in Annular Spaces	Projection above Vacuum Jacket
Mm.	*Mm.*	*1/cc.*	*Mm.*
4	Closed	..	7
8	6	0.05	3
12	10	0.05	1
16	14 (special size)	0.05	..

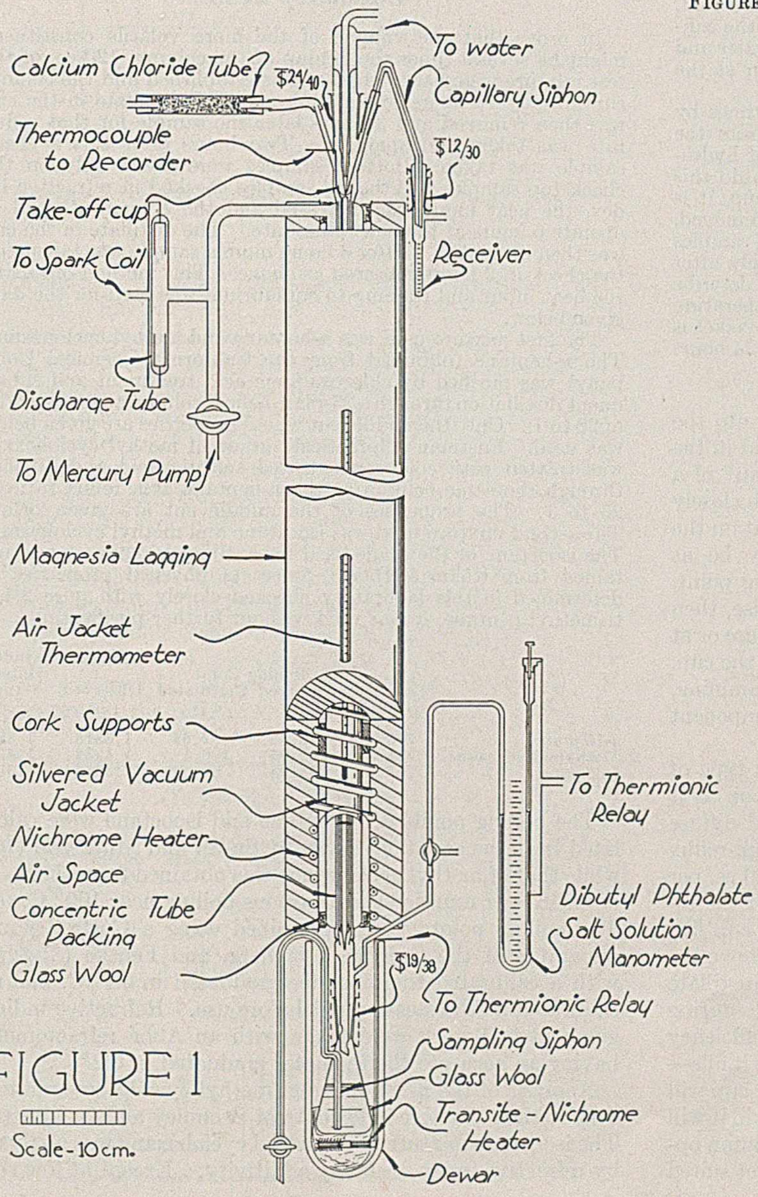


FIGURE 1

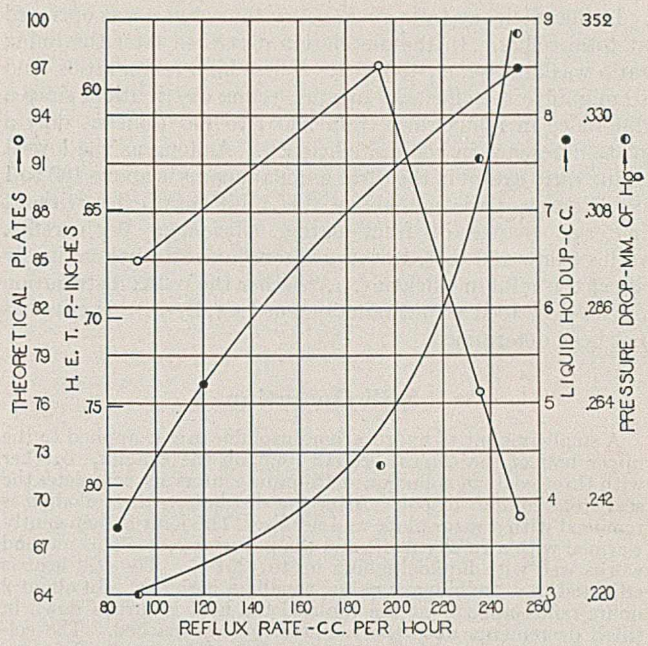


FIGURE 2. CHARACTERISTICS OF CONCENTRIC TUBE PACKING

In the efficiency tests given below the column was operated at total reflux. In the distillation described later the reflux ratio was high—i. e., 450 to 1. These high reflux ratios tend to minimize the effects of unequal reflux distribution, since a difference in reflux ratio from 200:1 to 400:1 means only a plate difference in column efficiency. As long as the lowest reflux ratio extant in the three annular spaces is above 100 to 1 considerable variation above this limit may exist without material change of fractionating efficiency. With reflux ratios below 100 to 1, variations in reflux ratio will seriously affect the column efficiency. Whether the reflux distribution device described would function successfully in this case has not been determined.

Still Operation

A small amount of hydrocarbon-insoluble grease applied to the upper half of the conical ground joint on the column, together with three coats of collodion at 15-minute intervals, completes the seal from column to pot. After the distillation the collodion is removed with a razor blade and needle. The joint is then gently warmed with a smoky flame and the pot removed. This method works well with liquids boiling up to 125° C. The still heat is adjusted to a preliminary value, usually a high one. In about 2 hours reflux appears at the top and the heat is turned down in small decrements until the required level is reached. The column is at approximate equilibrium after 10 hours of reflux at a given heat input when starting with the column and liquid cold. The reflux rate is determined by timing the drops from the calibrated dripper at the bottom of the column. All reflux rates and reflux ratios given are calculated from the reflux return at the bottom of the column.

Samples are taken from the head at predetermined times by starting the capillary siphon with a rubber syringe from the sample tube as shown in Figure 1. Since the vapors of hydrocarbons are toxic to some extent, it is not advisable to do this with the mouth. When the siphon has emptied the cup, it is left to drain itself for a few minutes; the sample tube is removed, and a closed-end ground joint replaced on the siphon. If samples are to be taken from the pot they are taken immediately after this with the still-pot siphon. All the data necessary to describe column operation and sample properties, including temperature of the head, are taken at the same time. If the heated jacket is used, it is adjusted to the required temperature at least 24 hours before use.

Since the thermocouple is inserted several inches into the column, it does not give the boiling point of the liquid in the cup. In the case of successive samples on a "plateau" of a distillation, the thermocouple temperatures will agree closely with the microboiling point of the cup condensate, but on the "breaks" between fractions the thermocouple may be as much as 20° C. high compared with the true boiling point. Each time the cup is emptied the temperature will rise, then fall back and level out either at the previous temperature or at one higher, but lower than the initial rise on draining the cup. This is due to establishment of total reflux after sampling, with consequent enrichment of the lowest boiling component in the head of the column.

A knowledge of the actual take-off rate with this type of head can be gained only by emptying the cup as soon as it fills. When the reflux rate is low, vapor and liquid diffuse slowly to the cup, which means slow take-off and high reflux ratio with maximum efficiency. At the low rate of 80 cc. per hour refluxed the cup would fill once every hour. If the reflux rate is now increased to 125 cc. per hour, the cup fills every 15 minutes because the vapor now condenses above the cup and drains into it. When the cup is emptied the distillate fills it very rapidly. This means that the reflux ratio during the filling at the higher reflux rate is low and the efficiency drops. If, however, the cup is not emptied as soon as it fills—i. e., every 15 minutes—but just once every hour the cup will overflow at least three times its volume and the liquid in it will be replaced with that extant in the head when the column operates at total reflux. Thus the Craig-type head is not suited for distillation other than at low reflux rates because increasing the reflux rate does not allow increase in take-off rate.

Still Holdup

The holdup of the still under operating conditions was determined (*12*) by taking a known volume of a volumetric solution of stearic acid in *n*-heptane and methyl cyclohexane mixture and determining the concentration when the still was operating. This was done by evaporating the solvent from a known volume siphoned from the still pot and weighing the residue. In one case the still pot was run to dryness, the heat shut off, and the total drainage determined. Heating the vacuum jacket to within 5° C. of the boiling point decreases the holdup perceptibly. The reflux rate was determined by timing the drops from the dripper in the still pot. The flooding point was not determined.

TABLE II. HOLDUP *vs.* REFLUX RATE

Reflux Rate	Holdup	Method
Cc./hr.	*Cc.*	
252	8.5	Stearic acid
120	5.2	Drainage
84	3.7	Stearic acid
	Heated Vacuum Jacket	
114	3.4	Stearic acid

Efficiency Tests

In order that the volume of the more volatile constituent might be several times the holdup of the column, 120 cc. of the test mixture were used. Reflux was established and the column run initially 10 hours to equilibrium. The distillate in the cup was then removed and 3 hours later the sample for that reflux rate was taken and analyzed. Two hours after this a check sample was taken. Bottom samples were taken only on the check top samples. If the top samples checked in refractive index, the heat input was increased and the column allowed to operate 6 hours at the new reflux rate. The distillate in the cup was then discarded. After 3 hours more a sample was taken and the check in 2 hours repeated as above. This method of raising the heat input and running to equilibrium was used for the data given below.

The first mixture used was *n*-heptane and methyl cyclohexane. The *n*-heptane (obtained from the California Chemical Company) was purified by chlorosulfonic acid treatment and subsequent distillation through a 25-plate helices column at a reflux ratio of 20 to 1. Only the middle cut whose properties are given below was used. Eastman's "practical" grade of methyl cyclohexane was treated with cold concentrated sulfuric acid and distilled through the same column as the *n*-heptane at a reflux ratio of 25 to 1. The properties of the middle cut are given below. The second mixture used was isooctane and methyl cyclohexane. The isooctane of the grade used for antiknock purposes was obtained from Röhm & Haas. Since its physical properties as determined in this laboratory checked closely with pure 2,4,4-trimethyl pentane, it was used without further purification.

	Pressure	Boiling Point Observed	Boiling Point Calculated	Refractive Index Observed	Refractive Index Literature
	Mm. Hg	*° C.*	*° C.*	*20° C.*	
n-Heptane	743.3	97.63	97.65	1.3878	1.3877
Methyl cyclohexane	741.8	100.05	100.1	1.4232	1.4232
Isooctane	747.2	98.68	98.64	1.3917	1.3916

The boiling points of *n*-heptane and isooctane were calculated from the equations given by Smith and Matheson (*10*), while that of methyl cyclohexane was obtained from the *dt/dp* of 0.046° per mm. for hydrocarbons boiling near 100° C. (*6*). The boiling points were determined using a Cottrell pump apparatus of the Quiggle, Tongberg, and Fenske (*8*) type, with a calibrated thermometer graduated in 0.1° C. and recalibrated at the steam point before use. Refractive indices given in this work were taken with an Abbé refractometer having an accurate thermometer graduated in 0.2° C.

Analysis of the *n*-heptane and methyl cyclohexane mixture was by the refractive index data of Bromiley and Quiggle (*3*). The isooctane mixture with methyl cyclohexane was analyzed by refractive index assuming additivity. Except at low con-

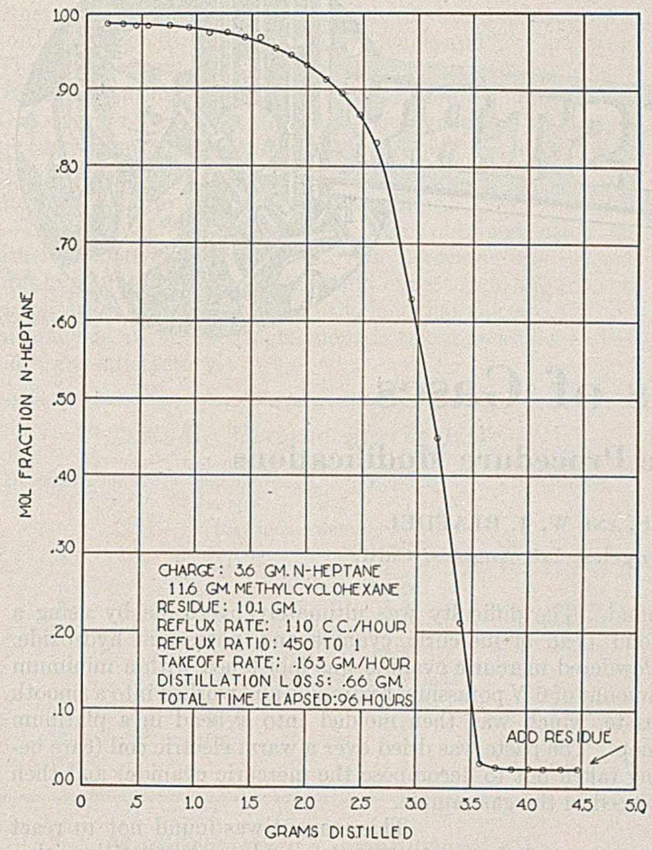


FIGURE 3. DISTILLATION OF *n*-HEPTANE AND METHYL CYCLOHEXANE MIXTURE

centrations of either component this is probably correct to within a few per cent. A more serious objection to the use of this mixture is the fact that its deviation from ideality is unknown. Beatty and Calingaert (*1*) have shown that small variations in ideality of solutions lead to serious errors in the calculation of column efficiencies when the relative volatility approaches 1. The data obtained by its use are therefore not reliable and are given merely for comparison with the *n*-heptane and methyl cyclohexane mixture which is very nearly ideal. However, with this latter mixture it is necessary to use the extremes of concentration when the still efficiency is near 100 plates. This means that the formula for calculating efficiency is used in the range where the accuracy of the data has considerable effect on the calculated efficiency.

The mixture of *n*-heptane and isooctane is ideal within 0.02 per cent (*1*) and would be excellent for efficiency tests except that the refractive index would then have to be determined to the fifth place. The formula used for calculation of efficiency was that given first by Fenske (*7*) and then generalized for any reflux ratio by Smoker (*11*). In comparing data on efficiency obtained by use of different mixtures, it must be kept in mind that the number of plates necessary to separate a mixture increases as the average molecular weight of the mixture increases (*4*). Relative volatility, alpha, for the *n*-heptane and methyl cyclohexane mixture used was that calculated from the data of Beatty and Calingaert (*1*) for the boiling point of the mixture in the still; alpha is 1.0726 for the data given in Table III. For the isooctane and methyl cyclohexane mixture, alpha was calculated from the vapor pressures for methyl cyclohexane given by Beatty and Calingaert (*1*) and those for isooctane by Smith and Matheson (*10*) to be 1.045. In Table III one plate has been subtracted to correct for the still pot.

TABLE III. EFFICIENCY TESTS

Reflux Rate	Back Pressure	Refractive Index		Mole Fraction-*n*-Heptane		Plates	H. E. T. P.
		Head	Still	Head	Still		
Cc./hr.	*Mm. Hg*						*Inch*
			n-Heptane, Methyl Cyclohexane				
93	0.22	1.3887	1.4201	0.972	0.076	84.9	0.67
194	0.26	1.3882	1.4202	0.987	0.074	97.2	0.59
236	0.32	1.3901	1.4211	0.927	0.052	76.7	0.74
252	0.35	1.3932	1.4218	0.827	0.034	69.0	0.82
			Isooctane, Methyl Cyclohexane				
				Mole Fraction-Isooctane			
84	0.19	1.3940	1.4173	0.924	0.185	89.4	0.64
120	0.23	1.3952	1.4174	0.887	0.184	79.6	0.72
126	0.25	1.3980	1.4176	0.797	0.177	64.9	0.88
180	0.28	1.3969	1.4180	0.832	0.164	72.2	0.79
210	0.36	1.3966	1.4183	0.842	0.155	75.5	0.76

Distillation of Known Mixture

Several distillations were carried out with the vacuum jacket heated to 1° C. below the boiling point of the low-boiling component. Since the separation obtained was no better than that with the vacuum jacket alone, the heated vacuum jacket was not used in the efficiency tests. In the distillation of small quantities the heated vacuum jacket decreases the holdup and is useful in this respect. If the heated jacket is used, care must be taken to overcome the time lag between the air-jacket temperature and the packing temperature. At temperatures above 100° C. the heated jacket would be most useful. Figure 3 gives the distillate composition curve obtained from a charge of 3.6 grams of *n*-heptane and 11.6 grams of methyl cyclohexane which was 0.233 mole fraction of *n*-heptane. The reflux ratio was 450 to 1. Reflux rate was 110 cc. per hour and take-off rate 0.163 gram per hour. The jacket was kept at 75° C. The distillation was run until the distillate showed no appreciable change in composition. The amount of the low-boiling material present is just about the holdup of the column, so that the curve given represents the break in an analytical distillation curve with several components.

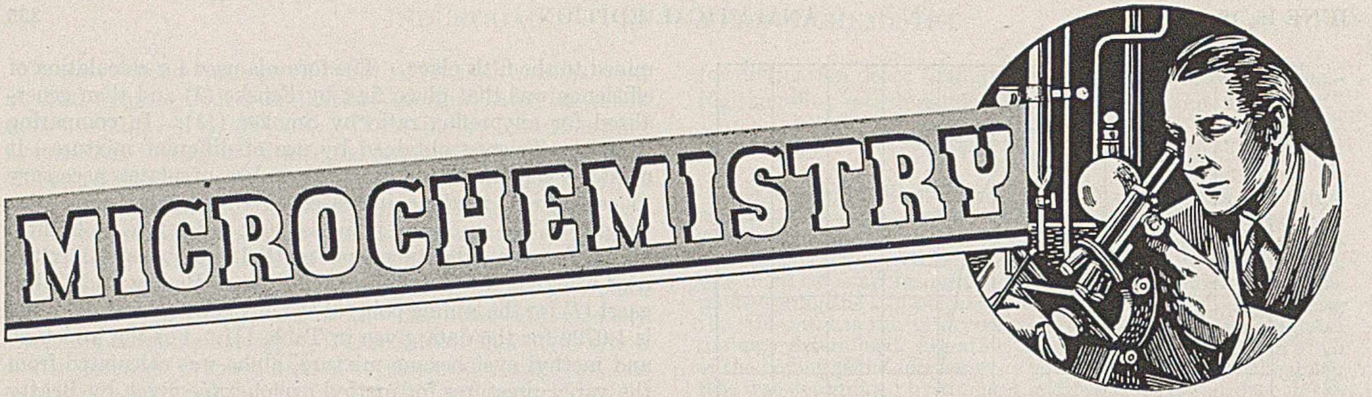
The distillation took 96 hours, during 28 of which samples were taken. The still was run continuously day and night, but take-off was only by day. At the end the column was drained 3 hours and the residue weighed. The material loss was 0.66 gram.

Acknowledgment

The writers wish to acknowledge the suggestion pertaining to back pressure measurement made by A. L. Glasebrook of the Research Laboratories Division, General Motors Corporation.

Literature Cited

(1) Beatty, H. A., and Calingaert, G., IND. ENG. CHEM., 26, 504–8 (1934).
(2) Bragg, L. B., *Ibid.*, Anal. Ed., 11, 283–7 (1939).
(3) Bromiley, E. C., and Quiggle, D., IND. ENG. CHEM., 25, 1136–7 (1933).
(4) Carswell, T. S., *Ibid.*, 18, 294–5 (1926).
(5) Craig, L. C., *Ibid.*, Anal. Ed., 9, 441–3 (1937).
(6) Dunstan, A. E., Nash, A. W., Tizard, Henry, and Brooks, B. T., "Science of Petroleum", Vol. II, p. 1281, London, Oxford University Press, 1938.
(7) Fenske, M. R., IND. ENG. CHEM., 24, 482–5 (1932).
(8) Quiggle, D., Tongberg, C. D., and Fenske, M. R., *Ibid.*, Anal. Ed., 6, 466–8 (1934).
(9) Rose, A., IND. ENG. CHEM., 28, 1210–12 (1936).
(10) Smith, E. R., and Matheson, H., *J. Research Natl. Bur. Standards*, 20, 641–50 (1938).
(11) Smoker, E. H., *Trans. Am. Inst. Chem. Engrs.*, 34, 165–72 (1938).
(12) Tongberg, C. D., Quiggle, D., and Fenske, M. R., IND. ENG. CHEM., 26, 1213 (1934).



Microanalysis of Gases

Acetylene, Benzene, and Some Procedure Modifications

F. E. BLACET, A. L. SELLERS, AND W. J. BLAEDEL
University of California at Los Angeles, Los Angeles, Calif.

A method of analysis for acetylene in the presence of propylene and carbon monoxide uses as the absorbing reagent solid mercuric cyanide and potassium hydroxide. In the microanalysis for benzene vapor both fuming sulfuric acid and ammoniacal nickel cyanide are satisfactory reagents.

A new combustion coil for the burning of gases is described, and a change in the method of preparing a cupric oxide–potassium hydroxide reagent for hydrogen is given.

SINCE the appearance of the fourth paper of this series there have accumulated in this laboratory some new methods of analysis and modifications of old procedures for the microanalysis of gases.

Acetylene

Acetylene can be determined quantitatively in the presence of ethylene and saturated hydrocarbons by using a bead of solid cuprous chloride and potassium hydroxide as the reagent (*2*). However, in a recent research problem of this laboratory it was important to analyze for acetylene in the presence of carbon monoxide and propylene. The cuprous chloride–potassium hydroxide reagent reacts slowly with carbon monoxide, the solid silver oxide normally used to remove carbon monoxide reacts rapidly with acetylene, and sulfuric acid, being the common reagent for absorbing unsaturated hydrocarbons, will combine with both propylene and acetylene. Obviously a new reagent was needed, preferably one which would remove acetylene and not react with the other two gases.

Treadwell and Tauber (*5*) recommended a solution made by dissolving 20 grams of mercuric cyanide in 100 cc. of 2 *N* sodium hydroxide. The authors found that such a solution introduced in a gas sample by means of a sintered-glass bead (*2*) absorbs acetylene quantitatively in 10 minutes from a 50 per cent mixture with nitrogen. The results compare favorably with those obtained by using either cuprous chloride–potassium hydroxide or sulfuric acid as the absorbent. Unfortunately, this solution also absorbs propylene to an appreciable extent and could not be used for the problem at hand. The difficulty was ultimately overcome by using a solid bead of mercuric cyanide and potassium hydroxide. Powdered mercuric cyanide was moistened with a minimum amount of 6 *N* potassium hydroxide and worked into a smooth paste, which was then molded into a bead in a platinum loop. The paste was dried over a warm electric coil (care being taken not to decompose the mercuric cyanide) and then placed in the gas sample.

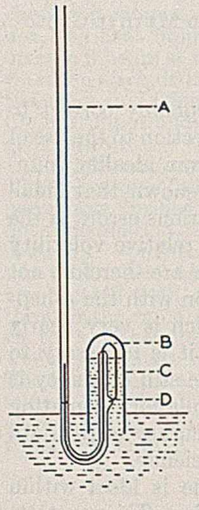


FIGURE 1. COMBUSTION COIL IN OPERATING POSITION

This reagent was found not to react to a measurable extent with either propylene or carbon monoxide during an exposure of 1.5 hours. Several known mixtures of acetylene, propylene, and carbon monoxide were made and analyzed for acetylene with satisfactory results. A single bead of absorbent and a time of 20 minutes were found sufficient for complete reaction in every analysis. Table I is typical of results which were obtained. In this case approximately equal volumes of the three gases were mixed. A complete analysis would require the subsequent introduction of concentrated sulfuric acid to remove ethylene and silver oxide to absorb carbon monoxide, a procedure which offers no difficulties.

