INDUSTRIAL AND ENGINEERING CHEMISTRY

Analytical Edition
Vol. 7, No. 6

November 15, 1935

Vol. 27, Consecutive No. 38
Published by the American Chemical Society
Harrison E. Howe, Editor

Publication Office: Easton, Pa. . 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

CONTENTS

16,100 Copies of This Issue Printed

Subscription to nonmembers, Industrial and Engineering Chemistry, $7.50 per year. Foreign postage $2.10, except to countries accepting mail at American domestic rates. To Canada, 70 cents. Analytical Edition only, $2.00 per year, single copies 75 cents, to members 60 cents. Foreign postage, 30 cents; Canada, 10 cents. News Edition only, $1.50 per year. Foreign postage, 60 cents; Canada, 20 cents. Subscriptions, changes of address, and claims for lost copies should be referred to Charles L. Parsons, Secretary, Mills Building, Washington, D. C. The Council has voted that no claims will be allowed for copies of journals lost in the mails, unless such claims are received within 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. If change of address implies a change of position, please indicate its nature.

The American Chemical Society also publishes the *Journal of the American Chemical Society* and *Chemical Abstracts*.

ELECTRIC HEAT FOR THE LABORATORY

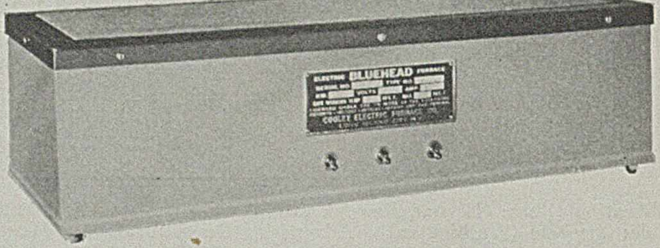
1 HOT PLATES
Type H.P.

ADVANTAGES

No metal top plate; no pitting or corroding from spillings; no warping.
Vessels heated directly and quickly.
High temperature, 1000 degrees F. standard maximum.
Three heat control.
Protected Doreco element.
Adjustable feet for leveling plate.

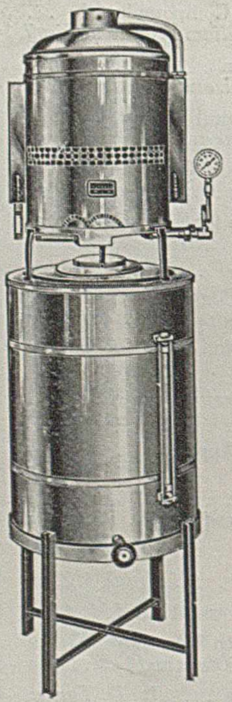
TYPE No.	SIZE in inches	PRICE
HP1	6 x 18	$28.00
HP2	12 x 12	33.00
HP3	12 x 18	42.00
HP4	18 x 24	By quotation
HP5	4½ x 24	28.00

For detailed description on hot plates or muffle combustion or crucible furnaces, consult your dealer or write for catalogue No. 34.



Type HP1. Metal top plates are unnecessary. Vessels are heated directly by the protected Doreco element

COOLEY ELECTRIC FURNACE COMPANY
INDIANAPOLIS, INDIANA



PRECISION WATER STILLS

"Precision" Automatic Water Stills, with their many excellent features, comprise ideal units for the production of chemically pure distilled water for every laboratory requirement. They unite every factor conducive to efficient, low-cost production of pure distilled water.

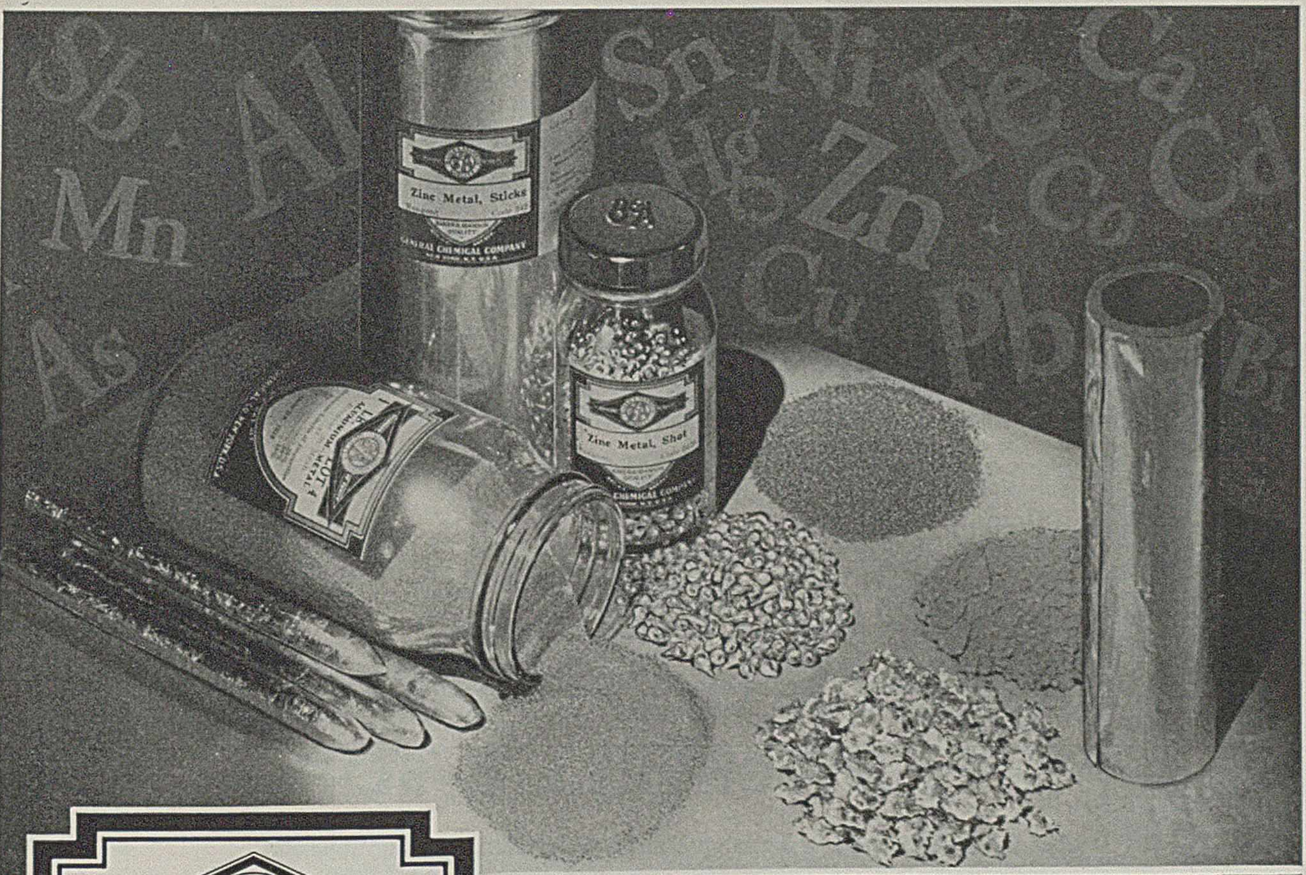
Models are available heated by electricity, steam, gas or gasoline, in capacities ranging from one to four gallons of pure distilled water per hour. Capacity ratings apply to normal free-running still operation, although steam heated stills are capable of delivering as much as 100% more distilled water than their minimum ratings indicate, to meet emergency needs. All "Precision" Automatic Water Stills are identical as to the process of distillation, differing only in their respective means for supplying the heat required to cause vaporization.

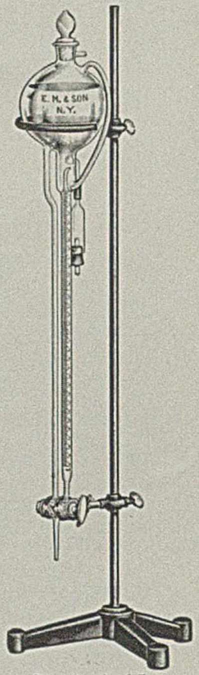
Illustration shows catalog No. 14334 Still, steam heated, and No. 14338 Storage Tank.

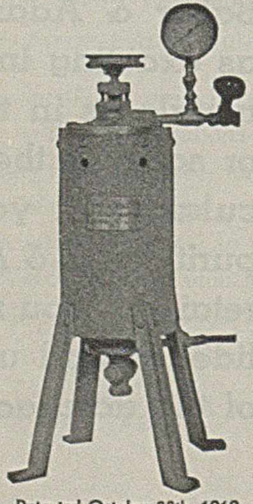
Write for complete descriptive bulletin.

W. J. GILMORE DRUG COMPANY
LABORATORY APPARATUS DIVISION
422 Blvd. of the Allies Pittsburgh, Pennsylvania

Published by the American Chemical Society, Publication Office, 20th & Northampton Sts., Easton, Pa.
Entered as second-class matter at the Post-Office at Easton, Pa., under the act of March 3, 1879, as 42 times a year. Industrial Edition monthly on the 1st; News Edition on the 10th and 20th; Analytical Edition bimonthly 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.


Sb
Al
Mn
As
Sn
Ni
Fe
Ca
Hg
Zn
Co
Cd
Cu
Pb
Bi
Zinc Metal, Sticks
GENERAL CHEMICAL COMPANY
Zinc Metal, Shot
LOT 4


E. M. & SON
N.Y.



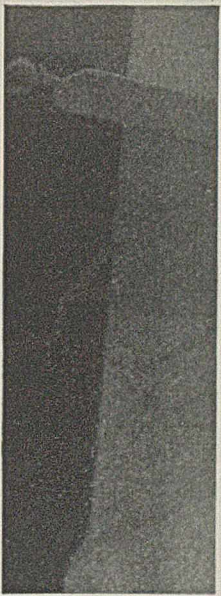
WHEN you specify Kimble Blue Line Exax Volumetric Flasks, you can be assured that nothing finer, nothing more accurate, nothing higher in quality and refinements is produced in a piece of technical glassware. Blue Line Exax flasks are made from blanks carefully selected to eliminate blisters, stones and streaks. The walls are heavy enough to resist the shocks of daily service. Bottoms are wide enough to stand (unstoppered) on a 15° slope without tipping—a requirement of the National Bureau of Standards.

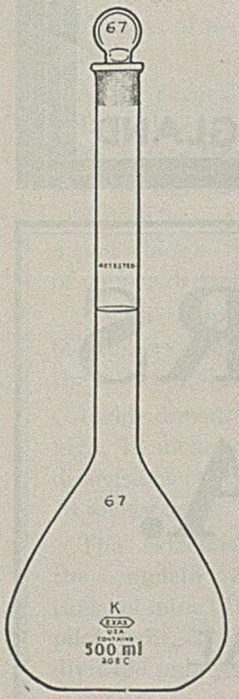
All lines and numbers are deeply acid-etched and filled with a brilliant and durable BLUE GLASS, fused in. Every flask—from the 10 ml. to the 2000 ml. size—is calibrated at 20° C. and RETESTED and RETEMPERED (strain-free).

Stoppers and necks are carefully ground to a leak-proof fit, and flasks and stoppers sandblasted with corresponding serial numbers. These flasks are guaranteed to the following tolerances:

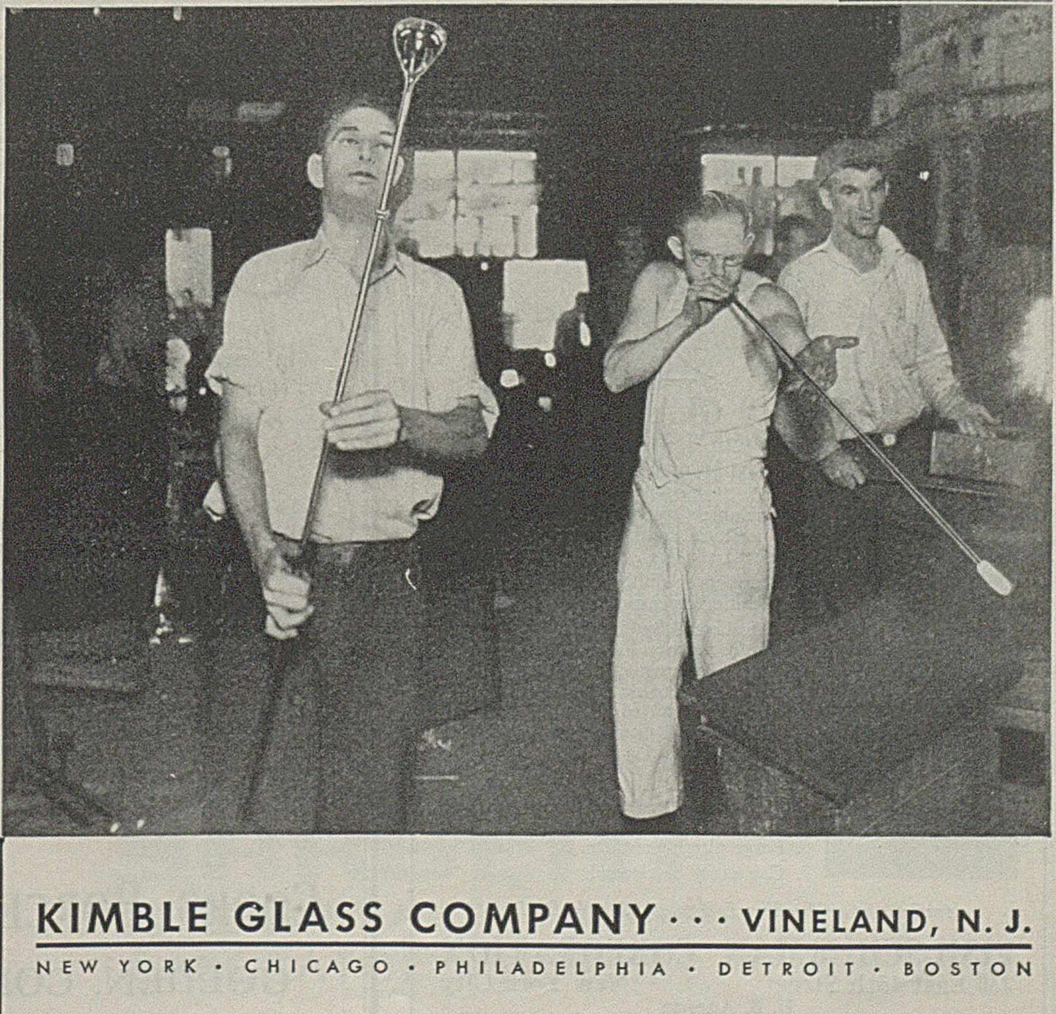
Size	*Calibrated to Contain*	*Calibrated to Deliver*
10 ml.	±0.06 ml.	±0.10 ml.
25 ml.	0.06 ml.	0.10 ml.
50 ml.	0.10 ml.	0.20 ml.
100 ml.	0.16 ml.	0.30 ml.
200 ml.	0.20 ml.	0.40 ml.
250 ml.	0.24 ml.	0.50 ml.
500 ml.	0.30 ml.	0.60 ml.
1000 ml.	0.60 ml.	1.00 ml.
2000 ml.	1.00 ml.	2.00 ml.

Blue Line Exax Flasks—as well as a full line of Kimble Laboratory Glassware—are stocked by Laboratory Supply Houses throughout the United States and Canada. For the sake of assured accuracy and service, SPECIFY EXAX.





BOOTHS 279-280
•
CHEMICAL INDUSTRIES EXPOSITION
•
GRAND CENTRAL PALACE
DECEMBER, 1935



KIMBLE GLASS

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

NEW YORK · CHICAGO · PHILADELPHIA · DETROIT · BOSTON

SARGENT

Electric Drying Oven

Automatically Controlled

Accuracy 1° C

$35.00

Any temperature up to 160° C may be maintained within ± 1°C by simple adjustment of a three heat switch and regulator conveniently placed on the front panel of the oven.

Considerably higher temperatures ranging from 195° to 200° C are readily obtained, with but a slight loss of accuracy, by closing inlet and outlet holes.

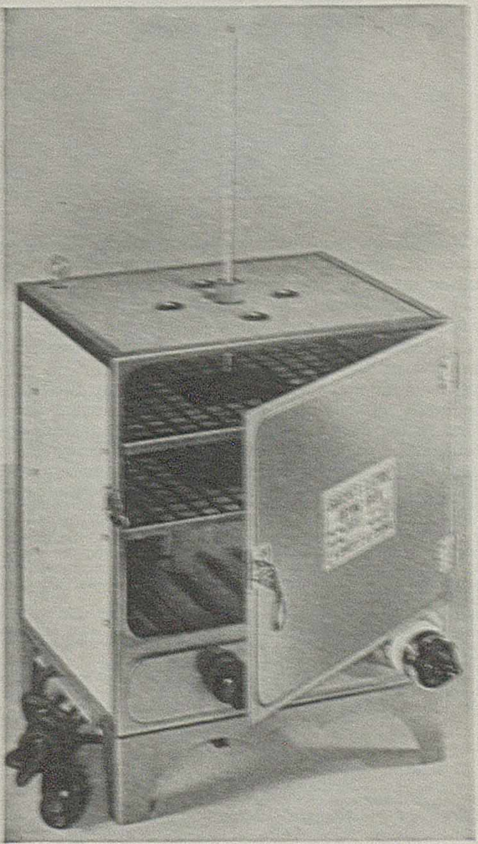
As the rugged welded frame and both sides of the well insulated door are made of Monel metal, the oven is free from corrosion and disintegration as well as the possibility of contamination of the sample when opening and closing the door, a condition which so frequently occurs with constructions of copper or treated iron.

A wide temperature range, reliable maintenance of temperature and freedom from corrosion make the oven suitable for a large number of applications.

Inside dimensions of working chamber, 10 inches high, 12 inches wide and 10 inches deep; outside dimensions over all, 16 inches high, 13 inches wide, 13 inches deep; maximum power input, 900 watts.

The extremely low price of $35.00 includes the complete oven with a thermometer having a range of minus 10 to plus 200° C in 1° sub-divisions, pilot light, 2 perforated metal shelves, cord and divisible plug for attaching to standard outlet.

All changeable parts are easily removed and economically replaced.



Bulletin on request to
E. H. Sargent & Co. 155 E. Superior St. Chicago

SARGENT
E. H. SARGENT & CO. CHICAGO
LABORATORY SUPPLIES

Two absorbent mixtures for carbon combustions in steel analysis

ASCARITE

Over 25 tons of Ascarite have been sold by us throughout the world since its introduction in 1918

ASCARITE. Prepared in accordance with the formula of James B. Stetser for the absorption of CO_2 in the determination of carbon in iron and steel. See *The Iron Age, Vol. 102, No. 8.* In universal use in the steel and iron industry throughout the world.

While originally designed for use in the Stetser-Norton modification of the Midvale Absorption Bulb, it can be used with equal satisfaction in the Fleming, Nesbitt and similar bulbs and is particularly recommended for use with the Miller Bulb; 60 grams of Ascarite (the contents of a Midvale Absorption Bulb) will absorb from 10 to 15 grams of CO_2. Therefore 500 grams of Ascarite provides for from 2,000 to 4,000 determinations. In much laboratory practice it is used without an additional dryer but, where use of the latter seems advisable, we recommend Dehydrite. Because of the difference in color between the used and unused portions of the absorbent, it is possible to determine exactly when a bulb should be discarded.

Ascarite is used for carbon dioxide absorption in carbon-hydrogen determinations. See J. S. Buck, *Industrial and Engineering Chemistry, Vol. 18, No. 12 (December, 1926), p. 1321.*

Ascarite is also used for the removal of carbon dioxide in the analysis of respiratory gases. See Paul G. Ledig and Richard S. Lyman, *The Journal of Clinical Investigation, Vol. IV, No. 4 (Oct. 20, 1927), p. 495.*

It is also recommended as a carbon dioxide absorbent in quantitative organic microanalysis by Pregl. See "*Die Quantitative Organische Mikroanalyse,*" 3rd edition (Berlin, 1930), p. 47.

			Code Word
Mesh 8 to 20	Per 1 lb. c.s.b.	4.10	*Ulvrf*
	" 500 gram c.s.b.	4.50	*Ulvuz*
	" 1 kilo c.s.b.	8.50	*Ulvyr*
Mesh 12 to 20	Per 1 lb. c.s.b.	4.10	*Ulwsc*
	" 500 gram c.s.b.	4.50	*Ulwuy*
	" 1 kilo c.s.b.	8.50	*Ulwwu*
Mesh 20 to 30	Per 1 lb. c.s.b.	4.10	*Ulxga*
	" 500 gram c.s.b.	4.50	*Ulxju*
	" 1 kilo c.s.b.	8.50	*Ulxoj*

DEHYDRITE

A new Anhydrous salt, at lower price, and with almost double the moisture absorbing capacity of the Trihydrate salt previously supplied

DEHYDRITE, Anhydrous Granular Magnesium Perchlorate—Smith. A dehydrating agent for use as a water absorbent in carbon combustions in steel analysis, in the ultimate analysis of organic substances, and in the drying of gases, including respiratory gases and carbon monoxide in air and blood.

This new anhydrous salt has almost double the moisture absorbing capacity of the trihydrate salt previously supplied under our registered trade mark, "DEHYDRITE." In addition, it possesses the following advantages:

Facility in charging, since the drying agent does not become sticky while momentarily in contact with atmospheric moisture.

Channels do not form in the salt and decrease its efficiency.

The deterioration of the reagent is accompanied by contraction in volume, thus reducing the tendency of drying tubes to clog.

On account of its porous nature, it offers almost no resistance to the passage of gas.

Cotton can be used as plugs.

The spent reagent is easily removed from its container.

See *Industrial and Engineering Chemistry, Vol. 16, No. 1 (January, 1924), p. 20; The Journal of Clinical Investigation, Vol. IV, No. 4 (Oct. 20, 1927), p. 495;* and *American Journal of Public Health, Vol. XIX, No. 3 (March, 1929), p. 293.*

	Price	Code Word
Per 250 gram c.s.b.	1.92	*Vyphe*
Per 500 gram c.s.b.	3.52	*Vypic*

ARTHUR H. THOMAS COMPANY

RETAIL—WHOLESALE—EXPORT

LABORATORY APPARATUS REAGENTS

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

ANALYTICAL EDITION
INDUSTRIAL
AND ENGINEERING
CHEMISTRY

Volume 7
Number 6

November 15,
1935

Harrison E. Howe, Editor

Direct Simultaneous Microdetermination of Carbon, Hydrogen, and Oxygen

II. Analysis of Pure Compounds Containing Carbon, Hydrogen, Oxygen, and Sulfur

W. R. KIRNER, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

THE purpose of this paper is (1) to extend the development of the direct simultaneous microdetermination of carbon, hydrogen, and oxygen to compounds which also contain sulfur; (2) to get information regarding the ultimate fate of the sulfur present in different types of linkage in organic compounds, after being subjected to combustion; and (3) to study the mechanism of the reaction between oxides of sulfur and the absorbents which are present in the combustion tube filling.

The elementary analysis of organic substances containing sulfur has caused relatively little difficulty. Different investigators seem to disagree as to whether sulfur dioxide or trioxide is the final oxidation product of the sulfur present in the molecule. It is common practice to remove either, or both, of these substances by the addition of a suitable absorbent to the combustion tube filling. The absorbents generally used are lead chromate or lead peroxide, both of which fix the oxides of sulfur as relatively nonvolatile lead sulfate. The efficacy of metallic silver as an absorbent for oxides of sulfur was pointed out by Dennstedt (*1*), but its use for this purpose seems to have been completely overlooked.

In the direct determination of oxygen by an oxidation process it is important to know whether sulfur dioxide or trioxide is formed. If both are formed, the proportion of the one to the other must be determined, since more oxygen is consumed in forming sulfur trioxide than in forming the dioxide. In most previous investigations using this method, it has been assumed that either sulfur dioxide (*2*) or sulfur trioxide (*3, 15–18*) is the sole final oxidation product of the sulfur present in the molecule.

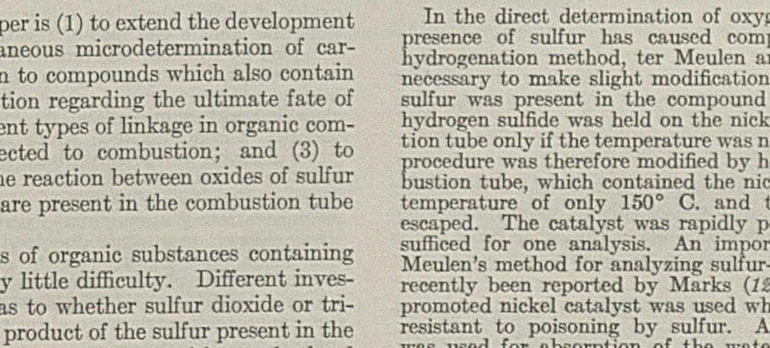


Figure 1. Temperatures Existing in Microcombustion Tube

In the direct determination of oxygen by other methods the presence of sulfur has caused complications (*14*). In their hydrogenation method, ter Meulen and Heslinga (*13*) found it necessary to make slight modifications in their procedure when sulfur was present in the compound being analyzed. All the hydrogen sulfide was held on the nickel catalyst in the combustion tube only if the temperature was not too high. The ordinary procedure was therefore modified by heating the end of the combustion tube, which contained the nickel-asbestos catalyst, to a temperature of only 150° C. and then no hydrogen sulfide escaped. The catalyst was rapidly poisoned by the sulfur but sufficed for one analysis. An important improvement to ter Meulen's method for analyzing sulfur-containing substances has recently been reported by Marks (*12*). In his work a thoria-promoted nickel catalyst was used which was found to be quite resistant to poisoning by sulfur. Anhydrous calcium sulfate was used for absorption of the water formed; this absorbent does not retain ammonia, hydrogen sulfide, or carbon dioxide.

Experimental

The apparatus and procedure used in the present investigation were identical to that already described (*9*).

In order to get information regarding the effect of the type of sulfur linkage present in the compound on the direct determination of oxygen, two substances were selected for analysis. The first was a sulfone, which would be expected to yield sulfur dioxide when subjected to thermal decomposition (*7*), and the second was a sulfonic ester, which would be expected to yield sulfur trioxide on thermal decomposition (*8*).

From theoretical considerations one would predict that the extent of the oxidation of the sulfur in the substance analyzed would be a function of the sulfur dioxide–sulfur trioxide equilibrium at the temperature existing in the combustion tube. There was a large excess of oxygen always present and the temperature of the palladium asbestos catalyst varied from a maximum of 588° C. down to a minimum of about 425° C. before the gases reached absorbents which made further equilibration impossible. Figure 1 illustrates the combustion tube and its filling and shows the temperatures which existed at various points in the tube. These temperatures were measured with a chromel-alumel thermocouple imbedded in the palladium-asbestos with oxygen flowing at the rate of 3 cc. per minute. The conditions existing during these temperature measurements were made to simulate, as closely as possible, those of the actual determinations. The combustion tube had an internal diameter of 8 mm., so that with this gas flow the linear flow rate was 1 cm. in 12.8 seconds.

Under these conditions one would expect 99 to 100 per cent of sulfur trioxide as the final product, since, according to Knietsch (*10*), who made a study of the equilibrium reaction

$$2SO_3 \overset{\text{Pt}}{\rightleftharpoons} 2SO_2 + O_2$$

under conditions similar to those used here, the percentages of sulfur trioxide shown in Table I exist at the indicated temperatures.

TABLE I. SULFUR DIOXIDE-TRIOXIDE EQUILIBRIUM

(According to Knietsch)

Temperature	SO_3
° *C.*	%
300	76[a]
350	95[a]
400	100
450	99
500	96
550	88
600	80

[a] Equilibrium not attained.

Table II gives the experimentally determined values for the "oxygen consumed" and also the calculated values, assuming in one case that sulfur trioxide and, in the other, that sulfur dioxide is the total final oxidation product of the sulfur.