Benzene

In studying the feasibility of analyzing for benzene vapor in small volumes, it was found that two of the recognized macroanalytical reagents can be used with results which appear satisfactory. One is fuming sulfuric acid followed by a solid potassium hydroxide bead, and the

TABLE I. ANALYSES FOR ACETYLENE IN THE PRESENCE OF PROPYLENE AND CARBON MONOXIDE

Determination	Volume of Sample	Acetylene Theoretical	Acetylene Determined	Acetylene Difference
	Cu. mm.	%	%	%
1	45.44	33.10	33.09	−0.01
2	40.75	33.10	32.98	−0.12
3	37.66	33.10	33.15	+0.05
4	40.82	33.10	33.11	+0.01
5	42.61	33.10	32.80	−0.30
		Av.	33.03	0.10

other is an ammoniacal nickel cyanide solution made according to the detailed directions given by Dennis and McCarthy (*4*). The latter reagent must be followed by solid phosphorus pentoxide or concentrated sulfuric acid to remove ammonia (*1*). Gas samples for testing these analytical methods were made by slowly bubbling nitrogen through liquid benzene at room temperature and then adding approximately 10 per cent more nitrogen to the resulting gas volume.

Table II gives results which were obtained using the different analytical procedures. The percentages of benzene obtained are about what one would expect from the mode of preparation of the sample, and the fact that the two methods of analysis are in good agreement is taken as evidence that both are satisfactory.

Table II. Determination of Benzene

Determination	Volume of Sample	Benzene	Deviation from Average
	Cu. mm.	%	%
	By Fuming Sulfuric Acid		
1	97.06	4.50	−0.01
2	102.83	4.57	+0.06
3	99.80	4.29	−0.22
4	98.90	4.50	−0.01
5	98.66	4.69	+0.18
		Av. 4.51	±0.10
	By Ammoniacal Nickel Cyanide		
1	101.33	4.54	+0.05
2	96.72	4.57	+0.08
3	99.05	4.37	−0.12
		Av. 4.49	±0.08

Modification of Combustion Coil

The platinum combustion coil now in use in this laboratory for the burning of gases is more satisfactory than the one previously described (*3*) and is illustrated, drawn to scale, in Figure 1.

The soft-glass holder, *A*, is a 1-mm. capillary with a 2.5-mm. external diameter. During construction of the coil the lower end of this tube is shrunk around the proper length of 24-gage platinum wire and then bent into a loop as shown. Sufficient wire is allowed to extend into the unconstricted portion of *A* to give a good electrical contact when this portion is filled with mercury. The other end of the wire extends beyond the glass about 2 mm., is bent sharply at *B*, and is attached to the holder at *D* with the aid of a glass bead. The tip of the glass below *B* should be well rounded and carefully polished to prevent introduction of small air bubbles into the sample. The distance between *B* and *D* is about 15 mm.

At bend *B* the wire is carefully filed and ground down on a fine whetstone until a diameter is obtained at one point which is from one fourth to one fifth of that which was originally present. This gives a cross section at this point roughly one twentieth that of the rest of the wire, a ratio which may be compared to one third as previously used (*3*). The strong anchorage at *D* holds the wire in place and has made possible the substantial reduction in diameter at *B*. This in turn has decreased the current necessary to produce the hot spot, and as a consequence, has diminished the operating temperature of the rest of the wire to the point where the danger of mercury oxidation has been greatly reduced, if not completely eliminated. Anchorage *D* is placed low so that it will be well below the mercury surface in the gas holder, *C*, at all times, and any small air bubbles which may be trapped at *D* will not be introduced into the combustion mixture. This type of construction has overcome the difficulties encountered earlier, when attempts were made to attach the wire beyond *B* to the glass (*3*).

Hydrogen Reagent

The method of preparing a cupric oxide–potassium hydroxide absorbent for hydrogen has been practically reversed from that described before (*1*). The bead is prepared now by fusing potassium hydroxide in a platinum loop and touching this while molten to powdered cupric oxide, allowing it to enclose as much of the oxide as it will and still give a smooth external surface on cooling. This reagent is easier to prepare than the one formerly used and gives just as satisfactory results.

Literature Cited

(1) Blacet and MacDonald, Ind. Eng. Chem., Anal. Ed., 6, 334 (1934).
(2) Blacet, MacDonald, and Leighton, *Ibid.*, 5, 272 (1933).
(3) Blacet and Volman, *Ibid.*, 9, 44 (1937).
(4) Dennis and McCarthy, *J. Am. Chem. Soc.*, 30, 233 (1908).
(5) Treadwell and Tauber, *Helv. Chim. Acta*, 2, 601 (1919).

Microdetermination of Sulfur in Organic Compounds

An Absorption Apparatus for Use with the Combustion Method

L. T. HALLETT and J. W. KUIPERS, Kodak Research Laboratories, Rochester, N. Y.

IT IS well known that organic material must burn at a much slower rate in the determination of sulfur by the method of combustion with oxygen gas than in other determinations where combustion is involved.

While studying the use of tetrahydroxyquinone as an indicator for the microvolumetric determination of sulfur (*5*) it became apparent that it would be desirable for routine work to reduce the burning time to 15 minutes, so that the total time for a determination would not be over 30 minutes. The well-known Pregl combustion tube with spiral absorber is not suited to rapid combustion and is not convenient because the tube must be removed from the furnace before the combustion products can be washed out.

If a sample is burned rapidly (15 minutes) in the Pregl combustion tube with spiral absorber or in the absorption apparatus designed by Hallett (*4*) with the oxygen flowing at the rate of 75 to 100 ml. in 5 minutes, low results are usually obtained, owing to the loss of sulfur trioxide as mist. This electrically charged mist is formed by the union of sulfur trioxide and water vapor; once formed, it cannot be absorbed in chemical reagents and so escapes from the absorption train.

A study was made, therefore, of the type of absorber that would allow rapid combustion and be convenient for removal of the absorbed combustion products.

It was found that hot gases containing sulfur oxides traveling rapidly readily formed the sulfur trioxide mist. Any constriction, therefore, at a point at the end of the combustion tube near the absorber would increase the speed of the gases and the tendency to mist formation.

Apparatus

The first type of absorber used (Figure 1) was similar to that previously described (*4*) but smaller, having a 6-mm. bore and 1-mm. wall. The absorption spiral is 8 cm. long with 2 mm.

between the coils. The upper expansion chamber, *C*, is 4 cm. long and 1.7 cm. at the wide part of the lower bulb. The size of the upper section above the absorption spiral is not critical, but if it is larger than the above dimensions it is difficult to rinse this part of the absorber thoroughly with distilled water. This expansion chamber helps to cool the gases from the combustion tube, *A*, and thereby prevent the formation of mist. Into the dome, *B*, at the top of the expansion chamber is sealed a tube and funnel, *F*, which is closed by a ground-in stopper, *G*, during the run. After the combustion, *G* is removed and the absorbed products are washed from the absorber through *D* by adding water through the funnel. The "dome" structure is necessary to spread the rinse water to all points of the expansion chamber. Between the absorber and the combustion furnace an electric heating coil, consisting of a few turns of No. 25 Nichrome wire wound around the combustion tube, prevents the condensation of sulfuric acid.

The temperature of the furnaces is kept at 750° C. and the Nichrome coil at approximately 400° C. If the coil is heated above this temperature, mist that cannot be absorbed will often form. That part of the combustion tube heated by a 22.5-cm. (9-inch) furnace is filled with platinum foil to facilitate the complete oxidation of the organic vapors. The automatic combustion unit used in this work has been previously described (*3*).

One to 2 ml. of 1 per cent potassium hydroxide solution is used as an absorbing agent and is carefully added by means of a pipet through the left arm of the funnel, *F*, into the bulb, *E*. Bromine water is later used to oxidize any sulfur dioxide to sulfur trioxide. Where the sulfur is determined gravimetrically as barium sulfate, the regular dilute (5 to 6 per cent) solution of hydrogen peroxide should, of course, be used to moisten the spiral.

This absorber in actual use gives good results with a burning time of 15 to 20 minutes, when the flow of oxygen is at the rate of 50 ml. in 5 minutes. While the actual time of a determination is approximately 30 minutes with this apparatus, the total elapsed time is approximately 1 hour because 20 to 30 minutes must be allowed to heat the solution in order to remove the bromine before the final titration.

This apparatus is superior to the standard Pregl combustion tube for sulfur, using the familiar glass absorption spiral, because at the end of the run the combustion tube need not be removed from the furnace. The speed of the flow of oxygen and consequent rate of burning have been increased by the new type of absorber. The products of oxidation are readily washed from the receiver. The weakness of the apparatus lies in the fact that compounds which burn almost explosively, with a consequent temporary but sudden increase in gas flow, may under such conditions produce loss of sulfur trioxide by formation of mist. These same conditions will produce mist in the Pregl tube. Such compounds are not frequently encountered, however. The apparatus offers advantages to laboratories which do not have a sufficient quantity of work to warrant purchasing the necessary equipment for the electroprecipitator described below.

However, apparatus so designed that mist would be positively dissipated and absorbed would serve the needs of a routine industrial laboratory much more efficiently and require less attention. Into a second type of absorber (Figure 2), therefore, a small electroprecipitator was built. This method of precipitating charged particles is well known for its efficiency and is widely used in industrial installations. Grote and Krekeler (*2*) used the method as a final check on the efficiency of their macrocombustion method for the determination of sulfur in organic material.

The absorber is fabricated from clear quartz tubing of 8-mm. bore and 1-mm. wall. The helix is made of Pyrex glass. The Pyrex stopcock, at *E*, is attached to the bottom of the absorber by a rubber connection. The quartz tube passing through the helix has a 2-mm. bore and a 1-mm. wall. *G* and *B* are ground-in Pyrex stoppers through which are sealed tungsten lead wires. Stopper *G* is slotted at the ground joint, so that the unabsorbed gases may escape. The tungsten wire projects about 1 cm. into chamber *C*; to it is spot-welded a 4-cm. length of B. & S. No. 24 platinum wire, and to this is spot-welded 3 cm. of No. 32 platinum wire. This fine wire gives a high current density on a small area, which has been found most efficient. The stiffer wire keeps the fine wire from vibrating excessively and thus making contact with the wall. The electrode in *F*, 3 cm., is No. 24 platinum wire, spot-welded to the tungsten. The platinum is filed to a sharp point. This electrode is really required only if a large volume of sulfur trioxide is momentarily formed; under such conditions, and with one precipitator, a small amount of sulfur trioxide mist might escape.

An electric heating coil of B. & S. No. 24 Nichrome wire is placed at *A* and kept at approximately 400° C. to prevent the condensation of sulfuric acid at this point. Around the outside of chamber *C* is wrapped metal foil, such as platinum, 2.5 cm. in height. Chamber *F* does not require an outer electrode because the foil on *C* is sufficiently close to serve this area also. A 25,000-volt transformer and Variac complete the apparatus. An effective potential of 10,000 to 13,000 volts is maintained between the electrodes when making a run. The cost of the transformer and Variac (115-volt, 5-ampere maximum) is approximately $40. It is not necessary that the apparatus shown in either Figure 1 or 2 be made of quartz, but if a competent glass-blower is available, the quartz apparatus costs very little more than that made of ordinary hard-glass combustion tubing.

Another modification consists of placing a ground joint between the absorber and combustion tube, as demonstrated by

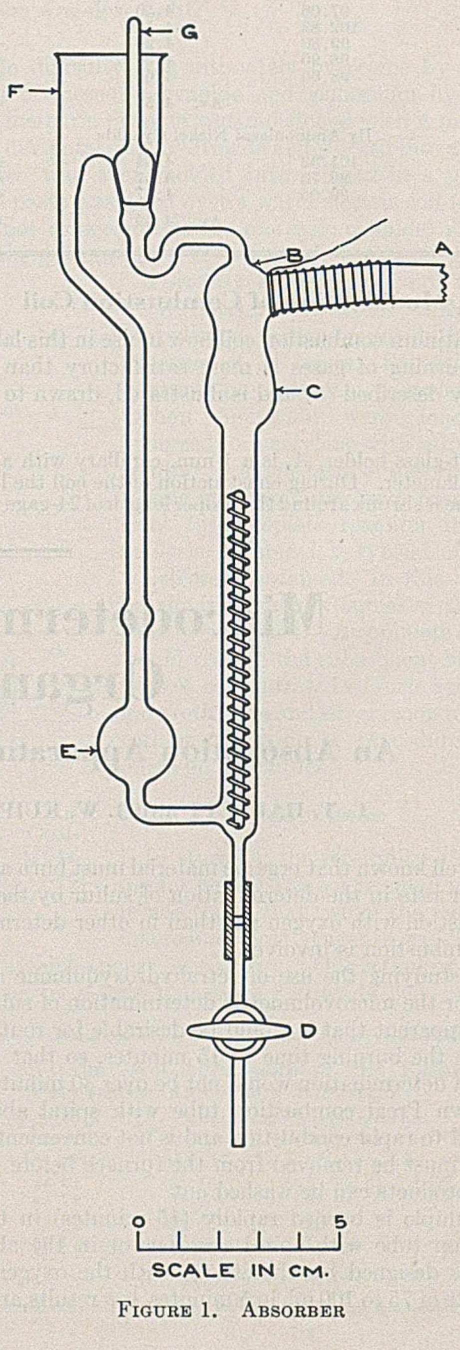


FIGURE 1. ABSORBER

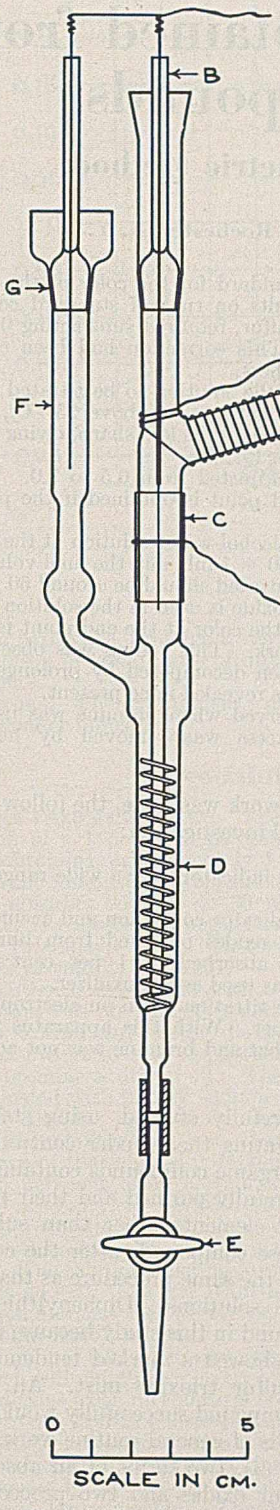


FIGURE 2. ABSORBER WITH ELECTROPRECIPITATOR

Beazley (*1*). This permits the absorber to be constructed entirely of Pyrex. The weakness of this construction is the possibility of leakage at the ground joint. For this reason it is best to draw the oxygen through by applying reduced pressure at the exit end, as in this way the pressure is directed inward at the joint.

The helix, *D*, is moistened with approximately 1 ml. of distilled water added through *F*. The oxygen is passed through at the rate of 75 to 100 ml. in 5 minutes. The electrodes, *B* and *G*, are put in place and the stopper of *B* is sealed with a few drops of water. The connection to the transformer is made and the current turned on. The heater at *A* is switched on and the automatic combustion furnace is brought into the burning position. Any sulfur trioxide mist formed is precipitated in *C*. The gases pass on to the bottom of *D* and around the helix into *F* where any remaining mist is precipitated. The excess gases pass out through the slot in *G*.

The combustion is completed in 15 minutes. The heater at *A* is turned off and 5 minutes more are allowed for the combustion tube to be cleared of sulfur oxides and for that section of the tube at *A* to cool.

The contents of the absorber are now washed into a 125-ml. Erlenmeyer flask through the stopcock at the bottom. After opening the stopcock, electrode *G* is first removed and the tip carefully washed, allowing the wash water to run through the absorber; then electrode *B* is removed and likewise washed. Chambers *F* and *C* are alternately washed until a volume of 30 to 35 ml. has been collected.

The apparatus incorporating the electroprecipitator is superior in routine work for several reasons. It gives positive dissipating of any sulfur trioxide mist; thus, the limitations of careful burning are reduced to the one factor, actual burning of the organic material. The ozone produced by the precipitator oxidizes any sulfur dioxide to sulfur trioxide. This is most important when the sulfate is determined volumetrically with the indicator tetrahydroxyquinone, because experience shows that the use of bromine as the oxidizing agent gives less accurate results and hydrogen peroxide cannot be used (*5*). If the precipitator is not turned on during the run, low results are invariably obtained.

Summary

Two forms of an absorber which can be used for the determination of sulfur by the method of combustion are described. One meets the needs of the average laboratory and allows more rapid burning of the sample. It is designed so that the products of combustion can be washed from the absorber without removing the tube from the furnace. Sulfur trioxide mist, which once formed cannot be absorbed, is eliminated with this type of absorber except in those infrequent cases where the compound burns very rapidly.

The other absorber meets the needs of routine laboratories where a large number of sulfur compounds must be analyzed. An electroprecipitator positively dissipates the sulfur trioxide mist and any lower oxides of sulfur are oxidized to sulfur trioxide because of the formation of ozone. This absorber retains the advantages of the one above but allows slightly more rapid burning, uses water as an absorbent, and allows the titration of the sulfate using the indicator tetrahydroxyquinone as soon as it is washed from the absorber.

Literature Cited

(1) Beazley, C. W., IND. ENG. CHEM., Anal. Ed., 11, 229 (1939).
(2) Grote, W., and Krekeler, H., *Angew. Chem.*, 46, 108 (1933).
(3) Hallett, L. T., IND. ENG. CHEM., Anal. Ed., 10, 101 (1938).
(4) *Ibid.*, 10, 111 (1938).
(5) Hallett, L. T., and Kuipers, J. W., *Ibid.*, 12, 360 (1940).

PRESENTED before the Division of Microchemistry at the 98th Meeting of the American Chemical Society, Boston, Mass. Communication No. 751 from the Kodak Research Laboratories.

Microgram and Millimicrogram

THE Committee on Nomenclature, Spelling, and Pronunciation of the AMERICAN CHEMICAL SOCIETY has approved the following recommendation of the Division of Microchemistry:

> For 0.001 milligram the term "microgram", designated by the symbol γ (the word "gamma" should not be used as a substitute for "microgram"). For 0.001 microgram, the term "millimicrogram", designated by the symbol mγ (the term "milligamma" should not be used).

Microdetermination of Sulfate Obtained from Combustion of Organic Compounds

Tetrahydroxyquinone as an Indicator in a Volumetric Method

L. T. HALLETT AND J. W. KUIPERS, Kodak Research Laboratories, Rochester, N. Y.

WHILE the microgravimetric procedure for the determination of sulfur as barium sulfate is accurate, it is tedious and time-consuming. A volumetric procedure approaching the accuracy of the gravimetric procedure would be welcomed by analysts who must run sulfur in a large number of organic compounds. There are several volumetric methods and the authors, during the past 5 years, have studied some of the more promising ones:

1. Precipitation of the sulfur as barium sulfate with barium chromate, and titration of iodine liberated from potassium iodide by the chromic acid formed. The method did not prove reliable and the conclusions of Manov and Kirk (*5*) were confirmed.
2. ter Meulen's (*12*) hydrogenation method is accurate, but because of the frequent burning out of the coke formed in the combustion tube the method is not an ideal routine procedure.
3. Precipitation of the sulfur as benzidine sulfate and subsequent titration with sodium hydroxide. Unless great care is taken to prevent loss of benzidine sulfate through solution while washing the precipitate, poor results are obtained (*2*). The method has not been found suitable for routine use here.

Recent studies (*6, 8–11, 13*) on the use of tetrahydroxyquinone as an indicator in the direct titration of the sulfate ion led the authors to study its use in a micromethod for the direct titration of sulfur as sulfate, following burning of the sulfur-containing compound in oxygen in the regular manner. Sheen and Kahler (*10*) used 0.025 *N* barium chloride, but this is too high a concentration for microwork. An investigation of the errors and color change, using barium chloride solutions on the order of 0.01 *N*, was therefore necessary. The work of Ampt (*1*), Manov and Kirk (*5*), and Gibson and Caulfield (*3*) would indicate that the indicator change is not sufficiently sharp for microtitration.

A preliminary investigation showed:

1. That a reproducible end point, using 0.01 *N* barium chloride in a solution containing 1 mg. of sulfur, could be obtained. The operator, however, requires practice in order to detect the color change and cannot see the change if the color of the solution is observed by reflected light. The use of strong artificial illumination when titrating has been suggested by Sheen and Kahler (*9*). However, the exact conditions under which the color change is observed are important if the end point is to be readily detected. For microwork a ground-glass screen illuminated with a 60-watt daylight bulb is employed. A small-sized darkroom safelight may be readily converted to serve the purpose. The operator with his eye on a level with the solution sees the color change best with the light coming through the solution. Observed under these conditions and when the flask is tilted back and forth, the solution at the end point will have a distinct reddish hue. It has been the authors' experience that a sharp end-point color is not observed if the operator is looking down upon the solution as is normally done.
2. The end-point color which is chosen by an operator can be reproduced by him, but another operator may or may not succeed in selecting the same color. Any one operator can easily reproduce the end point to ±0.05 ml. of 0.01 *N* barium chloride.
3. A color standard to which the end-point color can be matched is absolutely essential for accurate work. After working with dye solutions as color standards, it was found that a No. 21 Wratten filter (5 × 5 cm., 2 by 2 inches) cemented to the ground glass served much better as a standard because of the permanence of the color. In this way, it was easier to discern when the solution approached the end point. Later, two layers were used and the end point was reached when the color of the solution matched the color of the two layers of the filter. By this means, different operators can titrate to the same end point.
4. Before a definite standard for the color of the end point had been established, results on runs of standard compounds, when titrating 1 mg. of sulfur, required subtracting 0.10 ml. as an indicator correction. This correction had been established by the previous work of others.
5. The temperature of the solution to be titrated should be 15° to 25° C. If the temperature is above 25° C., the color change at the end point seems to be less sharp, owing to the decomposition of the indicator (*9*).
6. The pH should be adjusted from 6.5 to 7.0. A sharper and more reproducible end point is obtained if the pH is held within these limits.
7. The volume of the alcohol-water solution at the beginning of the titration should be 50 ± 1 ml., and the final volume of the solution after it has been titrated should be around 60 ± 4 ml.
8. When hydrogen peroxide is used in the solution to oxidize sulfur dioxide to trioxide, the color at the end point fades much too rapidly for precise work. This fading was observed even when the peroxide had been decomposed by prolonged heating and ordinary chemical tests revealed none present.
9. No fading was observed when bromine was used as the oxidizing agent. The excess was removed by heating the solution.

After this preliminary work was done, the following points seemed to warrant careful investigation:

1. The accuracy of the indicator over a wide range of sulfur concentration.
2. The effect on the indicator correction and accuracy of the titration when the sulfur oxides obtained from burning pure organic compounds were absorbed in 1 per cent potassium hydroxide, and bromine was used as the oxidizer.
3. The accuracy of the titration when an electroprecipitator was used with the absorber. With this apparatus water was used to moisten the absorber and bromine was not added as an oxidizer.

These points were carefully studied, using standardized sulfate solutions and titrating them under controlled conditions and by analyzing organic compounds containing sulfur. The compounds were carefully purified and their purity was checked by analysis for elements other than sulfur. The sulfur obtained from these compounds after the combustion was determined by using the same procedure as that followed in titrating the sulfate solutions. Diphenylthiourea was chosen as the key compound in this study because it could be obtained pure. It also showed a marked tendency to burn rapidly and to form sulfur trioxide mist. An apparatus which could burn this compound successfully would therefore adequately meet the needs of general routine work.

In such an apparatus (*4*), two forms of an absorber were built to collect the sulfur oxides and two procedures were followed in treating the solution washed from the absorber before the final titration with 0.01 *N* barium chloride.

The indicator used in the present study was the disodium salt of tetrahydroxyquinone, dispersed in an organic medium (sold under the trade name of THQ by W. H. and L. D. Betz, Philadelphia, Penna.). The color of the indicator in solution is at first golden yellow and, at the end point, a finely divided deep red precipitate, the barium salt of the indicator, imparts a distinct reddish hue to the solution.

Reagents

Barium chloride, 0.01 *N;* hydrochloric acid, approximately 0.02 *N;* sodium hydroxide, approximately 0.02 *N;* 1 per cent

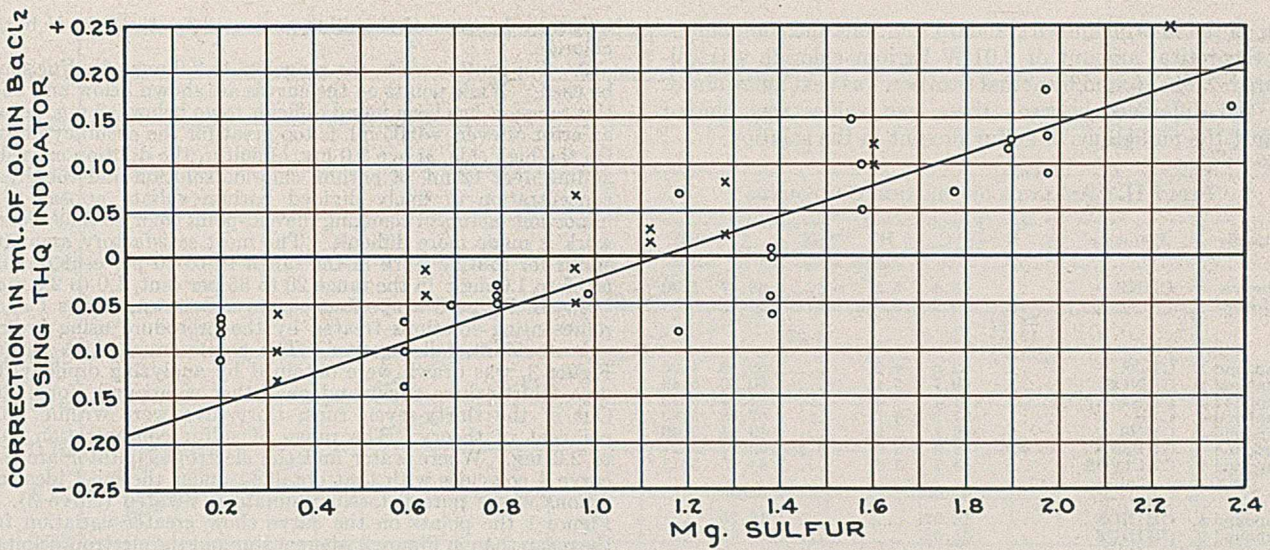


FIGURE 1. DETERMINATION OF SULFUR

×. Standard potassium sulfate solution treated with bromine water
○. Standard sulfuric acid solution treated with bromine water

potassium hydroxide, bromine water; 95 per cent ethyl alcohol; and a solution of equal parts of distilled water and 95 per cent ethyl alcohol.

INDICATORS. Phenolphthalein, methyl orange, and tetrahydroxyquinone indicator.

Procedure

BROMINE USED AS OXIDANT. The absorber is moistened with 1 to 2 ml. of a 1 per cent potassium hydroxide solution. A sample containing approximately 1 mg. of sulfur is burned in oxygen in the combustion tube, and the oxides of sulfur are rinsed from the absorber with 25 to 30 ml. of distilled water. The rinse water is collected through the stopcock at the bottom in a 125-ml. Erlenmeyer flask. The procedure of Sheen and Kahler (*10*) is now essentially followed.

The solution is made acid with 1 *N* hydrochloric acid, using methyl orange as an indicator, and 1 ml. of bromine water is added to oxidize any sulfur dioxide to sulfur trioxide. The solution is evaporated to approximately 20 ml., during which time the bromine is driven off. The solution is cooled, and the pH is adjusted with 0.02 *N* sodium hydroxide and hydrochloric acid until the pink color of the solution (when the solution is basic to phenolphthalein) just disappears (pH = 6.5 to 7.0). The volume of the solution is brought up to 25 ± 1 ml. and 25 ml. of 95 per cent ethyl alcohol are added. The solution is cooled, if necessary, to between 15° and 25° C. A measured scoop (approximately 0.15 gram) of tetrahydroxyquinone indicator is added and the solution is titrated with 0.01 *N* barium chloride. The solution must be constantly shaken as the barium chloride is added. The end point is reached when the color of the solution matches the two layers of No. 21 Wratten filter and persists for at least 3 minutes.

The amount of 0.01 *N* barium chloride required to produce the color which will match two layers of the filter is 0.20 ml., under ideal conditions when no sulfate is present.

NO OXIDANT ADDED (electroprecipitator used with absorber). The absorber is moistened with 1 ml. of distilled water. After the combustion, the absorber is rinsed with 30 to 35 ml. of a solution made by mixing equal volumes of distilled water and 95 per cent ethyl alcohol. The solution is neutralized with potassium hydroxide (approximately 0.1 *N*) until added phenolphthalein indicator turns pink. The pH of the solution is then adjusted with 0.02 *N* hydrochloric acid until the pink color just disappears. The volume of the solution is brought up to 50 ± 1 ml. by adding the alcohol-water mixture. The solution is cooled and titrated as previously described.

The variation in reproducibility of the end point is not over ±0.05 ml. When the sulfur concentration in the solution is below 0.5 mg., the end point is not so reproducible. Royer (*7*) also found that it was difficult to obtain a reproducible stoichiometric end point unless strict conditions were adhered to. Titration of standard sulfate solutions prepared from sulfuric acid gave him different end points, depending upon the base—i. e., ammonium or potassium hydroxide—used to bring it to the neutral point. Different stoichiometric end points were also found, depending upon the volume of titrating solution and the amount of sulfate present. The reproducibility under one set of conditions, however, was found to be as good as ±0.05 ml. when the colored filter (Wratten No. 21) standard was used with the same titration procedure.

TABLE I. ORGANIC COMPOUNDS[a] USED

Sample	Elements	Weight of Sample	Weight of Sulfur, Calcd.	0.01 *N* $BaCl_2$ Corrected from Curve	Sulfur	
					Found	Calcd.
		Mg.	*Mg.*	*Ml.*	%	%
Diphenylthiourea[b]	CHNS	11.086	1.55	9.80	14.17	14.03
		3.180	0.45	2.76	13.91	
		6.630	0.93	5.81	14.05	
		15.134	2.12	13.17	13.95	
Compound 1[c]	CHOS	3.186	0.71	4.43	22.29	22.25
		6.535	1.45	9.03	22.15	
Compound 2	CHNOS	5.604	0.65	4.03	11.53	11.56
		10.688	1.23	7.69	11.53	
Compound 3	CHNS	9.714	0.88	5.54	9.14	9.07
Compound 4	CHS	4.951	1.37	8.58	27.78	27.72
Compound 5	CHOS	5.977	2.28	14.27	38.27	38.13
		2.643	1.07	6.34	38.45	
Compound 6	CHBrNS	12.617	0.92	5.71	7.25	7.28
		22.140	1.61	10.11	7.32	
Compound 7	CHClNOS	10.200	1.01	6.26	9.84	9.94
Compound 8	CHINOS	21.402	0.99	6.14	4.60	4.61
Compound 9	CHINOS	12.884	1.029	6.42	8.07	7.99
		10.026	0.801	4.99	8.06	

[a] The 55 points on the curve shown in Figure 2 are from runs on 12 compounds. Representative figures from some of the runs are shown in this table.
[b] Average of 28 determinations, 14.01; maximum, 14.17; minimum, 13.84; 27 out of 28 are ±0.14 from theory.
[c] Average of 7 determinations, 22.23.

Table I shows the type of organic compounds run and the data from which Figure 2 was drawn. The compounds were considered 100 per cent pure, and, as shown by analysis for other elements (Table II), for the purposes of this study this assumption is justified. Analysis of diphenylthiourea for carbon, hydrogen, and nitrogen showed that this compound, with ordinary care, can be obtained in a high state of purity.

The standard potassium sulfate and sulfuric acid solutions were used as a check on the validity of the curves obtained by analyzing the organic sulfur compounds by the method of combustion.

In all the runs on known standard solutions and compounds, the theoretical amount of 0.01 *N* barium chloride was calculated. That found by actual titration was next determined, and the difference between these two values was plotted against the milligrams of sulfur present in the solution.

Table II. Analysis of Organic Compounds

Sample	Elements	Found N	Found C	Found H	Calcd. N	Calcd. C	Calcd. H
		%	%	%	%	%	%
Diphenylthiourea	CHNS	..	68.4	5.2	...	68.37	5.30
		..	68.4	5.2	...	...	..
		12.3 12.3 12.2	...	...	12.27	...	..
Compound 1	CHOS	..	62.6	4.2	...	62.46	4.20
Compound 2	CHNOS	..	60.7	5.4	...	60.60	5.46
Compound 3	CHNS	..	81.7	5.4	...	81.53	5.42
Compound 4	CHS	..	67.8	4.7	...	67.48	4.80
Compound 5	CHOS	..	49.7	2.5	...	49.95	2.40
Compound 6	CHBrNS	9.6	62.9	5.3	9.5	62.84	5.27
Compound 7	CHClNOS	..	44.7	3.0	...	44.65	3.13
			Iodine			Iodine	
Compound 8	CHINOS	..	18.07	...	...	18.25	..
Compound 9	CHINOS	..	31.52	...	...	31.64	..

Two curves are given with all the points shown. One shows the type of curve obtained when solutions of standard sulfuric acid and potassium sulfate are treated by the procedure outlined, using bromine as the oxidizing agent (Figure 1). The other curve was obtained from the analysis of organic compounds containing sulfur, using the electroprecipitator and water as the absorbent; no bromine was used as an oxidizing agent (Figure 2). The area marked off by the light lines is ±0.05 ml. of 0.01 *N* barium chloride, which is the maximum variation caused by the indicator.

Figure 3 shows these "average correction" curves, together with two others obtained in the same manner, drawn on one graph for comparison.

A study of Table I and of these curves points to the following conclusions:

1. The indicator correction depends upon the amount of sulfur titrated and the treatment of the solution before titrating.
2. The reproducibility of the end point is within ±0.05 ml. of 0.01 *N* barium chloride. Figure 3 shows a curve (No. 3) for pure potassium sulfate. These titrations were carried out under ideal conditions because no foreign ions were present, and no adjustment of pH was necessary. In the twenty-six points from which this curve was drawn, in the range 0.3 to 2.4 mg. of sulfur, two fall outside the area ±0.05 ml. (1.9 mg. of sulfur off the curve 0.08 ml.; 2.2 mg. of sulfur off 0.1 ml.). These two points are at concentrations of sulfur which are more difficult to titrate because of the dilution caused by the 0.01 *N* barium chloride.
3. For routine work, the range 0.5 to 2.0 mg. of sulfur should be used. While points on the curves are shown below and above this range, it has been found difficult to go below 0.5 mg. because an error of even ±0.05 ml. is too great for the accuracy desired. On the high side, above 2.0 mg. of sulfur, the dilution caused by adding over 12 ml. of barium chloride solution and the greater concentration of finely divided barium sulfate appear to be important factors in changing the end-point color, so that accurate work is made more difficult. The most satisfactory amount of sulfur for routine work in the range 15 to 20 per cent of sulfur is 0.5 to 1.0 mg.; in the range 20 to 35 per cent, 1.0 to 2.0 mg.
4. In Figure 3 where four curves are shown, curves 1 and 2, representing solutions treated by the procedure using bromine as an oxidant, fall together. The points from which curve 1, Figure 3, was drawn were obtained by analyzing diphenylthiourea (thirty-three runs) and one other compound (four runs). Out of the thirty-seven runs, thirty-five were within ±0.25 per cent of theory. The range of sulfur concentration is 0.5 to 2.2 mg. Where water and the electroprecipitator are used, curve 4 coincides with that obtained under the most ideal conditions where pure potassium sulfate is titrated (curve 3). In Figure 1 the points on the curve show greater variation from the mean than in Figure 2 where water and the electroprecipitator method are used. Where the solutions are evaporated to remove bromine, there is some chance of mechanical loss during this operation.
5. This study shows that when bromine is used as the oxidizing agent, to determine sulfur in organic compounds by the method of combustion, the maximum variation in precision from the average 13.97 per cent is +0.29 to −0.17. In accuracy, the maximum variation is +0.23 to −0.29 from the theoretical 14.03 per cent. The values were obtained by two operators. This would indicate that, with a well-trained operator, the average accuracy and precision would be ±0.25 per cent.

When the electroprecipitator and water as an absorbent are used, the maximum variation in precision is +0.15 to −0.18 from the average 14.02; in accuracy, +0.15 to −0.19 from 14.03. The values were obtained by three operators. The range of sulfur concentration in these determinations was 0.5 to 2.0 mg. Taking into consideration the runs made on other compounds, the average accuracy and precision of the method appear to be ±0.15 when the percentage of sulfur is 14.

If a sample weight is chosen with respect to the percentage of sulfur present, this accuracy can be obtained over the range 5 to 35 per cent sulfur.

Table I also shows results obtained with a variety of compounds and combinations of elements including halogens. Iodine in the compound causes excessive mist formation when the electroprecipitator is used, possibly owing to the combination of iodine and ozone. Results for sulfur, however, do not seem to be adversely affected, since the twin precipitators do not allow any mist to escape.

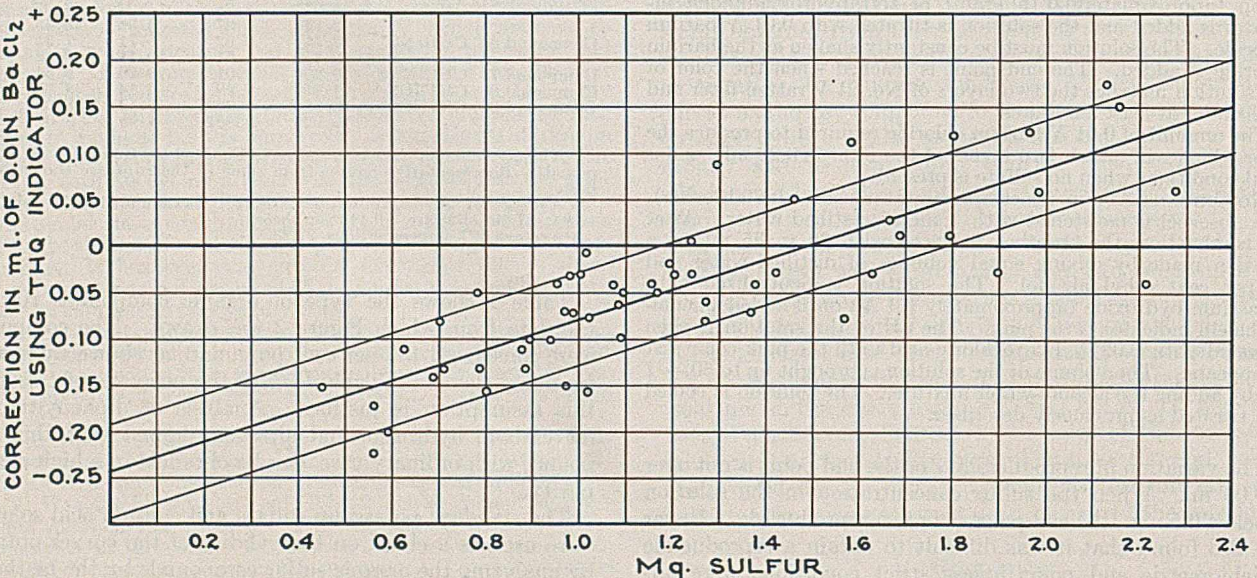


Figure 2. Determination of Sulfur

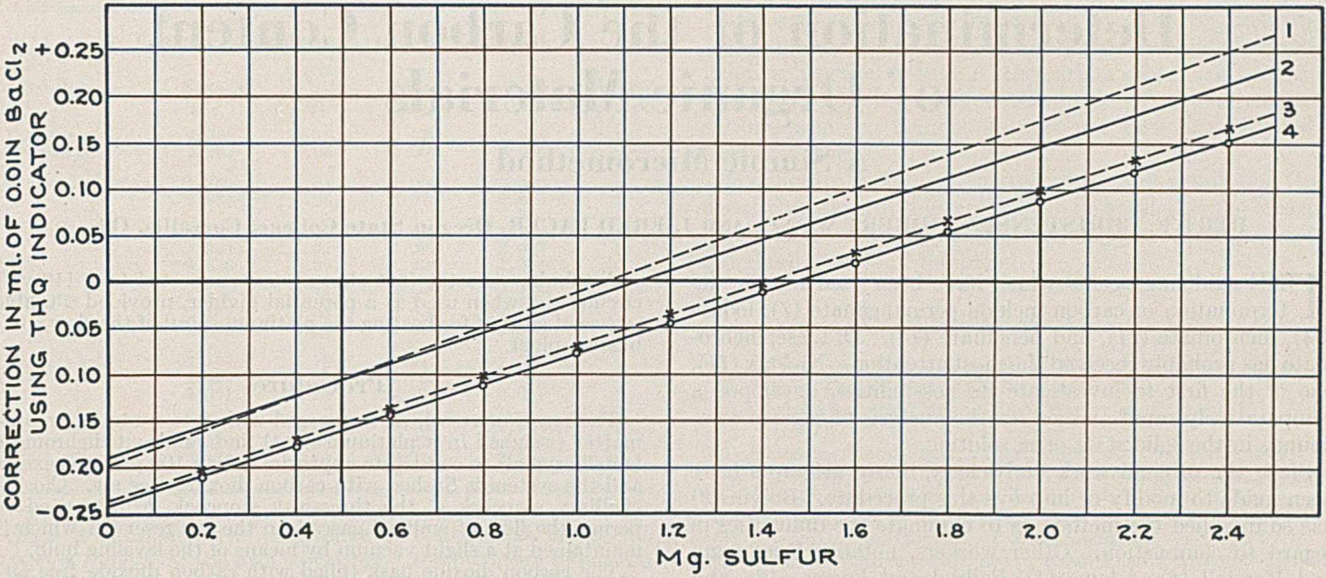


FIGURE 3. AVERAGE CORRECTION CURVES

1. Sulfur in organic compounds, bromine water used as oxidizing agent
2. Standard sulfuric acid treated by same procedure as in curve 1
3. Standard potassium sulfate solution, direct titration, no oxidizing treatment
4. Sulfur in organic compounds, using electroprecipitator

An oxidizing agent is not required when the electroprecipitator is used. The formation of ozone by the precipitator provides an oxidizing atmosphere. Low results are always obtained if the precipitator is turned off during a run.

The average time per determination for a series of twelve to fourteen runs, including calculating and weighing, is 30 to 35 minutes. This speed is possible only when an automatic combustion furnace is used, in which case the work is so coordinated that titrating, weighing, and calculating are carried out while the sample is burning. It has been found that the time of the 30-minute schedule should not be decreased if the operator is to perform consistent work day after day. This also holds true for other determinations.

Both methods normally require about the same burning schedule—15 minutes for burning and 5 minutes for sweeping, a total of 20 minutes. However, when the apparatus (4, Figure 1) is used, compounds are sometimes encountered which require slower burning to prevent mist formation. This, coupled with the fact that because an electroprecipitator is not used, bromine must be used as an oxidizer and time must be allowed to remove it by heating the solution, will increase the average time per determination by about 20 per cent.

It is hoped that others will use this method and check the findings of this study, especially in regard to the indicator correction. The indicator color change is sufficiently sharp and reproducible when the color filter is used as a standard for comparison.

The indicator correction is an empirical one, and the change of correction with increasing amounts of sulfur is difficult to explain logically. The amount of 0.01 N barium chloride which must be added to obtain the correct color at the end point is about 0.20 ml. In the range 0.5 to 2.0 mg. of sulfur, this amount is not subtracted and, in the higher concentrations, the titer is below that required. While the presence of finely divided barium sulfate does, no doubt, influence the color, its presence cannot wholly account for the behavior of the indicator.

In the hands of four operators in the microanalytical laboratory, over a period of 2 years, results have been obtained which compare favorably with the gravimetric procedure. The method, using the electroprecipitator, is now being applied for regular routine work in analyzing all types of organic compounds.

Summary

The conditions under which tetrahydroxyquinone may be used as an indicator in the determination of sulfur, using 0.01 N barium chloride, are described. Two procedures, together with correction curves for the indicator, are given; the one using bromine as the oxidizer of sulfur dioxide to sulfur trioxide is less rapid and accurate than the other. The accuracy and precision in analyzing a sample containing 14 per cent from theory vary ±0.25 per cent, where the amount of sulfur determined is 0.5 to 2.0 mg. The other method, using an electroprecipitator before and after the absorber, does not require the addition of an oxidizer. This method is better for routine work because the sulfur as sulfuric acid may be washed from the receiver and titrated directly. The precision and accuracy in analyzing a sample containing 14 per cent sulfur vary ±0.15 per cent from theory.

Literature Cited

(1) Ampt, G. A., *Australian Chem. Inst. J. & Proc.*, 2, 10 (1935).
(2) Friedrich, A., and Mandl, F., *Mikrochemie*, 22, 14–33 (1937).
(3) Gibson, D. T., and Caulfield, T. H., *Analyst*, 60, 522 (1935).
(4) Hallett, L. T., and Kuipers, J. W., IND. ENG. CHEM., Anal. Ed., 12, 357 (1940).
(5) Manov, G. G., and Kirk, P. L., *Ibid.*, 9, 198 (1937).
(6) Peabody, W. A., and Fisher, R. S., *Ibid.*, 10, 651 (1938).
(7) Royer, G. L., Calco Chemical Co., Bound Brook, N. J., private communication, 1938.
(8) Schroeder, W. C., IND. ENG. CHEM., Anal. Ed., 5, 403–6 (1933).
(9) Sheen, R. T., and Kahler, H. L., *Ibid.*, 8, 127 (1936).
(10) *Ibid.*, 10, 206 (1938).
(11) Sheen, R. T., Kahler, H. L., and Cline, D. C., *Ibid.*, 9, 69 (1937).
(12) ter Meulen, H., *Rec. trav. chim.*, 41, 112 (1922).
(13) Wilson, C. W., and Kemper, W. A., IND. ENG. CHEM., Anal. Ed., 10, 418 (1938).

PRESENTED before the Microchemical Section at the 96th Meeting of the American Chemical Society, Milwaukee, Wis. Communication No. 753 from the Kodak Research Laboratories.

Determination of the Carbon Content of Organic Materials

A Simple Micromethod

BERT E. CHRISTENSEN, ROBERT WONG, AND J. FRED FACER, Oregon State College, Corvallis, Ore.