Column 4 indicates that the found values are higher than the calculated values by a practically constant amount. The theoretical amount of sulfur present in the compounds was used in these calculations; in calculations made on unknown substances the percentage of sulfur present must be determined by an independent analysis. Column 5 gives the weight of oxygen equivalent to the weight of sulfur in the sample—i. e., the weight of oxygen involved in each single stepwise oxidation of the sulfur present. There is a close agreement between the figures in columns 1 and 6. The average value of the found oxygen consumed is 99.78 per cent of that calculated, assuming SO_4 formation. These figures are brought out in columns 7 and 8. The mean difference (column 7) corresponds to approximately the limits of accuracy of the gasometric determination of the oxygen consumed. However, since these differences all have the same sign and since the temperature (about 425° C., Figure 1) existing in the combustion tube at the point where the gases encounter the metallic silver after having passed over the catalyst is such that one would expect a small amount (1 per cent or less) of sulfur dioxide to still be present, it is also possible (*4*) that the discrepancy between the figures in columns 4 and 5 is due to the incomplete oxidation of the sulfur to sulfur trioxide and then to SO_4.

On the basis of these results it would appear that the lead peroxide in the combustion tube filling is not concerned in the absorption of the oxides of sulfur. If any oxides of sulfur reached the lead peroxide they would react according to Equations 1 and 2:

$$PbO_2 + SO_2 = PbSO_4 \quad (1)$$

$$2PbO_2 + 2SO_3 = 2PbSO_4 + O_2 \quad (2)$$

Experimentally, from the determined oxygen consumed, and theoretically, from the temperature which existed in the combustion tube, it is reasonably certain that sulfur trioxide is the predominating product of the oxidation of the sulfur present in the samples. If any sulfur trioxide came into contact with the lead peroxide an atom of oxygen would be evolved for every molecule of trioxide which reacted, whereas actually an additional atom of oxygen was consumed for every molecule of sulfur trioxide present.

While several investigators (*5*, *6*, *11*, *19*) have demonstrated that lead peroxide is a quantitative absorbent for oxides of sulfur, it was Dennstedt (*1*) who showed that metallic silver is also capable of quantitatively absorbing sulfur trioxide, forming silver sulfate, the increase in weight being due to the addition of SO_4.

In order to demonstrate that the silver had absorbed the oxides of sulfur, the silver filling in the middle of the combustion tube and in the rear of the tube adjacent to the position occupied by the boat was removed and added to distilled water containing a few crystals of barium chloride. A white precipitate immediately formed which consisted of a mixture of silver chloride and barium sulfate, the former being due to the metathetical reaction between silver sulfate and barium chloride. After digesting on the steam bath for a short time the characteristic curdy precipitate of silver chloride could be recognized. After cooling, the mixture was made alkaline with a few drops of concentrated ammonium hydroxide solution. The curdy silver chloride precipitate dissolved, leaving a fine silky precipitate which, after digestion on the steam bath, formed the microcrystalline precipitate characteristic of barium sulfate. Work is being started in this laboratory using this reaction as the basis for a microacidimetric method for the determination of sulfur in organic compounds.

The absorption of the sulfur trioxide by the metallic silver therefore fully explains the results obtained in the present work. Either the sulfur burns directly to sulfuric acid, as postulated by Dennstedt (in the presence of excess oxygen and water formed during the combustion), and then reacts with the silver, or, as seems more likely, the sulfur trioxide reacts directly with the silver, forming silver sulfite, which then immediately oxidizes to sulfate. Whatever the mechanism, this reaction satisfactorily explains the amount of oxygen which is consumed during the combustion of a sulfur-containing substance. It is immaterial whether the sulfur is eliminated from the sample as dioxide or trioxide during thermal decomposition, the final yield of trioxide being the same.

TABLE II. DETERMINATION OF OXYGEN CONSUMED

	Oxygen Consumed				Oxygen Consumed			
		Calculated, based on formation of:						
Compound	Found	SO_3	SO_2	Found minus calculated (SO_3)[a]	To convert SO_2 to SO_3 or SO_3 to SO_4	Calculated, based on formation of SO_4[b]	Difference	
	Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*[c]	%[d]
Diphenyl sulfone	16.204	15.705	15.181	0.499	0.524	16.229	−0.025	99.85
	16.348	15.876	15.347	0.472	0.529	16.405	−0.057	99.65
Phenyl p-toluene sulfonate	15.707	15.276	14.799	0.431	0.477	15.753	−0.046	99.70
	16.784	16.287	15.778	0.497	0.509	16.796	−0.012	99.93
						Mean	−0.035	99.78

[a] Column 1 − column 2.
[b] Column 2 + column 5.
[c] Column 1 − column 6.
[d] Column 1 ÷ column 6.

TABLE III. ILLUSTRATING METHOD OF CALCULATION

	Mg.
Weight of sample (diphenyl sulfone)	7.137
Weight of carbon dioxide, found	17.283
Weight of water, found	2.982
	%
Carbon, found	66.05
Carbon, theory	66.01
Difference	+0.04
Hydrogen, found	4.68
Hydrogen, theory	4.62
Difference	+0.06
	Cc.
Volume of oxygen at start (738.88 mm., 298.42° K.)	87.698
Volume of oxygen at start, NTP	78.026
Volume of mercury added	12.102
Volume of oxygen at end (736.47 mm., 300.79° K.)	75.607
Volume of oxygen at end, NTP	66.521
Volume of oxygen at end, NTP plus correction (0.166 cc.)	66.687
Volume of oxygen consumed, NTP	11.339
	Mg.
Weight of SO_4 formed, theory	3.143
Weight of oxygen consumed, found	16.204
	Mg.
Weight of actual oxygen consumed (found ÷ 99.78)	16.240
Weight of oxygen consumed, theory (based on SO_4 formation)	16.228
Difference	+0.012
Weight of oxygen in carbon dioxide, found	12.569
Weight of oxygen in carbon dioxide, theory	12.564
Difference	+0.005
Weight of oxygen in water, found	2.648
Weight of oxygen in water, theory	2.617
Difference	+0.031
Weight of oxygen in SO_4	2.094
Sum of oxygen in combustion products, found	17.311
Sum of oxygen in combustion products, theory	17.275
Difference	+0.036
Oxygen in sample, found (O_2 in combustion products minus O_2 consumed)	1.071
Oxygen in sample, theory (O_2 in combustion products minus O_2 consumed)	1.047
Difference	+0.024
	%
Oxygen in sample, found	15.01
Oxygen in sample, theory	14.67
Difference	+0.34

TABLE IV. RESULTS

		Found				Difference from Theory				
Compound	Sample	C	H	O	Oxygen consumed	C	H	O	Oxygen consumed	S
	Mg.	%	%	%	*Mg.*	%	%	%	*Mg.*	%
Diphenyl sulfone	7.137	66.05	4.68	15.01	16.204	+0.04	+0.06	+0.34	+0.012	14.70
	7.215	65.78	4.67	14.72	16.348	−0.23	+0.05	+0.05	−0.021	14.70
Phenyl *p*-toluenesulfonate	7.404	62.85	4.95	20.10	15.707	−0.01	+0.08	+0.76	−0.013	12.92
	7.894	62.90	4.98	19.97	16.784	+0.04	+0.11	+0.63	+0.025	12.92
					Mean	−0.04	+0.08	+0.45 ±0.12	+0.002 ±0.008	

Results

To illustrate the method of calculation, the complete data are given in Table III for one of the compounds. The actual oxygen consumed is obtained by dividing the found oxygen consumed by 99.78, the mean percentage difference between the found and theoretical oxygen consumed, based on SO_4 formation. This is justified by the possibility that a small amount of sulfur dioxide still persists in the combustion gases.

Finally, Table IV gives the summarized data for the two pure compounds analyzed.

The hydrogen determinations, particularly in case of the phenyl *p*-toluenesulfonate, are in error by amounts greater than desired. It is primarily this error which causes the error in the oxygen determination to reach the magnitudes indicated, since errors in the hydrogen determination are multiplied by 8 and errors in the carbon determination are multiplied by 2.67 in terms of oxygen. Although the samples were dried for some time in a vacuum desiccator over sulfuric acid, it may be that these substances tenaciously hold moisture.

Summary

The direct, simultaneous microdetermination of carbon, hydrogen, and oxygen has been extended to include compounds also containing sulfur.

Regardless of whether the sulfur linkage is such that, on thermal decomposition, sulfur dioxide or trioxide is primarily formed, the sulfur appears in the final combustion gases as sulfur trioxide, although it is possible that exceedingly small amounts of sulfur dioxide may also be present.

The sulfur trioxide is absorbed by the metallic silver present in the combustion tube filling and is quantitatively retained as silver sulfate, an atom of oxygen being consumed in converting the sulfur trioxide to SO_4.

Four analyses made on two different compounds indicate that the results are accurate to about 0.4 ± 0.1 per cent. The errors in the method are primarily due to the rather large multiplication of errors made in the determination of carbon and hydrogen. The gasometric determination of the oxygen consumed is of satisfactory accuracy.

Literature Cited

(1) Dennstedt, M., *Ber.*, 30, 1590–7 (1897).
(2) Dolch, M., and Will, H., *Brennstoff-Chem.*, 12, 166–9 (1931).
(3) Dumke, W., *Quart. Colo. School Mines*, 26, No. 2, 5–21 (1931).
(4) Friedrich, A., and Watzlaweck, *Z. anal. Chem.*, 89, 401–11 (1932).
(5) Guillard, *Chem. Zentr.*, 1883, 276.
(6) Henry, *J. Pharm. Sci. Accessories*, 20, 59 (1834).
(7) Hurd, C. D., "Pyrolysis of Carbon Compounds," p. 76, New York, Chemical Catalog Co., 1929.
(8) Hurd, C. D., *Ibid.*, p. 707.
(9) Kirner, W. R., IND. ENG. CHEM., Anal. Ed., 6, 358–63 (1934).
(10) Knietsch, R., *Ber.*, 34, 4069–4115 (1901).
(11) Kopfer, F., *Z. anal. Chem.*, 17, 1–53 (1878).
(12) Marks, M. E., IND. ENG. CHEM., Anal. Ed., 7, 102–3 (1935).
(13) Meulen, H. ter, and Heslinga, J., "Neue Methoden der organisch-chemischen Analyse," pp. 16–17, Leipzig, Akademische Verlagsgesellschaft, 1927.
(14) Mitscherlich, A., *Z. anal. Chem.*, 6, 136–66 (1867).
(15) *Ibid.*, 15, 371–417 (1876).
(16) Staněk, V., and Nemes, T., *Ibid.*, 95, 244–60 (1933); *Chem.-Ztg.*, 56, 285–7 (1932).
(17) Strebinger, R., *Z. anal. Chem.*, 58, 97–114 (1919).
(18) Stromeyer, A., *Ann.*, 117, 247–60 (1861).
(19) Warren, C. M., *Z. anal. Chem.*, 5, 169–74 (1866).

RECEIVED August 9, 1935. Presented before the Division of Physical and Inorganic Chemistry at the 89th Meeting of the American Chemical Society, New York, N. Y., April 22 to 26, 1935.

(Part III follows)

III. Analysis of Pure Compounds Containing Carbon, Hydrogen, Oxygen, and Nitrogen

THE purpose of this paper is to extend the development of the direct microdetermination of carbon, hydrogen, and oxygen in organic compounds to substances containing nitrogen, and to study the influence of the type of nitrogen linkage present upon the ultimate fate of the nitrogen after complete combustion of the sample.

The presence of nitrogen in organic compounds has always been a complicating factor in elementary analysis, necessitating the addition of some substance to the combustion tube filling which would either absorb any oxides of nitrogen formed by oxidation of the nitrogen present in the sample, or reduce them to elementary nitrogen. In the direct determination of oxygen by an oxidation process, the simultaneous presence of nitrogen introduces additional complications and, in many cases (*16, 17, 18*) has made the direct determination of oxygen impossible. In the gasometric combustion method (*4, 5*), it has previously been assumed that the nitrogen present in the samples analyzed was completely converted to elementary nitrogen, even in the case of trinitrobenzene (*5*). It is certainly difficult to visualize how the three nitro groups in trinitrobenzene could be completely deoxidized to elementary nitrogen in an atmosphere of oxygen.

In their hydrogenation method, ter Meulen and Heslinga (*11*) had to modify their procedure slightly when analyzing compounds containing nitrogen because the nitrogen appeared both as ammonia and in the elementary state. Analysis of an amide, oxime, nitro, and azo compound by a modification of this method (*14, 15*) generally yielded over 50 per cent of the nitrogen in the sample as ammonia, regardless of the type of nitrogen linkage present.

In the combustion of an organic nitrogen-containing compound, the nitrogen does not appear in the combustion products in any single combination unless the combustion tube filling contains a reagent which is capable of performing the necessary reaction (*2, 9, 12*). Any contrary assumption is not in agreement with the facts. Hence, in the direct determination of oxygen by an oxidation process it is important to know the amount of oxygen involved in the oxidation of the nitrogen present—i. e., the fate of the nitrogen after complete combustion of the sample.

Experimental

The apparatus and procedure used in the present work were identical to that already described (*7*). Five pure organic nitrogen-containing compounds were analyzed, the percentage of nitrogen varying from 5.6 to 10.4 per cent and the oxygen from 8.1 to 16.1 per cent. In order to get information regarding the effect of the type of nitrogen linkage on the ultimate fate of the nitrogen after complete combustion of the sample, the compounds selected had the following types of nitrogen linkages: (1) amido, (2) amino, (3) heterocyclic, (4) nitrile, and (5) nitro.

The "oxygen consumed" was first calculated, entirely neglecting the fact that nitrogen was present. The results are shown in Table I.

From Table I it is observed that, on the basis of oxygen consumed, the compounds group themselves into two classes: the found oxygen consumed is (1) less than the theoretical, and (2) greater than the theoretical. Strebinger (*17*) and also Staněk and Nemes (*16*) found, for the substances they studied, a similar division into two classes. One class, in which the nitrogen was quantitatively converted into ammonia and gave satisfactory results for oxygen consumed, likewise contained amino and amido groups. The other class, in which the oxygen consumed could not be successfully determined, because of the formation of a mixture of nitric acid and nitrogen, contained nitro, heterocyclic, azo, osazone, hydrazone, and betaine nitrogen.

Before proceeding to the determination of the oxygen content of the samples analyzed, using the combustion data obtained and including their nitrogen content, it was necessary to have some information as to the ultimate fate of the nitrogen present. It is assumed that, in the complete combustion of an organic substance, two distinct reactions occur: (1) the thermal decomposition of the substance, followed by (2) complete oxidation of the pyrolytic products. The rate of oxidation and the final state of equilibrium are determined by factors such as the amount of oxygen available, the temperature existing in the combustion tube, and the presence of catalysts and absorbents in the combustion tube filling. Sufficient oxygen should always be present so that this does not become a limiting factor and the rate of gas flow should be slow enough to permit complete equilibration under the conditions existing in the combustion tube before the gases reach any absorbent.

Table I. Theoretical and Observed Oxygen Consumed

Compound	N_2	Oxygen Consumed			
		Found	Theoretical (neglecting nitrogen)	Diff.	Found/Theory
	%	*Mg.*	*Mg.*	*Mg.*	%
Benzanilide	7.11	20.460	20.655	−0.195	99.06
p-Aminoacetophenone	10.37	16.593	16.785	−0.192	98.86
2-Phenylquinoline 4-carboxylic acid	5.62	18.252	17.855	+0.397	102.22
	5.62	18.307	17.932	+0.375	102.09
γ-Phenoxybutyronitrile	8.70	19.263	18.747	+0.516	102.75
	8.70	17.586	17.055	+0.531	103.11
p-Nitrobiphenyl	7.04	15.052	14.608	+0.444	103.04

If the thermal decomposition of the substances is first considered, it is noted that only the amino and amido groups have hydrogen attached to the nitrogen atom. It is postulated that these groups are split out of the molecule during the thermal decomposition, either directly as ammonia (recent evidence, *19*, as to the thermal decomposition of primary amines would indicate this to be the mechanism), or possibly as free amino or imino radicals which could then unite with hydrogen, formed during the same reaction, to form ammonia. The ammonia (or possibly the free amino or imino radicals) would then be subjected to oxidation and thermal dissociation under the conditions existing in the combustion tube. Since the nitrogen in these groups is attached to carbon as well as to hydrogen, other possible simple thermal scission products would include cyanogen and hydrogen cyanide. The compounds containing the nitrile and the heterocyclic nitrogen would, on this basis, be expected to yield cyanogen and possibly hydrogen cyanide. The nitro compound would be expected to yield nitrogen peroxide and cyanogen and possibly also nitric oxide and hydrogen cyanide. The complete list of simple thermal decomposition products expected would then include ammonia (or amino and imino free radicals), cyanogen, hydrogen cyanide, nitrogen peroxide, nitric oxide, and also elementary nitrogen, which might be evolved from nitrogen-containing cokes which are often formed during combustion.

Oxidation of the nitrogen-containing thermal decomposition products by the excess of oxygen present in the combustion tube at temperatures from the maximum of 600° C. (*8*) down to 181° C., the temperature of the lead peroxide, would yield only nitrogen peroxide and nitrogen (*1, 6, 10, 13*). The proportion of these two substances which finally results, under a given set of conditions, should primarily be a function of the manner in which the nitrogen is linked in the molecule.

With the combustion tube filling used in the present work, the nitrogen peroxide was absorbed by lead peroxide. According to Dennstedt (*3*), this reaction yields only lead nitrate. However, in an investigation conducted on the above reaction in this laboratory, the details of which will be communicated later, it was found that the reaction was not as simple as indicated above. When nitrogen peroxide was passed through a weighed microabsorption tube containing lead peroxide at a temperature of about 185° C., the increase in weight corresponded best with

$$2NO_2 + 2PbO_2 = Pb(NO_3)_2 + PbO + {}^1/_2O_2$$

This equation agrees with the increase in weight of the lead peroxide absorption tube and also with the fact that lead nitrate is formed, which could be extracted from the mixture of lead oxide and peroxide, as was done by Dennstedt. According to the above equation, an atom of oxygen is liberated each time a pair of nitrogen peroxide molecules react with the lead peroxide and must be considered in the calculation of the oxygen consumed. The calculations given later were all based on the use of the following equation:

$$2C_xH_yO_zN + nO_2 + 2PbO_2 \longrightarrow 2xCO_2 + yH_2O + Pb(NO_3)_2 + PbO$$

n = number of molecules of oxygen necessary to balance the above equation

On the basis of the above hypothesis regarding the fate of the nitrogen in the samples, the calculation of the oxygen content of the substances was undertaken. The theoretical amount of nitrogen present was used in these calculations: In studying substances of unknown composition the percentage of nitrogen must be determined by an independent analysis. Taking the combustion data collected for the first sample analyzed (benzanilide) and by a method of trial, the proportion of nitrogen peroxide and nitrogen assumed to be formed was varied until the determined and theoretical values for oxygen consumed agreed. Agreement occurred when 26 per cent of the nitrogen was considered to be in the form of nitrogen peroxide and 74 per cent as nitrogen. Using these figures, together with the combustion data, gave satisfactory agreement between the determined and theoretical oxygen content of the substance.

Since the combustion characteristics of *p*-aminoacetophenone are similar to benzanilide, as shown in Table I, it was expected that application of the same nitrogen peroxide–nitrogen ratio to the calculations made on the former substance would lead to a similar satisfactory agreement between the found and theoretical oxygen consumed and oxygen content of this substance. This was found to be the case despite the fact that the percentage composition of the two substances was quite different.

The combustion characteristics of the second group of substances, as indicated in Table I, are different from the first group. It was therefore anticipated that the nitrogen peroxide–nitrogen ratio applied to the first group would be invalid if used in the calculations on the second group of substances. This was confirmed. According to the hypothesis advanced above, the ratio of nitrogen peroxide to nitrogen should be much greater in the second group than in the first group. Using the method of trial mentioned previously it was found that when the ratio of 59 per cent nitrogen peroxide to 41 per cent nitrogen was used in the calculations made on the first substance analyzed in this group, satisfactory agreement was obtained between the found and theoretical oxygen consumed and the oxygen content. Satisfactory agreement was also obtained between all of these values when the same ratio was applied in the calculation of the data obtained for the other members of the group despite rather wide variations in the percentage composition of the substances analyzed.

To illustrate the method of calculation, the complete data for one of the substances analyzed are given in Table II.

TABLE II. ILLUSTRATING METHOD OF CALCULATION

	Mg.
Weight of sample (benzanilide)	8.342
Weight of carbon dioxide, found	24.197
Weight of water, found	4.179
	%
Carbon, found	79.11
Carbon, theory	79.15
Difference	−0.04
Hydrogen, found	5.61
Hydrogen, theory	5.63
Difference	−0.02
	Cc.
Volume of oxygen at start (743.66 mm., 297.66° K.)	87.700
Volume of oxygen at start, NTP	78.734
Volume of mercury added	15.945
Volume of oxygen at end (741.66 mm., 297.70° K.)	71.771
Volume of oxygen at end, NTP	64.251
Volume of oxygen at end, NTP plus correction (0.166 cc.)	64.417
Volume of nitrogen (assuming complete conversion to N_2)	0.474
74 per cent of this volume	0.351
Actual volume of oxygen at end = corrected end volume minus 74 per cent of nitrogen volume	64.066
Volume of actual oxygen consumed	14.668
	Mg.
Weight of actual oxygen consumed, found	20.961
Weight of oxygen necessary for complete combustion of carbon and hydrogen in sample, theory	20.655
Weight of nitrogen peroxide formed by complete combustion of nitrogen in the sample	1.947
Weight of oxygen in this nitrogen peroxide	1.354
26 per cent of this weight of oxygen	0.352
Weight of oxygen consumed, theory (including 26 per cent NO_2 formation)	21.007
Difference (theory minus found)	−0.046
Weight of oxygen in carbon dioxide, found	17.598
Weight of oxygen in carbon dioxide, theory	17.607
Difference	−0.009
Weight of oxygen in water, found	3.711
Weight of oxygen in water, theory	3.725
Difference	−0.014
Weight of oxygen in nitrogen peroxide (26 per cent formation)	0.352
Sum of oxygen in combustion products, found	21.661
Sum of oxygen in combustion products, theory	21.684
Difference	−0.023
Oxygen in sample, found (O_2 in combustion products minus O_2 consumed)	0.700
Oxygen in sample, theory (O_2 in combustion products minus O_2 consumed)	0.677
Difference	+0.023
	%
Oxygen in sample, found	8.39
Oxygen in sample, theory	8.12
Difference	+0.27

The complete data for all of the analyses are summarized in Table III.

TABLE III. RESULTS

Compound	Weight of Sample	Found				Difference from Theory				
		C	H	O	Actual oxygen consumed	C	H	O	Oxygen consumed	N
	Mg.	%	%	%	*Mg.*	%	%	%	*Mg.*	%
Benzanilide	8.342	79.11	5.61	8.39	20.961	−0.04	−0.02	+0.27	−0.046	7.11
p-Aminoacetophenone	7.267	71.04	6.69	11.57	17.230	−0.03	−0.03	−0.27	−0.003	10.37
2-Phenylquinoline 4-carboxylic acid	7.830	77.06	4.36	11.95	18.457	−0.02	−0.09	−0.89	+0.009	5.62
	7.864	77.10	4.36	12.53	18.515	+0.02	−0.07	−0.32	−0.013	5.62
γ-Phenoxybutyronitrile	7.704	74.36	6.84	10.23	19.578	−0.13	−0.04	+0.30	−0.072	8.70
	7.009	74.46	6.82	9.44	17.872	−0.03	−0.06	−0.50	−0.004	8.70
p-Nitrobiphenyl	6.859	72.32	4.64	16.40	15.278	−0.01	+0.08	+0.33	+0.020	7.04
					Mean	−0.03	−0.03	−0.15 ±0.13	−0.016 ±0.009	

Summary

The method for the direct simultaneous microdetermination of carbon, hydrogen, and oxygen has been extended to include substances which also contain nitrogen.

The hypothesis is advanced that in the combustion of nitrogen-containing compounds the nitrogen is split out, during the thermal decomposition of the substance, in the form of simple nitrogen containing products which then undergo oxidation, forming, under the conditions existing in the combustion tube, only nitrogen peroxide and nitrogen. The ratio of these products formed is a function of the manner in which the nitrogen is linked in the compound. The ratio for amines and amides was found to be 26 per cent nitrogen peroxide and 74 per cent nitrogen; for nitriles, nitro, and heterocyclic nitrogen compounds, 59 per cent nitrogen peroxide and 41 per cent nitrogen.

The mechanism of the reaction between nitrogen peroxide and lead peroxide, under the conditions generally used in microcombustions, has also been studied, and the details will be reported later.

The data show that this method is capable of directly determining oxygen in nitrogen-containing substances with a mean accuracy of about 0.2 to 0.3 per cent, although individual determinations may differ from theory by more than these amounts.

Errors in the oxygen determination are largely due to errors in the carbon-hydrogen determination. As has been previously pointed out, errors made in the determinations of these elements are multiplied by rather large factors. This is particularly true of errors made in the determination of hydrogen. The determination of the oxygen consumed can be made with considerable accuracy.

Literature Cited

(1) Abe, S., and Hara, R., *Tech. Repts. Tôhoku Imp. Univ.*, 7, 1–23 (1927).
(2) Baumhauer, E. H. von, *Z. anal. Chem.*, 5, 141–52 (1866).
(3) Dennstedt, M., and Hassler, F., *Chem.-Ztg.*, 33, 133 (1909).
(4) Dolch, M., and Will, H., *Brennstoff-Chem.*, 12, 166–9 (1931).
(5) Dumke, W., *Quart. Colo. School Mines*, 26, No. 2, 5–21 (1931).
(6) Hara, R., and Shinozaki, H., *Tech. Repts. Tôhoku Imp. Univ.*, 5, 71–113 (1925).
(7) Kirner, W. R., Ind. Eng. Chem., Anal. Ed., 6, 358–63 (1934).
(8) *Ibid.*, 7, 363 (1935).
(9) Klingemann, F., *Ber.*, 22, 3064–9 (1889).
(10) Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 8, p. 210, New York, Longmans Green & Co., 1928.
(11) Meulen, H. ter, and Heslinga, J., "Neue Methoden der organisch-chemischen Analyse," pp. 15–16, Leipzig, Akademische Verlagsgesellschaft, 1927.
(12) Pregl, F., "Die quantitative organische Mikroanalyse," 3rd ed., pp. 35–6, Berlin, Julius Springer, 1930.
(13) Richardson, A., *J. Chem. Soc.*, 51, 397–403 (1887).
(14) Russell, W. W., and Fulton, J. W., Ind. Eng. Chem., Anal. Ed., 5, 384–6 (1933).
(15) Russell, W. W., and Marks, M. E., *Ibid.*, 6, 381–2 (1934).
(16) Staněk, V., and Nemes, T., *Chem.-Ztg.*, 56, 285–7 (1932); *Z. anal. Chem.*, 95, 244–60 (1933).
(17) Strebinger, R., *Ibid.*, 58, 97–114 (1919).
(18) Stromeyer, A., *Ann.*, 117, 247–60 (1861).
(19) Taylor, H. A., and co-workers, *J. Phys. Chem.*, 34, 2761–70 (1930); 35, 2658–66 (1931); 36, 670–2 (1932).

Received August 29, 1935. Presented before the Division of Physical and Inorganic Chemistry at the 89th Meeting of the American Chemical Society, New York, N. Y., April 22 to 26, 1935.