THE oxidizing agents which have been used for the determination of carbon include permanganate (*7*), iodate (*14*), dichromate (*11*), and persulfate (*13*). Of these, dichromate has probably received the most attention. Nicloux (*11*), one of the first to investigate its possibilities, developed a comparatively rapid method for the analysis of organic compounds in the solid state or in solution.

Since the original work of Nicloux, many attempts have been made to modify or improve this procedure. Boivin (*2*) has so modified the method as to eliminate the difficulties in regard to combustion. Other workers, notably Friedmann and Kendall (*8*), Adams (*1*), Pollard and Forsee (*12*), and Kirk and Williams (*9*), have attempted to improve the method through the design of more suitable apparatus and methods for measuring carbon dioxide.

Both gravimetric and volumetric methods have been used to determine the carbon dioxide. Because of the nature of the gases (or vapors) evolved from the reaction mixture, a volumetric procedure is probably the more suitable of the two. The Pettenkofer (*10*) method, one of the simplest methods for the measurements of carbon dioxide, has received little attention in connection with this procedure (*4*); for this reason an apparatus which embodies the Pettenkofer principle has been devised, making it possible to decrease the time and operative skill required for this analysis.

Apparatus

The apparatus is illustrated diagrammatically in Figure 1. The reaction vessel, *A* (total volume 6 ml.), was constructed from a No. 11 standard taper joint and a capillary stopcock. The pressure-regulating unit, *C*, consisted of a three-way stopcock, a gas reservoir, and a leveling bulb. Mercury was used as a confining fluid. Complete combustion was ensured by means of the slow combustion pipet, *D* (*3*).

The train was equipped with two U-tubes, *B* and *E*, which served to control the rate of gas flow. The absorption flask, *F*, for the analysis of the carbon dioxide was designed from a 250-ml. Erlenmeyer flask, No. 20 standard taper joint, and a capillary stopcock.

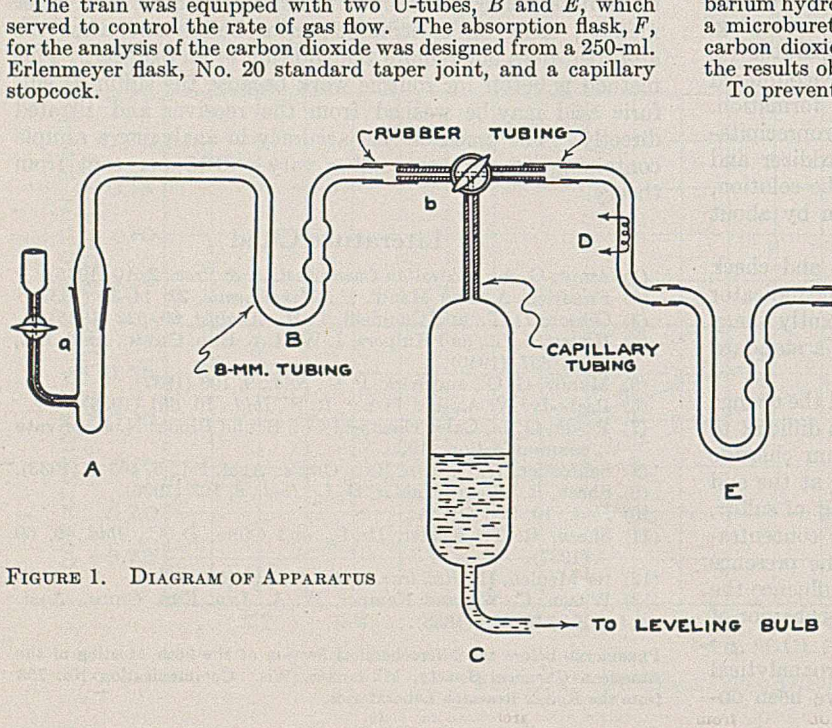


FIGURE 1. DIAGRAM OF APPARATUS

A tubular rheostat (not shown) was connected to a 110-volt circuit, and when used as a potential divider, provided a usable source of current for heating the platinum spiral of the slow combustion pipet.

Procedure

The reaction vessel, *A*, is charged with 2 to 5 mg. of organic matter (weighed in a platinum boat) and sufficient dichromate (small crystal) to constitute approximately a 100 per cent excess and the system is flushed with carbon dioxide–free air. Closing capillary stopcock *a*, the three-way stopcock, *b*, is opened to permit the flow of emitted gases into the gas reservoir which is maintained at a slight vacuum by means of the leveling bulb.

The carbon dioxide flask (filled with carbon dioxide–free air) is then charged with 5 ml. of standard 0.1 *N* barium hydroxide (measured with an automatic pipet), partially evacuated, and then connected to the other arm of U-tube *E*. One milliliter of concentrated (carbon-free) sulfuric acid is introduced into the reaction vessel by means of stopcock *a*. The charge is now ready for combustion.

Stopcock *a* and the standard taper joint of *A* are lubricated with concentrated sulfuric acid.

By means of an electrically heated phosphoric acid bath (*5*) the temperature of the reaction chamber is kept between 165° and 185° C. for 20 to 30 minutes. The gases which are generated during this time pass through *B*, containing 1 ml. of 50 per cent sulfuric acid solution, to the gas reservoir, *F*. At the completion of the heating operation, the charge is cooled, and 2 ml. of water are introduced into the reaction chamber through *a*. An Ascarite tower is then connected to the apparatus and sufficient carbon dioxide–free air is flushed through to sweep all the carbon dioxide into the gas reservoir. The platinum coil of the slow combustion pipet is brought to a fairly red heat. The gases are then slowly passed through U-tube *E* (charged with 1 to 2 ml. of acidified permanganate solution) to the evacuated flask, *F*. Absorption flask *F* is directly connected through stopcocks *a* and *b* to a source of carbon dioxide–free air, brought to atmospheric pressure, then removed and allowed to stand for 20 minutes (to ensure complete absorption of carbon dioxide). Five milliliters of acetone to improve the end point are introduced and the excess barium hydroxide is titrated with 0.05 *N* hydrochloric acid (using a microburet) to the thymol blue end point. The amount of carbon dioxide produced can be calculated from these data and the results obtained from the blank run.

To prevent diffusion of air into the flask during the titration, a rubber sheet (such as used for a dental dam) was loosely fitted over the mouth of the flask. The tip of the buret was inserted through a small hole in the rubber. This arrangement kept out all the air without complicating the procedure.

The hydrochloric acid used for this determination was standardized with the carbon dioxide evolved from the combustion of succinic acid by the above procedure. The normality of the acid obtained in this manner was 0.0553, and by iodate standard it was 0.0555.

Discussion and Result

From the results in Table I, it is apparent that this method for the determination of carbon dioxide compares favorably with that of Boivin and of Kirk and Williams.

TABLE I. DETERMINATION OF CARBON

Substance	Sample *Mg.*	0.0553 *N* HCl *Ml.*	C Found *Mg.*	C Calcd. *Mg.*	Error *P. p. 1000*
Potassium acid phthalate	4.366	6.18	2.050	2.054	2
	4.262	6.05	2.001	2.005	2
Cinnamic acid	2.754	6.01	1.994	2.006	6
	2.884	6.25	2.074	2.072	1
Succinic acid	4.838	5.93	1.963	1.963	..
	4.924	6.02	1.997	2.003	3
	4.830	5.89	1.955	1.964	5
Vanillin	3.939	7.46	2.477	2.487	5
	3.169	6.03	2.001	2.001	..
	2.876	5.45	1.815	1.808	4
Benzoic acid	2.768	5.78	1.913	1.905	4
	2.574	5.37	1.782	1.771	6
	3.047	6.34	2.104	2.097	4
Sucrose	5.205	6.60	2.190	2.192	1
	4.935	6.25	2.077	2.078	1
	5.474	6.81	2.260	2.305	22

Since it eliminates the possibility of contamination by the carbon dioxide of the atmosphere and the filtration of barium carbonate, it is less complicated and requires considerably less time.

Most carbon hydrogen and oxygen compounds can be oxidized with dichromate (*1*, *2*, *6*, *8*, *9*, *12*).

Nitrogen-containing compounds (*6*) such as acetanilide, pyridine, nicotinic acid, and leucine are quantitatively oxidized under the conditions here specified, the nitrogen remaining as ammonium sulfate. Ammonia is not oxidized even at temperatures as high as 200° C.

Halogen compounds are readily oxidized by dichromate (*15*). By slightly modifying the directions (using potassium iodide solution in U-tube *B*) the carbon content of these compounds should be easily determined. The combustion of sulfur-containing compounds has not been investigated in this laboratory.

By slightly modifying the technique and conditions (to fit the circumstances) this method can be applied to the measurement of the carbon content of physiological fluids, soils, and the alkali reserve of the blood.

Literature Cited

(1) Adams, IND. ENG. CHEM., Anal. Ed., 6, 277 (1934).
(2) Boivin, *Compt. rend.*, 187, 1076–9 (1928).
(3) Christensen and Carlton, IND. ENG. CHEM., Anal. Ed., 9, 400 (1937).
(4) Christensen and Facer, *J. Am. Chem. Soc.*, 61, 3001 (1939).
(5) Christensen and King, IND. ENG. CHEM., Anal. Ed., 8, 194 (1936).
(6) Christensen, Williams, and King, *Ibid.*, 9, 59, 293 (1937).
(7) De Nardo, *Giorn. chim. ind. applicata*, 10, 253–5 (1928).
(8) Friedmann and Kendall, *J. Biol. Chem.*, 82, 45–55 (1922).
(9) Kirk and Williams, IND. ENG. CHEM., Anal. Ed., 4, 403–4 (1932).
(10) Lunge and Ambler, "Technical Gas Analysis", p. 221, London, Gwiney and Jackson, 1934.
(11) Nicloux, *Compt. rend.*, 184, 890–1 (1927).
(12) Pollard and Forsee, IND. ENG. CHEM., Anal. Ed., 7, 77 (1935).
(13) Rischbieth, *Z. physik. chem. Unterricht*, 43, 132–4 (1930).
(14) Stanek and Nemes, *Z. anal. Chem.*, 95, 244 (1933).
(15) Zacherl and Krainick, *Mikrochemie*, 11, 61 (1932).

PUBLISHED with the approval of the Monographs Publication Committee, Oregon State College. Research Paper No. 31, School of Science, Department of Chemistry.

Determination of Iron in Liquid Food Products

H. L. ROBERTS, C. L. BEARDSLEY, AND L. V. TAYLOR, JR., American Can Company, Maywood, Ill.

THE importance of the determination of iron in foods and other biological material is reflected in the number of methods for estimation of the metal reported in the literature during recent years (*2–6*). Some of these methods, such as those of Stugart (*6*) and Jackson (*4*), have been proposed for determination of iron in all biological materials. Other methods (*2*, *3*, *5*) are reported as adaptable to specific food products or groups of food products.

The choice of a precedure for estimation of iron is properly a matter for individual determination by the particular laboratory concerned. Besides the usual requirement that the method be reliable within the range of iron content of the materials being analyzed, other factors often govern the type of procedure to be used. Thus the iron method selected must frequently not only be rapid, but also adaptable to the type and amount of material available for analysis. In addition, the procedure must often be capable of execution with existing laboratory facilities and be of such a nature as not to interfere with other work of the laboratory. It is therefore not surprising that available procedures for the quantitative estimation of iron in foods may not always satisfy the above imposed requirements.

The Stugart procedure, which is a colorimetric method using potassium thiocyanate and the principle of dry-ashing, had been used with considerable success in this laboratory. However, because of a program which required the rapid handling of a large number of samples, and because of limited dry-ashing facilities, this procedure was not found applicable to existing laboratory conditions. In addition, the amount of material available for analysis was frequently small. Consequently, the method described herein, which incorporates the basic principles of the Stugart procedure, was developed. This method differs from the Stugart procedure in that a sample of approximately 10 grams is employed; a wet-ashing procedure which is more rapid than dry-ashing is used; and the procedure for hydrolysis of pyrophosphates is eliminated. Although special microdigestion equipment is required for ashing, the procedure as outlined has been found to combine accuracy with speed and is not subject to interference by other metals and compounds in the amounts in which they normally occur in liquid foods.

The present procedure has been applied only to fluid products which can be readily mixed so as to obtain a homogeneous sample. The method has given good results with products such as citrus juices, grape juice, tomato juice, coffee, beer, and ginger ale. With slight modification, it can also be applied to liquid products relatively high in carbohydrate and protein, such as milk.

Preparation of Standard Iron Solutions

A stock iron solution is prepared by dissolving exactly 0.5000 gram of pure iron wire in 20 ml. of 25 per cent sulfuric acid. Solution of the wire is facilitated by the addition of 6 ml. of concentrated nitric acid. After the wire has completely dissolved the resulting solution is evaporated to white fumes, cooled, transferred quantitatively to a volumetric flask, and diluted to 100 ml. From this stock solution, working standards containing 0.01 and 0.02 mg. of iron per 10 ml. of solution are prepared. Sulfuric acid should be added to the latter standard solutions so that they will contain 150 ml. of concentrated sulfuric acid per liter. These working standards are transferred by pipet to separatory funnels, diluted to volume, and handled in the same manner as the unknown sample.

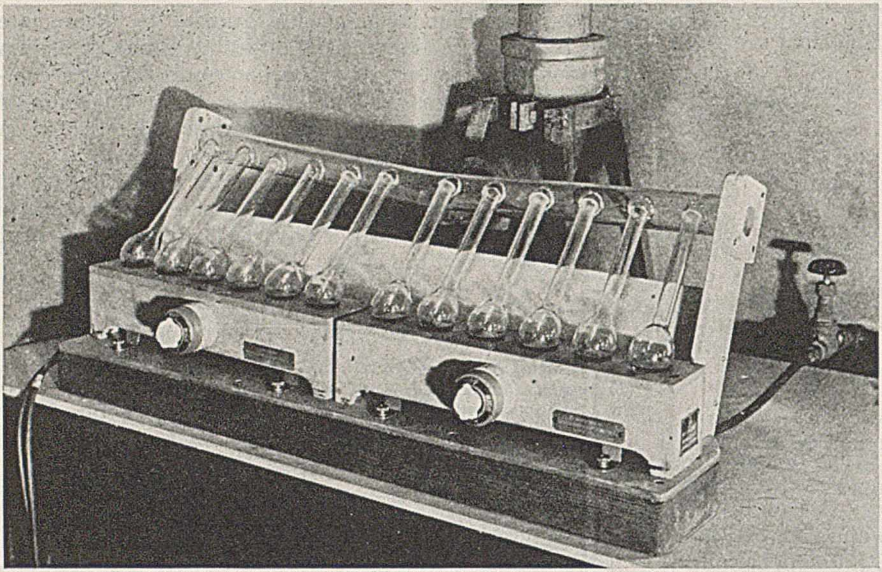


FIGURE 1. ARRANGEMENT OF ASHING EQUIPMENT

TABLE I. IRON RECOVERIES FROM FOOD PRODUCTS

Food Product	Fe Added		Fe Recovered		Recovery
	P. p. m.	*Micrograms*	*P. p. m.*	*Micrograms*	%
Beer	None	..	0.83	8.3	...
	0.20	2.0	1.04	10.4	101
	0.50	5.0	1.32	13.2	99
	0.70	7.0	1.51	15.1	99
	1.00	10.0	1.86	18.6	101
Brewed coffee	None	..	0.21	2.1	...
	0.20	2.0	0.42	4.2	101
	0.40	4.0	0.61	6.1	100
	0.60	6.0	0.77	7.7	95
	0.80	8.0	1.00	10.0	99
	1.00	10.0	1.21	12.1	100
Milk	None	..	0.43	4.3	...
	0.20	2.0	0.65	6.5	102
	0.40	4.0	0.84	8.4	100
	0.60	6.0	1.04	10.4	101
	0.80	8.0	1.24	12.4	101
	1.00	10.0	1.46	14.6	101
Tomato juice	None	..	5.08	25.4	...
	1.00	5.0	6.10	30.5	100
	2.00	10.0	7.08	35.4	100
	3.00	15.0	8.02	40.1	99
	4.00	20.0	9.00	45.0	99
	5.00	25.0	9.96	49.8	99
Pineapple juice	None	..	4.26	21.3	...
	1.00	5.0	5.27	26.4	102
	2.00	10.0	6.18	30.9	96
	3.00	15.0	7.25	36.3	100
	3.00	15.0	7.47	37.4	107
	4.00	20.0	8.28	41.4	100
Grapefruit juice	None	..	2.54	12.7	...
	0.50	2.5	3.06	15.3	104
	1.00	5.0	3.54	17.7	100
	1.50	7.5	4.04	20.2	100
	2.00	10.0	4.46	22.3	96
	2.50	12.5	5.02	25.1	99
Lemon juice	None	..	1.41	7.1	...
	0.50	2.5	1.92	9.6	100
	0.75	3.8	2.18	10.9	100
	1.00	5.0	2.32	11.6	90
	1.50	7.5	2.84	14.2	95
	2.00	10.0	3.14	15.7	86

Procedure

ASHING. Approximately 10 grams of the sample—or an amount estimated to contain not more than 40 micrograms of iron—are weighed differentially into a 30-ml. micro-Kjeldahl flask containing a glass bead and evaporated almost to dryness on the electric digestion microheater (Laboratory Construction Co., micro electric heater No. 2250). Construction of a fume tube for this equipment has been described by Blair (*1*), and Figure 1 shows the details of arrangement.

The digestion rack consists of a frame on which a fume tube is mounted in such a manner that the flasks when placed on the heater and supported by the fume tube will rest at an angle of about 45°. It is important that the neck of the flask barely enter the fume tube. By such an arrangement approximately one half of the flask opening is exposed and thus introduction of reagents into the flask during ashing is permitted. The escape of fumes into the room is prevented by application of compressed air to the aspirator connected with the fume tube.

If frothing occurs during evaporation, 2 drops of caprylic alcohol may be added. The glass bead should remain in the flask during both evaporation and digestion. After dehydration, 1 ml. of concentrated nitric acid is added and the flask is heated gently, either on the warm heater or over a gas burner, to start reaction. After the initial violent reaction has subsided, 2 ml. of concentrated sulfuric acid are added and digestion is begun. As the digestion proceeds, 3- to 4-drop increments of concentrated nitric acid are added to ensure an excess of this acid for complete oxidation of all organic material, as evidenced by production of a clear or straw-colored solution after digestion. The increments are conveniently added by use of a special buret shown in Figure 2, and usually a total of about 4 ml. of nitric acid is required.

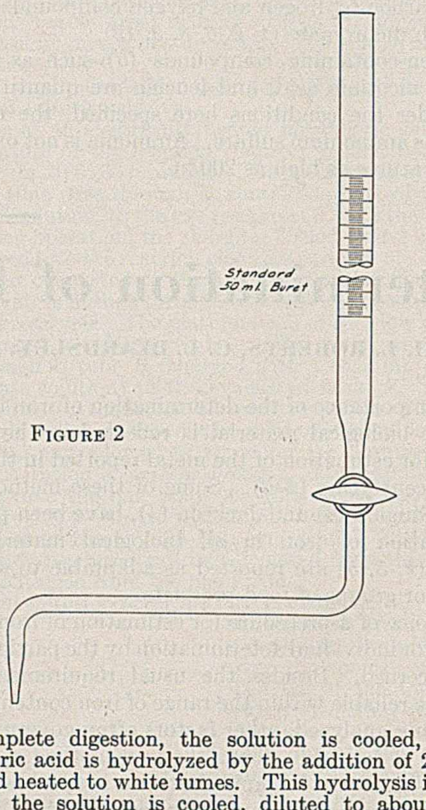


FIGURE 2

After complete digestion, the solution is cooled, and the nitrosylsulfuric acid is hydrolyzed by the addition of 2 to 3 ml. of water, and heated to white fumes. This hydrolysis is then repeated, and the solution is cooled, diluted to about 20 ml., thoroughly cooled again, and finally transferred with washings to a 125-ml. separatory funnel.

For beer and ale, the above ashing procedure is used, except that the initial addition of nitric acid is 3 ml. For milk, 1 ml. of nitric acid is added prior to dehydration. The flask should be gently heated and tapped during the dehydration procedure, removed from the burner when frothing occurs, and cooled. Two milliliters of sulfuric acid are then added and the ashing is completed as described above. Nitrosylsulfuric acid cannot be removed by the usual hydrolysis procedure; the calcium of the milk precipitates as the sulfate in the diluted solution, causing superheating with possible explosions. A drop by drop addition of 1 ml. of Superoxol (30 per cent hydrogen peroxide) to the warm concentrated sulfuric acid solution, however, will completely decompose the nitrosylsulfuric acid and from that point on the procedure outlined above may be followed.

EXTRACTION OF IRON AND COLORIMETRIC COMPARISON. To the sample in the separatory funnel, diluted to 95 ml. with cold water, one drop of approximately 0.10 *N* potassium permanga-

TABLE II. IRON RECOVERIES IN THE PRESENCE OF OTHER METALS

	Element Added	Iron Added	Iron Recovered	Deviation	Recovery
	Micrograms	*Micrograms*	*Micrograms*	*Micrograms*	%
Tin	5.0	5.0	5.0	0	100
	5.0	5.0	5.0	0	100
	50.0	5.0	5.0	0	100
	50.0	5.0	5.0	0	100
	500.0	5.0	5.1	+0.1	102
	500.0	5.0	5.0	0	100
Aluminum	5.0	5.0	5.0	0	100
	5.0	5.0	5.1	+0.1	102
	10.0	13.3	13.0	−0.3	98
	50.0	5.0	5.2	+0.2	104
	50.0	5.0	5.0	0	100
	50.0	11.4	11.9	+0.5	104
	100.0	11.4	11.7	+0.3	102
Lead	5.0	5.0	5.2	+0.2	104
	5.0	5.0	5.0	0	100
	5.0	5.0	5.0	0	100
	5.0	5.0	4.9	−0.1	98
	50.0	5.0	5.1	+0.1	102
	50.0	5.0	5.1	+0.1	102
	50.0	5.0	4.8	−0.2	96
Zinc	10.0	26.3	25.0	−1.3	95
	50.0	8.2	7.9	−0.3	96
	100.0	8.8	8.5	−0.3	97
	100.0	5.1	5.6	+0.5	110
	100.0	5.2	5.8	+0.6	112
	100.0	5.5	5.3	−0.2	96
	100.0	5.2	5.6	+0.4	108
	100.0	13.7	14.1	+0.4	103
	100.0	15.0	14.6	−0.4	97
	100.0	14.0	14.7	+0.7	105
Nickel	500.0	5.0	5.1	+0.1	102
	500.0	5.0	5.0	0	100
Copper	2.0	6.5	6.5	0	100
	2.0	13.5	14.1	+0.6	104
	5.0	4.4	4.3	−0.1	98
	5.0	13.5	14.0	+0.5	104
	20.0	13.5	13.0	−0.5	96
	20.0	13.5	13.3	−0.2	98
	40.0	13.5	13.1	−0.4	97
	40.0	13.5	13.0	−0.5	96
Calcium	100.0	7.2	7.8	+0.6	108
Sodium pyrophosphate	100.0	7.2	7.7	+0.5	107
	100.0	7.2	7.2	0	100
	100.0	7.2	7.6	+0.4	106
	1000.0	20.0	20.0	0	100
	1000.0	20.0	19.8	−0.2	99
	1000.0	20.0	20.0	0	100
Calcium 10,000 and phosphorus 10,000 as pyrophosphate		9.7[a]	10.3	+0.6	106
		9.7[a]	10.3	+0.6	106

[a] Iron added as ferric pyrophosphate.

nate is added, the solution is mixed, and 10 ml. of isoamyl alcohol are then accurately added, followed by the addition of 5 ml. of 20 per cent potassium thiocyanate solution. The funnel is shaken vigorously for 30 seconds, the mixture allowed to separate, and the water layer drawn off. A suitable portion of the alcohol layer is drawn into a colorimeter cup, care being taken to exclude any droplets of water, and comparison is made with the standard.

Iron Recoveries from Food Products

In Table I are listed the percentage recoveries of iron from various fresh or bottled liquid food products to which the method has been applied. The iron was added before ashing.

IN THE PRESENCE OF OTHER METALS. The possible interference of metals which may be present in foods has been studied by their addition to pure iron solutions. In this manner, zinc, copper, aluminum, tin, and even the less common metal, lead, in amounts greater than are usually found in foods have been found to be without interference. Likewise, calcium and phosphorus are apparently without effect upon the accuracy of the method.

Effect of Acid Concentration on Development of Ferric Thiocyanate Color

In order to compare the intensity of color developed in solutions which have been acidified with hydrochloric acid with those acidified with sulfuric acid, a study of this relationship was made. A neutral standard iron solution was acidified with varying concentrations of the acids in question and the color developed and compared with the standard in the usual manner.

It was found that the weakest acid solution used developed the most color and, conversely, the stronger acid solution developed the less intense color. For a given molarity of acid during the extraction with isoamyl alcohol, sulfuric acid produced a more intense color than hydrochloric acid.

The intensity of color of a standard made according to the Stugart method (3 ml. of hydrochloric acid) compares favorably with that of a standard made as previously described (1.5 ml. of sulfuric acid). This latter concentration was arrived at by assuming a loss of 0.5 ml. of sulfuric acid during the ashing procedure.

Comparison of Hydrochloric Acid and Wet-Ashing Hydrolysis

The Stugart method (6) makes use of a hydrochloric acid hydrolysis to break down any pyrophosphate present in the solution. In order to compare the effectiveness of the wet-ashing procedure for hydrolyzing pyrophosphates with the Stugart method, triplicate samples of ferric pyrophosphate were analyzed by both methods.

Table III shows the results of this test. The data listed indicate that the wet-ashing hydrolysis employed is as effective in hydrolyzing pyrophosphate as the hydrochloric acid procedure specified in the Stugart method.

TABLE III. IRON RECOVERED BY HYDROCHLORIC AND SULFURIC ACID HYDROLYSIS

Hydrochloric Acid Hydrolysis	Wet-Ashing	No Hydrolysis
Micrograms	*Micrograms*	*Micrograms*
11.2	11.3	9.8
10.4	10.5	9.7
11.6	11.7	9.9
Av. 11.1	11.2	9.8

TABLE IV. IRON CONTENT OF LIQUID FOOD PRODUCTS

Fruit Juice	Number of Samples	Maximum	Minimum	Average
		P. p. m.	*P. p. m.*	*P. p. m.*
Orange juice (fresh)	4	10.7	1.2	1.5[a]
Lemon juice (fresh)	2	1.7	1.4	1.6
Grapefruit juice (fresh)	4	2.5	1.0	2.0
Pineapple juice (bottled)	1	..	..	4.2
Apple juice (bottled)	2	10.7	5.7	8.2
Grape juice (bottled)	4	3.1	1.6	2.0
Tomato juice (fresh)	6	33.0	5.1	6.4[a]
Prune juice (bottled)	1	..	..	55.0
Cider (hard) (bottled)	1	..	..	1.0
Cherry juice (canned)	1	..	..	9.0
Miscellaneous				
Brewed coffee (fresh)	3	0.30	0.15	0.21
Whole milk (bottled)	2	..	..	0.42
Beer (bottled)	8	0.22	0.07	0.15
Ale (bottled)	2	0.40	0.30	0.35
English beer (canned)	2	5.0	1.7	3.4
English ale (canned)	4	4.2	0.37	1.4
Evaporated milk (canned)	26	2.0	1.0	1.5
Ginger ale (bottled)	7	0.50	0.30	0.40

[a] Maximum value omitted in average.

Acknowledgment

The authors wish to acknowledge the helpful criticisms and suggestions furnished by Miss Mignon Gill and R. H. Lueck of this department.

Literature Cited

(1) Blair, J. S., IND. ENG. CHEM., Anal. Ed., 10, 112 (1938).
(2) Byrne, J., Saywell, L. G., and Cruess, W. V., *Ibid.*, 9, 83 (1937).
(3) Gray, P. P., and Stone, I. M., *Ibid.*, 10, 415 (1938).
(4) Jackson, S. H., *Ibid.*, 10, 302 (1938).
(5) Saywell, L. G., and Cunningham, B. B., *Ibid.*, 9, 67 (1937).
(6) Stugart, R., *Ibid.*, 3, 390 (1931).

A Color Test for Elementary Sulfur

In Pyridine and Other Solvents

HERMANN SOMMER, George Williams Hooper Foundation, University of California, San Francisco, Calif.

Pyridine is an excellent solvent for crystalline and amorphous sulfur. On addition of a small amount of aqueous alkali to a solution of sulfur in pyridine, colors are obtained which allow a roughly quantitative estimation of the amount of sulfur present. As little as 2 micrograms in 1 cc. may be detected by a light blue color.

IN WORKING with alkaline pyridine solutions a blue-green coloration was accidentally observed which could be traced to contamination of the solvent by elementary sulfur from the rubber stopper. From this observation the following color reaction for sulfur was worked out. To the knowledge of the author there is, at present, no simple test for elementary sulfur.

A subsequent search of the literature revealed that a similar although less sensitive test had been proposed many years ago.

In 1894 Gil (*4*) discovered the blue color produced by polysulfides in boiling alcohol. Orloff (*6*) mentioned acetone as solvent in the Gil reaction. The limit of sensitivity as given by Gil is 430 micrograms of sulfur per 50 cc. of alcohol. Another type of color test was described by Schoenberg (*11*), who used benzylimido-(*p*-methoxyphenyl)-methane to detect free sulfur in minimum amounts of 40 micrograms. In the test of Zmaczynski (*14*) iron sulfide is formed in glycerol in the presence of levulose. Like all tests with heavy metals, such as plumbate or mercuric chloride, this reaction is not particularly sensitive for free sulfur—i. e., of the order of 100 micrograms per cc. [In connection with these studies, however, it was found that in the presence of pyridine as little as 10 micrograms per cc. of free sulfur give a visible reaction with doctor solution (sodium plumbate)]. With regard to Thornton and Latta's test for free sulfur in petroleum distillates (*12*) using cottonseed oil, carbon disulfide, and pyridine, it is interesting to note that pyridine is essential for the production of this color also, a fact which Gastalt (*3*) pointed out, in improving the original Halphen reaction (*5*) for cottonseed oil.

Solubility of Sulfur in Pyridine

That pyridine is an excellent solvent for sulfur does not seem to be generally known, although Raffo and co-workers (*8*, *9*) made use of the affinity of pyridine for free and organically bound sulfur. In an approximate solubility determination 100 cc. of pyridine were found to dissolve 1.13 grams of sulfur at room temperature (approximately 20° C.). At the boiling point (115° C.) 4 cc. of the solvent will readily dissolve 1 gram of sulfur. Pyridine has the advantage over carbon disulfide and other solvents that it also dissolves the amorphous modification. On cooling, the sulfur is deposited in crystalline form, entirely soluble in carbon disulfide or toluene. By means of pyridine, amorphous sulfur may thus readily be transformed into the crystalline forms. On slow cooling large crystals may be obtained.

Procedure

The pyridine should be water-clear and remain so on boiling with strong alkali. It should be kept in a glass-stoppered bottle; samples which give a discoloration with alkali are likely to have been contaminated by sulfur. Small amounts of water or ammonia do not interfere in the qualitative test, but must be removed for more accurate work. The sulfur used was prepared from sodium thiosulfate and hydrochloric acid.

The material to be tested for elementary sulfur is extracted with hot pyridine and the solution is filtered if necessary. One-tenth volume of 2 *N* sodium hydroxide is added to the filtrate and after brief shaking at room temperature the color of the pyridine layer is noted immediately.

As indicated in Table I, the presence and approximate amount of sulfur are demonstrated by a blue, green, olive-brown, or brown-red color. With sodium carbonate or sodium bicarbonate instead of sodium hydroxide the color develops only on boiling and shows various intensities of blue over the entire range of sulfur concentrations. The coloration fades within a few minutes. The presence of about 10 per cent of water is essential; greater dilution causes a diminution of the color. The amount of alkali necessary to bring out the maximum color is proportional to the amount of sulfur. The limit of sensitivity is of the order of 2 micrograms of sulfur per cc.

Table I. Colors Obtained with Sulfur in Pyridine

(1 cc. of pyridine with 0.1 cc. of 2 *N* sodium hydroxide or saturated sodium bicarbonate)

Concentration of Sulfur in Pyridine	Color Developed	
	With NaOH	With $NaHCO_3$
1:100	Deep red-brown	Deep greenish blue
1:1,000	Dark olive-green	Dark Prussian blue
1:10,000	Greenish blue	Strong blue
1:100,000	Light sky blue	Sky blue
1:300,000	Trace of blue	Very light blue
1:500,000	Questionable	Very faint blue
1:1,000,000	No color	Questionable

For the demonstration of sulfur in amounts of 10 micrograms or less the use of sodium bicarbonate has been found somewhat more advantageous. To 1 cc. of the pyridine solution of the unknown, 0.1 cc. of saturated aqueous sodium bicarbonate is added. The resultant mixture is boiled for a few seconds and observed immediately for color. The crystalline sodium bicarbonate which is deposited under these conditions forms a convenient white background for the visual observation of the blue color. For colorimetric comparison by transmitted light, in the presence of small amounts of sulfur, the saturated bicarbonate solution can be replaced by one of 1/100th saturation which gives a clear solution with pyridine. An approximation to the quantity of sulfur present can best be obtained by serial dilution of the unknown and comparison with known standards prepared simultaneously. The progressive fading is evidently the main obstacle to an accurate determination.

Specificity

The reaction is positive with free sulfur and substances containing loosely bound sulfur, such as sodium and ammonium polysulfides. No color is given by sodium sulfide, sodium thiosulfate, sodium hyposulfite, and similar compounds. Elementary selenium and phosphorus likewise show no color. The pyridine may be replaced by other alkaline organic solvents such as aniline or triethanolamine, but a high sensitivity is obtained only with pyridine or quinoline. Triethanolamine and other aliphatic amines may also replace the inorganic alkali.

Interference

Some organic solvents, especially carbon disulfide and hydrocarbons, inhibit the reaction, evidently by disturbing the solubility equilibrium. The lower alcohols do not interfere and may be used instead of water in the test. That chloroform and other polyhalogenated hydrocarbons cannot be present is evident, since these compounds give purple colors with a mixture of alkali and pyridine (*1, 2, 10*). Traces of free halogens give brown colorations.

Nature and Mechanism of Test

In an investigation of color as a function of the degree of dispersion of colloids, Ostwald (*7*) demonstrated the existence of blue sulfur in hot glycerol and paraffin, and found that it was due to the most highly dispersed colloidal form of sulfur. von Weimarn (*13*) extended the experiments to a series of other solvents and discussed various kinds of colloidal and molecular sulfur of many different colors.

Based on these earlier experiments, it is logical to assume that the colors obtained in the reaction herein described are due to colloidal dispersion of the sulfur in the aqueous pyridine. It is assumed that the sulfur is in molecular solution in pyridine; by the addition of water it is aggregated into a milky colloidal form. In the presence of alkali the colored forms appear, the highest dilution giving the most highly dispersed blue form. Increasing concentrations of sulfur give rise to the increasingly less disperse green and red colors. Whether the pyridine or the added alkali enters into the colored product, a question which has been variously discussed in the case of ammonia and caustic alkalies, cannot be decided here. The fading of the color apparently is due to oxidation of the sulfur to thiosulfate; on vigorous shaking in the presence of air, the colored reaction mixture takes up oxygen until the color has completely faded. The resulting solution then gives the reactions for thiosulfate but not for sulfide ions.

Use of Reaction

The color reaction has been tested in this laboratory by demonstrating free sulfur—e. g., in ultramarine, in rubber, in certain drugs and insecticides, and in matches. Pyridine has been found useful for the extraction of sulfur on numerous occasions, as in the analysis of heavy metals for the separation of sulfur from the sulfide precipitates.

Literature Cited

(1) Cole, W. H., *J. Biol. Chem.*, 71, 173 (1926).
(2) Fujiwara, K., *Sitzber. Abhandl. naturforsch. Ges. Rostock*, 6, 1 (1914).
(3) Gastalt, *Chem.-Ztg.*, 35, 688 (1911).
(4) Gil, J. C., *Z. anal. Chem.*, 33, 54 (1894).
(5) Halphen, *J. pharm. chim.*, (6) 6, 390 (1897).
(6) Orloff, N. A., *J. Russ. Phys. Chem. Soc.*, 34, 52 (1901).
(7) Ostwald, W., *Kolloidchem. Beihefte*, 2, 409 (1911).
(8) Raffo, M., and Balduzzi, O., *Gazz. chim. ital.*, 47, 65 (1917).
(9) Raffo, M., and Rossi, G., *Ibid.*, 44, 104 (1914).
(10) Ross, J. H., *J. Biol. Chem.*, 58, 641 (1923).
(11) Schoenberg, A., *Nature*, 134, 628 (1934).
(12) Thornton, M. K., and Latta, J. E., Ind. Eng. Chem., Anal. Ed., 4, 441 (1932).
(13) Weimarn, P. P. v., *Kolloidchem. Beihefte*, 22, 38 (1926).
(14) Zmaczynski, E., *Z. anal. Chem.*, 106, 32 (1936).

Photographic Silver-Gelatin Paper as a Reagent in Spot Analysis[1]

G. SCHWARZ, Gevaert Photo-Producten N. V., Antwerp, Belgium

Photographic paper developed to complete blackness becomes more brightly reflecting upon dipping in hot water. This brightening is prevented by all mercaptans and seleno alcohols, by certain heterocyclic substances containing imino groups, by salts of the nobler metals such as silver, by iodides, and by substances which easily split off selenium or tellurium. On this reaction is based a microanalytical test for these substances which is here described in detail and theoretically discussed. The reaction is carried out with a drop of the test solution; the limiting concentration is of the order of magnitude of 1 to 100,000. The method has been extended to the detection of other substances, and a further increase in the sensitivity of the reaction is possible.

THE drying of photographic pictures in heated presses strongly decreases their contrast, depending upon the temperature and other working conditions (*2*). This phenomenon, undesired in photography, can be prevented by means of surface changes in the silver particles—i. e., by changing into a silver compound, by covering with a nobler metal, or by adsorption of quite different substances on the surface of the silver. For this such a small amount suffices that application of this behavior of the silver of photographic paper to analytical purposes appears promising. The results so far obtained, although in no way complete, may be of interest in microchemical analysis.

Principles of the Method

As was mentioned (*2*), the decrease of the blackening of a photographic picture which has been dried by heat depends upon a change of the structure of the silver caused by the heat and pressure. The action of heat is the important factor. In the drying process the effect of pressure is important only in so far as it prevents rapid evaporation which results in a cooling. Obviously the change in structure consists in a decrease of the degree of dispersion of the silver, and a consequent marked increase in reflecting power. The decrease in the degree of dispersion occurs not only as the result of agglomeration of the single particles, but also as a result of a partial crystalline coalescing. The irreversible nature of the change favors this assumption.

The increase in reflecting power brought about by the

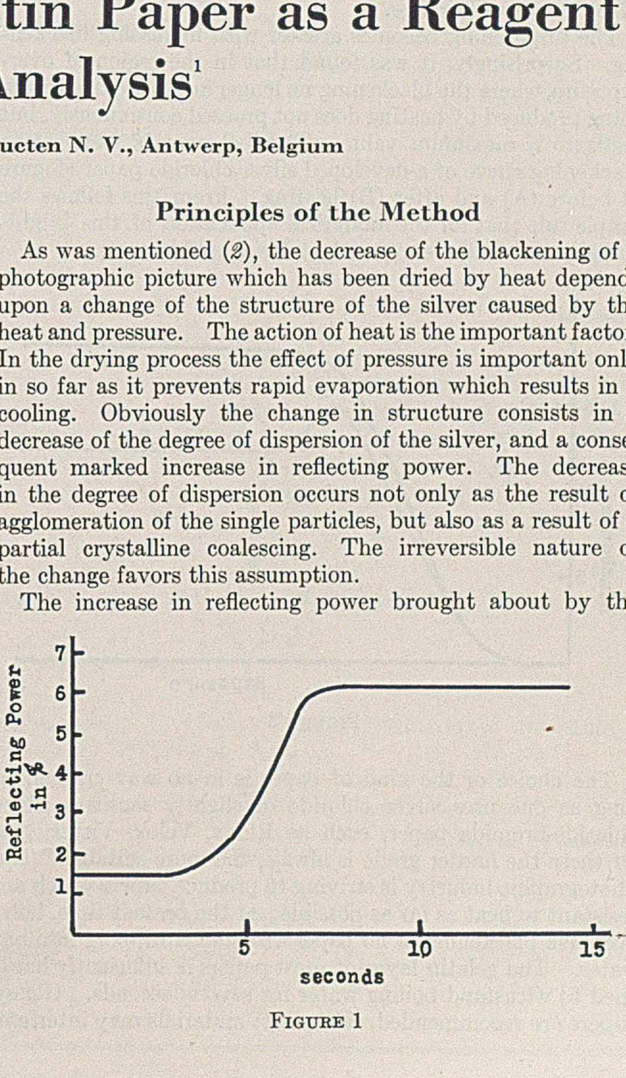


Figure 1

---

[1] Translated by D. Weiblen, University of Minnesota, Minneapolis, Minn.

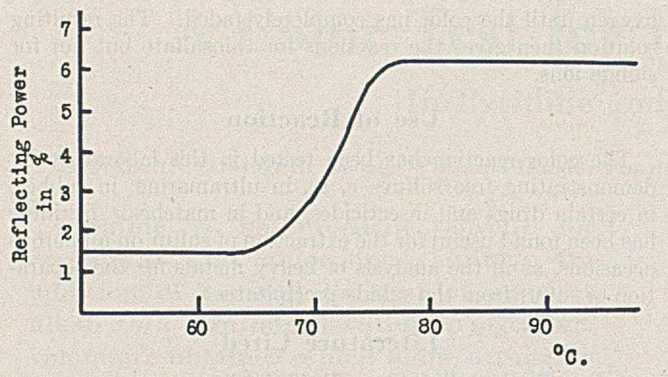


FIGURE 2

heat-drying process takes place before the pictures are really dry—that is, while they are yet moist—for if pictures are dried without heat, the contrast is not decreased upon subsequent heating without moistening. To attain brightening it is not necessary to dry the photographic papers; exposure in a moist condition to heat, as for example, by dipping for a few seconds in hot water, is sufficient. The change of the reflecting power rapidly reaches a maximum value, as seen in Figure 1, for an arbitrarily chosen temperature of 70° C. In Figure 2 is given the change of the reflecting power with the temperature upon dipping for 5 seconds. In order to obtain a sufficiently distinct change of reflecting power, dipping for at least 5 seconds in water heated to at least 75° C. suffices; exceeding this time and this temperature is without effect over a wide range.

The brightening becomes greater with increasing blackening. Surprisingly, it was found that in the region of overexposure, where the blackening no longer increases, the brightening produced by heating does not proceed continuously, but tends to a maximum value. This behavior is seen in the blackening curve of a developed silver chloride paper (Figure 3) before (A) and after (B) heating. From this follows the simple rule that for the analytical application of this brightening, somewhat overexposed papers should be used.

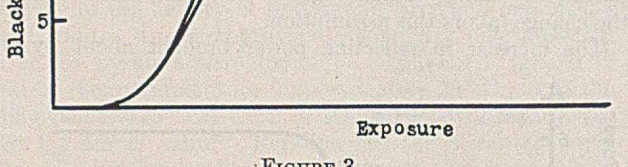


FIGURE 3

The choice of the kind of paper is in no way critical, so long as one uses silver chloride or slightly sensitive silver chloride-bromide paper, such as Ridax, Velox, Vittex, etc. Of these the harder grade is always the more suitable. The photographic industry is striving to produce papers which are resistant to heat as far as possible; at the present time, however, the blackening of no paper withstands dipping into hot water. The gelatin layer of most papers is sufficiently hardened to withstand boiling water for several seconds. Glossy papers are recommended, since matt materials may interfere.