A Fatigue Cracking Test for Tire Tread Compounds

Some of the Laws of Fatigue

E. T. RAINIER AND R. H. GERKE, U. S. Rubber Products, Inc., Passaic, N. J.

AN IMPORTANT factor in the service rendered by a tire tread is its ability to resist cracking. Cracking of tire treads in service may be classified into two kinds or phases—the initiation or start of cracks, and the growth of cracks or cuts once started—and the two phases must be differentiated. Nearly all tires in service soon develop small cracks or "checking" due to the action of ozone in the atmosphere (*9*), and may suffer cuts due to sharp objects on the road. In many cases such cuts and ozone cracks may be harmless, but if the cracks grow too rapidly they will extend to the carcass before the tire is worn out (*4*). We define the growth of cracks under the influence of mechanical action as fatigue cracking.

The quality of rubber in respect to its resistance to fatigue cracking can be improved by addition of antioxidants (*3, 7*), and by such factors as the proper choice of accelerators (*4*), the proper balance of fillers (*1, 3*), and the proper cure. The quantitative evaluation of such chemicals and compounding ingredients in the laboratory depends upon the validity and precision of a test. It is the purpose of this paper to describe a laboratory test which has been found to correlate with shoulder cracking in tires, and to present data from which certain laws of fatigue cracking have been deduced.

In general, a laboratory test to be valid for the prediction of service should give results in agreement with those obtained in service, and should be reproducible. A laboratory fatigue cracking test for tire tread stocks should simulate service by measuring the rate of growth of cracks after their initiation (*4*), should operate between constant strain limits rather than constant stress limits (*3*), and should be capable of operation within the range of strains actually encountered in tires. The cracks should occur in a definite region on the test piece, and the mechanism of their growth should be of the same nature as in tires. The ratings should be quantitative. For the laboratory study of tread compounds the test specimens should be easily, accurately, and cheaply prepared. A large number of samples must be tested simultaneously. The test should be fairly rapid.

A number of laboratory cracking tests have been described in the literature, but none meets all the above-mentioned conditions.

The test herein described consists of starting cracks in a grooved, molded test specimen by means of ozone; causing the cracks to grow by bending the test specimen through repeated cycles of strain with a suitable machine; and estimating the degree of cracking from the loss of bending moment as measured in a suitable apparatus. The test meets most of the conditions outlined above. The cracks are produced in much the same way as in service, and the cracked specimens have the same appearance as do cracked tires. The method of rating the cracking is independent of any judgment on the part of the operator, and the test does not require close attention.

The chief disadvantage of the test is that it is slow compared with some other laboratory tests (*1*, *8*), for the flexing machine cannot be operated at the very high speeds of which some other machines are capable. When the tests are run at low strain limits they may last several weeks, but in such cases it is believed that what is lost in time is gained in validity. In certain cases, the time required for a test may be reduced by working to high strain limits or by running the test at elevated temperatures.

One of the reasons for using rubber in tires is its unusual resistance to fatigue. The quantitative measurement of resistance to fatigue cracking is therefore of importance as an aid in the development of tread compounds and in tire design.

A new laboratory test for evaluating the resistance to fatigue cracking of tire tread stocks is described. The precision of the strain cycle, the quantitative measurement of the degree of cracking, and the initiation of the cracks with ozone are novel features which enhance the validity of the test.

Data are given which show that ozone cracking and fatigue cracking are additive, that the rate of growth of cracks is a function of the maximum strain, that endurance limits may exist, and that the addition of antioxidants decreases the rate of growth of cracks and raises the endurance limit. The test has been found to correlate with shoulder cracking in tires.

Description of Test

TEST SPECIMEN. A diagram of the molded test specimen is shown in Figure 1.

It consists entirely of tread rubber without any fabric backing. Its essential feature is the single U-shaped groove, running across the center. The groove has a half-round bottom of 0.1588-cm. (0.0625-inch) radius, with straight sides exactly tangent, and it extends half-way through the test piece. It is important that the mold rib which forms the groove should be accurately machined and polished.

The authors have found it convenient to mold the samples in slabs about 15.8 cm. (6.25 inches) long, from which six test specimens may be cut. The test specimens are usually cut 2.5 cm. (1 inch) wide, but the exact width is not important.

Strains may be induced in the test specimen by bending it so as to open or close the groove, and the maximum surface strain always occurs in the bottom of the groove. Figure 2 shows the relationship between the angle of bend and the surface strain in the bottom of the groove of an uncracked test specimen. By "angle of bend" is meant the angle of displacement from the straight, molded shape—that is, the difference between 180° and the dihedral angle formed by the back of the test specimen. Thus, an angle of bend of 60° means that the test specimen is bent to a dihedral angle of 120°. The surface strain data shown in Figure 2 were obtained by placing short marks in the bottoms of the grooves of about 60 test specimens and measuring the lengths of the marks by means of a microscope, when the test specimens were bent to various angles in the flexing machine. It will be noted that there is a considerable variation in the measured surface strain at any given angle of bend. Some of this variation may be due to actual variations among the samples, but it is believed that most of the variation is due to errors in the measurements. The authors have observed no systematic variations in the relationship between angle of bend and surface strain for samples molded from stocks with widely differing moduli.

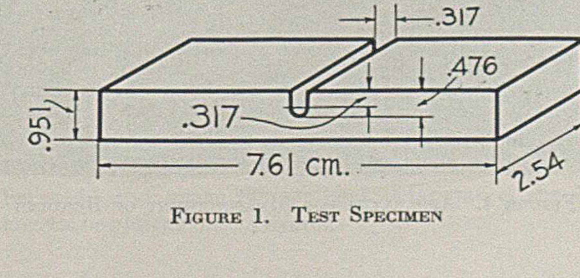


FIGURE 1. TEST SPECIMEN

FLEXING MACHINE. The essential feature of the flexing machine is the mechanism pictured in Figure 3, which consists of hinged angle bars for holding the test pieces.

The test pieces fit loosely into a slot in the lower or stationary bar, and are tightly clamped to the upper or movable bar, by means of metal strips held by thumb screws. The hinges are so constructed that their axis is collinear with the approximate center-of-bend of the test pieces—i. e., the axis is 0.238 cm. (0.094 inch) in front of the faces of the back bars and in line with the centers of the grooves in the test pieces. The edges of the bars are placed 1.27 cm. (0.5 inch) apart, so that the center sections of the test pieces are left free of clamping.

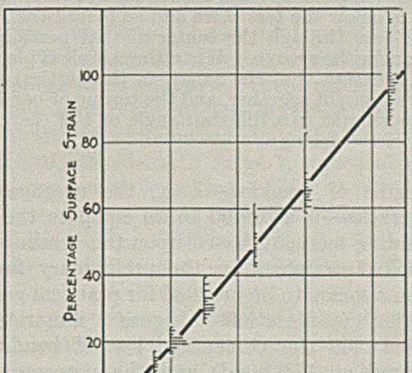


FIGURE 2. RELATIONSHIP BETWEEN ANGLE OF BEND AND SURFACE STRAIN IN UNCRACKED TEST SPECIMENS

The position of the fixed bar is adjustable within an angle of about 90°. Through the adjustment of the throw of the crank, the movable bar may be vibrated through any angle within +45° and −45° from its central position. Thus the angle of bend to which the test pieces are to be submitted may be varied through large limits.

To develop fatigue cracking in the test pieces, the movable bar is vibrated by driving it with any suitable mechanism. One mechanism consists of a slide driven by an inverted

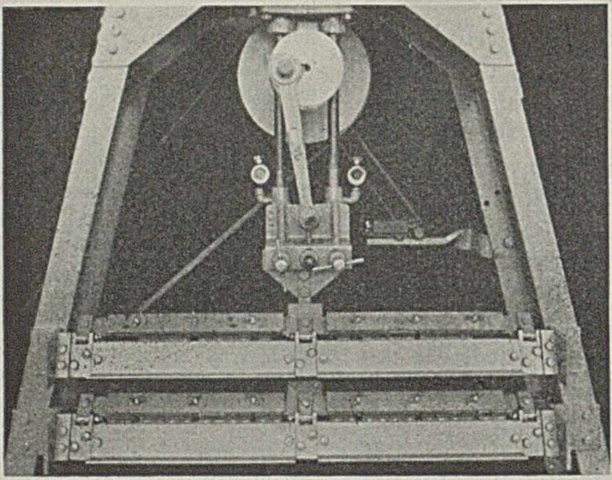


FIGURE 3. FLEXING MACHINE

DeMattia flexing machine, as shown in Figure 3. In another type of machine a simple system of levers driven by a cylindrical cam is used. The machines are usually run at the maximum speed at which they will run smoothly—i. e., 350 to 400 cycles per minute.

MEASUREMENT OF DEGREE OF CRACKING. The degree of cracking in a test piece at any time is determined by measuring its bending moment when it is bent to a definite dihedral angle—namely, 135°. Figure 4 shows the apparatus that is used.

It consists of a hinged clamp, one end of which is fastened to a board and the other end of which carries a pointer and is movable. The back side of the movable end is cut away so that the test piece may slip slightly and adjust itself to its natural position. The hinge is below the test piece and so placed that its extended axis would pass through the center of that portion of the test piece just under the groove. When the sample is placed as shown in Figure 4, except that the axis is in the vertical position, the pointers are brought together, and the torque or bending moment to bend the sample to a dihedral angle of 135° is read from the elongation of the spring.

The degree of cracking—i. e., the average percentage depth of cracks—is assumed to be equal to the percentage loss of bending moment, based upon the bending moment of the uncracked sample after the preliminary flexing. This assumption appears to be justified for practical purposes from the following considerations. Figure 5 illustrates the relationship between the percentage loss of bending moment (as measured at 45° bend) and the percentage depth of smooth, straight, even cuts made with a razor blade. The solid curve represents the average experimental relationship, while the dotted line shows the relationship required for equality. It will be observed that, for the cuts, the percentage loss of bending moment is usually a little greater than the percentage depth of cut. However, fatigue cracks are usually irregular and of uneven depth. For a given loss of bending moment the deepest portions of the cracks (which count most in service) are undoubtedly deeper than the even cuts. Hence for cracked test pieces the percentage loss of bending moment is probably more nearly equal to the percentage depth of cracks than in the case of the cuts. In one case the depth of a crack was measured microscopically at two points and gave percentage depths of 35 and 42, respectively. The loss of bending moment was 39 per cent.

If the bending moment is to give a definite measure of the degree of cracking, it is necessary that the modulus of the rubber should not change appreciably between the determination of the initial bending moment and subsequent determinations of bending moment. It has been found that unflexed samples are always stiffer than samples which have been flexed. The uncracked samples suffer a loss of bending moment during the first few cycles of flexing without any visible cracking, but after from 5 to 100 kilocycles (depending upon the angle of bend) the bending moment becomes constant for tests at room temperature, and there is no further loss until cracks appear. The "initial bending moment" upon which the degree of cracking is based is always taken on samples which have had considerable flexing, and in which the bending moment has become constant.

Thus it appears that for tests run at room temperature the percentage loss of bending moment gives a direct measure of the average percentage depth of cracks.

The measurement of the bending moment at a dihedral angle of 135° is more or less arbitrary, and it is likely that any angle greater than 90° could be used, so long as the same angle was used for all samples which are to be compared. The authors have chosen 135° merely because it is a convenient angle for their particular test specimen and gives reproducible values of the bending moment over a suitable range. Angles too near 180° should not be used, however, since there are small variations due to the way in which different samples fit into the clamps. At a dihedral angle of 135° such variations are of relatively small consequence, but at greater angles the relative effects would be greater.

Procedure for Testing

1. The samples are placed in the flexing machine and are flexed for 5 to 10 kilocycles if tested at a high angle of bend (85°) or for 50 to 200 kilocycles if tested at a low angle of bend (20° to 30°). This removes the stiffness from the samples and makes the bending moment reproducible.
2. The samples are removed from the flexing machine and their bending moments are measured to get the values for the uncracked samples, using the apparatus shown in Figure 4. The sample is placed in the apparatus with the groove out. The pointer is moved to an angle of about 75° and vibrated several times, then allowed to come back to about 30°, and again vibrated. Finally, the spring is stretched with one hand, while the pointer is vibrated with the other, until the pointer holds at 45°. The value of the bending moment is read from the scale.
3. It is usually well to repeat steps 1 and 2. This gives two readings of the bending moment on the uncracked samples. The average is taken as the zero load.
4. The samples are cracked in ozone as follows: They are placed in frames which hold them to a 20° bend, and are then put into an ozonized atmosphere until the entire surface of the groove is checked—covered with many very small cracks. These cracks should not be too deep, but just barely visible to the naked eye.

The samples are removed from the 20° frames and placed in

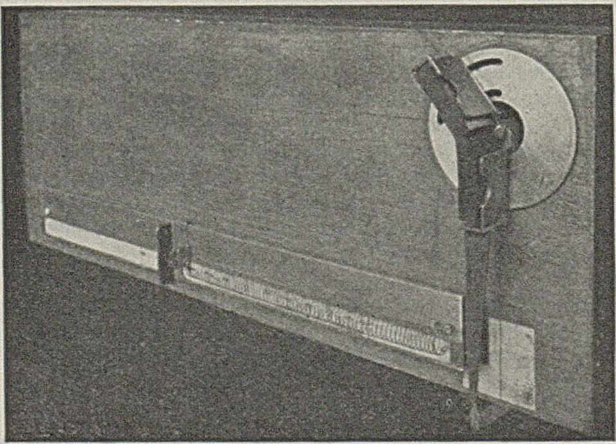


FIGURE 4. APPARATUS FOR MEASUREMENT OF BENDING MOMENT

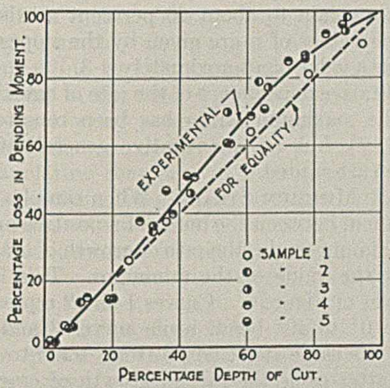


Figure 5. Relationship between Percentage Loss of Bending Moment and Percentage Depth of Cuts or Cracks

frames which hold them to 7° bend. They are again put into the ozonized atmosphere until the ozone cracking is completed—that is, until the samples would show from 10 to 15 per cent loss in bending moment, which is the amount required to eliminate the induction period. (Figure 6.) A little experience will enable the operator to judge when the cracking is sufficient. When the ozone cracking has been properly done, the sample has a single broken line of ozone cracks all the way across the sample and in the bottom of the groove.

In the ozone cracking treatment the concentration of ozone is immaterial except as it determines the time necessary to get cracking. The authors prefer a low concentration, which is high enough so that the odor is very noticeable and considerably higher than atmospheric concentrations. The checking of the surface when the samples are at an angle of bend of 20° leads to a series of small cracks similar to those observed on tires in service. If this step is omitted the ozone cracks may be few and large and difficult to reproduce. For the final ozone cracking an angle of bend of about 7° must be used, so that only the bottom of the groove will suffer deep cracking. The exact amount of ozone cracking (within limits) is immaterial, since the effects of variations in the amount of ozone cracking are eliminated in the method of rating.

5. The bending moment is measured as described in step 2, from which the degree of ozone cracking may be calculated.

6. Fatigue cracking is induced in the samples by flexing them in the flexing machine. At intervals during the test the samples are removed from the machine, their bending moments are measured as in step 2, and the counter reading is recorded. The frequency at which data are taken depends upon the rate of cracking, and must be judged by the operator upon the basis of experience. In general, the intervals should be such as will give 5 to 10 per cent loss in the bending moment. For high-angle tests data should be taken about every 150 kilocycles. For low-angle tests the intervals might be 500 to 3000 kilocycles.

Rating the Samples

By Rate of Growth of Cracks. It has been found experimentally that, for most stocks and most flexing cycles, the rate of growth of cracks, as measured by the rate of loss of bending moment in terms of cycles of flexing, is constant up to about 60 per cent loss of bending moment. Hence the authors prefer to rate the samples in terms of $\Delta Kc/\Delta$ per cent—i. e., the number of kilocycles of flexing required to produce 1 per cent deterioration in the sample. The $\Delta Kc/\Delta$ per cent values may be calculated as follows: For each sample the bending moment data are calculated to percentage deterioration—i. e., percentage loss of bending moment, based upon the zero load values. The percentage deterioration is plotted against the total number of kilocycles of flexing, using cartesian coördinate paper. The best straight line is drawn graphically through the plots and its slope is taken as the $\Delta Kc/\Delta$ per cent value. In drawing the straight lines, points below 10 and above 60 per cent deterioration should in general be neglected.

In Terms of a Definite End Point. In some cases it may be desirable to rate the samples in terms of a definite end point, such as 50 per cent fatigue cracking. The percentage deterioration values are calculated as directed above. From these values, the values for ozone cracking are subtracted in each case to give the percentage fatigue cracking. The number of kilocycles of flexing for 50 per cent (or any other degree) of fatigue cracking may be estimated by interpolation.

Characteristics of Test

Induction Period. When an uncracked specimen is flexed in air there is a period during which there is no loss of bending moment and no visible cracking. This may be termed an induction period. Following the induction period, cracks appear and grow at a steady rate. Curve 1 of Figure 6 shows typical data on a sample which was not subjected to ozone cracking. This curve represents a flexing test in which the strain cycle was −5° minimum bend to +60° maximum angle of bend. When the maximum bend is higher, say 90°, the induction period is shorter, both absolutely and relative to the life of the sample.

In other flexing tests which have been described (*1*, *6*, *7*, *8*) the induction period occurs, and in general the ratings of these tests include both the induction period and the rate of growth of cracks after they form.

Elimination of Induction Period by Ozone. If the cracks are initiated by the action of ozone, the induction period is eliminated, as is illustrated by curves 2, 3, and 4 of Figure 6. It is believed that for tires in service the cracks are usually initiated by the action of ozone. Often small ozone cracks may be observed on tires which have been in service only a few hours. It is partly for this reason that the authors start the cracks with ozone in their test. Initiation of cracks with ozone shortens the time of the test. Gray, Karch, and Hull (*4*) obtain a similar result with cuts.

Additivity of Static Ozone Cracking and Fatigue Cracking. The effects of static ozone cracking and of fatigue cracking appear to be additive. (Figure 6.) If curves 2, 3, and 4, which represent samples in which the cracks were started with ozone, were moved along the X-axis they could all be made to coincide with curve 1, representing a sample which had no ozone cracking. This shows that cracks produced by ozone are the same in their effect as cracks produced by flexing only. Within limits, the amount of ozone cracking has no effect upon the subsequent rate of fatigue cracking.

Rate of Growth of Cracks vs. Degree of Cracking. When the minimum strain in the flexing cycle is nearly zero, the rate of growth of cracks is nearly constant and is inde-

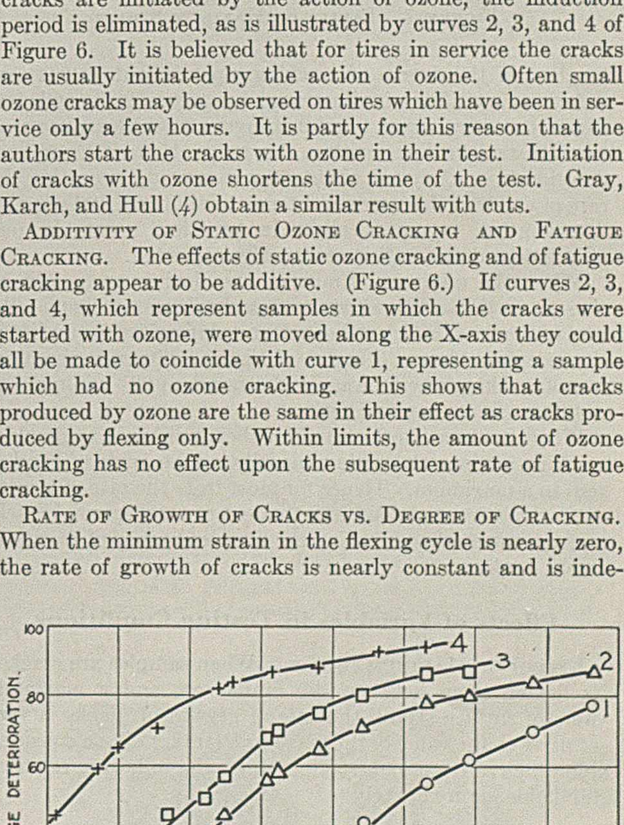


Figure 6. Additivity of Static Ozone Cracking and Fatigue Cracking

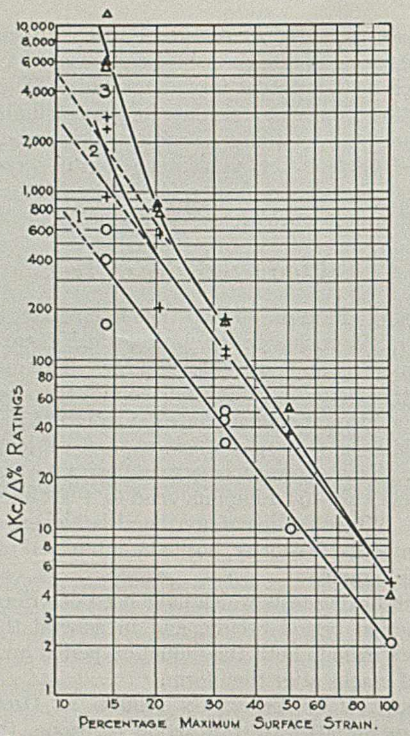


FIGURE 7. EFFECT OF MAXIMUM STRAIN

pendent of the degree of cracking, up to about 60 per cent deterioration. This is illustrated by curves 2, 3, and 4 of Figure 6 and by curves 1 and 2 of Figure 8, which are approximately straight lines within the range 15 to 60 per cent deterioration. Beyond about 60 per cent deterioration the rate of cracking decreases and tends to approach 100 per cent deterioration asymptotically. In practice, points beyond 60 per cent deterioration are usually neglected.

When the minimum strain in the flexing cycle is positive—i. e., the sample is not brought back to zero bend—the rate of cracking may not be constant during the entire life of the sample. Curves 3 and 4 of Figure 8 illustrate the progress of cracking when the angle of strain is +20° minimum to +40° maximum angle of bend.

When stocks are to be rated for their resistance to shoulder cracking in tires, the authors usually use an angle of bend of zero to a maximum. Hence for most tests the rate of growth of cracks is constant and independent of the degree of cracking, and the method of rating the samples by rate of growth of cracks applies.

Effects of Variables in Testing Conditions

EFFECT OF MAXIMUM STRAIN. When samples are cracked by flexing them between the limits zero and a maximum value of surface strain, the rate of growth of cracks is very sensitive to the value of the maximum strain. For a considerable range of maximum strain values, the following relationship holds approximately:

$$R = k/S^n$$

where R is the number of kilocycles of flexing required to cause 1 per cent deterioration in the test specimen—$\Delta Kc/\Delta$ per cent—S is the percentage maximum surface strain as measured on the uncracked specimens, while k and n are constants for any particular stock and cure.

If the values of R and S are plotted on logarithmic scales, straight-line curves are obtained, as is illustrated by the curves of Figure 7, which are straight lines from 100 per cent maximum surface strain to about 20 per cent maximum surface strain. The values of n are given by the slopes. For most stocks, n has a value of approximately +3.

The qualitative dependence of the rate of cracking upon the value of the maximum strain has been reported by other workers (*3*, *7*), but no quantitative generalizations appear to have been attempted.

EFFECT OF MINIMUM STRAIN. When samples are cracked by flexing them between the limits of a positive minimum and a given maximum strain, the rate of growth of cracks is slower the greater the value of the minimum. This is illustrated by the curves of Figure 8. Curves 1 and 2 represent samples flexed from 0° to 40° bend, while curves 3 and 4 represent samples of the same stock flexed from +20° to +40° bend. With the latter cycle the rate of growth of cracks was only about one-fifth of that obtained with the former cycle.

A similar effect has been observed by Busse (*2*) in regard to tear resistance.

It is recognized that surface strains as measured on uncracked test specimens are lower than the actual strains in the bottom of the cracks (*2*), but for cracks of any given depth and sharpness the actual strains in the cracks are probably proportional to the over-all strain in the specimen—i. e., to the measured surface strains. The true endurance limits of strain for rubber compounds would therefore be higher than those calculated, but should be proportional to the calculated values. For purposes of tire design we are limited to the over-all strains instead of the actual strains in the cracks; hence the authors measured the strains in test specimens as over-all strains in order to facilitate correlation with tires.

The knowledge of "safe limits" for tread stocks has been useful in controlling shoulder cracking in tires.

Busse (*2*) has observed a kind of endurance limit in connection with tears started from cuts. He flexed cut samples to constant maximum over-all strains, varying the minimum strains, and found that as the minimum was increased the lives of the samples became infinite. In the author's tests, however, the cracks never branch into arrowheads and grow backwards, as Busse observed with the cuts.

ENDURANCE LIMITS. Curves 3 and 4 as plotted in Figure 7 are similar in shape to the *S-N* curves which are plotted in the fatigue testing of metals (*5*). At low values of maximum strain, the curves depart from the straight-line relationship and tend to become parallel with the log ($\Delta Kc/\Delta$ per cent) axis. This indicates that an "endurance limit" is being approached at which the rate of growth of cracks would be indefinitely slow.

In the authors' experiments no true endurance limit was reached, for in no case was the strain so low that no cracking at all took place, but for practical purposes "safe limits" were reached in many cases. It has been calculated that for shoulder cracking in passenger size tires a rate of crack growth corresponding to a $\Delta Kc/\Delta$ per cent value of about 3500 is

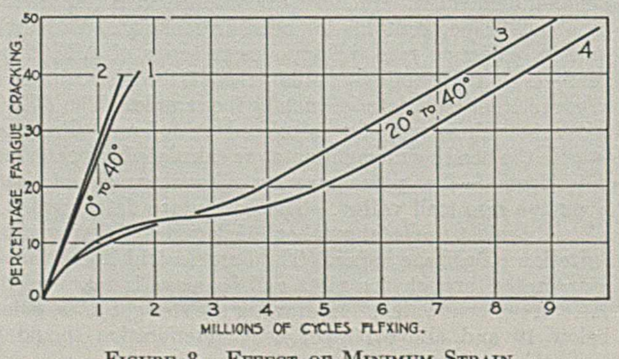


FIGURE 8. EFFECT OF MINIMUM STRAIN

safe for the life of a tire, allowing a safety factor of 5 in the rate of crack growth. The values of maximum surface strain corresponding to this safe rate of cracking may be read from curves of the type shown in Figure 7. Curve 1 represents a stock which contained no antioxidant. In this case the safe limit was not reached in the laboratory tests, but by extrapolating the curve as a straight line we would arrive at a value of about 6 per cent surface stretch. Curve 2 represents the same stock with 0.5 part BLE added. (BLE is a commercial antioxidant which is a diarylamine-ketone reaction product.) The estimated safe limit is about 12 per cent. Curve 3 represents the same stock with 1.0 part BLE added. The estimated safe limit is about 16 per cent.

Effect of Speed of Testing. The rate of cracking is measurable in terms of cycles of flexing, and when so measured is independent of the speed of the machine. This is in agreement with the observations of other workers (*7*). Also, no effects of short rest periods have been observed.

Effect of Temperature. Increasing the temperature of the air surrounding the samples always increases the rate of cracking in the authors' test. This is contrary to the observations of Somerville (*7*) who found that the rate of cracking decreased with increased temperature. His test pieces took on considerable permanent set at elevated temperatures, while the authors believe their test pieces to be fairly free from permanent set even at elevated temperatures, although other effects must sometimes be taken into consideration.

For rating shoulder cracking in tires the authors always test stocks at room temperature, about 25° C.

Effects of Variables in Stocks

Antioxidants. In agreement with other workers, the authors find that the addition of antioxidants decreases the rate of cracking. This is illustrated by the curves of Figure 6. Curve 1 is for a tread stock without antioxidant, while curves 2 and 3 are for the same stock with 0.5 and 1.0 part of BLE added. The relative effect of the antioxidant is greater at the low angle tests than at the high angle tests. The addition of antioxidant raises the endurance limit.