TABLE I. COMPOUNDS TESTED

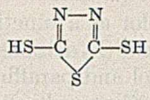
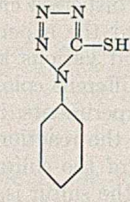
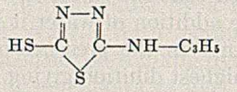
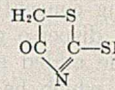
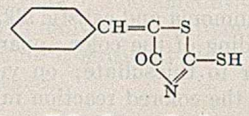
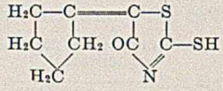
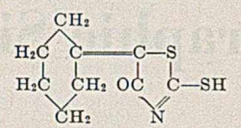
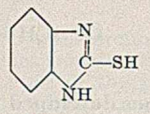
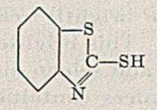
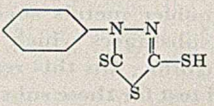
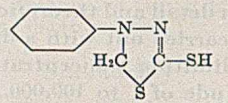
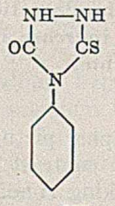
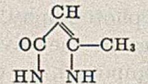
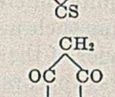
Substance	Formula	Limiting Concentration Alkaline medium	Limiting Concentration Acid medium
Dimercapto-thiadiazole		1:100,000	1:100,000
N-phenylmercapto-tetrazole		1:500,000	1:500,000
Allylaminomercapto-thiadiazole		1:100,000	1:500,000
Rhodanine		1:100,000	1:20,000
Benzylidene-rhodanine		1:100,000	Insoluble
Cyclopentylidene-rhodanine		1:100,000	1:20,000
Cyclohexylidene-rhodanine		1:100,000	1:20,000
Mercapto-benzimidazole		1:500,000	1:200,000
Mercapto-benzothiazole		1:100,000	1:200,000
Phenyldithiobiazolone sulfhydrate		1:100,000	1:100,000
N-phenylmercapto-thiadiazole		1:100,000	1:100,000
4-Phenylthiourazole		1:2000	..
2-Thio-4-methyl-uracil		1:100,000	1:100,000
Thiobarbituric acid		1:1,000,000	1:200,000

Table I. Compounds Tested (*Cont'd*)

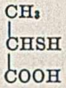
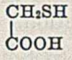
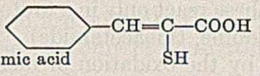
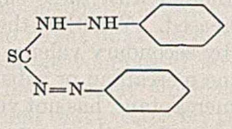
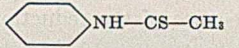
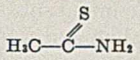
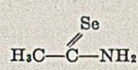
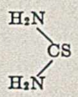
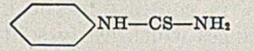
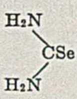
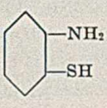
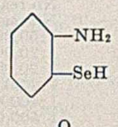
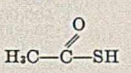
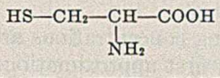
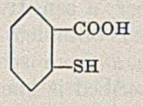
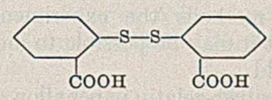
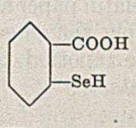
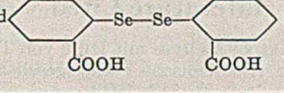
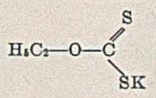
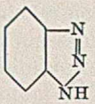
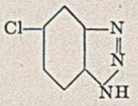
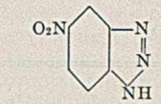
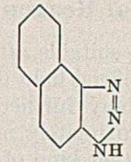
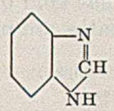
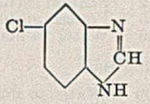
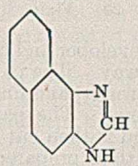
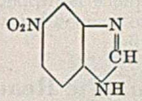
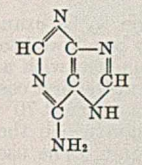
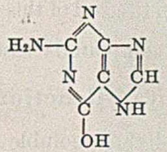
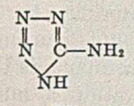
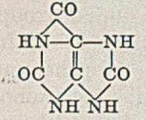
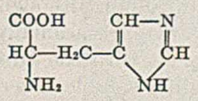
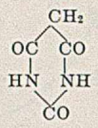
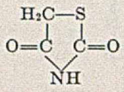
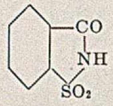
Substance	Formula	Limiting Concentration Alkaline medium	Limiting Concentration Acid medium
Thiolactic acid (α-mercapto propionic acid)	 $\begin{array}{l}CH_3\\ CHSH\\ COOH\end{array}$	1:100,000	1:20,000
Thioglycolic acid (mercapto acetic acid)	 $\begin{array}{l}CH_2SH\\ COOH\end{array}$	1:100,000	1:100,000
α-Sulfhydryl-cinnamic acid (α-mercapto cinnamic acid)		1:100,000	1:20,000
Thiosemicarbazide	$H_2N-CS-NH-NH_2$	1:20,000	1:100,000
Diphenylthiocarbazone		1:100,000	1:100,000
Dithiooxamide	$H_2N-CS-CS-NH_2$	1:500,000	1:100,000
Thioacetanilide		1:100,000	1:5000
Thioacetamide	 $H_3C-\overset{S}{\overset{\|}{C}}-NH_2$	1:20,000	1:1000
Selenoacetamide	 $H_3C-\overset{Se}{\overset{\|}{C}}-NH_2$	1:100,000	1:10,000
Thiourea	 $\begin{array}{l}H_2N\\ \quad CS\\ H_2N\end{array}$	1:100,000	1:1000
Phenylthiourea		1:50,000	1:50,000
Selenourea	 $\begin{array}{l}H_2N\\ \quad CSe\\ H_2N\end{array}$	1:50,000	1:50,000
o-Aminothiophenol		1:100,000	1:100,000
o-Aminoselenophenol		1:100,000	1:100,000
Thioacetic acid	 $H_3C-\overset{O}{\overset{\|}{C}}-SH$	1:20,000	1:20,000
Cysteine	 $HS-CH_2-\underset{NH_2}{CH}-COOH$	1:100,000	1:100,000
Cystine	$[S-CH_2-CHNH_2-COOH]_2$	1:20,000	1:20,000
Thiosalicylic acid		1:100,000	1:100,000
Dithiosalicylic acid		1:5000	1:5000
Selenosalicylic acid		1:100,000	1:100,000
Diselenosalicylic acid		1:5000	1:5000
Potassium xanthogenate	 $H_5C_2-O-\overset{S}{\overset{\|}{C}}-SK$	Without reaction	
Benzotriazole		1:50,000	No reaction
5-Chlorobenzotriazole		1:200,000	No reaction
5-Nitrobenzotriazole		1:200,000	1:2000
1,2-Naphthotriazole		1:200,000	No reaction
Benzimidazole		No reaction	No reaction
Chlorobenzimidazole		1:1000	No reaction
1,2-Naphthimidazole		1:5000	No reaction
Nitrobenzimidazole		1:2000	No reaction
Adenine		1:100,000	No reaction
Guanine		1:100,000	No reaction
Aminotetrazole		1:20,000	No reaction
Uric acid		No reaction	No reaction
Histidine		No reaction	No reaction

Table I. Compounds Tested (*Conc'd*)

Substance	Formula	Limiting Concentration Alkaline medium	Limiting Concentration Acid medium
Barbituric acid		No reaction	No reaction
2,4-Thiazoledione		No reaction	No reaction
Saccharine		No reaction	No reaction

Preparation of Reagent Paper

The kind of paper found suitable after a few preliminary tests is fully exposed by artificial light or daylight (Figure 3) and is developed without any further precautions against light for as long as is approximately necessary for the production of the image upon that kind of paper. For this the usual developer and fixing baths are used.

Developer

	Grams		Grams
p-Methylamino phenol sulfate	2	Sodium carbonate, crystalline	50
Hydroquinone	5	Potassium bromide	1
Sodium sulfite, crystalline	50	Water to make to 1 liter	

Fixing Bath

Sodium thiosulfate, crystalline	200	Water to make to 1 liter
Sodium bisulfite	20	Fixing time, about 10 minutes

Copious amounts of the developer and fixing baths are used and the used baths are poured away. The paper is then washed, first about 1 hour in flowing tap water, and finally with distilled water which is changed many times. The paper is allowed to hang free, is dried in clean air, and is then cut in the usual form of reagent papers. The paper thus prepared is stable indefinitely. To test the reagent paper, a piece is dipped halfway into water at 70° to 80° C. In about 3 to 5 seconds a very distinct decrease of the blackening must be visible.

Carrying Out the Reaction

A small drop of the solution to be examined is placed upon the dry reagent paper and may be allowed to evaporate, or after 5 minutes the excess may be removed with a strip of filter paper. The reaction is more sensitive in the first case. The strip is then dipped, using tweezers, into hot water at 70° to 90° C. The reaction is positive if the spot upon which the drop was placed is black against a gray background. The used reagent paper can be dried and kept as a permanent record of this reaction.

Tables I and II list the compounds tested as above.

Application of Reaction

Compounds which form slightly soluble silver salts give positive results, since according to the Paneth-Fajans adsorption rule these compounds can be easily adsorbed on silver. Among the organic compounds these are, first of all, the mercaptans, and in addition a number of substances containing the heterocyclic imino group. The mercaptans can be distinguished with fair certainty from the heterocyclic imino substances, since they give the reaction in acid as well as in alkaline medium, while the imino substances do not give the reaction in acid medium, although if present in very high concentration they may occasionally react. This behavior is in good agreement with the adsorption rule, since the mercaptans form slightly soluble silver salts in both acid and alkaline medium, while the imino substances do this only in neutral or best in alkaline medium. The reaction can accordingly be designated as strictly specific for mercaptans.

In the iodoazide reaction described by Feigl (*1*) we have a very valuable test for mercaptans, yet fairly large amounts of substances which combine with iodine interfere. Thiosulfates do not show the reaction with silver-gelatin paper, but clearly react with iodoazide solution. Substances with a SeH— group, such as selenophenol, give a positive reaction in contrast to the iodoazide reaction. Many other divalent sulfur-containing substances also give the reaction; it is probable, however, that these react only in a tautomeric sulfhydryl form (thiourea, rhodanine, thioacetamide).

Disulfides formed by the oxidation of mercaptans, as well as diselenides formed from seleno alcohols, likewise give a positive reaction, although with these substances the sensitivity is greatly decreased. Whether the disulfides are adsorbed on the silver by secondary valence effects, or whether they still contain some mercaptan or substances which could be transformed into mercaptans, has not yet been determined. In the author's experiments in the presence of reducing substances the test for mercaptans has occasionally been more sensitive, probably because of the reduction of disulfides to mercaptans.

The presence of heterocyclic imino substances is recognized by a positive reaction in alkaline and a negative reaction in acid medium. However, the reaction is not applicable to all substances in this group, for, surprisingly, the imidazoles react only very weakly. A >CO group in the ortho position to an imino group interferes with the test, since these substances do not form slightly soluble silver salts—i. e., 2,4-thiazoledione, barbituric acid, uric acid, etc.

Among the inorganic substances the strong reaction of iodides is remarkable, in contrast to the inactivity of the other halides. Substances which easily split off selenium or tellurium likewise give a sensitive reaction. In addition, the salts of noble metals and mercuric ions react, the latter only weakly.

Table II. Compounds Tested

Substance	Limiting Concentration	
Potassium iodide	1:100,000	
Potassium bromide	No reaction	
Potassium chloride	No reaction	
Potassium fluoride	No reaction	
Sodium thiosulfate	No reaction	
Sodium selenosulfate	1:50,000	in the presence of 1% $Na_2S_2O_3$
Sodium selenite	1:20,000	
Sodium tellurite	1:20,000	
Sodium selenosulfide	1:20,000	
Silver nitrate	1:1000	
Chloroauric acid	1:500,000	
Chloroplatinic acid	1:20,000	
Mercuric nitrate	1:5000	
Mercurous nitrate	No reaction	

The specified limiting concentrations are in no way exact, but serve merely as a first approximation. If the test solution is allowed to dry on the reagent paper without removing the excess with filter paper, a sensitivity five times greater than the values given here is obtained. Further experiments are in progress to make a more sensitive reagent paper. Although the method described is one of the most sensitive of microanalytical methods the experiments so far performed indicate that it may be possible to increase the sensitivity five- or tenfold.

The reaction with silver-gelatin paper allows still other practical applications—for example, the detection of sugar, ascorbic acid, etc. More will be reported concerning this upon completion of the experiments.

Literature Cited

(1) Feigl, F., "Qualitative Analyse mit Hilfe von Tüpfelreaktionen", 3rd ed., Leipzig, Akademische Verlagsgesellschaft, 1938.
(2) Schwarz, G., *Phot. Ind.*, 31, 317 (1933).

Determination of Carbon Disulfide in Air

By Means of Copper and Diethylamine in 2-Methoxyethanol

FREDERICK F. MOREHEAD, American Viscose Corporation, Roanoke, Va.

THE development of a satisfactory micromethod for the determination of carbon disulfide in air has been especially desirable for use in the viscose rayon industry, where the problems involved are not only those of hygiene, but also of the efficiency and economy of ventilating systems, the detection of leaks, etc.

The chief limitations of both volumetric and colorimetric modifications of the generally accepted xanthate method (*4*) for carbon disulfide in gas mixtures are that they require the aspiration of such large volumes of air (56,000 ml., 2 cubic feet, or more) for the extremely small concentrations usually found in practice, and that excessively large blank corrections are necessary.

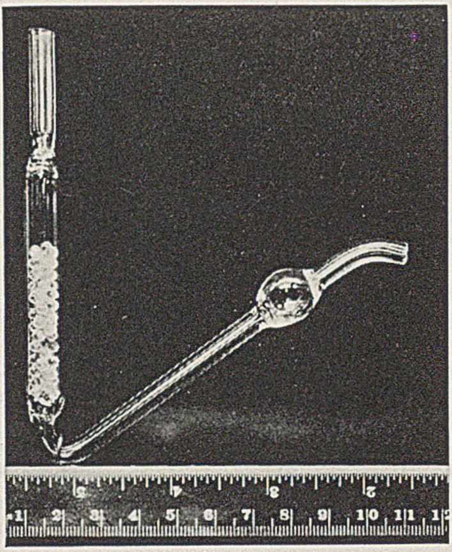


FIGURE 1. NEW TYPE OF ABSORPTION BULB

The recently published procedures (*1, 2, 3, 6, 7*), based upon the production of a yellow or golden-brown coloration by the action of carbon disulfide on diethylamine in the presence of copper ions, are considerably more sensitive and accurate than the xanthate methods, but the colors obtained in ethanol are rather unstable and subject to fading. However, the present author has discovered that the 2-methoxyethanol recently recommended by Winsor (*8*) as a reaction medium in the colorimetric thiocyanate method for iron is also ideal for the determination of carbon disulfide by the copper-diethyldithiocarbamate reaction. The color obtained in this medium is not only more intense than that produced in ethanol, but is also stable for 24 or even 48 hours. Further, only comparatively small samples (100 to 1000 ml.) are necessary with this modification.

Apparatus

The absorption train first used in this investigation consisted of three Huff (*5*) five-bulb tubes blown from 6-mm. tubing, the first two being sealed together and the third attached by a ground-glass joint. This type proved satisfactory so long as the rate of aspiration did not exceed 5 ml. per minute; but in the course of the work it became necessary to sample at the rate of 50 ml. per minute or more. Hence, a new absorption tube which can easily be constructed by the average amateur glass blower was designed to incorporate the following desirable features: small volume; provision for intimate contact between gas and liquid; very low resistance to the flow of gas; and ease of complete washing with small volumes of liquid.

A small bulb, 10 to 15 mm. in diameter, is blown about 2 cm. from the end of a 12- to 16-cm. length of 1-mm. Pyrex capillary tubing; and the other end is sealed to a 6- to 7-cm. piece of 10-mm. Pyrex tubing (Figure 1). Small indentations are placed in the tubing near the joint, to prevent the filling of 3-mm. solid glass beads from dropping down and sealing the capillary. Next, a 3- to 4-cm. length of 7-mm. Pyrex tubing is sealed on, the 10-mm. section is nearly filled with beads, and the joint between the two is constricted to prevent them from falling out when the tube is inverted. Finally, the capillary tubing is bent to an angle of 60° near the joint for ease in washing, and to some convenient obtuse angle near the other end, as shown in Figure 1. The outlet tube may also be bent to an angle if desired. This single absorption tube may be used alone in many cases, or in connection with a purification train. Resistoflex tubing, obtainable from the Resistoflex Corporation, Belleville, N. J., is a satisfactory substitute for ground-glass connections.

Figure 2 shows a convenient arrangement for rapid sampling of small volumes of air.

A Klett colorimeter was used in this investigation, the 2-ml. microcups being employed.

Reagents

2-Methoxyethanol, obtained from the Carbide and Carbon Chemicals Corporation under the name of methyl Cellosolve. If not colorless, it may be rendered so by distillation in glass.

Diethylamine, 1 per cent by volume in 2-methoxyethanol, obtained from the Eastman Kodak Company. The product boiling at 55–56° C. was found to be satisfactory.

Cupric acetate, 0.1 per cent by weight in 2-methoxyethanol.

Cupric sulfate, 5 per cent by weight in water, for removal of hydrogen sulfide in the purification train. Lead acetate paper may be substituted.

FIGURE 2. METHOD FOR TAKING RAPID SAMPLES

Table I. Analysis of Known Air-Gas Mixtures

Carbon Disulfide Taken	Carbon Disulfide Found	Difference
Micrograms	*Micrograms*	*Microgram*
7.89	8.03	0.14
14.58	14.54	−0.04
28.60	28.36	−0.24

Table II. Analysis of Air Samples Encountered in Practice

Carbon Disulfide Found		
Xanthate method	Copper-diethylamine method	Difference
Micrograms	*Micrograms*	*Microgram*
7.50	8.02	0.52
10.60	10.20	−0.40
11.20	11.50	0.30
12.00	11.80	−0.20
15.20	14.95	−0.25

Sulfuric acid, c. p., concentrated, for the purification train. Other drying agents may be substituted.

Carbon disulfide, c. p., redistilled, for the preparation of standards.

Experimental Procedure

When hydrogen sulfide is present, it must be removed by absorption in 5 per cent cupric sulfate solution, or by passing over lead acetate paper, since copper sulfide would otherwise be precipitated in the copper-diethylamine reagent. The gas stream is then dried by sulfuric acid or other suitable desiccating agent; if hydrogen sulfide is absent, the entire purification train can often be omitted. The reaction tube itself should contain 1 ml. of the diethylamine reagent, plus 2 drops of the 0.1 per cent cupric acetate solution.

To make a determination, a known volume of air is aspirated through the apparatus, followed by 100 ml. of carbon disulfide-free air when the purification train has been used, to sweep the latter free from carbon disulfide. Then the reaction mixture is rinsed into a 2-ml. calibrated flask and made up to the mark with 2-methoxyethanol. At the same time a suitable standard, containing 5 to 20 micrograms of carbon disulfide, is prepared, using the same quantities of reagents; and after 20 minutes, they are compared in the colorimeter.

Typical Results

Several milligram lots of carbon disulfide were weighed in sealed bulbs on a microbalance, and broken in a 12-liter bottle. After allowing sufficient time for the gas to diffuse through the bottle, samples were withdrawn and analyzed. The results in Table I show good agreement with the theoretical values, for the small amounts involved.

Discussion

The reaction was found to be almost instantaneous when used as directed. It was observed in a number of runs using the Huff (*5*) tubes on air containing small quantities of carbon disulfide that the yellow color was produced only in the first bulb, and that there was practically no spray carried over into the second. When ethanol was used as the reaction medium, it was necessary to increase the number of tubes to take care of both the spray carried over and the apparently slower rate of reaction.

In comparing the intensities of colors produced in ethanol and in 2-methoxyethanol, using 20 micrograms of carbon disulfide in each case, colorimeter readings were 20.0 and 13.5 mm., respectively, showing an increase of 67.5 per cent in intensity for the latter.

Standards containing 20 micrograms of carbon disulfide in 2-methoxyethanol matched similar freshly prepared standards even after 48 hours; longer standing produced some fading.

The sensitivity of the reaction was not appreciably affected by as much as 20 per cent of water in the mixed reagent, but fading was much more rapid in this case; for this reason, it is usually desirable to insert a drying tube in the train, even in the absence of hydrogen sulfide, which of course must be removed.

Passage of large volumes of carbon disulfide-free air through the mixed reagent caused no blank, nor did it affect the intensity of color produced by the addition of a known amount of carbon disulfide.

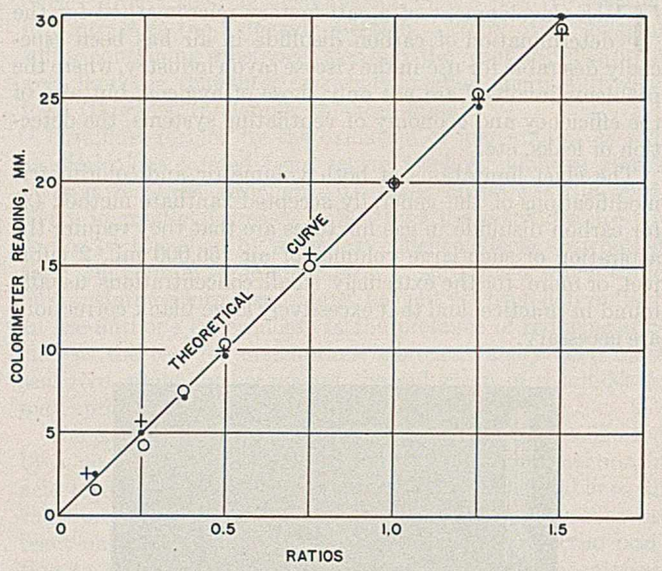


Figure 3. Determination of Carbon Disulfide

Unknown set at 20.0 mm., 2-ml. microcups used.
Reading for standard, micrograms of carbon disulfide: ○, 20; ●, 10; +, 5.

The most satisfactory range for this method proved to be from 1 to 30 micrograms, higher concentrations than these giving colors too dense for accurate comparison. The curves in Figure 3 for standards containing 5, 10, and 20 micrograms of carbon disulfide, respectively, show that Beer's law is obeyed satisfactorily for the entire range recommended in this paper. Proportional parts of these standards were taken, the unknown being placed in the colorimeter cup set at 20.0 mm., and then matched by the standard.

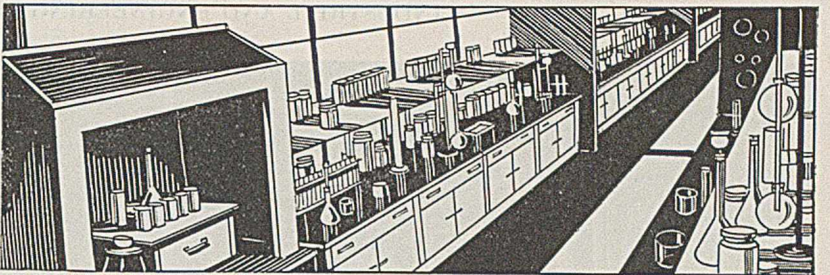
Summary

The copper-diethylamine method for the determination of carbon disulfide has been made sufficiently sensitive for the determination of low concentrations in reasonably small samples of air by the use of 2-methoxyethanol as the reaction medium. Very good agreement with Beer's law has been shown, and the results compare favorably with those obtained by the xanthate method when used on air. A new and very satisfactory type of absorption tube is described. The investigation is being continued with the object of improving the apparatus and technique, and of adapting it to the determination of copper.

Literature Cited

(1) Callan, T., Henderson, J. R., and Stafford, J., *J. Soc. Chem Ind.*, 51, 193–4T (1932).
(2) Conn, L. W., Johnson, A. J., Trebler, H. A., and Karpenko, V., Ind. Eng. Chem., Anal. Ed., 7, 15–23 (1935).
(3) Dept. Sci. Ind. Research, *Leaflet* 6, London, England, Stationery Office (1939).
(4) Desy, G., *Proc. Am. Gas Assoc.*, 1927, 1440–1.
(5) Huff, W. J., *J. Am. Chem. Soc.*, 48, 81–7 (1926).
(6) Snell, F. D., "Colorimetric Methods of Analysis", New York, D. Van Nostrand Co., 1936.
(7) Tishler, N., Ind. Eng. Chem., Anal. Ed., 4, 146 (1932).
(8) Winsor, H. W., *Ibid.*, 9, 453–5 (1937).

Presented before the Division of Microchemistry at the 97th Meeting of the American Chemical Society, Baltimore, Md.



MODERN LABORATORIES

New Chemical and Metallurgical Engineering Building at Purdue University

J. L. BRAY, Purdue University, West Lafayette, Ind.

THE new building for the School of Chemical and Metallurgical Engineering at Purdue University was completed in the fall of 1939 and will be dedicated at the Regional Meeting of the AMERICAN CHEMICAL SOCIETY to be held on June 15, 1940, in cooperation with the American Institute of Chemical Engineers and the American Institute of Mining and Metallurgical Engineers. The building, made possible in its present form through a PWA grant of $271,584, represents an investment of about $600,000, but a great deal of equipment in the way of evaporators, stills, filter presses, dryers, etc., was available from the old laboratories. Not only is it the newest and largest structure of its kind in the country, but it embodies many original features of design and construction.