Cure. In tests on unaged samples at room temperature no general law for effect of cure has been observed with the authors' test. For any given stock, differences in rates of cracking among different cures are usually observed; with some stocks the undercures crack the faster, while with others the overcures crack the faster. In tests on aged samples, the overcures usually tend to crack the faster, although exceptions have been observed.

Other workers (*1*, *4*, *7*) have found that overcures crack worse than undercures.

Aging. Samples which have been shelf-aged, aged in the Geer oven, or aged in the oxygen bomb, almost invariably crack faster than the unaged samples. Other workers (*4*) have found that oven aging of tires causes them to crack more rapidly.

Precision of Test

The relative deviation from the mean of duplicate samples depends somewhat upon the angle of bend used in the test. Long-time tests run at low angles of bend are usually less reproducible than short-time tests run at a high angle of bend. In one test run at 0° to 60° bend, wherein 3 groups of 6 duplicate samples were tested, the percentage probable errors of the means were 4.48, 4.38, and 3.86 per cent, respectively. In another series of tests run at 0° to 30° and 0° to 20° bend, the average percentage probable error of the means of groups of 8 or 9 duplicates was about 25 per cent.

According to the theory of probability, it may be shown that if the difference between two quantities which are to be compared is 1.4 times the probable error of each quantity, there will be about 9 chances out of 10 that the difference is real. It follows that, if the test is capable of giving ratings for stocks with a probable error of 4.3 per cent it is capable of detecting differences in stocks of the order of 6 per cent. If the probable error of the ratings is 25 per cent, it can detect differences only of the order of 35 per cent. Differences in the rates of cracking of tread stocks as great as 500 per cent have been observed, while differences of the order of 60 per cent are not uncommon.

The variations observed with this test are not all due to errors in the cracking test itself, but may be due in large part to actual variations in the samples tested, caused by uncontrolled variables in mixing, molding, and curing.

Fatigue cracking tests are, in general, among the least reproducible of the physical tests on rubber. In order to get reliable results it is necessary to test many duplicate samples. The authors recommend testing at least 6 duplicates, and preferably more.

Correlation with Service

Analyses of data from the test have shown good correlation with tire cracking in service. Compounds which have shown up well in the laboratory test have shown less tendency to crack in tires. The test has been useful in the evaluation of such factors as antioxidants, accelerators, and softeners for their effects upon the resistance to cracking of tread stocks.

In certain cases where correlation tests have been made, the laboratory test has shown good quantitative agreement with shoulder cracking in tires. From laboratory data, together with a knowledge of the strains suffered by tire treads in service, the authors have been able to predict with fair accuracy the mileages at which troublesome shoulder cracking is likely to occur.

Literature Cited

(1) Booth, E. W., *India Rubber World*, **82**, No. 6, 53–5 (1930).
(2) Busse, W. F., Ind. Eng. Chem., **26**, 1194–9 (1934).
(3) Cooper, L. V., *Ibid.*, Anal. Ed., **2**, 391 (1930).
(4) Gray, H., Karch, H. S., and Hull, B. F., *Ibid.*, **6**, 265–8 (1934).
(5) Moore, H. T., and Kommers, J. B., "The Fatigue of Metals," 1st ed., pp. 122–4, New York, McGraw-Hill Book Co., 1927.
(6) Neal, A. M., and Northam, A. J., Ind. Eng. Chem., **23**, 1449 (1931).
(7) Somerville, A. A., *Inst. Rubber Ind. Trans.*, **6**, 130–70 (1930).
(8) Torrence, P. M., and Peterson, L. C., *India Rubber World*, **80**, No. 4, 62 (1929); *Rubber Chem. Tech.*, **2**, 525–7 (1929).
(9) Van Rossem, A., and Talen, H. W., *Kautschuk*, **7**, 79–86, 115–17 (1931); *Rubber Chem. Tech.*, **4**, 490–504 (1931).

Received April 26, 1935. Presented before the Division of Rubber Chemistry at the 89th Meeting of the American Chemical Society, New York, N. Y April 22 to 26, 1935.

Chemical Lead-Lined Steel Stock Base, Titanium Paint Company

The Kauri Butanol Test for Solvent Power

E. L. BALDESCHWIELER, W. J. TROELLER, AND M. D. MORGAN
Esso Laboratories, Standard Oil Development Company, Elizabeth, N. J.

DURING the course of recent work pertaining to the study of hydrogenated petroleum solvents, it was necessary for this laboratory to investigate the various solvency tests for thinners used by the varnish and lacquer industry. The following solvency tests were considered: (1) kauri butanol value, (2) aniline point, (3) dimethyl sulfate value, and (4) dilution ratio.

The first three of these tests find extensive application in both the varnish and the lacquer industry, whereas the dilution ratio is restricted to the latter. Comparison revealed that although the aniline point and dimethyl sulfate tests were valuable indexes for ordinary petroleum solvents, they were inadequate for hydrogenated solvents, inasmuch as the latter are generally found to be 100 per cent miscible with dimethyl sulfate and their aniline points are much below the freezing point of aniline. The kauri butanol test and the dilution ratio were therefore the only solvency criteria suitable for the purpose.

The kauri butanol test has been used almost exclusively by this laboratory for the following reasons:

1. According to published data (*4*, pages 148 and 149) and the authors' experience, both the kauri butanol test and the dilution ratio classify petroleum solvents in the order of their aromaticity.
2. Specifications for the use of petroleum solvents as lacquer diluents (*4*, page 145) often include a minimum kauri butanol value.
3. The kauri butanol test is a more sensitive index for indicating change in aromaticity than the dilution ratio (*4*, pages 148 and 149).

Extensive investigation has been centered on the kauri butanol test in an effort to overcome some of its objectionable features and to improve upon its general reproducibility. The work is fully discussed in this paper and an improved method of standardization is suggested. The new method has been found most satisfactory and is shown to be independent of the wide variations in the composition of kauri gums used in the preparation of standard kauri butanol solution.

Kauri Butanol Test

The kauri butanol test was officially adopted in 1931 by the Paint and Varnish Superintendents' Club of the Philadelphia District (*4*). The kauri butanol value of a solvent is defined as the number of cubic centimeters of the solvent that must be added to 20 grams of the standard kauri solution at 77° F. to produce sufficient precipitation of the gum so that a printed sheet of paper (10-point print) will appear blurred and be illegible when viewed through the flask containing the solution.

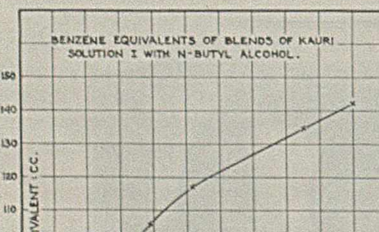


FIGURE 1

In practice the standard kauri solution is weighed into a 250-cc. flat-bottomed extraction flask. This is held by hand in a water bath kept at 25° C. (77° F.) preferably in a large crystallizing dish, the printed sheet being placed under the dish. After temperature equilibrium has taken place (about 5 minutes) the solvent is added from a buret at a fairly rapid rate until a permanent turbidity has formed. The titration is then made drop by drop to the above prescribed end point. The additional amount of solvent required to render the print illegible generally does not exceed 0.5 cc.

It is evident that, inasmuch as similar flasks are always used for the titration, the same depth of liquid will be compared for solvents of equal kauri butanol value. The magnitude of the error introduced in comparing solvents of widely different kauri butanol value due to different depths of liquid does not exceed 0.3 cc. which is smaller than the error inherent to the method. This error, moreover, will be compensated by standardizing the standard kauri solution against solvents of both high and low kauri butanol values as proposed in this paper.

The standard kauri solution is prepared by adding 100 grams of carefully selected kauri gum to 500 grams of *n*-butyl alcohol (distilling between 114.4° and 116.6° C.). The mixture is heated gently in a flask provided with a water-cooled reflux condenser, allowed to cool, and after 96 hours decanted into a clean dry bottle always kept well stoppered. While *n*-butyl alcohol of the specified boiling range has been used throughout this work (this was the material of highest purity obtainable at the time) a material boiling between 116° and 119° C. (C. P. *n*-butanol boils at 117.7° C.) is now commercially available and should be preferable.

The various factors affecting the test and the preparation of the standard solutions have been discussed at length by Beard, Shipp, and Spelshouse (*1*), who conclude that "all sources of inconsistency in results of the kauri butanol test can be easily eliminated by adopting a standard procedure, with the exception of the uniformity of the basic material, the kauri gum." These authors proposed the use of two standards, *n*-heptane and toluene; they suggested determining the curve or relationship between the toluene-heptane concentration ratio and kauri butanol value for a given kauri solution, from which the solvent power of any solvent treated with this gum solution may be expressed in terms of per cent toluene or toluene number.

The authors have been using C. P. benzene as the 100 per cent solvency standard, this procedure having been originally advocated by Kiehl (*3*). Kiehl as well as this laboratory found that the kauri butanol value of C. P. benzene or the benzene equivalent of the gum solution, as determined by the prescribed method, with standard kauri solutions prepared as specified, varied between 102 and 105 cc., depending on the grade of gum used.

To allow for this variation, data on solvents were expressed in terms of "solvent power" or the kauri butanol value multiplied by the ratio of 100 to the benzene equivalent of the gum solution used. This index should not be confused with the kauri butanol value.

Until recently it was possible to purchase kauri gum of such quality and composition that the benzene equivalents of standard solutions did not exceed 105 cc. Now, however, for some unexplained reason, the best gum obtainable has a benzene equivalent of 113 cc., while some of the lower grades tested have values as high as 159. Table I gives the benzene equivalent of a number of samples obtained from various dealers in New York.

TABLE I. BENZENE EQUIVALENTS OF STANDARD SOLUTIONS PREPARED WITH KAURI GUMS FROM DIFFERENT SOURCES

Sample	Type of Gum	Benzene Equivalent *Cc.*
1	Bush kauri	124.6
2	Bush dust	159.0
3	Bush dust	158.5
4	Rescraped brown chips (fossil)	152.0
5	Fossil XX	124.1
6	Fossil GXX	113.8
7	Fossil XXX	119.5
8	Fossil XXXX	123.8
9	Fossil (dark chips)	132.0
10	Fossil (light chips)	113.0
11	Fossil (small chips)	117.7
12	Fossil (superior chips)	149.5

A correction for the wide variations shown would of course be made in calculating the solvent power—i. e., its kauri butanol value divided by the benzene equivalent and multiplied by 100. However, by making determinations on a number of pure hydrocarbons it was found that even this correction does not give identical solvent power values for a given hydrocarbon in the range between *n*-heptane and benzene, when using various gum solutions. This is shown by the data in Table II, which gives the kauri butanol values and also the solvent power of six pure hydrocarbons as obtained with some of the standard kauri solutions listed in Table I.

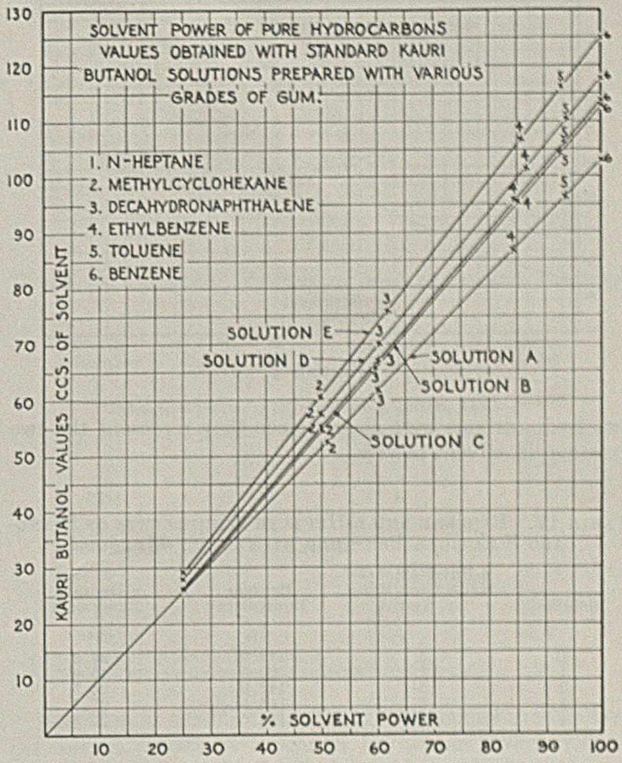


FIGURE 2

TABLE II. SOLVENT POWER OF PURE HYDROCARBONS OBTAINED WITH VARIOUS STANDARD KAURI SOLUTIONS

	Solution A		Solution B		Solution C		Solution D		Solution E	
	Kauri butanol value	Solvent power	Kauri butanol value	Solvent power	Kauri butanol value	Solvent power	Karui butanol value	Solvent power	Kauri butanol value	Solvent power
Benzene	103.0	100.0	113.0	100.0	113.8	100.0	117.7	100.0	124.6	100.0
Toluene	96.6	94.8	104.3	92.4	106.0	93.1	110.5	93.9	116.0	93.1
Ethylbenzene	87.6	85.1	96.0	84.9	96.4	84.7	102.3	87.0	106.7	84.7
Decahydronaphthalene	62.4	60.6	65.9	58.3	66.7	58.6	70.0	59.5	75.7	60.7
Methylcyclohexane	52.5	51.0	54.4	48.3	54.7	48.1	57.3	48.7	60.1	48.2
n-Heptane	26.2	25.4	26.3	23.3	26.3	23.1	27.9	23.7	29.1	23.4

The data on solution A were obtained 2 years earlier but, inasmuch as the pure hydrocarbons used throughout these experiments are stable and were the original materials used for solution A, the results should be comparable. The benzene and toluene were C. P. materials purchased from Eimer and Amend, New York. The ethylbenzene, methylcyclohexane, and decahydronaphthalene were obtained from the Eastman Kodak Company. The boiling points of these compounds were found to check the values given in the literature. The *n*-heptane, as obtained from the California Chemical Company, had the specifications given in Table III.

TABLE III. PHYSICAL CONSTANTS OF NORMAL HEPTANE

	Found	Literature (*2*)
Boiling point, ° C.	98.4	98.4
Freezing point, ° C.	−90.7	−90.0
Specific gravity at 20°/4° C.	0.6837	0.6840
Index of refraction n_D^{20}	1.3878	1.3850

The results given in Table II show wide variations in the kauri butanol values for a given solvent, particularly in the upper values when different gum solutions are used. The maximum variations for toluene, for instance, between solution A and solution E, is approximately 20 cc. Variations are greatly reduced, however, when data are converted to solvent power. The agreement between the results in the upper range of solvent powers is as close as may be expected for determinations made by different laboratories. The agreement is also fair in the lower ranges of solvent powers, provided the results obtained with solution A are omitted. However, the data originally published (*3*) and all the previous work were obtained with standard kauri solutions similar to solution A or of about 103 to 105 benzene equivalent. The results obtained with solutions similar to B, C, D, and E therefore must be correlated with the data previously obtained. Again, there is no assurance that the next batch of kauri gum purchased will not give a lower value. Inasmuch as the preparation of a standard kauri solution is a rather long and tedious process, it was felt that much time and effort would be saved if a method of preparing a standard solution or a procedure for standardizing the latter could be worked out to avoid these difficulties and thereby secure greater uniformity in the results.

In this direction, the authors first attempted to adjust the kauri solution by adding either additional gum or *n*-butyl alcohol to obtain a desired standard. For this purpose solutions of several concentrations were required.

Concentrated kauri solution 1 was prepared by dissolving 200 grams of gum in 200 grams of *n*-butyl alcohol; the gum used for this purpose being the same as that used in the preparation of standard solution B. Solution 2 was prepared by diluting solution 1 with *n*-butyl alcohol to the specified 5 to 1 (*4*) *n*-butyl alcohol–kauri gum ratio, without heating under reflux. Solution 3 was similar to solution 2, except that it was heated for 24 hours under a reflux condenser. Standard kauri solution 4 was prepared with kauri gum which had been dried for 12 hours at 105° C. The gum lost 2.8 per cent of its weight on drying.

The benzene and *n*-heptane equivalents of these various solutions were determined and are given in Table IV. These

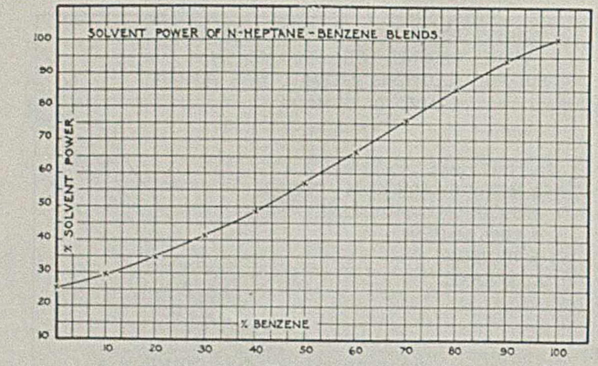


FIGURE 3

two hydrocarbons were chosen since they represent the two extremes in solvent powers.

TABLE IV. BENZENE AND *n*-HEPTANE EQUIVALENTS OF STANDARD SOLUTIONS PREPARED BY VARIOUS METHODS

Solution	*n*-Butyl Alcohol–Kauri Gum Ratio by Weight	Benzene Equivalent	*n*-Heptane Equivalent
		Cc.	*Cc.*
B	5	113.0	26.3
1	1	80.5	15.0
2	5	142.0	26.5
3	5	145.5	27.7
4	5	144.5	26.5

Table IV shows that the benzene equivalent is greatly affected by the method used in preparing the solution, while the *n*-heptane equivalent is practically independent of the method of preparation, except in the case of solution 3 where the equivalent is about 5 per cent higher. The most remarkable results are, however, the large discrepancies in benzene equivalent between the values obtained with solution B on the one hand and solutions 2, 3, and 4 on the other hand. No logical explanation for these discrepancies has been found.

To solution 1 various amounts of *n*-butyl alcohol were added and the relationship between the benzene equivalents and the amounts of *n*-butyl alcohol added plotted in order to determine the amount required to give a standard kauri solution having a benzene equivalent of as nearly 100 as possible. The results are given in Table V and the curve is shown in Figure 1.

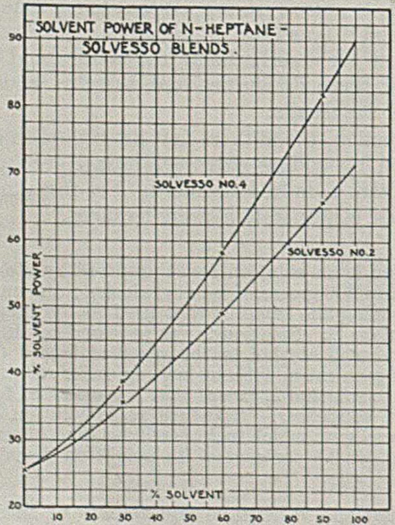


FIGURE 4

TABLE V. BENZENE EQUIVALENTS OF VARIOUS BLENDS OF KAURI SOLUTION 1 WITH *n*-BUTYL ALCOHOL

Blend	*n*-Butyl Alcohol–Kauri Gum Ratio by Weight	Benzene Equivalent
		Cc.
1	1.00	80.5
1-A	1.66	99.6
1-B	1.93	105.9
1-C	2.57	117.0
1-D	4.25	134.6
2	5.00	142.0

Solution 1-A of 99.6 cc. benzene equivalent was prepared from solution 1 by adding 33$^1/_3$ per cent of its weight of *n*-butyl alcohol. The kauri butanol value of most of the various hydrocarbons listed in Table II were then determined with this solution. The results are given in Table VI. In this case the solvent powers are practically equal to the kauri butanol values, since the benzene equivalent of the standard solution is nearly 100.

TABLE VI. SOLVENT POWERS OF PURE HYDROCARBONS OBTAINED WITH STANDARD SOLUTION 5

	Kauri Butanol Value	Solvent Powers
	Cc.	*%*
Benzene	99.6	100.0
Toluene	91.0	91.4
Ethylbenzene	81.4	81.7
Methylcyclohexane	41.2	41.4
n-Heptane	21.3	21.4

These results are very much lower than those obtained with standard solutions listed in Table II and show that it is practically impossible to adjust a standard kauri solution to a benzene equivalent of 100 and obtain comparable values throughout. Even if satisfactory, the method would be tedious, involving at least three extra benzene and *n*-heptane equivalent determinations.

Modified Method

These difficulties have been surmounted by what is believed to be a much simpler procedure. This consists of determining the *n*-heptane and benzene equivalents of each standard solution and plotting these values against the solvent power as determined with solution A of these two hydrocarbons. A straight line is drawn between the two points from which the solvent power corresponding to any kauri butanol value (as obtained with this particular standard solution) can be directly read. The solvent powers obtained with solution A are used as standard, inasmuch as the benzene equivalent of 103.0 is close to the 104.5 cc. given by Kiehl (*3*, page 590); the *n*-heptane equivalent of 26.2 also checks the value of 26.0 found by Beard, Shipp, and Spelshouse (*1*); and moreover the curve drawn through these points passes through the origin.

Solvent power of various solvents determined with gum solutions listed in Table II interpolated from the curve, as compared with values calculated in old way, are given in Table VII and illustrated graphically in Figure 2.

The solvent powers obtained from the curves using solutions B, C, D, and E agree more closely with the data obtained with solution A than do the calculated results. This agreement is particularly apparent in the lower ranges, as for instance, for methylcyclohexane. The maximum deviation from the standard values is given by solution B for toluene and amounts to 2 per cent. The average deviation is about 1 per cent, which is considered to be within the limits of error for this type of determination.

An additional test of this procedure was made by checking the solvent power curve of *n*-heptane–benzene blends. This curve was determined in 1932 by this laboratory, using standard solution A and again recently with solution B. The results are given in Table VIII.

TABLE VII. SOLVENT POWER OF PURE HYDROCARBONS OBTAINED WITH VARIOUS STANDARD KAURI BUTANOL SOLUTIONS

Hydrocarbons	Solution A Calculated	Solution A From Figure 2	Solution B Calculated	Solution B From Figure 2	Solution C Calculated	Solution C From Figure 2	Solution D Calculated	Solution D From Figure 2	Solution E Calculated	Solution E From Figure 2
Benzene	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Toluene	94.8	94.8	92.4	92.8	93.3	93.9	93.9	94.0	93.1	93.5
Ethylbenzene	85.1	85.1	84.9	85.5	84.7	85.0	87.0	85.8	84.7	86.1
Decahydronaphthalene	60.6	60.6	58.3	59.7	58.6	60.0	59.5	60.5	60.7	61.7
Methylcyclohexane	51.0	51.0	48.3	49.8	48.1	49.8	48.7	49.9	48.2	49.8
n-Heptane	25.4	25.4	23.3	25.4	23.1	25.4	23.7	25.4	23.4	25.4

TABLE VIII. SOLVENT POWER OF *n*-HEPTANE–BENZENE BLENDS (BY VOLUME)

Blend		Solution A		Solution B	
n-Heptane	Benzene	Kauri butanol value	Solvent power	Kauri butanol value	Solvent power
%	%				
0	100	103.0	100.0	113.0	100.0
20	80	87.5	85.0	95.6	85.2
40	60	68.0	66.0	73.3	66.0
60	40	49.7	48.2	51.8	47.4
80	20	36.0	35.0	37.1	34.5
100	0	26.2	25.4	26.3	25.4

Results with both solutions show very good agreement, the widest variation amounting to 0.8 per cent for the 60 per cent *n*-heptane blend.

The kauri butanol values of certain hydrogenated products which contain some hydronaphthalene cannot be determined directly. This is caused by the fact that the gum, at the end point of the titration, precipitates very slowly in the form of a transparent gel and therefore the prescribed end point in this method is not applicable. The solvent power of such products can be found only by determining the solvent power curve of a number of blends with *n*-heptane and obtaining the data for the pure solvent by extrapolation.

The accuracy of this extrapolation method is shown by the results obtained with two hydrogenated solvents, Solvesso No. 2 and Solvesso No. 4. The solvent power curves of *n*-heptane blends with both solvents are shown in Figure 4 and the values given in Table IX, which shows a comparison of the solvent power of Solvesso No. 2 as directly obtained and also as found by extrapolation from the blending curve. The solvent power of Solvesso No. 4, however, can be obtained only by extrapolation and is included here only as a typical example.

TABLE IX. SOLVENT POWERS OF *n*-HEPTANE AND SOLVESSO BLENDS

Blends		Kauri Butanol Value	Solvent Power
n-Heptane	Solvesso No. 2		
%	%		
Benzene equivalent of standard solution, 113.8 cc.			
0	100	80.4	71.8[a] 71.6[b]
10	90	73.7	65.8
40	60	54.0	49.0
70	30	38.3	35.7
100	0	26.3	25.4
	Solvesso No. 4		
Benzene equivalent of standard solution, 113.8 cc.			
0	100	No end point	90.3[b]
10	90	92.9	82.0
40	60	64.7	58.2
70	30	42.1	38.9
100	0	26.3	25.4

[a] Obtained by direct determination.
[b] Obtained by extrapolating the solvent power curve.

Inasmuch as the pure paraffin hydrocarbons have the lowest solvent powers as measured by aniline, kauri butanol value, or dimethyl sulfate value, it is very unlikely that commercial solvents will have solvent powers lower than that of *n*-heptane. For this reason the position of the curve lower than 25.4 per cent solvent power has not as yet been investigated by the authors.

Literature Cited

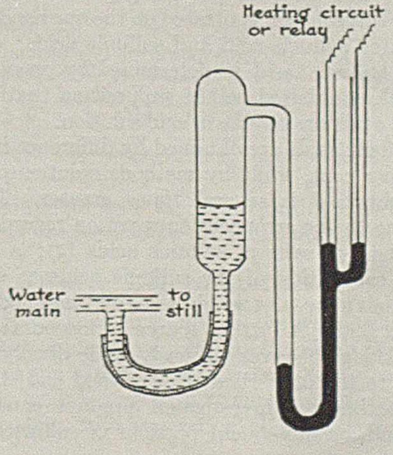
(1) Beard, L. C., Shipp, V. L., and Spelshouse, W. E., IND. ENG. CHEM., Anal. Ed., 5, 307 (1933).
(2) International Critical Tables, Vol. 1, p. 215 (1926).
(3) Kiehl, J. R., *Am. Paint Varnish Mfrs. Assoc., Circ.* 319, 585–96 (1927).
(4) Stewart, J. R., *Ibid., Circ.* 378, 143–53 (1931).

RECEIVED July 19, 1935.

A Simple Automatic Cut-Off for Electric Stills

M. R. ASWATHNARAYANA RAO AND
BASRUR SANJIVA RAO
Central College, University of Mysore, South India

INTERMITTENT water supply in laboratories often causes the burning out of the electric heating unit of the apparatus for distilling water. An automatic cut-off, supplied by the manufacturers of a certain still and involving the use of a float actuating a mercury switch, failed to work after use for a few months and caused in this laboratory the loss of the heating units of two stills. The stills are now fitted up with the simple automatic cut-off indicated in the accompanying figure. The glass parts are made of Pyrex and the electrodes dipping in the mercury are of nickel. The device is easily constructed and has been found to be extremely satisfactory.



RECEIVED July 18, 1935.

Analysis of Acid Sludge from Mineral Oil Treatment

E. HOLZMAN AND STEFAN SUKNAROWSKI, Malopolska Petroleum Corporation, Refinery Jedlicze, Poland

PARALLEL to the development of scientific research in the petroleum industry has been work on refining wastes, the most important of which are perhaps the acid sludges after mineral treatment. With regard to the product obtained, the proposed and patented methods of acid sludge utilization can be divided into regeneration of sulfuric acid, obtaining of fuel and oil, production of asphalt and tar, and separation of sulfonic acids and their derivatives (*14*).