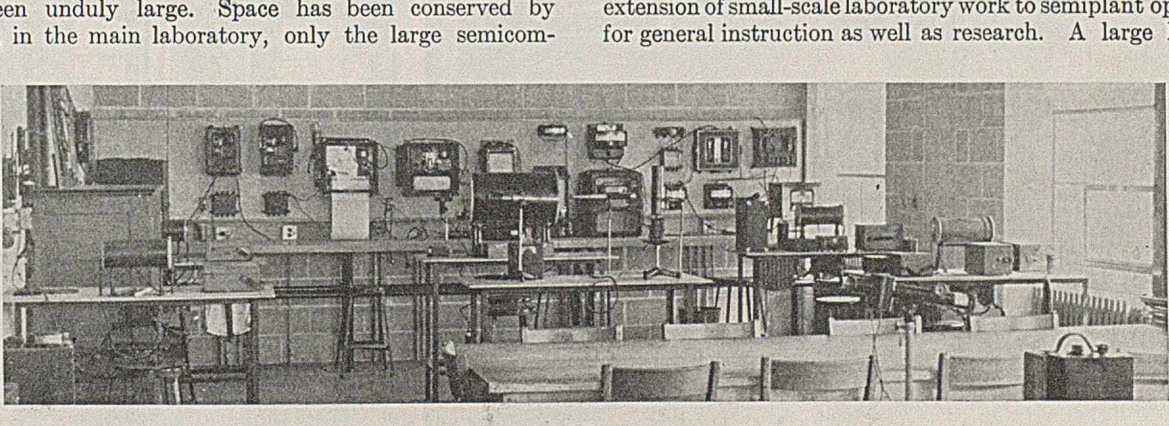
The building will eventually take the form of a quadrangle, of which only a little more than one L has now been completed. The front (220 × 36 feet) and short wing (54 × 54) have four stories and an attic, and the longer wing (186 × 54) has a basement, giving a total floor area of 78,952 square feet. It is of heavy reinforced concrete construction (many of the laboratories being designed for loads in excess of 200 pounds per square foot) with a rough brick facing, tile roof, and Indiana limestone trim. Approximately 120 per cent more space can be provided by completing the quadrangle and adding a large laboratory or lecture hall or a small four-story building in the space now occupied by a parking area.

UNIT OPERATIONS LABORATORY. Enrollment in this school has increased very rapidly in the last few years; a laboratory built along conventional lines to take care of the 120 to 160 students ordinarily enrolled in the summer session, would have been unduly large. Space has been conserved by erecting, in the main laboratory, only the large semicommercial units such as the evaporator, rectification column, batch stills, dryers, filter presses, etc. This laboratory, which extends through two stories, is 72 × 50 feet with a mezzanine 72 × 32 feet, offering 5900 square feet of working space. Beneath it in the basement is a large storage space where small equipment, such as pumps, tanks, pipe assemblies, blowers, etc., can be stored and brought up to the main laboratory, by means of a 2-ton electric crane through an 8 × 6 foot hatch for study or the erection of semicommercial units. Both the main floor and the mezzanine are waterproofed by means of a diaphragm. The laboratory, lighted by windows on three sides and provided with very flexible service connections, constitutes an unusually commodious and well-equipped unit.

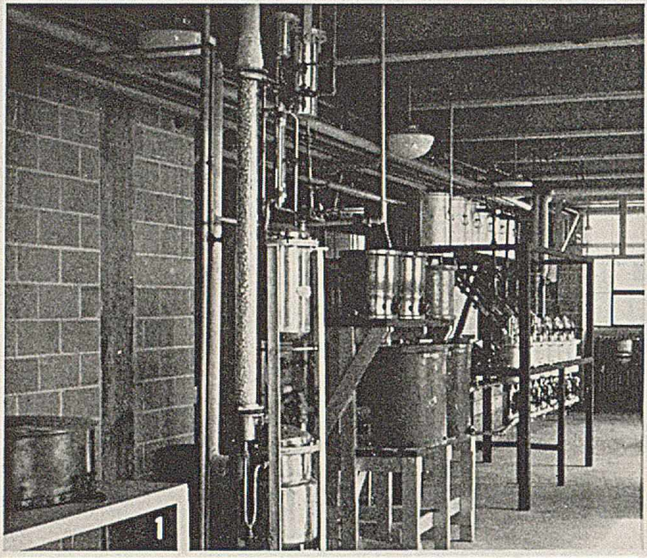
A large control laboratory with chemical desks, hoods, and a balance room, accommodating 96 students, is provided on the second floor. Here the students carry out analytical work in connection with the manufacturing processes that are a part of the laboratory course.

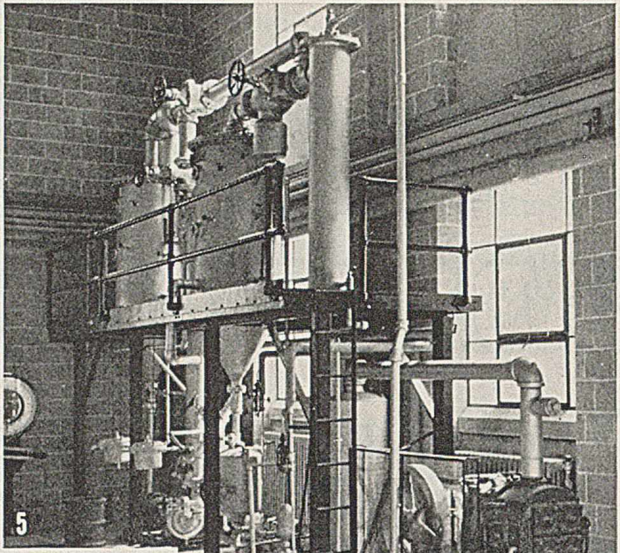
Report writing is carried on in four computation rooms distributed about the building, since it has been found to be more effective to carry this out in groups, as a self-contained course, than to allow students to write up reports at home.

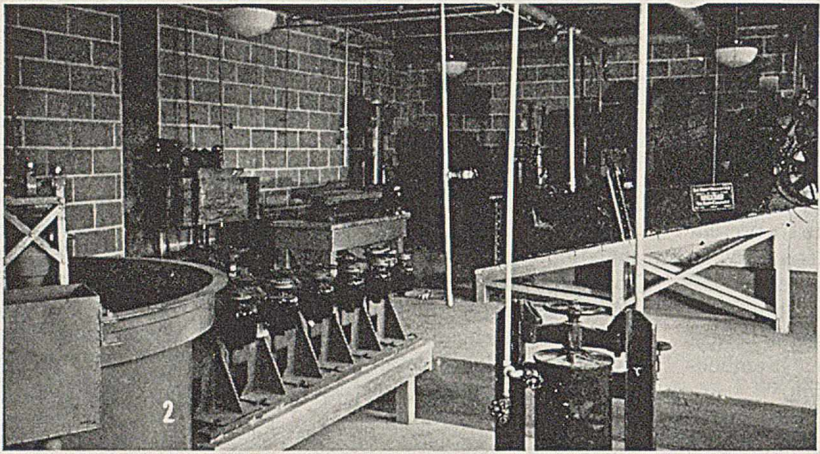
UNIT PROCESSES LABORATORY. This laboratory, for chemical technology, covers 54 × 80 feet on the third floor. It consists of eight individual research laboratories along the side, each accommodating two graduate students. The remainder of the space is taken up by pilot-plant hydrogenators, sulfonators, esterification units, nitrators, etc., permitting the extension of small-scale laboratory work to semiplant operation for general instruction as well as research. A large hood is



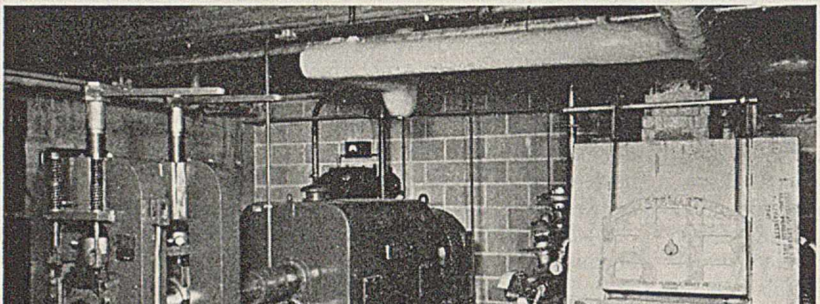
PYROMETRY LABORATORY

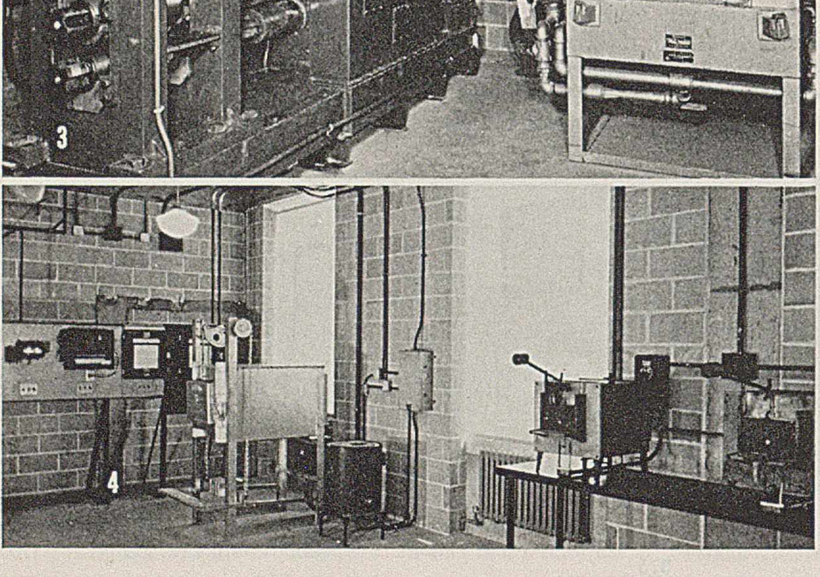


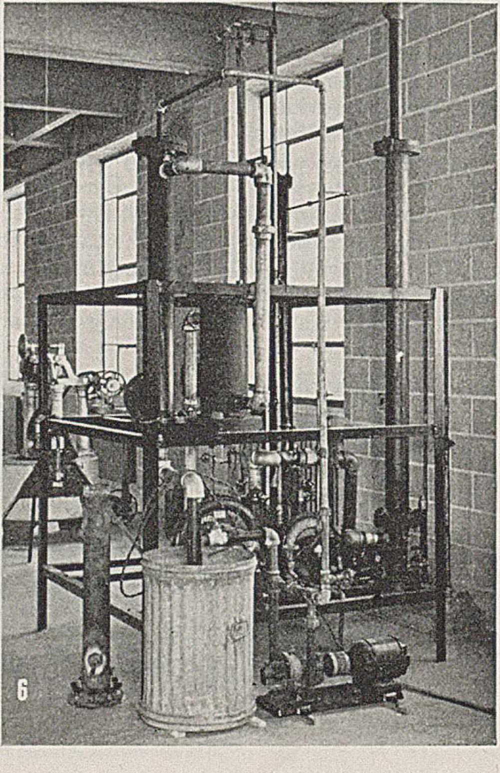


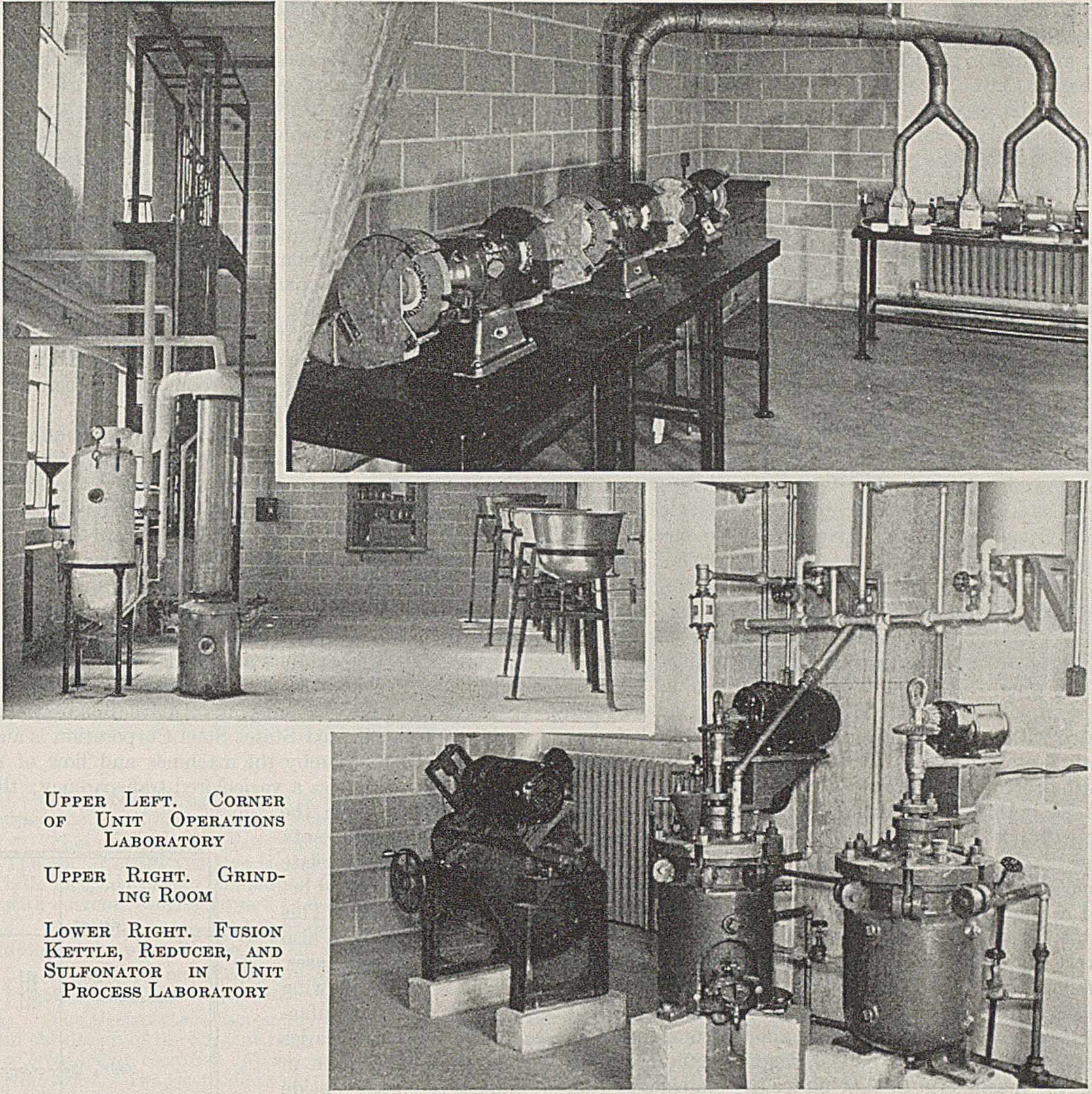


1. Esterification Unit in Unit Process Laboratory
2. Ore-Dressing Laboratory
3. Rolling Mill and Billet Furnace
4. Heat-Treatment Laboratory
5. Multiple-Effect Evaporator
6. Pilot Plant for Study of Carbon Dioxide Absorption









Upper Left. Corner of Unit Operations Laboratory

Upper Right. Grinding Room

Lower Right. Fusion Kettle, Reducer, and Sulfonator in Unit Process Laboratory

provided at one end. To accommodate an autoclave (designed for a pressure of 3500 pounds per square inch at 350° C.) as well as for carrying out hazardous reactions in any semicommercial unit, a safety room built of 0.5-inch armor plate is provided at the other end of the laboratory.

Production Metallurgy. One innovation is space on the ground floor devoted to a very flexible concentrating plant with a capacity of about 300 pounds of ore per hour. The ore can be crushed on the first floor in Blake and gyratory crushers or rolls and then dropped through the floor into a terraced room. On the different levels (about 16 inches apart) are Hardinge mills, classifiers, sand pumps, jigs, tables, conditioners, flotation apparatus, thickeners, etc., permitting wide variations in the kind of treatment. The floor is sealed off by a lead pan to avoid leaks, and connections are made through floor drains to a large settling tank in the basement, so that a close material balance can be made for mill runs.

A second feature is an 8 × 12 inch rolling mill in the basement with a motor-generator control offering a wide variation in speed. This mill is equipped with a pressure meter and a variety of rolls, so that both hot and cold rolling can be carried on for undergraduate instruction as well as for research projects. In the summer session, the students in metallurgical engineering refine steel in an electric furnace, reheat the billets, and roll them into shapes for examination in the courses in physical metallurgy and metallography of the senior year. Such work improves morale, heightens interest, and serves to correlate these fundamental metallurgical courses.

On the first floor is a production metallurgy laboratory 18 × 39 feet in area equipped with a 1200-ampere motor-generator set furnishing current at 55 to 120 volts, a 35-kva. high-frequency melting furnace, a small rotary kiln, and a variety of arc, resistance, and gas furnaces for the roasting and calcining of ores and the reduction, refining, and melting of metals.

Three high-temperature stacks are provided, each 12 × 16 inches in area—two for assay and production metallurgy and one for the billet furnace. These offered a design problem since, for esthetic reasons, the administration did not care to expose them outside the building. To avoid overheating important structural members, the stacks are built double and cooled by air, and, to ensure stability and provide for expansion, are enclosed in a frame of angle irons.

On the ground floor is an 18 × 46 foot laboratory for fire assaying, equipped with twelve gas-fired muffle furnaces; adjoining are rooms for the parting and weighing of buttons.

ELECTROMETALLURGY AND ELECTROCHEMISTRY. In these laboratories on the second floor are chemical desks, a storage battery, and motor generator sets. A switchboard furnishes direct current (2 to 120 volts) to any one of 48 stations. This current may be derived from the large storage battery (60 cells), when constant voltage is desired, or from one of the motor-generator sets for power purposes. One motor generator furnishes 500 amperes with which it is possible to refine copper, lead, and zinc and operate an aluminum pot.

PHYSICAL METALLURGY AND METALLOGRAPHY. These laboratories, which occupy most of the second floor, are laid out on the production principle. The crude metal samples, after being sawed and rough ground, pass successively through laboratories devoted to paper polishing, wet polishing, etching, microscopic examination, photography, dark-room processing, x-ray examination, dilatometric and physical testing, and heat treatment. These laboratories are well equipped with 24 student microscopes, two Bausch & Lomb and one Leitz research microscopes, and a wide variety of apparatus for x-ray examination, physical testing, and heat treatment. There is also a pyrometry laboratory, 18 × 47 feet, exceptionally well equipped with apparatus for the measurement of temperatures and with gas and electric furnaces.

CLASSROOMS AND OFFICES. More than half of the first story is devoted to offices, a library, a mimeograph room, and two conference rooms. Four classrooms and a large design room are provided on this floor, while on the third floor are three more classrooms, a student society room, and a large lecture room with seats for 156 students. This lecture room is provided with a fully equipped chemical lecture desk and an automatic lantern, is wired for sound, and has an adjoining preparation room with complete laboratory facilities.

SERVICES. All the main hallways have false ceilings which, in combination with hollow interior walls having an 18-inch free space, facilitate cheap and rapid equipment changes by providing steam, 25 and 150 pounds per square inch; air, 20 and 150 pounds per square inch; vacuum; constant-pressure water; 110- and 220-volt alternating current; 2- to 120-volt direct current (storage battery and motor-generator); gas; distilled water; and soft water. The building is served by a freight elevator with a capacity of 2500 pounds.

In the basement is a commodious shop with milling machine, hack saw, lathes, drill presses, welding equipment, and woodworking machinery, so that either the students or staff mechanics may build equipment.

A locker and shower room with accommodations for 150 students is on the ground floor. The undergraduate laboratory work is concentrated in the summer; consequently, it has been found well worth while to provide these facilities.

The building is well ventilated by 40 fans located in the attic but controlled by switches in the various laboratories. Also in the attic are stills for supplying distilled water to the building and six 500-gallon steady-head tanks. Headers run to the main laboratories as well as to a number of the research laboratories, for use in study and research in fluid flow and heat transfer.

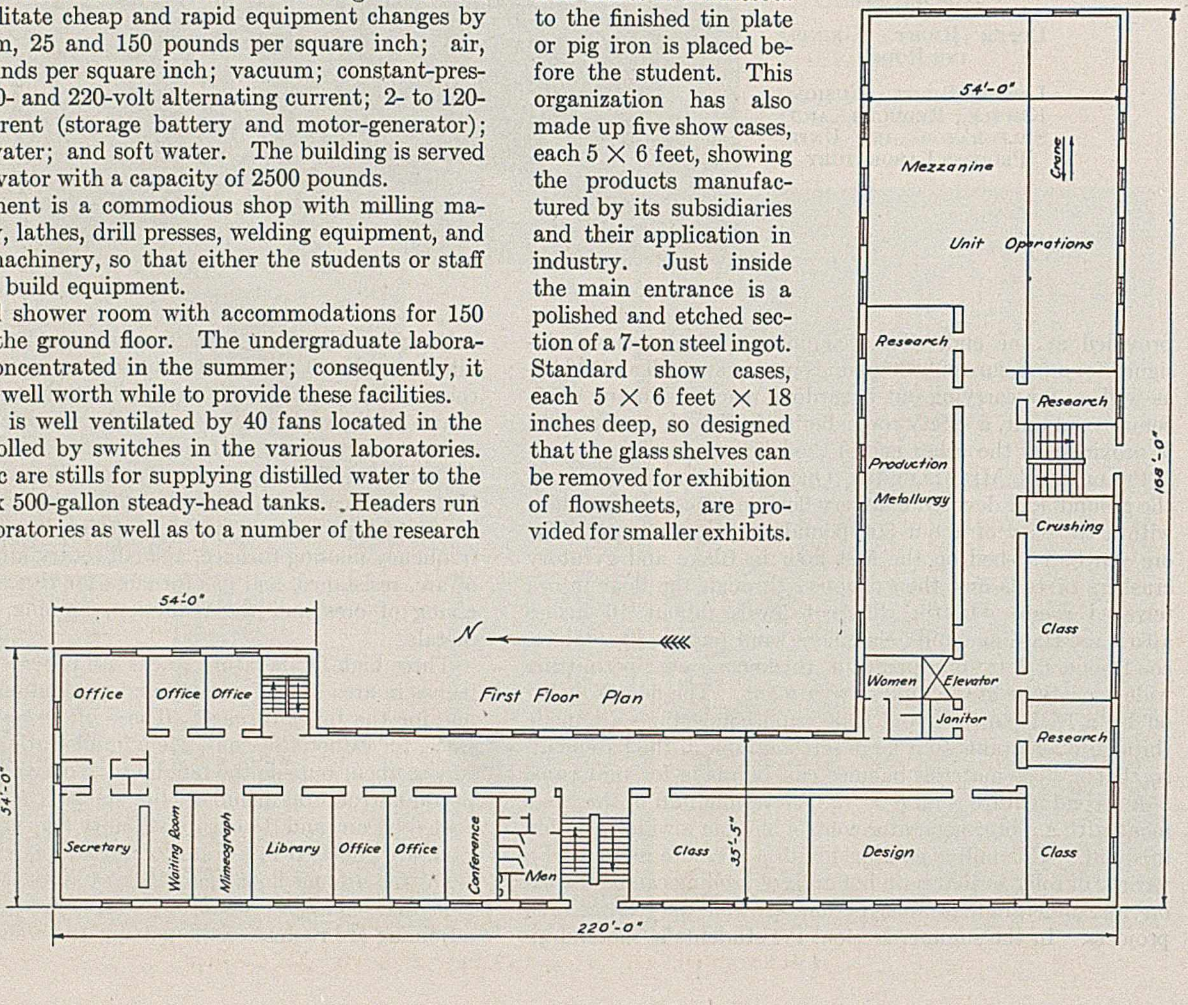
RESEARCH. The school now has an enrollment of 43 graduate students, of whom about two thirds are working towards the Ph.D. degree. In the building are 23 research laboratories, each of which will accommodate comfortably two graduate students and is provided with complete equipment in the way of hoods, sinks, steam tables, and all service facilities.

On the third floor are laboratories where extensive research is carried on in the manufacture and utilization of gas for the Indiana Gas Association. These are provided with chemical desks, gas analysis apparatus, meters, pumps, and blowers for testing equipment using gas as a fuel.

PHOTOGRAPHY. For the courses in photography, quarters in the basement include a classroom, four undergraduate dark rooms, a large graduate dark room, and a room devoted to copying, enlarging, and portrait work.

GEOLOGY, MINERALOGY, AND CRYSTALLOGRAPHY. This group of courses appears to be more closely associated with metallurgical engineering than any other group on the campus. Laboratories are provided on the ground floor and consist of a large laboratory for mineralogy, smaller ones for geology and crystallography offices, and classrooms.