The acid sludge treatment for sulfonic acid recovery has been developed only in recent years, according to patents of Pilat and Sereda (*9*), Klipper, Suknarowski, and Chierer (*6*), and others (see literature cited in *7, 10, 12, 13*). The scientific investigation of sulfonic acids was first carried out by Pilat and his collaborators (*7, 10, 12, 13*).

In spite of remarkable progress in investigation and utilization of acid sludges, the literature still lacks methods of their full analysis, permitting the determination of all fundamental groups of constituents. The known methods chiefly have to do with determination of the sulfuric acid left unchanged, and moreover are not always applicable to all acid sludges.

Bacon (*1*) describes four methods of determining free sulfuric acid in light-oil sludge:

1. Gravimetric determination as barium sulfate from a water extract of a fresh sludge.
2. Methods in which the sulfuric acid is titrated with alkali under different conditions, depending upon the means of separation of the other constituents of acid sludge.
3. A method in which the heat of dilution of the sludge with water is determined and the amount of free sulfuric acid is estimated by comparison with the data on the heat of dilution of pure sulfuric acid.
4. A method in which the sludge is treated with a boiling solution of aniline in chloroform with formation of insoluble aniline sulfate, which is filtered off and analyzed for sulfuric acid.

These methods determine merely the unchanged sulfuric acid from light-oil sludge, neglecting other constituents. Pilat and Starkel (*11*) determine in water solution the total acid content by titration with 0.1 *N* sodium hydroxide, and the sulfuric acid by precipitation with barium chloride. The difference between the two determinations is due to the sulfonic acids. On the same principle is based a method (*5*) which is commonly used in petroleum laboratories. According to this method, the sludge is washed with warm water and this solution is titrated on the one hand with caustic soda for free sulfuric acid and sulfonic acids; on the other hand the sulfuric acid is determined by precipitation with barium chloride, based on the supposition that barium salts of sulfonic acids are soluble in acid solution.

The sulfonic acids are obtained by difference in an amount of a few per cent, while by methods mentioned above, the amount obtained is several times greater. This discrepancy is due to the erroneous supposition regarding the solubility of barium salts of sulfonic acids (*2*); a second error arises by calculation of the sulfonic acids as sulfuric acid, whereas their molecular weight is many times higher than that of sulfuric acid. A further source of inaccuracy is the fact that acid sludge behaves variously while dissolving in water, according to the properties of oil refined and stage of treatment—whether the investigated product comes from the first, second, or subsequent portions of sulfuric acid. Thus the paraffin-base oil sludge does not dissolve entirely in water, in consequence of which the sulfonic acids occluded by hydrocarbons cannot be completely washed out; naphthene-base oil sludge dissolves readily in water, except the first and sometimes the second acid sludge, as well as the sludge obtained from very heavy stocks. This dissimilar behavior of acid sludge is probably the reason why Gurwitsch (*3*) calls Seidenschnur's data on complete solubility of sludge in water "*höchstmerkwürdig.*"

According to Chierer and Primost (*2*) sodium chloride precipitates sulfonic acids, which permits their separation from sulfuric acid; on the other hand Pilat and Sereda (*8*) state that sodium chloride does not precipitate all sulfonic acids.

The method outlined below is in general applicable to all kinds of acid sludge, including products obtained from both paraffin-base and naphthene-base oils, treated with diluted, concentrated, or fuming sulfuric acid. The method permits the separation and determination of neutral constituents (oil-dissolved, and oil polymerization, condensation, and oxidation products), sulfonic acids, insoluble parts, and remaining free sulfuric acid.

The principle of distribution is based on benzene application as a solvent for neutral constituents (after previous sludge neutralization) and the use of amyl alcohol for sulfonic acid extraction from acid solution, the unchanged sulfuric acid remaining in the aqueous solution.

The course of analysis is as follows:

About 20 grams of sludge are weighed into a 300-cc. Erlenmeyer flask and a 25 per cent sodium hydroxide solution is added, until the reaction becomes strongly alkaline. Usually 100 cc. of caustic soda solution will be sufficient. Then 50 cc. of benzene and 20 cc. of alcohol are added and the mixture is refluxed until solution is complete. (If the sludge is easily soluble in water, refluxing becomes superfluous and complete dissolving will be accomplished by stirring. In case of failure to dissolve, which sometimes takes place with paraffin-base oil sludge, the dissolved part is decanted and the rest is boiled for the second time with diluted caustic soda and benzene. Sometimes boiling will be unnecessary and careful mixing with water will be sufficient.)

Mineral Oil

After the sludge is completely dissolved, the contents of the flask are poured into a 1000-cc. separator through a funnel, adding the benzene and water used for flask washing, and then carefully stirred. A few minutes later the mixture forms two layers. The lower is poured into another 1000-cc. separatory funnel, together with the middle layer which sometimes forms (sodium salts of sulfonic acids, readily soluble in water). The alkaline aqueous solution is extracted several times with benzene until the extract becomes almost colorless, and the benzene extract is added to the upper benzene layer. The collected benzene portions are washed again with hot water until the alkaline reaction disappears, and the wash water is added to the primary alkaline solution. To break an emulsion sometimes arising when benzene is washed with water, a small quantity of alcohol is added or the emulsion warmed. The benzene solution is filtered off through a dried and weighed filter. After the benzene is distilled the residue is dried at 105° C. to constant weight, with an accuracy of 0.01 gram.

Sulfonic Acids

The alkaline solution being extracted with benzene is strongly acidified with concentrated hydrochloric acid and shaken out several times with amyl alcohol till appearance of a yellowish coloring, dissolving all the sulfonic acids and small quantities of sulfuric acid. The amyl alcohol used was a pure commercial product. To remove the small amount of sulfuric acid, the amyl alcohol solution is washed with a little water until the water begins to appear colored, when the sulfonic acids might on further washing pass into the aqueous solution. The wash water is added to the main aqueous layer. The washed alcohol solution is filtered through a dried and weighed filter into a weighed flask and the amyl alcohol is distilled off under diminished pressure from an oil bath at 100° C. The flasks used for distillation should be fitted with interchangeable stoppers (Fr. Greiner flasks). After distillation the residue is dried one hour *in vacuo* at an oil bath temperature of 115° C. having in mind that according to Pilat, Sereda, and Szankowski (*8*) sulfonic acids visibly decompose above this temperature. After drying, the flask is washed on the outside with gasoline to remove oil and weighed.

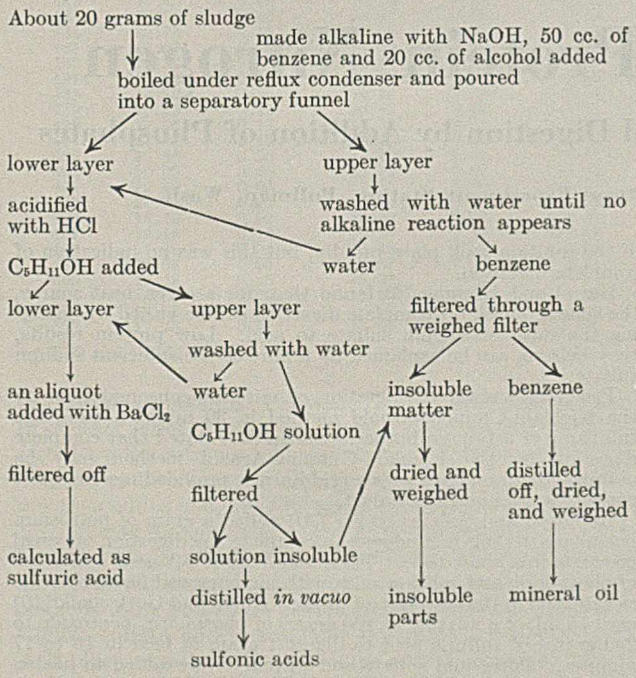
Insoluble Matter

The insoluble parts of sludge are obtained by weighing the dried filtrate from the benzene and amyl alcohol filtering.

Sulfuric Acid

The remaining acid is made up to a known volume, usually 1000 to 1500 cc., and an aliquot (25 cc.) is taken for sulfuric acid determination by precipitating with barium chloride.

An outline of the method is given below:



Tables I, II, and III give results of sludge analyses carried out by means of the method elaborated by the writers. To check the validity of the method two parallel determinations of each sludge were conducted, while control determinations were performed by Miss Geschwind.

The sulfonic acids separated by the authors by means of amyl alcohol may be divided according to Pilat and collaborators (*7*, *10*, *12*, *13*) into at least two species, differing in solubility of their calcium salts. The sulfonic acids called by them γ-acids give calcium salts soluble in water and insoluble in ethyl ether; the calcium salts of α-sulfonic acids are insoluble in both water and ether.

To conduct this distribution, the sulfonic acids separated in the manner described above are dissolved in a small quantity of water and lime-water is added until the reaction is alkaline to phenolphthalein. (The transition is immediately visible, because the acid solution changes in alkaline medium from dirty green to brown.) To the alkaline solution amyl alcohol is added and stirred carefully in a separatory funnel. After settling and clarifying two layers form, while calcium salts, insoluble in both water and amyl alcohol, separate as a solid in amyl alcohol on the border of the lower water layer. From this lower water solution, after evaporating in a dry and weighed beaker and drying at 130° C. to constant weight, water-soluble salts are obtained, called by Pilat γ-sulfonic acids. The alcohol layer is filtered through a glass filter which has been dried at 130° C. and weighed, and is washed with amyl alcohol. This glass funnel-filter with the sediment is dried at 130° C. to constant weight to obtain the calcium salts of sulfonic acids, insoluble in both amyl alcohol and in water. Unlike free sulfonic acids, the salts are more stable and decompose at 180° C. (*7*, *10*, *12*, *13*). The calcium salts soluble in amyl alcohol and insoluble in water are determined last by distilling off the amyl alcohol and drying the residue at 130° C. to constant weight.

TABLE I. SLUDGE ANALYSES

(Second acid sludge from a naphthene-base transformer oil)

	Test I (20.78 grams)		Test II (24.65 grams)	
	Grams	*Per cent*	*Grams*	*Per cent*
Mineral oil	3.20	15.41	3.86	15.65
Sulfonic acids	7.70	37.05	9.17	37.20
Sulfuric acid	9.458	45.51	11.289	45.79
Insoluble matter	0.0214	0.10	0.0258	0.10
Total	20.379	98.07	24.34	98.74

TABLE II. SLUDGE ANALYSES

[Acid sludge from treatment with oleum (20 per cent SO_3) of a stock of specific weight d/15, 0.917; viscosity at 20° C., 7.18° E.; pour point, −48° C.; flash, 162° C.]

	Test I (20.10 grams)		Test II (21.33 grams)	
	Grams	*Per cent*	*Grams*	*Per cent*
Mineral oil	0.95	4.69	0.95	4.46
Sulfonic acids	12.70	63.18	13.79	64.65
Sulfuric acid	5.801	29.29	6.312	29.57
Insoluble matter	0.019	0.09	0.018	0.08
Total	19.47	97.25	21.07	98.76

TABLE III. SLUDGE ANALYSES

(First acid sludge from treatment of a paraffin-base stock of: specific weight d/15, 0.925; viscosity at 50° C., 4.31° E.; pour point, 0° C.; flash, 203° C.)

	Test I (20.51 grams)		Test II (19.79 grams)	
	Grams	*Per cent*	*Grams*	*Per cent*
Mineral oil	12.13	59.19	11.85	59.83
Sulfonic acids	3.67	17.89	3.27	16.52
Sulfuric acid	4.264	20.78	4.063	20.54
Insoluble matter	0.330	1.61	0.331	1.67
Total	20.39	99.47	19.52	98.56

TABLE IV. SEPARATION OF SULFONIC ACIDS

(Sulfonic acids taken for analysis, 13.79 grams)

	Calcium Salts		
	Grams	Sulfonic acids %	Sludge %
Soluble in water	3.125	22.66	14.65
Soluble in amyl alcohol	11.29	81.87	52.93
Insoluble in amyl alcohol	0.584	4.24	2.74
Total	14.999	108.77	70.32

Table IV gives the separation of sulfonic acids obtained by analysis II.

The water-insoluble salts are noncrystalline and dark in color when dry; water-soluble calcium salts are brown.

Water Determination

In the sludge analysis given above, the water content was not taken into consideration. It was found by the authors that in this case the Holde (*5*) xylene method is of no use because, when sludge is heated with xylene, the sulfuric acid acts as a strong oxidant with separation of water and sulfurous anhydride. Then a considerable amount of water is formed from sulfuric acid decomposition and oxidation of organic substances (*4*).

The acid sludge (Table II) of 29.29 per cent free sulfuric acid content showed after heating with xylene 28 per cent water, with almost complete decomposition of sulfuric acid, as is indicated by 0.136 per cent of sulfuric acid left after heating. Otherwise if the same sludge is previously neutralized by mixing 100 grams of dry anhydrous sodium carbonate with 25 grams of acid sludge, only 7.2 per cent of water is obtained after distillation with xylene—i. e., the water included by the acid and arising from acid neutralization.

For lack of a method of water determination in acid sludge, the water content was not taken into consideration in the present determinations, but further work is to be done in this connection.

In working out a method of sludge analysis as complete as possible, the authors neglected also the small amounts of sulfurous anhydride.

A difficulty in the described method involves the removal of the final traces of amyl alcohol owing to the instability of sulfonic acids, which gives higher results for sulfonic acids.

Acknowledgment

The authors acknowledge their grateful indebtedness to Miss O. Geschwind for conducting control analyses.

Literature Cited

(1) Bacon, F. S., Ind. Eng. Chem., Anal. Ed., 1, 89 (1929).
(2) Chierer, F., and Primost, J., *Przemysl Chem.*, 15, 49 (1931).
(3) Gurwitsch, "Wissenschaftliche Grundlagen der Erdölverarbeitung," p. 322.
(4) *Ibid.*, p. 44.
(5) Holde, D., and Bleyberg, W., "Kohlenwasserstofföle und Fette," 7th ed., p. 433, Berlin, Hirschwaldsche Buchhandlung, 1933.
(6) Klipper, Suknarowski, and Chierer, Polish Patent 11,030.
(7) Neyman, E., and Pilat, S., Ind. Eng. Chem., 26, 395 (1934).
(8) Pilat, S., and Sereda, J., *Fettchem. Umschau*, 41, 171–4, 200–4, 237–41 (1934).
(9) Pilat, S., and Sereda, J., Polish Patent 15,021, French Patent 694,256, British Patent 34,353.
(10) Pilat, S., Sereda, J., and Szankowski, W., *Petroleum Z.*, 29, No. 3, 1–11 (1933).
(11) Pilat and Starkel, *Ibid.*, 6, 2177 (1911).
(12) Pilat, S., and Szankowski, W., *Ibid.*, 31, No. 10 (1935).
(13) Sereda, J., *Ibid.*, 30, No. 19 (1934).
(14) Sereda, J., *Przemysl Naftowy*, 9, 627 (1934).

Received June 18, 1935.

Determination of Protein Nitrogen

Accelerating the Kjeldahl-Gunning-Arnold Digestion by Addition of Phosphates

H. W. GERRITZ AND J. L. ST. JOHN, Agricultural Experiment Station, Pullman, Wash.

ALTHOUGH the official (*1*) Kjeldahl-Gunning-Arnold method for protein nitrogen gives good results, it requires a long digestion period, especially if the source of heat is not entirely adequate. Various rapid methods of digestion have been reported.

Mears and Hussey (*13*) and Bimmerman and Frank (*2*) used perchloric acid to accelerate the Kjeldahl digestion. Kleeman (*9*) and Heuss (*8*) found that 25 ml. of 30 per cent hydrogen peroxide added to 1-gram samples of plant or animal material before addition of sulfuric acid shortened the digestion period.

Sborowsky and Sborowsky (*22*) and Richards (*19*) reported more rapid digestion of carbonaceous matter by substitution of mercurous iodide for mercuric oxide. Hassig (*7*) found no acceleration by the use of mercurous iodide and reported that its use is disadvantageous because of the sublimation of iodine on the neck of the flask. Parri (*16*) obtained more rapid clearing of the solution when a mixture of vanadium pentoxide and cupric oxide was used than when either of these catalysts was used alone. Lepper (*12*) used 5 grams of copper sulfate, 15 grams of potassium sulfate, and 20 ml. of sulfuric acid. He reported clearing of the solution for 1-gram sample of feeding stuff in 15 minutes and complete digestion in 45 minutes.

Lauro (*11*) substituted selenium oxychloride for mercury and obtained digestion of 1-gram samples of cereals in 12 to 55 minutes. Sandstedt (*21*) and Rich (*18*) also reported rapid digestion and satisfactory results using selenium or its compounds as catalyst. Messman (*14*) obtained digestion in 20 minutes, using mercury and selenium together as catalysts on a 550-watt electric heater. Osborn and Krasnitz (*15*) found no more rapid digestion using selenium as a catalyst than when using mercury but advise a combination of selenium with either mercury or copper; later they advised the combined use of selenium and mercury. They analyzed a wide variety of materials for nitrogen and obtained a 25 per cent saving of time over the use of mercuric oxide alone. Davis and Wise (*3*), after a survey of cereal laboratories, concluded that selenium as a Kjeldahl catalyst does not appear to be as universally adaptable to general laboratory conditions as does mercury, and its use in combination with common catalysts, especially mercury, is to be discouraged. Snider and Coleman (*24*) found that selenium, as a Kjeldahl catalyst, gave low results, caused undue frothing, and produced obnoxious odors. Clearing of the solution took place rapidly, but this was no indication of complete digestion.

Harrel and Lanning (*6*) found that, for a given heat source, the time required for complete digestion can be varied by changing the ratio of sodium sulfate to acid. Low protein results, they believe, can be explained by failure to use sufficient sodium sulfate.

Pickel (*17*) obtained digestion of miscellaneous materials by the Kjeldahl-Gunning-Arnold method in 30 minutes using the full flame of a Bunsen burner. Shedd (*23*) stated that complete digestion by the Kjeldahl-Gunning-Arnold method may be obtained in 20 minutes over a grid burner, provided mercury, not copper, is used as the catalyst.

Robinson and Schellenberger (*20*) added a gram of potassium persulfate to their microdigest to complete the digestion of cereal products in a short time. Folin and Wright (*4*) used a mixture of phosphoric and sulfuric acids with mercury and ferric chloride as catalysts in the digestion of urine. Kuehl and Gottschalk (*10*) used 15 ml. of a mixture of 100 grams of phosphorus pentoxide to 200 grams of sulfuric acid to digest 1 gram of feed in 15 to 17 minutes. Potassium sulfate and mercury were added to hasten the reaction. Guillemet and Schell (*5*) used 4 ml. of sulfuric acid and 10 drops of glacial phosphoric acid for the microdetermination of protein in cereal products. In the following work potassium phosphate or equivalent reagents are substituted in part for sodium sulfate in the Kjeldahl-Gunning-Arnold digestion.

Experimental

Samples of mixed feed, wheat products, pasture grasses, poultry feces, dried blood, fish meal, soy-bean meal, and dried skim milk were digested in duplicate by phosphate modifications of the Kjeldahl-Gunning-Arnold method and at the same time duplicate determinations were made by the official (*1*) Kjeldahl-Gunning-Arnold method. Blank determinations for the two methods were the same. Distillations were made on an electric still equipped with block tin condensers. The standard acid and alkali used were 0.1142 *N*. One milliliter of the standard acid is equivalent to 1 per cent of protein (factor 6.25) when a 1-gram sample is used. Milliliters of acid multiplied by 0.16 give per cent of nitrogen.

Replacing Sodium Sulfate Completely by Potassium Phosphate. Two grams of mixed feed were placed in a 500-ml. Kjeldahl flask and 12 grams of dipotassium phosphate trihydrate or 10 grams of the anhydrous salt, 0.7 gram of mercuric oxide, and 0.3 gram of copper sulfate were added. The salts were well mixed with the feed, 25 ml. of concentrated sulfuric acid were then added, and the flask was well shaken. Heating and charring occurred. The flask was placed over the full flame of a Bunsen burner. Vigorous digestion took place immediately, almost filling the flask with froth, but this seldom reached the neck of the flask. Clearing took place in about 20 minutes and digestion was continued for another 20 minutes.

Analyses are reported in Table I. Clearing time was decreased appreciably by use of the phosphate, but low results were obtained on replacing sodium sulfate completely by 10 grams of potassium phosphate when compared with the official (*1*) method.

Table I. Protein Determinations on Mixed Feeds

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method		Digested with K_2HPO_4 and H_2SO_4[a]		
		Difference between duplicates		Difference between duplicates	Difference between Methods
	%	%	%	%	%
482	19.40	0.05	19.28	0.15	−0.12
483	20.98	0.05	20.83	0.05	−0.15
484	22.76	0.18	22.45	0.10	−0.31
485	21.47	0.10	21.22	0.12	−0.25
486	19.98	0.15	19.84	0.07	−0.14
487	20.87	0.10	20.72	0.04	−0.15
488	14.50	0.20	14.27	0.00	−0.23
489	20.45	0.22	20.41	0.02	−0.03
490	17.44	0.15	17.28	0.15	−0.16
491	21.87	0.10	21.58	0.12	−0.29
492	33.46	0.20	33.40	0.00	−0.06
493	20.00	0.30	19.74	0.07	−0.26
494	22.40	0.05	22.15	0.00	−0.25
495	21.79	0.02	21.26	0.12	−0.53
496	18.19	0.02	18.08	0.05	−0.11
497	19.16	0.12	19.00	0.10	−0.16
498	15.68	0.05	15.49	0.13	−0.09
499	22.08	0.05	21.97	0.00	−0.11
500	19.13	0.05	19.00	0.10	−0.13
501	15.05	0.20	14.62	0.10	−0.43
502	19.38	0.05	19.20	0.30	−0.18
503	17.76	0.02	17.53	0.15	−0.23

[a] HgO and $CuSO_4$ catalysts.

Adding Potassium Persulfate to Cleared Digest. In another series of analyses, samples of mixed feeds were digested by the mixture just described. Clearing occurred in from 15 to 25 minutes. One gram of potassium persulfate was then added and, after bringing the solutions to boiling, the heating was discontinued. The data are reported in Table II. The results are still slightly lower than those obtained by the official method and also lower than those obtained by rapid methods using potassium phosphate together with 6 grams of sodium sulfate which are later described. While clearing took place rapidly with potassium phosphate, these results seem to substantiate the findings of Snider and Coleman (*24*) with selenium that digestion is not necessarily complete when the solution becomes clear.

Table II. Protein Determination on Mixed Feeds

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method		Digested with K_2HPO_4 and H_2SO_4[a]		
		Difference between duplicates		Difference between duplicates	Difference between Methods
	%	%	%	%	%
508	21.75	0.00	21.45	0.10	−0.30
509	19.90	0.00	19.60	0.10	−0.30
510	20.54	0.13	20.38	0.15	−0.16
511	20.03	0.05	19.80	0.00	−0.23
512	18.40	0.00	18.13	0.05	−0.27
513	20.38	0.01	20.15	0.20	−0.23

[a] $CuSO_4$ and HgO used as catalysts. 1 gram of $K_2S_2O_8$ added after clearing.

Combining Potassium Phosphate and Sodium Sulfate. Since 1 gram of potassium persulfate added to the potassium phosphate apparently did not complete the digestion, 6 grams of anhydrous sodium sulfate were added to the above to bring about more complete digestion. Although the gas supply available for this work was barely sufficient to keep the digest boiling, clearing took place on 2-gram samples in 15 to 20 minutes over Bunsen flames. One gram of potassium persulfate was then added and the boiling was continued 5 minutes more. All digestions were terminated in less than 30 minutes. The results on mixed feeds, pasture grass, and poultry feces are given in Tables III, IV, and V. They agree closely with analyses by the official Kjeldahl-Gunning-Arnold method.

A further modification of this method was also used which included the substitution of phosphorus pentoxide plus potassium hydroxide for the potassium phosphate. Phosphorus pentoxide equivalent to 10 grams of anhydrous dipotassium phosphate was added to the sample with the sulfuric acid and potassium hydroxide was then added. Two-gram samples were placed in 500-ml. Kjeldahl flasks and 6 grams of anhydrous sodium sulfate, 0.7 gram of mercuric oxide, and 0.3 gram of copper sulfate were added. Twenty-five milliliters of the sulfuric acid–phosphoric anhydride mixture, containing 16 grams of phosphorus pentoxide per 100 ml. of sulfuric acid, were added and then mixed with the sample. About 4 grams of stick potassium hydroxide were added and the flask was swirled. After the initial vigorous action ceased the flask was placed over the burner. Vigorous digestion began immediately. Using the gas flames available, clearing took place in 15 to 20 minutes and the flask was removed after 25 minutes. These results are presented in the second part of Table III.

Table III. Protein Determinations on Mixed Feeds

Sample No.	Digested with Kjeldahl-Gunning-Arnold Method		Digested with H_2SO_4, K_2HPO_4, and Na_2SO_4[a]		
		Difference between duplicates		Difference between duplicates	Difference between Methods
	%	%	%	%	%
482	19.40	0.05	19.43	0.15	+0.03
483	19.98	0.05	21.03	0.05	+0.05
488	14.50	0.20	14.40	0.10	−0.10
508	21.75	0.00	21.60	0.00	−0.15
509	19.90	0.00	19.80	0.04	−0.10
510	20.54	0.13	20.45	0.06	−0.08
511	20.03	0.05	20.09	0.18	+0.06
512	18.40	0.00	18.39	0.13	−0.01
513	20.38	0.01	20.30	0.20	−0.08
514	19.20	0.10	18.92	0.05	−0.28
515	16.45	0.00	16.40	0.20	−0.05
516	15.75	0.00	15.72	0.05	−0.03
517	22.85	0.10	22.82	0.10	−0.03
518	19.94	0.17	20.00	0.10	+0.06
519	21.50	0.10	21.22	0.00	−0.28
520	22.73	0.25	22.73	0.05	0.00
521	18.70	0.00	18.51	0.08	−0.19
522	15.50	0.00	15.35	0.10	−0.15
523	24.00	0.10	23.90	0.00	−0.10
400	19.11	0.07	18.96	0.06	−0.15
402	16.13	0.10	16.32	0.02	+0.19
408	19.84	0.20	19.98	0.10	+0.14
410	16.38	0.08	16.21	0.11	−0.17
414	18.44	0.14	18.34	0.02	−0.10
424	16.58	0.05	16.53	0.06	−0.05
445	18.43	0.14	18.43	0.04	0.00
381	16.47	0.06	16.45	0.06	−0.02
373	15.19	0.08	15.22	0.03	+0.03
41	16.30	0.13	16.24	0.12	−0.06
23	16.44	0.05	16.39	0.05	−0.05
42	18.36	0.03	18.28	0.15	−0.08
68	17.98	0.15	17.76	0.07	−0.22
58	15.87	0.02	15.72	0.05	−0.15
46	16.31	0.01	16.16	0.01	−0.15
			Digested with H_2SO_4, P_2O_5, Na_2SO_4, HgO, $CuSO_4$, and KOH		
485	21.47	0.10	21.44	0.13	−0.03
486	19.97	0.15	19.90	0.00	−0.07
487	20.87	0.10	20.95	0.10	+0.08
488	14.50	0.20	14.40	0.15	−0.10
489	20.45	0.22	20.54	0.07	+0.09
490	17.43	0.15	17.27	0.00	−0.16
491	21.87	0.10	21.73	0.10	−0.14
494[b]	22.40	0.05	22.19	0.17	−0.21
495[b]	21.79	0.02	21.50	0.05	−0.29
496[b]	18.19	0.02	18.15	0.00	−0.04
497[b]	19.16	0.12	19.09	0.17	−0.07
498[b]	15.68	0.05	15.66	0.12	−0.02
499[b]	22.08	0.05	21.96	0.12	−0.12
500	19.13	0.05	19.13	0.05	0.00
501	15.05	0.20	14.80	0.10	−0.25
502	19.38	0.05	19.06	0.22	−0.32

[a] HgO and $CuSO_4$ as catalysts. 1 gram of $K_2S_2O_8$ added after clearing.
[b] No $K_2S_2O_8$ was added to these digestions.

Table IV. Nitrogen Determination on Poultry Feces

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method		Digested with H_2SO_4, K_2HPO_4, and Na_2SO_4[a]		
		Difference between duplicates		Difference between duplicates	Difference between Methods
	%	%	%	%	%
50	3.92	0.03	3.88	0.02	−0.03
51	3.99	0.02	4.02	0.00	+0.03
52	3.78	0.06	3.79	0.03	+0.01
53	3.81	0.04	3.81	0.05	0.00
54	3.66	0.00	3.69	0.00	+0.03
55	3.77	0.02	3.74	0.02	−0.03
56	3.94	0.00	3.90	0.01	−0.04
57	4.08	0.01	4.05	0.02	−0.03
58	3.87	0.01	3.83	0.01	−0.04
59	4.03	0.01	4.01	0.01	−0.02
60	4.42	0.04	4.36	0.01	−0.06
61	4.06	0.04	4.04	0.02	−0.02

[a] HgO and $CuSO_4$ catalysts. 1 gram of $K_2S_2O_8$ added after clearing.

Table V. Protein Determinations on Pasture Grass

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method		Digested with H_2SO_4, K_2HPO_4, and Na_2SO_4[a]		
		Difference between duplicates		Difference between duplicates	Difference between Methods
	%	%	%	%	%
B	27.00	0.00	26.95	0.20	−0.05
C	26.50	0.20	26.43	0.25	−0.07
D	25.18	0.05	25.35	0.20	+0.17
E	22.85	0.10	22.70	0.00	−0.15
F	21.50	0.00	21.53	0.25	+0.03
G	23.18	0.15	23.00	0.20	−0.18
H	20.17	0.03	20.15	0.00	−0.02
M	30.54	0.01	30.38	0.04	−0.16
O	29.03	0.02	28.84	0.08	−0.19
P	29.31	0.07	29.25	0.10	−0.06

[a] HgO and $CuSO_4$ catalysts. 1 gram of $K_2S_2O_8$ added after clearing.

Table VI. Protein Determination on Wheat Products

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method		Digested with H_2SO_4, P_2O_5, KOH, and Na_2SO_4[a]		
		Difference between duplicates		Difference between duplicates	Difference between Methods
	%	%	%	%	%
30	15.32	0.00	15.21	0.02	−0.11
31	14.68	0.05	14.49	0.08	−0.19
32	14.88	0.05	14.89	0.02	+0.01
34	14.55	0.04	14.46	0.11	−0.09
35	14.09	0.02	14.00	0.07	−0.09
39	13.65	0.06	13.65	0.00	0.00
41	16.75	0.00	16.86	0.14	+0.11
42	10.15	0.00	10.21	0.08	+0.06
43	11.25	0.00	11.33	0.05	+0.08
44	13.33	0.05	13.15	0.00	−0.18
36	13.30	0.00	13.33[b]	0.00	+0.03
37	11.81	0.09	11.82[b]	0.03	+0.01
38	13.20	0.10	13.23[b]	0.05	+0.03
40	14.78	0.13	14.75[b]	0.10	−0.03
45	18.23	0.05	18.25[b]	0.00	+0.02
46	11.88	0.05	11.88[b]	0.00	0.00
25	13.10	0.10	12.93[c]	0.07	−0.17
26	12.41	0.08	12.31[c]	0.10	−0.06
27	13.45	0.08	13.43[c]	0.20	−0.02
28	15.56	0.01	15.48[c]	0.05	−0.08
29	14.27	0.17	14.12[c]	0.02	−0.15
33	13.60	0.10	13.61[c]	0.11	+0.01

[a] HgO, $CuSO_4$, and $Fe_2(SO_4)_3$ used as catalysts.
[b] K_2HPO_4 used in digestion instead of P_2O_5 and KOH.
[c] Digested in 9 minutes on glimmer heater.

Attempts were made to substitute sodium phosphate, phosphoric acid plus potassium sulfate, or phosphorus pentoxide without potassium hydroxide, in place of dipotassium phosphate. The clearing time for any such substitution was longer than where dipotassium phosphate was used. The addition of larger quantities of the potassium phosphate caused vigorous frothing, while smaller quantities resulted in slower digestion.

Another modification following Folin and Wright's (*4*) suggestion included the addition of iron to the mixture of sodium sulfate, mercuric oxide, copper sulfate, potassium hydroxide, and sulfuric acid–phosphorus pentoxide mixture. The results of the addition of iron in the form of ferric sulfate to this digestion mixture previously described, when used in the analysis of wheat, flour, and bran, are given in Table VI.

A 700-watt hot plate was used to determine the effect of more intense heat. When the flasks were placed on the preheated hot plate, clearing occurred in 4 to 5 minutes and the digestion was completed in about 9 minutes, as indicated in Table VI. The results agree well with those by the official method.

The method is also applicable to high-protein samples.

An acid mixture was made by adding 16 grams of anhydrous phosphorus pentoxide per 100 ml. of sulfuric acid in a Kjeldahl flask, cooling, and adding 16 grams of potassium hydroxide with cooling. Fifteen to twenty milliliters of this mixture were added to the sample in a Kjeldahl flask together with 6 grams of sodium sulfate and 0.7 gram of mercuric oxide. Over grid burners clearing occurred in 5 to 8 minutes and digestion was terminated at 15 minutes. Over Bunsen burners clearing occurred in 25 minutes and digestion was terminated after 45 minutes and 90 minutes to determine the effect of longer boiling. At the same time, samples were digested by the Kjeldahl-Gunning-Arnold method for 120 minutes. Results are given in Table VII.

Table VII. Protein Determination on High-Protein Materials

Substance Analyzed	Weight of Sample	Digested with Na_2SO_4 and H_2SO_4[a] 15 minutes Grid burner	45 minutes Bunsen burner	90 minutes Bunsen burner	Kjeldahl-Gunning-Arnold Digestion 120 Minutes Bunsen Burner
	Grams	%	%	%	%
Meat scrap	1.0	59.93	59.55	59.95	60.00
Herring meal	0.8	68.71	69.18	69.03	69.11
Mixed feed	1.0	48.23	47.75	47.90	48.00
Meat meal	0.8	56.88	56.82	57.12	56.71
Dried blood	0.8	63.20	62.40	61.94	63.19
Meat meal and bone	0.8	58.50	58.37	58.25	58.80
Herring meal	0.7	72.96	72.83	73.00	72.94
Herring meal	0.7	73.13	73.28	73.11	73.28
Soy-bean meal	1.0	47.65	47.50	47.50	47.15
Dried skim milk	1.5	36.23	36.05	36.02	36.08

[a] 6 grams of Na_2SO_4 and 20 ml. of H_2SO_4 containing 3.5 grams of P_2O_5 and 3.5 grams of KOH-HgO catalyst.

The results obtained by the rapid digestion of high-protein materials, wherein potassium phosphate is substituted in part for sodium sulfate, agree well with the longer Kjeldahl-Gunning-Arnold method. Satisfactory results were also obtained when using Bunsen flames, although a somewhat longer digestion period was required.

Discussion

The substitution of dipotassium phosphate for part of the sodium sulfate in the Kjeldahl-Gunning-Arnold protein digestion shortened the required digestion time. Using Bunsen flames total digestion time for low-protein materials was reduced to 25 minutes or less. Trials made with a 700-watt plate indicated that digestion time may be reduced to 10 minutes or less. With high-protein samples digestion was completed in 15 minutes with a grid burner. The results of analysis of mixed feeds, wheat products, pasture grasses, and poultry feces, as well as difficultly digestible high-protein material, agreed well with results obtained by the official method. The mixture served a double purpose by shortening the digestion period and at the same time furnishing a solution, the vapors from which condensed and washed the sides of the flask. The charred material carried to the top of the flask and into the bottom of the neck by rapid heating on the hot plate was washed down rapidly by condensing vapors, thus obviating the necessity of swirling the flask during digestion. The solution cooled much more without solidifying than digests using sodium sulfate.

Similar results were obtained with a sulfuric acid solution to which 16 grams of phosphorus pentoxide and 16 grams of potassium hydroxide per 100 ml. were added. When 15 to 25 ml. of this solution were added to samples, together with 0.7 gram of mercuric oxide and 6 grams of sodium sulfate, rapid digestion occurred and good results were obtained.

Low results were obtained when the sodium sulfate was completely replaced by 10 grams of potassium phosphate. The addition of iron to the catalysts and the use of potassium persulfate to complete the digestion were not shown to be necessary.

The use of phosphate partially to replace sulfate will, of course, slightly increase the cost of reagents used in the protein determination. The saving in gas or electricity during the shorter digestion period should, however, more than offset the increase in reagent cost. If anhydrous dipotassium phosphate is used, a mixture of 64 per cent dipotassium phosphate and 36 per cent sodium or potassium sulfate may be prepared and added to the sample from a dipper. When the phosphorus pentoxide–potassium hydroxide modified digestion is employed, a sulfuric acid solution containing 16 grams of phosphorus pentoxide and 16 grams of potassium hydroxide per 100 ml. may be prepared. The digestion mixtures in either case should be added to the sample not more than a few minutes before placing the flasks on the heaters.

Summary

Ten grams of anhydrous dipotassium phosphate or 12 grams of dipotassium phosphate trihydrate, or an equivalent quantity of phosphorus pentoxide plus potassium hydroxide, were substituted for ten-sixteenths of the sodium or potassium sulfate used in the digestion of samples for protein nitrogen determinations.

Two-gram samples of feeds and wheat products were digested in 25 minutes or less over the Bunsen flames available and in 9 minutes on a preheated 700-watt electric plate. Samples of dried blood, fish meal, soy-bean meal, and dried skim milk were digested in 15 minutes over grid burners. The results obtained compared well with analysis by the official Kjeldahl-Gunning-Arnold method.

Literature Cited

(1) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, 3rd ed., 1930.
(2) Bimmerman, P. H., and Frank, W. L., *J. Am. Assoc. Cereal Chem.*, 8, 49–53 (1923).
(3) Davis, C. F., and Wise, M., *Cereal Chem.*, 10, 488–93 (1933).
(4) Folin, Otto, and Wright, L. E., *J. Biol. Chem.*, 38, 461 (1919).
(5) Guillemet, R., and Schell, C., *Bull. soc. chim. biol.*, 15, 1631–6 (1934).
(6) Harrel, C. G., and Lanning, J. H., *Cereal Chem.*, 6, 72–8 (1929).
(7) Hassig, M., *Mitt. Lebensm. Hyg.*, 14, 101–2 (1923).
(8) Heuss, R., *Z. ges. Brauw.*, 44, 162–4 (1921).
(9) Kleeman, *Z. angew. Chem.*, 34, 625–7 (1921).
(10) Kuehl, H., and Gottschalk, P. G., *Cereal Chem.*, 6, 512–14 (1929).
(11) Lauro, M. F., Ind. Eng. Chem., Anal. Ed., 3, 401 (1931).
(12) Lepper, W., *Landw. Vers.-Sta.*, 111, 159–61 (1930).
(13) Mears, B., and Hussey, R. E., J. Ind. Eng. Chem., 13, 1054–6 (1921).
(14) Messman, H. C., *Cereal Chem.*, 9, 357–8 (1932).
(15) Osborn, R. A., and Krasnitz, A., *J. Assoc. Official Agr. Chem.*, 16, 110–12 (1933); 17, 339–41 (1934).
(16) Parri, W., *Giorn. farm. chim.*, 71, 253–9 (1922).
(17) Pickel, J. M., J. Ind. Eng. Chem., 7, 357 (1915).
(18) Rich, C. E., *Cereal Chem.*, 9, 118–20 (1932).
(19) Richards, E. S., *Chem. Eng. Mining Rev.*, 15, 369 (1923).
(20) Robinson, R. J., and Schellenberger, J. H., Ind. Eng. Chem., Anal. Ed., 4, 243 (1932).
(21) Sandstedt, R. M., *Cereal Chem.*, 9, 156–7 (1932).
(22) Sborowsky, M., and Sborowsky, L. A., *Ann. chim. anal. chim. appl.*, 4, 266–7 (1922).
(23) Shedd, O. M., *J. Assoc. Official Agr. Chem.*, 10, 507 (1927).
(24) Snider, S. R., and Coleman, D. A., *Cereal Chem.*, 11, 414–30 (1934).

Received May 1, 1935. Published as Scientific Paper No. 322, College of Agriculture and Experiment Station, State College of Washington.

Determination of Manganese and Magnesium in Soils and Silicate Rocks

L. A. DEAN AND E. TRUOG, University of Wisconsin, Madison, Wis.

THE methods of rock, mineral, and soil analysis commonly suggested by Hillebrand and Lundell (*4*) and the Association of Official Agricultural Chemists (*1*) require that manganese be determined on a separate portion of the sample, because of incompleteness of separation of manganese by precipitation with bromine, persulfate, and ammonium sulfide. Furthermore, because of this incompleteness of separation, Hillebrand and Lundell recommend that the magnesium, when determined, be corrected for contaminating manganese. Thus, if both manganese and magnesium are to be determined, it requires that two fusions and two determinations of manganese be made.

Since manganese may be quantitatively precipitated as manganese ammonium phosphate, and since it generally exists in soils and silicate rocks in much smaller quantities than magnesium, it appeared possible to develop a method in which the manganese and magnesium are precipitated and weighed or titrated together as the phosphate, after which the manganese is determined colorimetrically or volumetrically and the amount of magnesium obtained by difference.

Precipitation and Titration of Manganese Ammonium Phosphate

The first step in this investigation was to determine whether manganese could be completely precipitated under the same conditions as magnesium and ultimately titrated by the method developed by Handy (*3*).

Measured portions of standardized 0.05 N potassium permanganate were mixed with 100 cc. of 0.5 N hydrochloric acid and a few drops of a 1 per cent solution of oxalic acid added to bring about complete reduction. The solution was neutralized with ammonia, and 20 cc. of a 10 per cent solution of sodium ammonium hydrogen phosphate were added, followed by 10 cc. more of concentrated ammonia. The solution was then boiled and allowed to cool at room temperature overnight. After filtration, the precipitate and paper were washed with 0.5 N ammonium hydroxide. The filter with precipitate were removed and allowed to dry at room temperature until ammonia-free—that is, until ammonia fumes could no longer be detected with bromocresol purple test paper. The filter paper containing the precipitate was then placed in a 250-cc. flask, 50 cc. of carbon dioxide-free distilled water and an excess of standard sulfuric acid were added, the flask was shaken until the paper was pulped, and the solution back-titrated to pH 4.5, using bromocresol green as an indicator. [J. A. Chucka (unpublished data) found that bromocresol green is superior for this purpose to the indicator used by Handy.] The filter paper pulp was then filtered off and the manganese determined volumetrically, using the bismuthate method of Park (*5*). The results of this test are given in Table I.

These data indicate that manganese may be quantitatively precipitated as manganese ammonium phosphate, and this in turn titrated according to the method of Handy (*3*).

TABLE I. DETERMINATION OF MANGANESE

Manganese Taken	Manganese Found by Precipitation and Titration as $MnNH_4PO_4$	Manganese Found by Bismuthate Method
Mg.	*Mg.*	*Mg.*
5.50	5.53	5.47
8.25	8.08	8.25
11.00	11.13	11.00

TABLE II. DETERMINATION OF MANGANESE AND MAGNESIUM

Manganese Taken	Manganese by Bismuthate Method	Magnesium Taken	Magnesium by Difference
Mg.	*Mg.*	*Mg.*	*Mg.*
5.50	5.47	5.98	5.97
1.10	1.11	5.98	5.97

Determination of Manganese and Magnesium

PRECIPITATION AND TITRATION AS PHOSPHATES. Aliquots of known solutions of potassium permanganate and magnesium chloride were mixed together with 100 cc. of 0.5 *N* hydrochloric acid and the combined amounts of manganese and magnesium determined by precipitation and titration as phosphate. The manganese was then determined by Park's bismuthate method and the amount of magnesium obtained by difference. The results obtained are given in Table II, and show that manganese and magnesium may be satisfactorily determined in this way.

DETERMINATION IN SOLUTIONS CONTAINING IRON, ALUMINUM, AND CALCIUM. The purpose of these tests was to determine whether there is any noticeable precipitation of manganese during the ammonia separation and the calcium precipitation as the oxalate, and, further, to compare the results for magnesium when the manganese is previously precipitated by either bromine or persulfate with those obtained by the difference method just explained.

Synthetic solutions were prepared which contained 100 mg. of R_2O_3 purified by reprecipitation, magnesium from recrystallized magnesium nitrate, calcium from calcite (free of manganese and magnesium), and manganese from potassium permanganate. The R_2O_3 was then separated from these solutions by two ammonia precipitations at pH 6.2. In two of the samples, the manganese was then precipitated as the dioxide with either bromine or persulfate, ignited, and weighed as Mn_3O_4. The Mn_3O_4 precipitates were fused with sodium carbonate and the manganese was redetermined by the bismuthate method. The calcium was separated from all samples as the oxalate at pH 4.4 according to the procedure of Chapman (*2*). The magnesium or manganese and magnesium together were then precipitated and determined by the method previously described.

The results, given in Table III, show that differences in procedure caused but slight differences in the values obtained for magnesium and calcium. However, the values for magnesium obtained by the difference method are uniformly higher. When the manganese was weighed as Mn_3O_4, high results were obtained for manganese, and when the Mn_3O_4 was fused and redetermined volumetrically, slightly low values resulted. The high values may be attributed to a contamination of R_2O_3, and low values to an incomplete precipitation of the manganese.

TABLE III. RESULTS WITH DIFFERENT PROCEDURES OF ANALYSIS

Procedure	Material Analyzed	Manganese	Manganese Found		Magnesium		Calcium	
		Taken	Weighed as Mn_3O_4	Bismuthate method	Taken	Found	Taken	Found
		Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
Mn pptd. with Br	Synthetic solution	1.65	2.74	1.35	9.75	9.61	9.90	9.98
Mn pptd. with persulfate	Synthetic solution	1.65	2.36	1.48	9.75	9.60	9.90	9.90
Mn and Mg pptd. as phosphate, Mg by difference	Synthetic solution	1.65	...	1.63	9.75	9.70	9.90	9.95
Mn pptd. with Br	Soil	..	10.7	1.42	..	3.66	..	5.1
Mn pptd. with persulfate	Soil	..	12.5	1.43	..	3.69	..	5.0
Mn and Mg pptd. as phosphate, Mg by difference	Soil	..	...	1.53	..	3.93	..	4.9

The magnesium precipitates obtained when the bromine or persulfate method was used for manganese gave in all cases a test for manganese.

In further tests, 1-gram samples of a soil (Miami silt loam) were treated with hydrofluoric and sulfuric acids to decompose the silicates and volatilize the silica. The residues were fused with potassium bisulfate, dissolved, and treated in the same manner as the synthetic solutions. The results are given in Table III and are in accord with those previously given. The results by the difference method are again slightly higher for both manganese and magnesium. The higher results for the manganese may be attributed to more perfect precipitation, and the lower results for magnesium in the bromine method to the possibility that sufficient ammonia salts may have been destroyed by the bromine to cause some precipitation of magnesium with the manganese dioxide.

Results for Manganese with the Two Procedures

In the direct method for manganese, 1-gram samples of a pyroxene were treated with hydrofluoric and sulfuric acids, and heated, and the residue was fused with potassium bisulfate. The fusion was dissolved in 3 *N* sulfuric acid and the manganese determined by the bismuthate method. In the second method, involving the indirect determination of magnesium, other samples of pyroxene were fused with sodium carbonate and treated with dilute hydrochloric acid, and the silica was removed after dehydration. The R_2O_3 was precipitated at pH 6.2 and filtered off, the calcium was precipitated at pH 4.4 and filtered off, and the magnesium and manganese were then precipitated as the phosphate which was ignited to the pyrophosphate form. This was fused with sodium carbonate and the manganese determined by the bismuthate method. The results are as follows: by the direct method, 0.51 mg., and by the method involving magnesium by difference, 0.48 mg. of manganese. These results agree within experimental error.

Details of Proposed Procedure

Fuse a sample of soil or mineral with sodium carbonate and remove the silica in the regular way. Precipitate the R_2O_3 with ammonia at pH 6.2 and filter off. Precipitate the calcium with oxalic acid at pH 4.4 and filter off. Remove the excess ammonia salts by evaporation with nitric acid (be careful to avoid spattering). Take up the residue with 5 cc. of concentrated hydrochloric acid diluted to 100 cc. and neutralize with ammonia. Add 20 cc. of 10 per cent sodium ammonium hydrogen phosphate solution, followed by 10 cc. excess of concentrated ammonia. Bring solution to a boil and allow to cool at room temperature overnight. Filter off the precipitate and wash with 0.5 *N* ammonium hydroxide. Remove the filter paper with precipitate, and air-dry until free of ammonia. Place the filter paper and precipitate in a 200-cc. flask, add 50 cc. of carbon dioxide-free water, and follow with an excess of standard sulfuric acid. Shake the flask until the paper is pulped, and back-titrate with standard sodium hydroxide to pH 4.5, using bromocresol green as the indicator. This titration represents the phosphate combined with manganese and magnesium.

In case large quantities of manganese are present, two drops of a 1 per cent solution of sodium oxalate adjusted to pH 4.5 should be added with the standard acid to assure complete solution, which is indicated by disappearance of brown color. Remove the filter paper pulp by filtration and determine the manganese in the solution by Park's sodium bismuthate method. Convert the manganese to equivalent value in cubic centimeters of the standard sulfuric acid and subtract this from the previous titration value, giving the magnesium by difference. When there is a large precipitate of magnesium and manganese phosphates, it may be more convenient to ignite the precipitate to the pyrophosphates, weigh, and then fuse the pyrophosphate with sodium carbonate and proceed with the bismuthate method for manganese.

Summary

The precipitation of manganese by oxidation with bromine or persulfate in the regular course of analysis of rocks and soils has not been satisfactory because of incompleteness of precipitation of the manganese, and at times contamination of the manganese precipitate with magnesium and the magnesium precipitate with manganese. To overcome these difficulties, it is suggested that the manganese be precipitated with the magnesium as the phosphate. The phosphates of manganese and magnesium are then weighed or titrated together, after which the manganese present is determined by means of the bismuthate method, and the amount of magnesium is obtained by difference. In a number of tests this procedure has given satisfactory results.

Literature Cited

(1) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, 2nd ed., p. 30 (1930).
(2) Chapman, H. D., *Soil Sci.*, **26**, 479 (1928).
(3) Handy, J. O., *J. Am. Chem. Soc.*, **22**, 31 (1900).
(4) Hillebrand, W. F., and Lundell, G. E. F., "Applied Inorganic Analysis," p. 743, New York, John Wiley & Sons, 1929.
(5) Park, B., Ind. Eng. Chem., **18**, 597 (1926).

Received July 22, 1935. Published with the permission of the director of the Wisconsin Agricultural Experiment Station.

Refractometric Estimation of the Total Solids Content of Whole Eggs and of Yolks

M. IRENE BAILEY, Columbia University, New York, N. Y.

A CORRELATION between the total solids contents and the indices of refraction of whole egg and of yolk magma obtained from hens' eggs shows that an estimation of the per cent total solids may be made by the use of a refractometer. A study made at the California Agricultural Experiment Station (*1*, *3*) has shown that the total solids content of egg white may be estimated refractometrically.

In the study herein reported, the eggs were taken from carload deliveries received at an egg-freezing plant in Jersey City, from various parts of the United States during the egg-producing season of the year 1931. No storage eggs were used.

Yolks were separated from whites in commercial fashion by girls accustomed to the work of a commercial egg-breaking plant supplying bakers and confectioners with whole egg, yolks, or whites according to demand. This plant prepared commercially two types of yolks, one known as "commercial yolk" and the other as "dry yolk." In the preparation of the latter, extra care was exercised to remove as much of the egg white as was practically feasible. Consequently, all the yolk samples studied contained some adhering whites. This paper, therefore, does not attempt to record the total solids in the egg yolk entirely free from egg white but nevertheless presents a method by which such determinations may be made if desired. A method for completely separating the egg white from the yolk is given by Pennington (*4*).

The whole egg magmas were prepared in the laboratory. Two grades were studied, U. S. Extras and U. S. Standards, the selection according to grade having been made by expert egg candlers. Samples were prepared for analysis in the following manner:

> Six (or three) eggs at about 5° C. were removed from the shells and then disrupted to a uniform magma by the operation of a typical malted milk mixer. (In the early part of the work a composite sample was made from six eggs, or yolks, but later the sample was reduced to three.) The yolks as received from the plant were disrupted and mixed in the same manner, in all cases, six yolks constituting one sample.

The magma was then submitted to analysis. The determination of total solids was carried out according to the Association of Official Agricultural Chemists method (*2*). The index of refraction was read in an Abbé type refractometer around the prisms of which water at 25 ± 0.01° C. was circulating. A drop or two of the remixed egg magma was pipetted onto the prism of the instrument. (Owing to danger of "creaming" of the fatty matter, the magma was always carefully mixed in the sample bottle immediately prior to placing it in the refractometer.) The prism was then closed and the index of refraction was read exactly one minute later. This procedure was adopted for two reasons, in order to allow time for temperature equilibrium and because the reading changes with time.

Egg white gives a sharp and easily read line of demarcation between the illuminated and dark segments of the field. In the case of yolk magma, the line of demarcation is less distinct, while whole egg magma in general gives a poorer boundary line than yolk magma. The distinctness varies with different specimens. However, with a little practice operators can readily learn to check each other to about 3 units in the fourth decimal place of refractive index in the case of whole egg magma and better in the case of yolk magma. A dipping or immersion refractometer was tried on yolk and whole egg magma. Owing to its greater sensitivity, the line of demarcation was too blurred and consequently this type of refractometer was found inapplicable for the purpose of this study.

Table I. Numbers of Specimens Studied

(Spring 1931)

	March	April	May	June	Total
Whole egg, U. S. Extras	38	14	10	15	77
Whole egg, U. S. Standards	38	13	9	9	69
Commercial yolks	19	20	16	9	64
Dry yolks	9	17	17	9	52

The number of specimens of fresh eggs examined is given in Table I according to the months of the year they were received and analyzed. When the total solids contents were plotted against the indices of refraction, the distribution of points indicated a straight-line relationship. On the assumption of this indication, the several sets of data were subjected to mathematical analysis by the method of least squares which produced the following equations, where R equals index of refraction and S equals per cent total solids:

Whole eggs, U. S. Extras	$S = 497.0R - 658.29$
Whole eggs, U. S. Standards	$S = 439.9R - 579.49$
Commercial yolks	$S = 503.1R - 663.15$
Dry yolks	$S = 542.4R - 718.19$
All yolks (combination of data on "dry" and "commercial" yolks)	$S = 565.4R - 750.76$

After having derived these equations, the total solids content for each specimen included in the data was calculated by substitution of the observed values for R. The differences, d, between the observed and calculated values for the per cent total solids were then used to calculate the standard deviation, $S.D.$, by means of the formula $S.D. = \sqrt{\frac{\Sigma d^2}{n}}$ where n equals the number of cases, with the following results:

Whole eggs, U. S. Extras	$S.D. = \pm 0.30$
Whole eggs, U. S. Standards	$S.D. = \pm 0.31$
Commercial yolks	$S.D. = \pm 0.59$
Dry yolks	$S.D. = \pm 0.45$
All yolks	$S.D. = \pm 0.55$

The standard deviations for the yolks are seen to be higher than those for the whole eggs, despite the more distinct line between light and shadow in the refractometer observed in the case of the yolks. Thus the relationship between refractive index and total solids is more variable with yolks of commerce than with whole eggs. This is to be expected in view of the fact that the yolks measured contained variable amounts of whites.