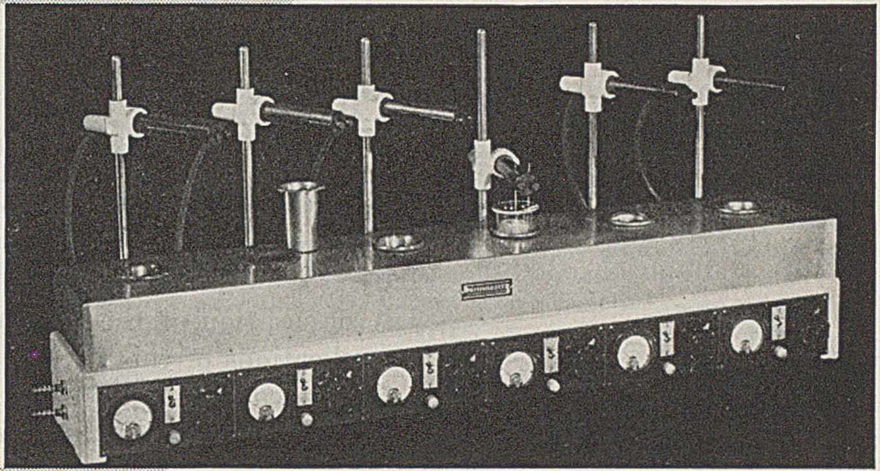
VISUAL EDUCATION. Where the free space between the double interior walls is not taken up by services, show cases and exhibits have been built in for visual instruction. Some of these industrial exhibits are special ones furnished by such organizations as du Pont, New Jersey Zinc, United States Steel, Commercial Solvents, and International Nickel. The exhibit of the United States Steel Corporation is an 8 × 13 foot flowsheet, whereby the machines and flow of raw materials are shown on a varicolored transparency; the whole steel industry from the iron mines in Minnesota to the finished tin plate or pig iron is placed before the student. This organization has also made up five show cases, each 5 × 6 feet, showing the products manufactured by its subsidiaries and their application in industry. Just inside the main entrance is a polished and etched section of a 7-ton steel ingot. Standard show cases, each 5 × 6 feet × 18 inches deep, so designed that the glass shelves can be removed for exhibition of flowsheets, are provided for smaller exhibits.



Deposition Time for Many Analyses Reduced 50% by New

HIGH SPEED ELECTROLYTIC METHODS

The special laboratory manual, "Sargent High Speed Methods for Electrolytic Analysis" is supplied with each Sargent analyzer and is available to laboratories without charge on written request.



SARGENT HIGH SPEED ELECTROLYTIC ANALYZER

The successful application of the fast electrolytic methods contained in the Sargent laboratory manual depends upon the use of high currents, adequate agitation of electrolytes, efficient cooling, and large electrode surface areas.

These essential instrumental characteristics are all incorporated in the Sargent High Speed Electrolytic Analyzer. The circuit of the analyzer is designed for currents as high as 10 amperes. This is essential because the new electrolytic methods specify comparatively high currents. Copper and zinc in various alloys, for instance, are electrolyzed with currents ranging from 8 to 9 amperes.

To obtain a smooth, bright deposit at these high currents, and at maximum speed, special electrodes have been designed for use with the Sargent analyzer.

Electrolytes are adequately cooled by permanently mounted, individual cooling jackets connected in series and located at each beaker position.

The electrolyte is thoroughly agitated electromagnetically. This refinement has made possible a radical change in the design of the Sargent High Speed Analyzer. *All mechanical stirring mechanisms and the concomitant difficulties of breakdowns, corrosion of parts, repair and replacement expenses, and critical electrode adjustment have been completely eliminated.* The electrode heads of the Sargent Analyzer are made entirely of bakelite, no metal other than platinum is exposed to corrosive fumes, electrodes are automatically centered, an electrode head is brought to any desired vertical or lateral position without any clamp adjustment whatsoever—only slight pressure of the hand is required.

A sturdy cast metal base, finished in acid resistant baked white enamel contains the entire electrical circuit and cooling system. Each position consists of a stainless steel beaker inserted into a hole in the stainless steel cover sealed by a rubber grommet against penetration of liquid, surrounded by a close fitting water cooling jacket and located in a strong magnetic field created by a concentric solenoid.

A direct current power supply is required; 110 volt for magnets, 10 to 11 volts for electrolysis and it must have a maximum current capacity of 1 ampere per magnet and 10 amperes per position.

A double output motor generator is available if needed.

S-29405 ELECTROLYTIC ANALYZER—Sargent, High Speed, Heavy Duty, Magnetic Stirring, Water Cooled, Parallel Circuit Model. As described above but without platinum electrodes or motor generator.

Number of positions	2	6
Each	$275.00	700.00

S-29620 ANODE—Platinum, Gauze, Sargent. Formed in two compressed cylindrical sections, and strengthened by reinforcement. Sand blasted. Approximate weight, 10 grams. . . . . *Price subject to market.*

S-29660 CATHODE—Platinum, Gauze, Sargent. Cylindrical form, reinforced, sand blasted. Approximate weight, 15 grams . . . . *Price subject to market.*

S-29425 MOTOR GENERATOR—Electroanalyzing, 11 and 110 volts. Especially designed to supply D.C. power at correct voltages for operation of switch board and magnets and supplying two circuits at 11 volts and 110 volts respectively. For operation from 110 volt 60 cycle single phase circuits. (Other power characteristics supplied to order).

Output capacity, K.V.A.	1/2	1
For size, analyzer, places	2	6
Each	$200.00	300.00

A technical bulletin and a manual of Sargent High Speed Methods for Electrolytic Analysis are available to any commercial laboratory without charge or obligation on written request.

SARGENT

LABORATORY SUPPLIES

E. H. Sargent & Co. · 155-165 East Superior St., Chicago

Now Available . . .

Universal Indicator Solution

EFFECTIVE RANGE—pH 4 to pH 10

ACCURACY—To within 0.5 pH

COLORS—Systematic succession of spectrum colors

COLOR CHANGES—At whole pH numbers

CATALOG LISTING—No. 4953, Universal Indicator Solution; 100 cc., $1.00

A description of the color changes, as well as suggested applications of this prepared universal indicator, will be forwarded promptly upon request. . . . Eastman Kodak Company, *Chemical Sales Division*, Rochester, N. Y.

BE SURE TO VISIT THE
KODAK BUILDING
AT THE NEW YORK
WORLD'S FAIR

EASTMAN ORGANIC CHEMICALS

Announcing The Second of Four Volumes on

Physical Constants of HYDROCARBONS

Cyclanes, Cyclenes, Cyclynes, and Other Alicyclic Hydrocarbons

by Gustav Egloff, Director of Research, Universal Oil Products, Chicago

A. C. S. Monograph No. 78—To be published in Four Volumes

THE scope of this work is such that it may be utilized in pure and applied science and in industries such as petroleum, natural and manufactured gas, chemical, rubber, plastic, resin and pharmaceutical. The ideal underlying this four volume study of the Physical Constants of Hydrocarbons, has been to contribute to the fundamental knowledge of hydrocarbons from the scientific as well as the pragmatic point of view. In the present work, the critical study of the hydrocarbon constants and their interrelationships to derive useful and sound generalizations has been the desired goal. The melting point, boiling point, specific gravity, and refractive index of all classes of pure hydrocarbons will appear in three volumes and their interrelationships in the fourth volume. The work is restricted to these four constants chiefly because they are the ones most frequently employed in identifying hydrocarbons and in industrial engineering. Bibliographical sources of all experimental values are given.

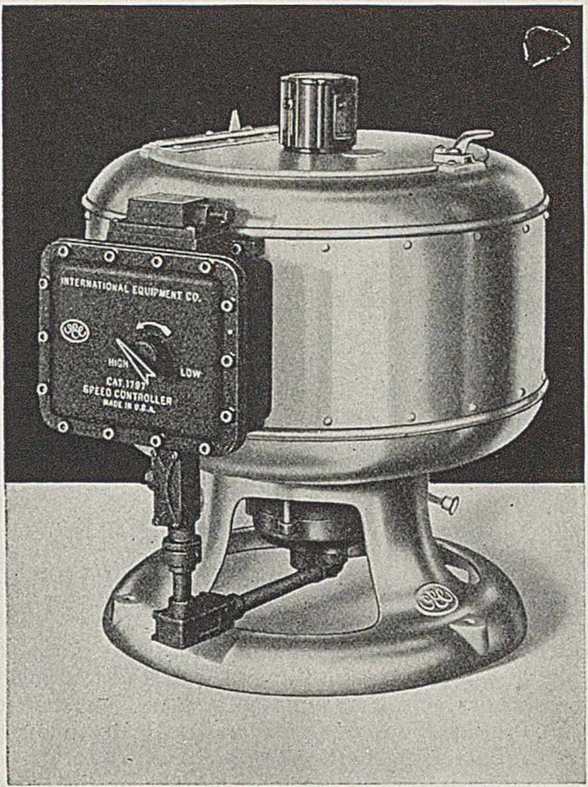
Volume I.—Covers paraffins, olefins, acetylenes, and other aliphatic hydrocarbons. 416 p., $9.00.

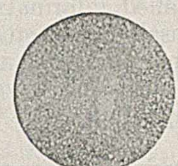
Volume II.—Includes the cycloparaffins, cycloölefins, cycloacetylene, bi- and dicycloparaffins and cycloölefins, olefin and acetylene substituted cycloparaffins and cycloölefins. 608 p., $12.00.

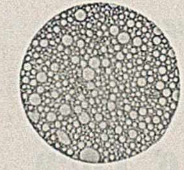
Volumes Three and Four to follow in rapid succession.

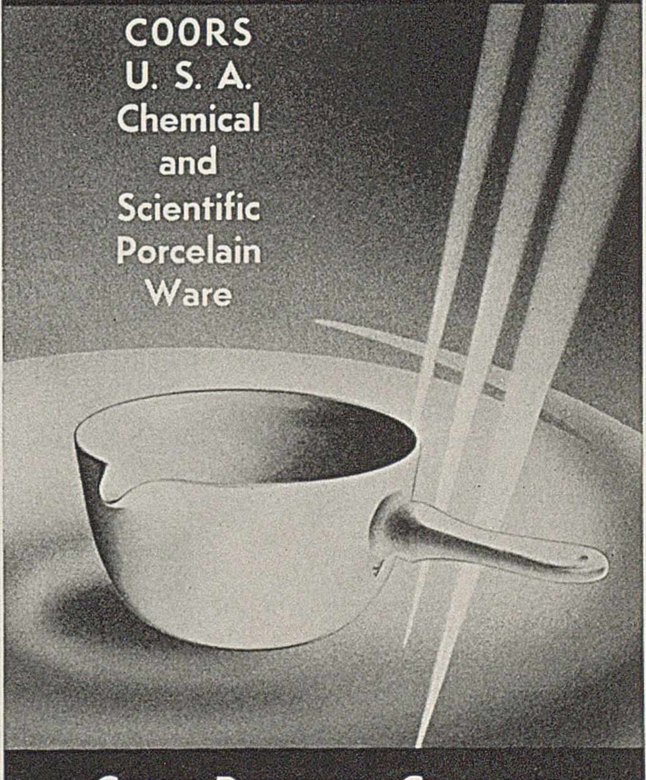
Place your order for complete set now.

Reinhold Publishing Corporation, 330 W. 42 Street, New York, U.S.A.


INTERNATIONAL EQUIPMENT CO.
HIGH
LOW
CAT. 1787
SPEED CONTROLLER
MADE IN U.S.A.







Spencer Instruments *for* INDUSTRIAL CONTROL

The Spencer No. 33 Microscope is adaptable to almost any type of microscopic examination and is designed for convenience in quickly changing magnifications or types of illumination, for photomicrography, for measuring, counting or examination of materials.

The Spencer Refractometer provides a quick and accurate method for determining the refractive indices of liquids and solids—essential in laboratory and plant control of food products, oils, fats, extracts, tars, colloids, waxes, resins, etc.

Direct result COLORIMETER is used wherever characteristic color is produced proportional in intensity to the concentration of a substance in solution.

Spencer Stereoscopic Microscopes are used in practically every industry for the examination of details too small to be seen by the unaided eyes—to examine impurities or inclusions in raw materials, flaws or irregularities in materials being processed, surface characteristics of finished products. A vivid three dimensional image is obtained.

The Spencer No. 41 Polarizing Microscope is used extensively in industrial laboratories for identification of crystalline materials by means of their optical constants. Ideally suited for research or routine inspection in the manufacture of ceramics, chemicals, petroleum, food, pharmaceuticals, textiles and paper.

The Spencer Microtomes are used for cutting cross-sections of frozen foods, for study of rate of freezing formations of ice crystals, leakage, cell rupture and color factors.

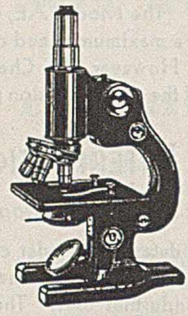
Write Dept. No. F48 for catalogs describing these instruments more completely.

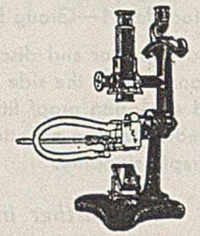
Spencer Lens Company

MICROSCOPES
MICROTOMES
PHOTOMICROGRAPHIC EQUIPMENT

SPENCER BUFFALO U.S.A.

REFRACTOMETERS
COLORIMETERS
SPECTROMETERS
PROJECTORS





PROPERTIES OF ORDINARY WATER-SUBSTANCE

In All Its Phases—Water-Vapor, Water, and All the Ices

Compiled by
N. ERNEST DORSEY
National Bureau of Standards

A. C. S. Monograph No. 81

A MONUMENTAL compilation of physical data, this volume represents a lifetime of effort on the part of the author, himself an eminent authority on the subject. In it he assembles, extends, and critically evaluates all the available information on water-substance, with special emphasis on the data published in the International Critical Tables. His statements are copiously documented and are accompanied at every point by data gathered by hundreds of observers.

The scope of this monograph is so comprehensive that only a few of the more general topics can be mentioned. Among these are the thermodynamic considerations involved in the synthesis and dissociation of water-substance; thermal energy of dilated water-vapor; molecular and pressure-volume-temperature data for all forms of water-substance; acoustic data; optical properties; the structure of water and ice as revealed by Raman Spectra and X-rays; the reflectivity of ice and snow; electrical properties of water-substance; the color of water and of the sea, etc.

That this exhaustive work will be of unique value to workers in many diverse fields, is evident from the fact that it contains 289 tables of data gathered from every available source and critically revised by the author. Of particular interest to aeronautical engineers is the material presented on such subjects as the mechanism of ice formation and the viscosity of fog; the data on icebergs and glaciers will be useful to geologists, oceanographers and hydrographers; and detailed information on rain, hail and snow will be indispensable for meteorologists. Hydraulic, steam and marine engineers, and physicists and physical chemists will also find a vast amount of vital information in this compilation.

An invaluable reference book for all working in these and related fields!

Circular sent on request

700 Pages **Illustrated** **$15.00**

Reinhold Publishing Corp.
330 West 42nd Street, New York, U. S. A.

"Time-It"

THE MODERN ELECTRIC STOPWATCH

BEING a split-second timer and second totalizer combined, "TIME-IT" is ideal for hundreds of laboratory and industrial timing jobs. Its large, legible, indicating counter reads direct to 1/10 second, totaling to 10,000 seconds (2 hrs. 46 minutes) before repeating, and can be reset to zero from any reading, or successive readings totalled.

★

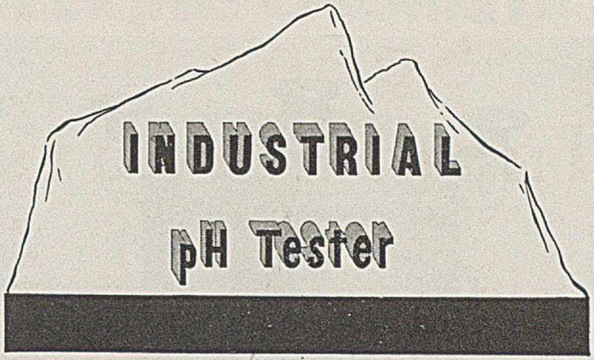
- No computations necessary for any intervals up to 10,000 seconds, in contrast to a 60-second stopwatch which requires computations to determine total seconds beyond 60.
- Run by a powerful, continuous-duty synchronous motor whose speed is governed by A.C. cycle constancy, "TIME-IT" is accurate within .02%. *Never needs standardizing.*
- Automatic built-in brake further insures accuracy—motor mechanism is several times more powerful than actually needed to run the counter.
- "TIME-IT" cuts out stopwatch repair bills once and for all—will save you money in the long run—is always ready when you need it, not off for repairs and adjustments.
- Only one set of large, legible figures to read instead of close, small dial figures. No guess-work in reading fractional seconds, no eye-strain even after all-day use.
- Sturdily built to take gruff handling which would quickly ruin a fragile stopwatch. Rugged aluminum housing; sturdy mechanism; dust shut out by non-breakable plastic window over counter.
- Compact handy size, only 4 x 5 x 3½", convenient for ordinary mounting or portable utility size.

With 6 ft. rubber covered cord and plug, for 110–115 Volts, 50 or 60 Cycles A.C. $32.50

A. DAIGGER & CO.

Laboratory Apparatus and Chemicals

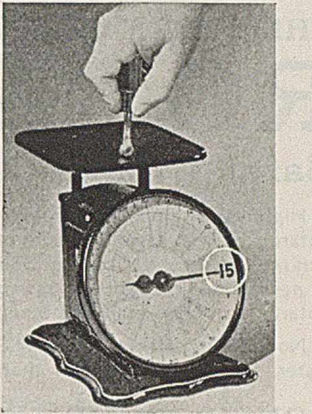
159 WEST KINZIE STREET • CHICAGO



After all . . .

the plant man is entitled to a SIMPLER pH tester than the chemist needs in his laboratory!

And he will want a more rugged glass electrode, for quick testing at the vat!



So the new Industrial pH Tester is simpler and the glass electrode is stronger! It will resist pressures up to 25 lbs. and it may safely be wiped and washed.

At half the price and over full glass electrode pH range, 0 to 12 pH, the industrial pH Tester makes more accurate pH control possible in the plant! Complete in metal case, ready for use.

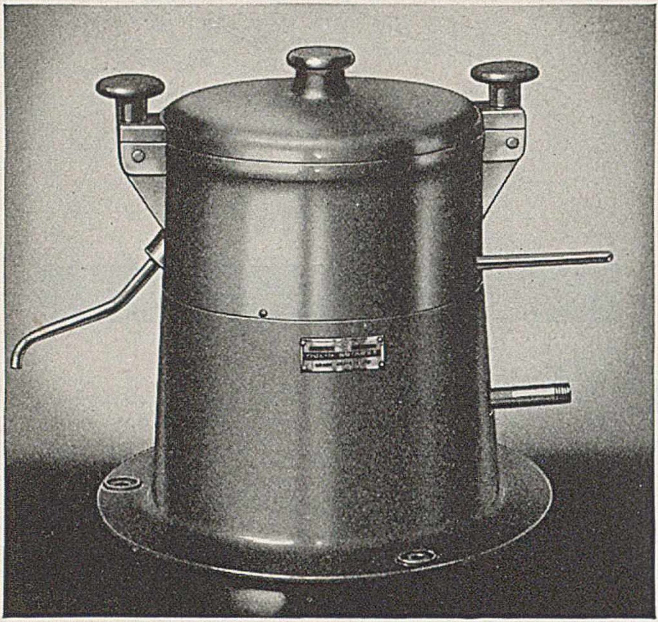
Complete $84.50

Ask for 5 Day Quick Trial

. . . or write for Bulletin IE615.

WILKENS-ANDERSON CO.

111 N. CANAL ST. CHICAGO



BRAUN DULIN ROTAREX, MODEL EP

Announcing

THE NEW MODEL EP BRAUN DULIN

ROTAREX

Safer • Faster • More Efficient

Highway engineers everywhere recognize the Braun Dulin Rotarex as the speediest and most efficient means of determining the bitumen content, and the character and gradation of aggregates in bitulithic paving materials. . . . For years the Rotarex has been standard equipment in highway laboratories.

Now Braun presents the new 1,000 gram Model EP Rotarex—faster, safer, more efficient than ever.

CONSIDER THESE NEW FEATURES

- **Explosion-Proof, Variable Speed Motor.** Underwriters approved for Class 1, Group D (hazardous) service. Operates on either A.C. or D.C. Model EP Rotarex is SAFE.
- **Quick Stopping Brake.** Model EP Rotarex decelerates rapidly without jarring contents. **Makes a fast test faster.**
- **Solvent can be Added while Running.** No need to stop the Rotarex during the test. Another time-saving feature.
- **Modern Design.** The new Rotarex has been re-engineered throughout. Handsomely modern in appearance. Efficient, accurate, up to the minute in every detail.

Highway Engineers and Inspectors, make sure that specifications are being followed exactly on your jobs by checking frequently with the new Model EP Rotarex.

Send today for your copy of Bulletin C-137 describing this Rotarex. Address Dept. I-6

BRAUN CORPORATION

2260 East Fifteenth Street
Los Angeles, California

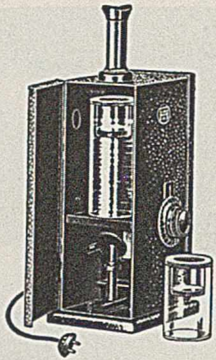
San Francisco, Calif.
BRAUN-KNECHT-HEIMANN-CO.

BRAUN

Seattle, Washington
SCIENTIFIC SUPPLIES CO.

HELLIGE TURBIDIMETER

for



Water Analysis, Sulfate Determinations and Measurements of Suspended Matter in Various Colorless and Colored Liquids

Recent improvements have greatly increased the convenience of this instrument for measuring turbidities without the preparation and use of standard suspensions. *An accurate test can be made in one minute.* Reads all turbidities down to zero.

The use of the Hellige Turbidimeter in sulfate determinations by the Betz-Hellige Method* gives sensitive and accurate results exceeding those obtainable by gravimetric analysis.

* *Turbidimetric Determination of Sulfate in Water, Betz-Hellige Method:* Sheen, R. et al., Ind. & Eng. Chem. (Anal). 7:262—July 15, 1935. *Reprint on request.*

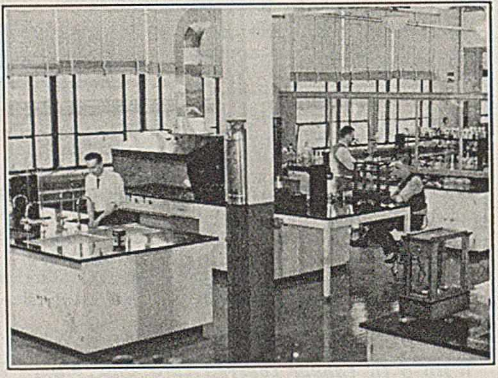
HELLIGE
INCORPORATED
3718 NORTHERN BLVD., LONG ISLAND CITY, N.Y.

SPECIFY

SHELDON

CAN YOUR LABORATORY EXPAND? WITH YOUR BUSINESS•

• SHELDON INDUSTRIAL SECTIONS—MATCHED AND INTERCHANGEABLE — are the answer when laboratories are being planned for present needs and provisions made for future production demands.



Write for No. 24 Catalog!

E. H. SHELDON COMPANY
Muskegon • Michigan
LABORATORY FURNITURE