Since a large fraction of the total solids of whole eggs and an even larger one in case of yolks is fatty matter emulsified in the continuous aqueous phase, it is remarkable that the refractometric method works at all. Since it does, there is evidently a relationship between the total fatty matter and the water-soluble matter, as is the case in cows' milk where a high fat content is accompanied by a high protein content and vice versa.

An examination of the data obtained in this study revealed an indication of a seasonal variation in the case of yolks and to a less extent in the case of whole eggs. The determined values for total solids of late June eggs were lower than those calculated by means of the equation, and to a smaller extent early March eggs showed calculated total solids lower than those actually determined. However, the number of specimens analyzed was insufficient to give more than a general trend. Further study is necessary to determine the extent of this seasonal variation.

For the benefit of those who may wish to apply the data at temperatures other than 25° C., temperature coefficients were determined by measurements upon 7 specimens of whole egg and 7 specimens of dry yolk. These showed that there is a straight-line variation between the temperatures of 20° C. (68° F.) and 30° C. (86° F.) The method cannot be applied outside of this temperature range. In the case of the refractive index of whole egg, 0.0001 should be added (or subtracted) for each degree Centigrade above (or below) 25° C. (77° F.) in order to reduce the reading to the 25° C. (77° F.) basis. The corresponding correction for dry yolk refractive index is 0.0002.

While the number of cases studied is small, the application of the equations derived from them to 1932 spring eggs and yolks gave such satisfactory results that it was decided to publish the results herein given as a rapid method for the estimation of the total solids content.

Acknowledgments

The author is indebted to M. E. Pennington for the suggestion of this study, to A. W. Thomas, in whose laboratory the work was done, and to the Borden Company for its material coöperation.

Literature Cited

(1) Almquist, H. J., Lorenz, F. W., and Burmester, B. R., Ind. Eng. Chem., Anal. Ed., 4, 305 (1932).
(2) Assoc. Official Agr. Chem., Official and Tentative Methods, 3rd ed., p. 244 (1930).
(3) Holst, W. F., and Almquist, H. J., *Hilgardia*, **6**, 45 (1931).
(4) Pennington, M. E., *J. Biol. Chem.*, 7, 109 (1910).

Received August 13, 1935.

A Short Method for Calculating Delta *D* in a Crystal Growth Process

MOSES GORDON,[1] University of North Dakota, Grand Forks, N. D.

IN ORDER to predict the screen analysis of the product from the analysis of seed it is necessary to calculate ΔD, the increase in size of opening (mesh) through which a crystal will pass after the growing process is completed. McCabe (*2*, *3*) does this by integrating the following equation graphically:

$$W_p = \int_0^{W_s}\left(1 + \frac{\Delta D}{D_s}\right)^3 dW_s \qquad (1)$$

where

W_s and D_s give the screen analysis of the seed
W_p = weight of crystal product

Values are assumed for ΔD, a curve of $\left(1 + \frac{\Delta D}{D_s}\right)^3$ against W_s is plotted for each value of ΔD, and the area under each curve measured. The ΔD giving the proper value for W_p is then used in calculating the final screen analysis.

The purpose of this paper is to eliminate the cut-and-try graphical integration by substituting for it a rapid method of finding ΔD. The method will be illustrated by applying it to the example on the crystallization of potassium chloride worked out by McCabe (*1*).

The screen analysis of the seed (D_s and W_s) is given. Calculations made from solubility data show that 156 pounds of product will be obtained per 100 pounds of seed. From these data ΔD may be calculated as follows:

To integrate Equation 1 it is necessary to obtain an expression for D_s in terms of W_s. This is done by plotting D_s against W_s and drawing the best straight line through the points. (The straight line is an approximation, since the cumulative screen analysis plot will curve at either end, but the approximation is sufficiently accurate for practical purposes.) This will give

$$D_s = b + mW_s \qquad (2)$$

where b is the intercept on the D_s axis and m is the slope.

---

[1] Present address, University of Minnesota, Minneapolis, Minn.

For the data in the problem being considered the values of b and m are found to be 0.09 and -0.0006, respectively.

Substituting Equation 2 in 1 we obtain

$$W_p = \int_0^{W_s} \left(1 + \frac{\Delta D}{b + mW_s}\right)^3 dW_s$$

which expanded gives

$$W_p = \int_0^{W_s} \left(1 + \frac{3\,\Delta D}{b + mW_s} + \frac{3\,\overline{\Delta D}^2}{(b + mW_s)^2} + \frac{\overline{\Delta D}^3}{(b + mW_s)^3}\right) dW_s \tag{3}$$

As a first approximation the last two terms in parentheses are negligible. Equation 3 then becomes

$$W_p = \int_0^{W_s} \left(1 + \frac{3\,\Delta D_t}{b + mW_s}\right) dW_s$$

where ΔD_t is the tentative value of ΔD. This integrates to

$$W_p = \left[W_s + \frac{3\,\Delta D_t}{m} \log_e (b + mW_s)\right]_0^{W_s} \tag{4}$$

Solving Equation 4 for ΔD_t, changing to the common logarithms, and substituting for $b + mW_s$ the values D_{s_0} and D_{s_i}, where D_{s_0} = intercept of straight seed line at $W = 0$, and D_{s_i} = intercept of straight seed line at $W = W_s$ we obtain

$$\Delta D_t = \frac{(W_p - W_s)(m)}{6.9 \log_{10} D_{s_i}/D_{s_0}} \tag{5}$$

Substituting in Equation 5 the values for W_p, W_s, m, D_{s_0}, and D_{s_i}, we obtain

$$\Delta D_t = 0.0102$$

Since ΔD is so small, the term containing $\overline{\Delta D}^3$ may be neglected. The turn containing $\overline{\Delta D}^2$ may be considered to be only a correction factor which can be estimated by using $\Delta D = \Delta D_t$, thereby converting Equation 3 again into a linear rather than a quadratic or cubic equation. The integrated form of 3 becomes

$$W_p = \left[W_s + \frac{3\,\Delta D}{m} \log_e (b + mW_s) - \frac{3\,\overline{\Delta D}_t^2}{m(b + mW_s)}\right]_0^{W_s}$$

Solving for ΔD we obtain

$$\Delta D = \frac{m(W_p - W_s) + 3\,\overline{\Delta D}_t^2 \left(\frac{D_{s_0} - D_{s_i}}{D_{s_0} D_{s_i}}\right)}{6.9 \log_{10} \frac{D_{s_i}}{D_{s_0}}} \tag{6}$$

Substituting in Equation 6 the values for m, W_p, W_s, D_{s_0}, and D_{s_i} we obtain $\Delta D = 0.009$, which is the value found by McCabe (*1*).

The steps then are as follows:

1. Plot the screen analysis of the seed and draw the best straight line through the points. This gives $D_s = b + mW_s$. Values for D_{s_0}, D_{s_i}, and m are read from this curve.
2. Obtain ΔD_t, a tentative value for ΔD, from Equation 5.
3. From Equation 6 obtain the final value for ΔD.

Literature Cited

(1) Badger and McCabe, "Elements of Chemical Engineering," p. 409, New York, McGraw-Hill Book Co., 1931.
(2) McCabe, W. L., Ind. Eng. Chem., 21, 30 (1929).
(3) *Ibid.*, 21, 112 (1929).

Received June 1, 1935.

Spectrophotometric Determination of Copper in Ores and Mattes

J. P. MEHLIG, Oregon State College, Corvallis, Ore.

THE colorimetric method for the determination of copper based upon the formation of the blue copper-ammonia complex ion $[Cu(NH_3)_4]^{++}$ by the addition of an excess of ammonium hydroxide to a solution of cupric ions has been known and used for many years (*2*, *8*). While it has given satisfaction, it has the disadvantage of requiring the preparation of a series of standard solutions of copper for comparison and there is a question as to the permanency of these standards.

With the development of photoelectric colorimeters it is now possible to dispense with the use of standard solutions. About 2 years ago such an instrument called the photelometer was devised by Sanford, Sheard, and Osterberg (*7*) and recently similar instruments have been described by Eimer and Amend (*1*), by Yoe and Crumpler (*9*), by Zinzadze (*10*), and by Müller (*6*). In using them the intensity of light transmitted by a colored solution is correlated with the concentration of the constituent responsible for the color. It is necessary to use a suitable light filter in order to provide light of the proper wave length.

The spectrophotometric method for copper depends upon the fact that the percentage transmittancy of light of a given wave length for an ammoniacal copper solution is a function of the copper concentration. It is possible to construct a reference curve by plotting percentage transmittancy at a given wave length of a series of standard solutions of ammoniacal copper sulfate against the known copper concentrations and then by use of this curve to convert the percentage transmittancy of an unknown ammoniacal copper solution into concentration of copper. A similar procedure was followed by the writer in determining manganese in steel (*4*). Once constructed, such a curve may readily be used permanently, but the labor involved in its construction is an objection to it.

Since Beer's law has been shown (*6*, *9*) to hold for ammoniacal copper solutions up to concentrations of almost 1 gram of copper per liter, the concentration of copper in a given solution can be calculated from the fundamental Lambert-Beer equation

$$I = I_0 \times 10^{-elc}$$

in which I_0 represents the intensity of the incident light of given wave length which enters the solution, I the intensity remaining after its passage through the solution, l the length in centimeters of the solution, c the moles of absorbing substance per liter of solution, and e a constant which is a measure of the absorption due to a single molecule and is called the molecular extinction coefficient.

The above equation may also be written

$$\log \frac{I}{I_0} = -elc$$

or

$$\log \frac{I_0}{I} = elc$$

The ratio $\frac{I}{I_0}$ may be evaluated by dividing 100 by the percentage transmittancy of the solution as determined by a spectrophotometer. To establish the value of the constant e for a given wave length it is necessary to determine the percentage transmittancy of a solution of known copper concentration. Theoretically a single measurement would be sufficient, but practically it is far better to take the average of a series of careful measurements made on solutions of different concentrations of copper.

Determination of Molecular Extinction Coefficients

A series of copper solutions was made by accurately weighing from 0.1 to 0.2 gram of copper wire, the purity of which had been determined electrolytically, and dissolving each portion in 5 ml. of concentrated nitric acid. After the addition of 5 ml. of concentrated sulfuric acid, the solution was evaporated on a hot plate to dense white fumes, allowed to cool, and then was diluted with 25 ml. of water. When all the copper sulfate had been dissolved, 30 ml. of 15 *N* ammonium hydroxide were added and the deep blue solution was diluted with 3 *N* ammonium hydroxide to 500 ml. at 30° C. in a volumetric flask. Various aliquots of these solutions were in turn diluted with 3 *N* ammonium hydroxide to 100 ml. at 30° C.

All transmission measurements were made with the photoelectric spectrophotometer built for Purdue University by the General Electric Company. This is the same instrument that was used and described by Mellon and Kasline in their recent work on solutions of ferric chloride (*5*). Measurements were made by setting the wave-length scale, adjusting the three slits to give the desired width of spectral band at the given wave length, and reading the transmission on the photometer scale. Readings were taken at 570, 580, and 590 mμ and each one was checked within ±0.1 per cent. The photometer scale was checked before each series of measurements by means of Bureau of Standards glasses. All transmittancies were obtained by dividing the transmission for the solution by that for the solvent at the same wave length. The cell used had a length of 1.968 cm.

As Yoe and Crumpler (*9*) point out, ammonia solutions show an appreciable absorption in the visible region and it is therefore necessary to use in measuring the transmission of the solvent an ammonia solution of the same concentration as is present in the copper solution. This was done by adding dropwise to the copper solution in the cell after the transmission had been observed just enough 1 *M* solution of potassium cyanide to decolorize the solution.

The average values obtained for e are

570 mμ	49.76
580 mμ	52.99
590 mμ	55.55

Determination of Copper in Ores and Mattes

The method was tested by applying it to the determination of copper in ores and mattes in which the copper had previously been determined by the iodide method. After the copper had been put into solution and excess ammonium hydroxide had been added, the copper was separated from the silica and the hydroxides of iron and aluminum by filtration as was done by Heath (*2*) in his colorimetric determination.

Procedure. Accurately weigh from 0.2500 to 1 gram of sample, depending upon the copper content, and transfer to a casserole. Cover with a watch glass, add 10 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid, and warm on the hot plate until all action has ceased and solution has been effected. Let cool, slowly add 5 ml. of concentrated sulfuric acid, and carefully evaporate from the uncovered casserole, keeping in constant motion until dense white fumes are evolved. This fuming is most conveniently done by use of an electric evaporating cone placed directly above the casserole. In such case it is not necessary to keep the casserole in motion. Let cool, carefully add 25 ml. of water, and warm to dissolve the copper sulfate.

Add slowly to the cool solution 30 ml. of 15 *N* ammonium hydroxide, and filter into a 250-ml. volumetric flask. Wash the residue with 3 *N* ammonium hydroxide until the washings come through colorless. By means of a stream of water from the wash bottle rinse the residue back into the casserole, being careful not to damage the filter, and add just enough concentrated sulfuric acid to dissolve the iron and aluminum precipitate. Reprecipitate by adding 5 ml. of 15 *N* ammonium hydroxide, add torn up bits of filter paper to hasten filtration, and filter through the original paper, catching the filtrate in the volumetric flask. Transfer the precipitate to the filter and wash with 3 *N* ammonium hydroxide until the volume of the filtrate is almost 250 ml. Make up the filtrate to the mark with 3 *N* ammonium hydroxide at 30° C. and mix thoroughly.

By means of the spectrophotometer determine percentage transmission of this solution in a 2-cm. cell at 570, 580, and 590 mμ. Then to the solution in the cell add dropwise just enough 1 *M* potassium cyanide to remove the color and determine the percentage transmission of this solution at the above wave lengths. The former figure multiplied by 100 and divided by the latter gives the percentage transmittancy of the copper solution.

Using the value of e given above for the wave length in question, calculate the percentage of copper in each case and take the average as the percentage of copper in the sample.

Notes

1. Convenient weights of sample: for ores containing less than 5 per cent of copper, 1 gram; from 5 to 10 per cent of copper, 0.5 gram; more than 10 per cent of copper, 0.25 gram.
2. The method of double precipitation of the iron and aluminum is more accurate, more conveniently carried out, and much more rapid than the process of precipitating the copper by aluminum that is generally used in the iodide method.
3. According to Heath (*2*), results with samples containing from 25 to 35 per cent of iron and aluminum oxides showed never more than 0.04 per cent of copper in the residue on the paper after the second precipitation and sometimes no copper at all.
4. Fuming down with sulfuric acid removes any lead as lead sulfate.
5. If the type of spectrophotometer is used in which the light passes through separate cells of solution and solvent simultaneously, the solvent is prepared by adding to a second portion of the solution just enough potassium cyanide solution to remove all the blue color.
6. Nickel and cobalt must be absent, since both give soluble colored complex ions with excess ammonia.
7. Other wave lengths might be chosen, but the three selected consistently gave the best results.
8. The following example will illustrate the method of calculation. Weight of sample, 0.2517 gram; transmission of solution at 580 mμ, 52.1 per cent; transmission of solvent, 89.1 per cent; cell length, 1.968 cm. The Lambert-Beer formula solved for c gives

$$c = \frac{\log \frac{I_0}{I}}{el} \text{ moles per liter}$$

$$c = \frac{\log \frac{I_0}{I} \times 63.57}{el} \text{ gram of copper per liter}$$

or,

$$\text{Since } I = \frac{\text{Transmission of solution} \times 100}{\text{Transmission of solvent}} \text{ and } I_0 = 100$$

$$\log \frac{I_0}{I} = \log 100 - (\log \text{transmission of solution} + \log 100 - \log \text{transmission of solvent})$$

$$\log \frac{I_0}{I} = \text{log transmission of solvent} - \text{log transmission of solution}$$

$$\log \frac{I_0}{I} = \log 89.1 - \log 52.1$$

$$\log \frac{I_0}{I} = 1.9499 - 1.7168 = 0.2331$$

Therefore,

$$c = \frac{0.2331 \times 63.57}{52.99 \times 1.968} \text{ gram of copper per liter}$$

Since the solution of the sample was made up to 250 ml.

$$\text{per cent copper} = \frac{0.2331 \times 63.57 \times 100}{52.99 \times 1.968 \times 4 \times 0.2517} = 14.12$$

The calculation can be made very quickly.

Copper was determined in nine low-grade sulfide ores and two mattes by following the procedure as given above. The results are shown in Table I, which also includes as a check the figures obtained by using the iodide method as given by Mahin (*3*).

TABLE I. RESULTS OBTAINED BY SPECTROPHOTOMETRIC METHOD

Sample No.	Sample Nature	Copper by Iodide Method	Copper Obtained from Transmittancy at: 570 mμ	580 mμ	590 mμ	Average Copper Found	Difference
		%	%	%	%	%	%
1	Ore	7.27	7.33	7.27	7.24	7.28	+0.01
2	Ore	6.27	6.27	6.29	6.29	6.28	+0.01
3	Ore	5.37	5.37	5.42	5.43	5.41	+0.04
4	Ore	3.94	3.98	3.93	3.90	3.94	0.00
5	Ore	3.03	3.09	3.09	3.08	3.09	+0.06
6	Ore	8.56	8.55	8.52	8.44	8.50	−0.06
7	Ore	8.22	8.27	8.26	8.25	8.26	+0.04
8	Matte	14.09	14.16	14.12	14.07	14.12	+0.03
9	Ore	2.24	2.22	2.20	2.17	2.20	−0.04
10	Ore	4.34	4.30	4.29	4.27	4.29	−0.05
11	Matte	21.61	21.80	21.61	21.61	21.67	+0.06

The spectrophotometric method is capable of giving results for copper in ores and mattes which are within ±0.10 per cent of the values given by the iodide method and many are much closer than that. Results may be duplicated on the same sample with a precision of about ±0.05 per cent. The method, while applicable especially to low-grade copper ores, may be used for ores of high copper content by suitable dilution of the solution.

Summary

The spectrophotometric method for copper, which depends upon measuring by a spectrophotometer the transmittancy of light of a given wave length through an ammoniacal solution of copper, has these advantages over the regular colorimetric method: It does not require a series of color standards, eliminates entirely matching color shades by eye, and gives results which are more dependable.

Its advantage over the photoelectric colorimetric methods consists in not requiring the use of a light filter or color screen. It is much easier merely to set the wave-length scale of a spectrophotometer at the desired figure than it is to find a suitable light filter. The instrument, however, is an expensive one that is not universally available.

The spectrophotometric method gives just as good results for copper as the iodide method does and is more rapidly and more conveniently carried out.

Acknowledgments

The writer wishes to express his sincere appreciation to M. G. Mellon, Department of Chemistry, Purdue University, in whose laboratory this investigation was carried on, and to thank him for the use of the Purdue spectrophotometer and for his helpful criticism and suggestions. Thanks are also given to H. W. Swank, W. B. Fortune, and G. Dragt of Purdue for their aid in adjusting the spectrophotometer.

Literature Cited

(1) Eimer and Amend, "A. P. C. Photoelectric Meter," *Bull.* **103**, Eimer & Amend Co., New York.
(2) Heath, G. L., *J. Am. Chem. Soc.*, 19, 24 (1897).
(3) Mahin, E. G., "Quantitative Analysis," p. 257, New York, McGraw-Hill Book Co., 1932.
(4) Mehlig, J. P., IND. ENG. CHEM., Anal. Ed., 7, 27 (1935).
(5) Mellon, M. G., and Kasline, C. T., *Ibid.*, 7, 187 (1935).
(6) Müller, R. H., *Ibid.*, 7, 223 (1935).
(7) Sanford, A. H., Sheard, C., and Osterberg, A. E., *Am. J. Clin. Path.*, 3, No. 6, 405 (1933).
(8) Yoe, J. H., "Photochemical Analysis," Vol. I, p. 176, New York, John Wiley & Sons, 1928.
(9) Yoe, J. H., and Crumpler, T. B., IND. ENG. CHEM., Anal. Ed., 7, 281 (1935).
(10) Zinzadze, Ch., *Ibid.*, 7, 280 (1935).

RECEIVED August 27, 1935.

Differences in the Lactic Acid Percentages in Butters

E. O. WHITTIER AND C. S. TRIMBLE, Bureau of Dairy Industry, U. S. Department of Agriculture, Washington, D. C.

WHEN unsalted butter is purchased for use in ice-cream manufacture, it is highly desirable from the standpoint of keeping quality to know whether the butter was made from sweet or sour cream. In many instances, the score is sufficiently indicative, but inquiries addressed to this bureau indicate that a test that eliminates the personal factor is needed.

The most obvious possibility of distinction would seem to be in the proportions of lactic acid, both free and combined, present in the butters. For practical use for this purpose, the lactic acid determination should be rapid, the proportions of lactic acid should not change during storage of the butter, and, either the values obtained should be highly accurate, or, in case a high degree of accuracy is not obtainable, the values for sweet-cream and sour-cream butters should be considerably different.

Even in the simpler methods of determination of lactic acid given in the literature, it is recommended that protein and carbohydrates be removed in a preliminary treatment of the sample, since in the presence of these substances too high values are obtained. The methods of removal are tedious and the proportional errors in the determinations on the prepared samples may be from 3 to 15 per cent of the quantity of the lactic acid being determined. It was decided, therefore, to use samples without preliminary treatment, on the assumption that the error due to protein and carbohydrate would be a fairly constant one. It was hoped, furthermore, that the proportional error would be insignificant in comparison with the differences measured. The results fulfilled hopes in these two respects.

Method

The method of determination adopted is that of Friedemann, Cotonio, and Shaffer (*1*), which consists of oxidizing an acidified sample by means of an oxidation-reduction system composed essentially of divalent and quadrivalent manganese compounds. The oxidant is renewed by means of addition of potassium permanganate solution. Under these conditions, lactates and lactic acid are oxidized to acetaldehyde. The aldehyde is absorbed in sodium bisulfite solution and the quantity of bisulfite thus bound is determined by titration with standard iodine solution. When 0.01 *N* iodine solution is used for the titration, the butter sample should weigh 10, 20, or 30 grams, depending on the percentage of lactic acid present. The sample is weighed directly into the flask in which the oxidation is to take place and the oxidation is carried out without any preliminary treatment of the sample.

Determinations

Preliminary determinations were made on fourteen commercial samples of unknown history and two samples of known history. Nine of the samples gave percentages of apparent lactic acid ranging from 0.012, for a sample known to be sweet-cream butter, to 0.023; the other seven samples gave percentages from 0.117 to 0.217, a known "centralizer" butter giving 0.185. The remarkable feature is that there were no butters giving values between 0.025 and 0.100 per cent. It is of passing interest that the titratable acidity of the low lactate butters was of the order of 0.08 per cent, and that of the high lactate butters was of the order of 0.16 per cent, these consistencies indicating, apparently, that none of these butters was from partially neutralized cream.

Forty samples of butter were then prepared from two lots of cream, each lot being subdivided and given various treatments before and after churning. Typical analytical results on these butters are given in Table I. All samples of butter were washed and worked in the customary way, unless it is otherwise stated.

TABLE I. APPARENT LACTIC ACID IN BUTTERS OF KNOWN HISTORY

History	Apparent Lactic Acid
	%
0.15[a] per cent acid in cream, butter unwashed	0.025
Same, butter washed and worked	0.015
Whey butter	0.017
0.23 per cent acid in cream	0.024
Same, starter added to butter in churn	0.038
0.30 per cent acid, mixture of raw and pasteurized	0.023
Same, butter worked with limewater	0.021
Same, worked further with limewater	0.016
0.26 per cent acid, reduced to 0.18 per cent by water	0.013
0.35 per cent acid, reduced to 0.25 per cent by skim milk, butter unwashed	0.099
Same, butter washed	0.027
Same, butter washed with $NaHCO_3$ solution	0.018
0.38 per cent acid	0.142
0.40 per cent acid, reduced to 0.22 per cent by water	0.058
0.42 per cent acid, neutralized to 0.14 per cent, butter unwashed	0.085
Same, butter washed	0.055
Same, butter washed with $NaHCO_3$ solution	0.033
0.45 per cent acid, neutralized to 0.05 per cent by limewater	0.061
0.80 per cent acid, moldy, bitter; butter unwashed	0.245
Same, butter washed	0.262
Same, butter washed with $NaHCO_3$ solution	0.110
0.80 per cent acid, neutralized to alkaline side, unwashed	0.099
Same, butter washed	0.038

[a] These values are in all cases titratable acidities.

In Table II are results obtained from twenty samples of butter made commercially in the South in several different creameries. All except four of these samples were made from partially neutralized cream. The sweet-cream butters show consistently less than 0.025 per cent of apparent lactic acid; the partially neutralized samples, consistently more than 0.050 per cent.

TABLE II. APPARENT LACTIC ACID IN SAMPLES OF COMMERCIAL BUTTER

Sample	Titratable Acidity of Cream		Apparent Lactic Acid in Butter
	Before neutralization	When churned	
	%	%	%
1-R	0.55	0.28	0.063
2-R	0.80	0.15	0.051
3-R	0.60	0.25	0.059
4-R	0.70	0.24	0.075
5-R	0.80	0.22	0.071
1-N	0.65	0.25	0.068
2-N	0.60	0.23	0.067
3-N	0.65	0.24	0.084
4-N	0.82	0.24	0.074
5-N	0.73	0.23	0.061
1-K	0.78	0.23	0.057
2-K	0.56	0.25	0.062
3-K	0.72	0.28	0.057
35-B	0.16	0.16	0.023
37-B	0.14	0.14	0.011
38-B	0.14	0.14	0.020
39-B	0.16	0.16	0.021
40-M	0.84	0.27	0.082
41-M	0.84	0.27	0.081
43	1.30	0.24	0.127

TABLE III. EFFECT OF STORAGE AT 15° C. ON PERCENTAGE OF LACTIC ACID IN BUTTER

Date	Apparent Lactic Acid
	%
April 2, 1934	0.018
June 15, 1934	0.017
May 5, 1934	0.018
June 14, 1934	0.018
April 2, 1934	0.047
June 14, 1934	0.052
April 28, 1934	0.071
June 14, 1934(moldy)	0.066
March 26, 1934	0.217
June 15, 1934(moldy)	0.226

Table III gives results of determinations on five samples before and after storage at 15° C. (60° F.). The authors have also analyzed samples of butter that had been in commercial storage for as long as 9 months and found less than 0.025 per cent of apparent lactic acid, this showing that sweet-cream butter, even on long storage, does not develop lactic acid in appreciable quantity.

Conclusions

Detailed discussion of the results seems unnecessary. Study of the tables will bring out several points not mentioned here, but the most important conclusions appear to be as follows:

1. Butter made without the use of starters from normal cream containing less than 0.25 per cent of titratable acid will contain less than 0.025 per cent of apparent lactic acid.

2. Butter made without the use of neutralizing agents from normal sour cream containing more than 0.40 per cent of titratable acid will contain more than 0.100 per cent of apparent lactic acid.

3. Butter made from sour cream neutralized to approximately 0.20 per cent titratable acidity will contain more than 0.050 per cent of apparent lactic acid.

4. Dilution of the cream with water or sweet skim milk, or washing of the butter with alkaline water, will somewhat decrease the percentage of apparent lactic acid in the butter. Such procedures are, however, not likely to be encountered commercially, since they injure the flavor and texture of the butter.

5. Storage of butter even at temperatures considerably higher than those customarily used for butter storage has no effect on the percentage of apparent lactic acid present.

Literature Cited

(1) Friedemann, T. E., Cotonio, M., and Shaffer, P. A., *J. Biol. Chem.*, 73, 335 (1927).

RECEIVED August 16, 1935.

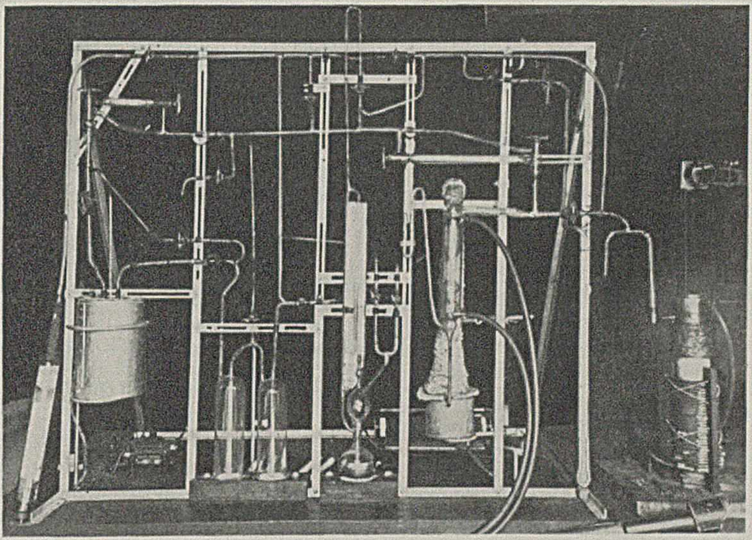


FIGURE 1. PHOTOGRAPH OF ASSEMBLED APPARATUS

Determination of Oxygen and Nitrogen in Steel

Improvements in the Vacuum-Fusion Method

JOHN CHIPMAN[1] AND M. G. FONTANA,[2] University of Michigan, Ann Arbor, Mich.

THE development of reliable methods for the determination of the gaseous elements in steel has done much to clarify our understanding of their occurrence and effects, and has played an important part in recent advances in steel-making practice based upon the control of ferrous oxide in the liquid steel. The vacuum-fusion or hot-extraction method, which was developed by Jordan (*6, 7, 15*) and his associates at the Bureau of Standards and by the late Professor Oberhoffer (*8, 9, 10, 14, 16*) and his students at Aachen, is to be regarded as the most dependable method for the determination of total oxygen and total nitrogen in ferrous metals. This paper describes the apparatus and technic employed in the Department of Engineering Research at the University of Michigan and introduces several changes which were designed to enhance the simplicity and speed of the determination, as well as to improve its accuracy for steels of low oxygen content.

Principle of the Method

At sufficiently high temperatures and low pressures all oxides are reduced by carbon, forming carbon monoxide. A graphite crucible is heated in vacuum to remove adsorbed gases. The steel sample is then melted in the crucible, its oxides are reduced to carbon monoxide, its nitrides and hydrides are decomposed, and any adsorbed or dissolved gases are liberated. The gases are pumped out continuously and are collected and analyzed. In order to effect the reduction of all the oxides that are found in steel, including alumina, it has been found necessary to employ temperatures above 1550° C. This is most easily accomplished by high-frequency induction heating, a method first applied by Jordan, by means of which the crucible may readily be heated to 1900° C. without endangering the silica furnace tube.

Limitation of Method and Sources of Error

The chief failing of the vacuum-fusion method is that as ordinarily employed it yields only total oxygen and total nitrogen and gives no information as to the form of combination of these elements in the sample. A fractional method has recently been suggested by Reeve (*11*) in which the gases evolved at four different temperatures are assumed to represent the four principal oxides in steels. While this modification has been very useful in the study of weld metal, it will doubtless require special development for each type of material to which it is applied.

The most important source of error is that due to the presence of metallic vapors in the furnace during the evolution of gases from the metal. These vapors condense as a metal film on the colder parts of the furnace and tend to reabsorb the gases. Manganese and aluminum are the two most volatile metals found in steels and both lead to "metal film" interference.

All the investigators of the method recognize this volatile metal interference, but there is some disagreement as to its seriousness. Von Seth (*12*), on one extreme, regards the manganese interference as an insuperable obstacle, whereas Bardenheuer (*1*) claims successful operation with manganese contents up to 1 per cent. Diergarten (*2, 3, 4*) states that the oxygen determination will be inaccurate if the material in the graphite crucible contains over 0.7 per cent manganese or 0.3 per cent aluminum. Vacher and Jordan (*15*) found that over 0.2 per cent manganese will interfere if several analyses are carried out successively in the same graphite crucible. The metal film error can be avoided by providing a high speed removal of the evolved gases, by avoiding the

---

[1] Present address, American Rolling Mill Co., Middletown, Ohio.

[2] Present address, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

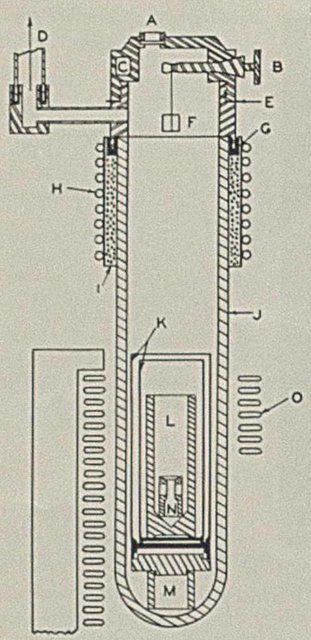


Figure 2. Section of Vacuum-Fusion Furnace

re-use of a crucible in which a sample containing high manganese or aluminum has been analyzed, and by cleaning the furnace tube after each such analysis.

There has been some uncertainty concerning the completeness of reduction of all the oxides present in the steel, especially the oxide of aluminum. There can be no doubt as to the complete reduction of the oxides of iron and manganese. Vacher and Jordan have shown that the silicates and silica as they ordinarily exist in steels are completely reduced. Attempts to show conclusively whether or not alumina is completely reduced have led to some contradictory reports. This uncertainty has been partially clarified by Ziegler's (*17*) work in which he showed that when powdered alumina is packed into a hole in a steel specimen it is not reduced in vacuum fusion even at 1700° C. On the other hand, when powdered graphite is mixed with the alumina and the mixture is analyzed in the same manner, the oxygen of the alumina is recovered. The effect of the graphite is merely to prevent lumping of the alumina. Further evidence that oxygen of the alumina in steel is determined by this method will be described in a later section of this paper.

Since it is virtually impossible to remove the last traces of gases from even the purest commercial graphite, it is necessary to apply a blank correction because of the continuous evolution of gas from the crucible. Obviously, the lower the gas content of the steel, the more important it is to reduce the blank correction to a minimum. Considerable work has been done in this laboratory on the deoxidation of steel and on the melting and refining of Chromel, an alloy of extremely low oxygen content. This necessitated the development of a technic by which the blank could be reduced to about one-fifth or one-tenth of its usual amount.

Description of Apparatus

Figure 1 is a photograph of the assembled apparatus showing, from right to left, the induction furnace in which the specimen is melted, the vacuum pump, McLeod gage, and analytical system.

Furnace. Figure 2 shows a section of the assembled furnace. The silica tube, *J*, is 30 cm. (12 inches) long by 6.8 cm. (2.625 inches) outside diameter. The graphite crucible, surrounded by the concentric radiation shields, *K*, is located at about the center of the field of the induction coil, *O*. The specimen, *F*, is suspended by fine nickel wire (36 B and S gage, 0.13 mm.) from the stainless steel windlass, *B*, which is ground into the brass head and lubricated by vacuum grease. The head is made of annealed, cold-rolled brass. Its upper portion is water-cooled and has a small Pyrex glass window, *A*, held down by a threaded brass ring and rubber washers. The two parts of the head are threaded together and made vacuum-tight by an ordinary mason jar ring, *E*. The lower part is cemented to the silica tube by picein wax held in the groove, *G*, which is formed by the outer brass ring and water cooled by the copper coil, *H*. The lower part of the head contains the outlet to the vacuum pump which is attached to the glass tubing, *D*, by an easily made picein seal. Duplicates of the lower part were made, so that each silica tube in use could be equipped with one, and the seal at *G* having once been made need never be broken. This simple and easily removable head construction permitted a quick exchange of tubes or crucibles and greatly facilitated the task of cleaning the tube.

A feature of the furnace which has been especially helpful in reducing the blank correction and increasing the operating temperature is the method of supporting the crucible and of protecting the outer tube from its intense radiation.

A photograph of the crucible, *L*, the two graphite shields, *K*, and the plug, *N*, is shown as Figure 3. These were all made from Acheson graphite. The shields were turned out from a solid 5-cm. (2-inch) electrode and have a wall thickness of 0.8 mm. (0.03 inch). The walls were slotted to prevent heating due to induced currents. The bottoms of the shields and crucible were recessed to diminish thermal contact with the base. The shoulders on the insides of the shields insured proper spacing.

The purpose of the shields is to protect the walls of the furnace from excessive heating by radiation. They not only accomplished this in excellent fashion, but also eliminated an important source of trouble that was encountered when refractory shields were used—namely, the evolution of gases that occurred when the hot crucible touched the refractory shield. The outer graphite shield stayed cold enough so that no appreciable disturbance appeared if the whole internal assembly tilted slightly and touched the silica walls of the furnace. The graphite shields also permitted rapid heating, and consequently rapid degassing, of the crucible because they were immune from cracking due to large temperature gradients, which was a very disturbing factor when porcelain or sillimanite protectors were used. These graphite shields, in addition to being fairly easy to make, possessed remarkable strength and failed only when subjected to severe mechanical shock. This shield arrangement made possible the heating of the crucible to 1900° C. without danger of the quartz tube crushing or becoming permeable.

The crucible was made by drilling a 22-mm. (0.875-inch) hole in a 32-mm. (1.25-inch) rod. The bottom was slotted to prevent overheating of the lower portion of the crucible. The purpose of the plug, *N*, is to prevent spattering of the molten metal during gas evolution. When the sample, resting on top of the plug after lowering, begins to melt, it slips down through the hole in the plug and is thus effectively covered before any appreciable amount of gas is given off. The bubbles of gas formed through reduction by the carbon are broken up and the loss due to spattering is minimized. The plug also increases the area of contact between carbon and molten metal, thus favoring more rapid reduction. The use of this arrangement was imperative in the analysis of metals of high gas content, wherein large globules of metal would have otherwise been completely ejected out of the crucible because of the violent ebullition of gas. On the other hand, it was found that when the sample contained large amounts of alumina the use of the plug was detrimental to its complete reduction. This point will be explained later.

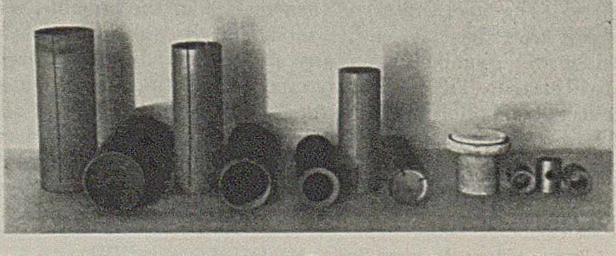


Figure 3. Photograph of Crucible, Graphite Shields, and Plug

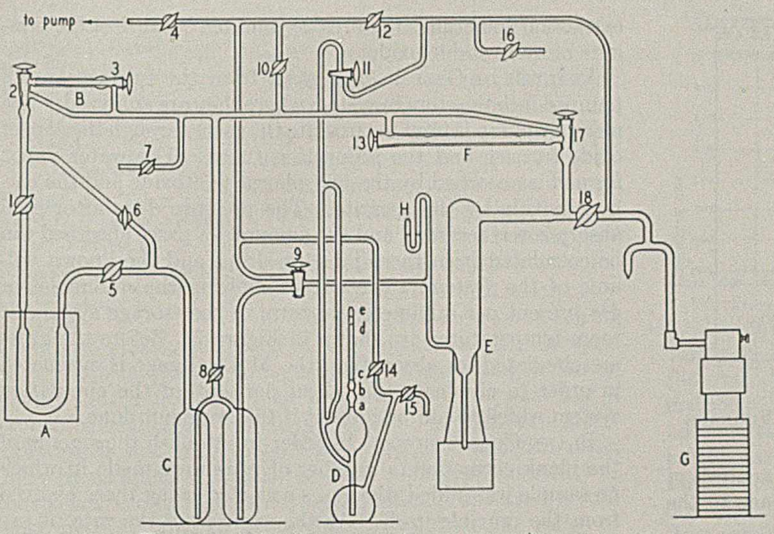


Figure 4. Diagram of Analytical Apparatus

The graphite assembly rests on a magnesia base and a magnesia ring, *M*, both made by tamping powdered fused magnesia into a graphite mold and firing by induction in the neighborhood of 2000° C. The reaction at the point of contact of the graphite shield and magnesia base is practically nil because of the small area in contact and the comparatively low temperature of the shield. This was an important factor in reducing the blank correction.

Analytical Train. The storage and analysis train are supported by a framework of 1.9-cm. (0.75-inch) angle iron resting on a heavy wooden base. Figure 4 is a sketch of the whole apparatus drawn approximately to scale.

The two-stage mercury diffusion pump, *E*, removes the gases evolved from the sample and stores them at low pressure in the reservoirs, *C*. After gas evolution has ceased, the same pump acts as a circulating mechanism to draw the gas through the copper oxide furnace, *A* (at about 340° C.) and through the absorption tubes, *B* and *F*. The tube to the left of stopcock 4 connects to a Cenco "hivac" or preferably the larger "megavac" oil pump. The mercury pump operates very efficiently against back pressures up to 12 mm.

The absorption tubes, *B* and *F*, are of an entirely new design. Previous experience with tubes which could be removed and weighed showed that the gravimetric determination was inferior in speed and accuracy to the volumetric. The removable feature was therefore eliminated, with the result of simplifying the construction and speeding up the circulation and absorption of gases. Tube *B* contains loosely packed phosphorus pentoxide, held in place by two wads of cotton, for removing water vapor from the system. This tube is efficient as long as there is any dry powder remaining in it.

Tube *F*, containing ascarite for absorbing carbon dioxide, is shown in better detail in Figure 5. The inner plug which forms the stopcock and holds the absorbing agent is easily removable and is made in duplicate so that the spent plug may be removed and a freshly loaded plug quickly inserted. The volume between the two constrictions is filled with ascarite, while that to the right of the right constriction is filled with phosphorus pentoxide, the two absorbents being held in position by wads of cotton. Before loading into the absorption tube, the ascarite is vacuum-desiccated over phosphorus pentoxide. One tube of ascarite is usually sufficient for about 15 analyses of steel of normal gas content.

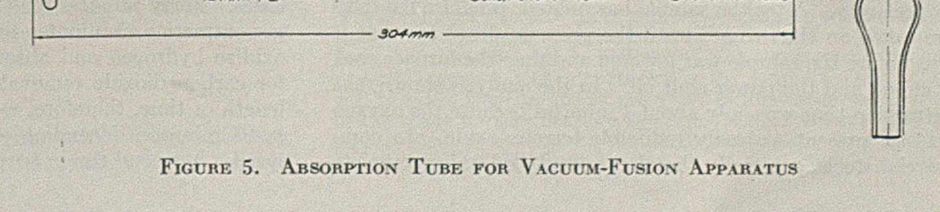


Figure 5. Absorption Tube for Vacuum-Fusion Apparatus

The McLeod gage, *D*, is a specially constructed multistage instrument carefully calibrated by mercury weighings. It is read by observing the height in the open arm when the mercury in the closed arm is brought to one of the designated points shown by letters in Figure 4. The factors by which the observed height must be divided to give the pressure are: *a*, 23.5; *b*, 120.2; *c*, 552; *d*, 2760; *e*, 5520.

Calibration. The storage system into which the gases are pumped during extraction consists of the exhaust side of the mercury pump, the two bulbs, *C*, the copper oxide furnace, the McLeod gage, and the connecting tubing. The volume of the storage system was determined with and without the absorption tubes open.

A known volume of purified nitrogen was admitted from a calibrated buret, which consisted of 8-mm. Pyrex tubing mounted on a meter stick and calibrated over its entire length by mercury weighings. The pressure before and after admission of the nitrogen was read with the McLeod gage. From these two pressures and the volume of gas admitted, the volume of the storage system was readily calculated. The total volume of the storage system, including the two absorption tubes, is 1810 cc. This was calculated to millimoles of gas per millimeter of pressure and expressed as a function of room temperature as in Figure 7.

Procedure

Preparation of Sample. The sample to be used for a determination should be as representative of the metal to be analyzed as possible. For example, a "pie slice" is usually taken from circular ingots or test bars. Whenever possible, a complete cross section is most desirable. The sample is first ground on an emery wheel to remove all surface scale, next pickled in alcohol and hydrochloric acid, and then washed first in alcohol and then in ether.

The weight of the sample should be chosen so as not to yield too much gas for the mercury pump to handle or too small an amount of gas to be accurately analyzed. In case considerably more gas is evolved than expected, some of the gas may be removed, after reading the total storage pressure, by the oil fore pump and only the remainder of it analyzed. This procedure prevents the too rapid exhaustion of the ascarite.

If the samples do not contain too much aluminum or manganese, two or three of them may be strung up in the furnace at the same time. When they are lowered, the first one in line drops off into the crucible when the nickel wire holding it melts and the others are then quickly raised and held in the upper part of the furnace until the first sample has been

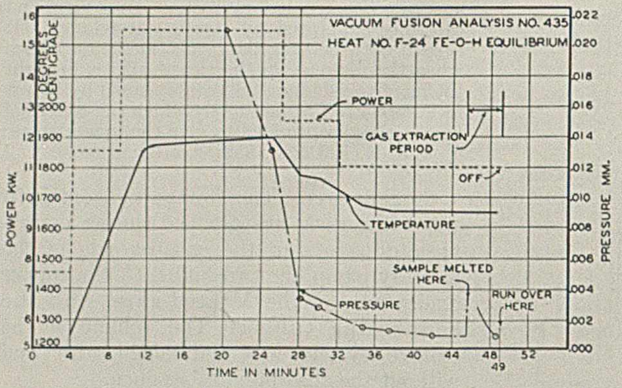


Figure 6. Performance Curves for Vacuum Furnace

completely analyzed. This procedure permits the analysis of two or three specimens without opening the furnace to the atmosphere.

Preparation of Analytical System. Except for the glass tubing between cock 9 and the mercury pump, all the storage system is thoroughly evacuated by the diffusion pump before any gases are pumped into it. The absorbents may be shaken up by turning the inner plugs of the absorption tubes (cocks 3 and 13). Air is occasionally admitted into the copper oxide furnace to oxidize any reduced copper that may be present. After air has been admitted into the storage system, the glass tubing is gently flamed under high vacuum with a Bunsen burner. The only important difficulty encountered in operating the analytical system has been in obtaining a satisfactory lubricant for the stopcocks. Formerly, it was possible to obtain a fairly good product by melting together the greases obtained from two supply houses. Unfortunately, one of these suppliers "improved" his product and now it is necessary to prepare one's own vacuum grease by the tedious method of Shepherd and Ledig (*13*).

Furnace Preparation. Figure 6 shows performance curves which give a graphic account of what occurs in the vacuum furnace from the time the power is turned on to the end of the gas extraction. In this particular analysis, a new graphite crucible was used and was degasified at a maximum temperature of 1900° C. and a converter setting of 15.5 kw. The preliminary heating time for any subsequent runs in a used crucible would be much shorter and at a converter setting of only about 12.5 kw. The first stages of the degasifying period are carried out under an oil pump vacuum. In the run illustrated, the diffusion pump was turned on to the furnace at the 18-minute mark or 2 minutes before the first pressure reading was taken. Prior to this the diffusion pump had been used to evacuate the storage system. The temperature is read by means of a disappearing filament-type optical pyrometer which is sighted through the prism shown in Figure 1. The pyrometer was calibrated using this prism and a similar sight glass.

Extraction of Gases. When the temperature of the crucible has been adjusted at about 1650° C., and after the pressure in the furnace has dropped to 0.001 mm. or less, the sample is lowered into the crucible and melted. The furnace pressures vary from e-2 to e-5 readings on the McLeod gage, which correspond to approximately 0.0004 to 0.0001 mm., respectively. After the sample has melted, pressure readings are taken on the furnace until the pressure drops to what it was before the sample was lowered and then the furnace cock is closed and the power shut off. In the analysis shown, the extraction time was only about 4 minutes because the oxygen was all present as easily reducible ferrous oxide. In commercial steels, especially the aluminum-killed ones, complete extraction sometimes requires 25 minutes because of the presence of more stable oxides.

Analysis of Gases. The gases from the furnace are all pumped into the storage system where they are analyzed. The mercury pump is used to circulate the gases through the copper oxide furnace and the absorption tubes. The water vapor formed is absorbed by the phosphorus pentoxide and the carbon dioxide by the ascarite. The pressure drop after each absorption is recorded and the amounts of gases absorbed can be calculated from these pressure drops and the known volume of the system. The curves showing the millimoles of gas present per millimeter pressure in the storage system at room temperatures are shown in Figure 7. Before the gases are circulated for absorption, the McLeod gage is evacuated in order to eliminate the "dead portion" of the circulation system which would be present if this were not done.

Blank Corrections. In order to establish the amount of the blank correction, a number of runs were made in which no sample was added, the gases collected being those evolved from the crucible itself. At the same time the rate of increase of base pressure in the storage system was determined at furnace pressures ranging from e-3 (0.0005 mm.) to e-8 (0.0015 mm.). In practice, the time used in computing the blank was the sum of the time that would have been required to accumulate the measured base pressure plus the elapsed time from measurement of base pressure to the end of the extraction. The time correction and the total blank are shown in Figures 8 and 9. It has been remarked elsewhere that a prerequisite of accuracy is a small blank. Virtually all the authors' runs have had a total blank correction of less than 0.01 millimole. The gases constituting the blank were found to analyze, on the average, 60 per cent carbon monoxide, 25 per cent hydrogen, and 15 per cent nitrogen.

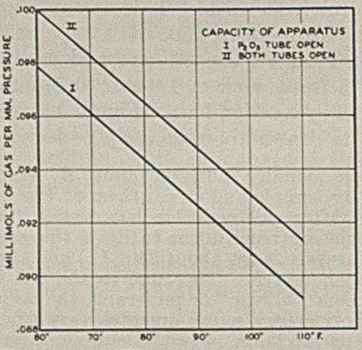


Figure 7. Volume of Apparatus Expressed in Millimoles per Millimeter

Discussion and Results

Speed, Precision, and Accuracy of Apparatus. The time required for a complete analysis by the vacuum-fusion method has been considerably shortened. A study of the performance curves in Figure 6 will indicate clearly the length of time required for the preparation of the furnace and the degasification of the sample. A new crucible was used in this run. The mean time required for the gas extraction is about 15 minutes, although 25 minutes has been required in some cases. Forty minutes for the bake-out, 5 to 15 minutes for gas extraction, 5 minutes to remove moisture, 10 minutes to oxidize hydrogen and absorb water vapor, and 15 minutes for carbon dioxide removal, represent good averages. The length of time, therefore, required for an analysis is from 75 to 85 minutes, depending on the type of steel or metal analyzed. A second run in a crucible requires a shorter bake-out

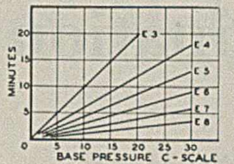


FIGURE 8. TIME CORRECTION FOR BASE PRESSURE

Time to be added to blank to compensate for base pressure in system.

period. Replacing the furnace is only a matter of minutes and the preparation of the next sample, or samples, can be accomplished during the absorption period. The storage system may be prepared during the time required to change furnaces and during that part of the bake-out period when the furnace is only under oil pump vacuum.

The precision and accuracy of the vacuum-fusion method have been greatly increased in this apparatus. For samples of not unusual gas contents, the oxygen and nitrogen can be readily determined with a precision of 0.001 per cent and a probable accuracy of ±0.002 per cent. The hydrogen determination is not very reliable and duplicate analyses often differ by as much as 0.0005 per cent. The reproducibility of the oxygen and nitrogen analyses by different operators is well illustrated in Table I. Note the two-hundred fold range of oxygen content covered with precision.

TABLE I. REPRODUCIBILITY OF ANALYSES

Sample	Date of Run	Sample	O	N	Operator
		Grams	%	%	
SMA-15	11-2-33	25.7	0.0011	0.0051	Fontana
SMA-15	12-5-33	48.0	0.0013	0.0052	Chipman
BS 7	8-19-34	9.3	0.110	0.0045	Fontana
BS 7	10-26-34	11.0	0.109	0.0044	Raynor
F 70	8-7-34	2.97	0.210	nil	Fontana
F 70	8-8-34	5.23	0.208	nil	Fontana

REDUCTION OF ALUMINA. In attempting to answer the question of the recovery of oxygen from the alumina in steel, it seemed best to employ steel samples containing large quantities of this oxide formed by reaction in the liquid steel. A method for determining oxygen in liquid steel was introduced by Herty (*5*) and has come into fairly general use. A spoonful of liquid steel is deoxidized by aluminum, cast into a mold, and analyzed for Al_2O_3 by solution of the metal in nitric acid. Samples secured by an improved form of this method from several heats of mild steel low in carbon, manganese, and impurities were analyzed for alumina and for oxygen. The results are given in Table II and show a recovery of 80 to 100 per cent of the oxygen by vacuum fusion. Duplicate samples are grouped together in brackets.

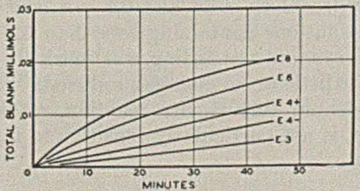


FIGURE 9. BLANK AS A FUNCTION OF TIME AND FURNACE PRESSURE

One cause of low results in these specimens was found in the tendency of the metal to melt away from the alumina leaving part of it as a dry powder adhering to the crucible wall. This error was increased by the presence of the plug in the crucible and was minimized by lowering the specimen into the molten residue from a previous analysis. Since the alumina content of any ordinary steel is of a lower order of magnitude than that of these specimens, it is altogether unlikely that incomplete reduction of alumina would ever constitute a serious source of error.

Summary

Improvements in technic and changes in construction have resulted in a vacuum-fusion apparatus that yields reliable results for the determination of oxygen and nitrogen in metals, chiefly in iron and steel. Except for very special cases, all the obstacles in the path of the successful operation of the method have been overcome. The accuracy of the method has been increased and the length of time required for a determination has been considerably shortened. It has been shown that the oxygen content of alumina formed in the deoxidation of liquid steel by aluminum is recovered by this method. Over six hundred successful vacuum-fusion analyses on a wide variety of steels, cast irons, and nonferrous materials have been completed in this laboratory.

TABLE II. ANALYSES OF ALUMINUM-KILLED SPECIMENS

No.	Oxygen by Al_2O_3	Oxygen Vacuum-Fusion
{1	0.057	0.052
{2	0.058	0.050
{3	0.066	0.056
{4	0.068	0.060
5	0.059	0.050 0.059
6	0.050	0.039 0.042
{7	0.049	0.042
{8	0.040	0.045

Acknowledgments

The writers gratefully acknowledge their indebtedness to D. W. Murphy for aid in setting up and standardizing the apparatus; to H. Hamner of the Union Carbide and Carbon Research Laboratories for suggesting graphite shields; and to C. W. Raynor for a number of analyses, including those on the aluminum-killed samples. The difficult glass parts were made by G. Kessler. Thanks are also extended to F. G. Norris and O. B. Ellis of the American Rolling Mill Company for sampling and analysis of the aluminum-killed samples.

Literature Cited

(1) Bardenheuer and Schneider, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, 13, 215 (1931).
(2) Diergarten, H., *Arch. Eisenhüttenw.*, 3, 557 (1930).
(3) Diergarten and Piwowarsky, *Ibid.*, 3, 627 (1930).
(4) Eilender and Diergarten, *Ibid.*, 4, 587 (1931).
(5) Herty, Gaines, Freeman, and Lightner, *Trans. Am. Inst. Mining Met. Engrs.*, Iron and Steel Div., p. 28 (1930).
(6) Jordan and Eckman, *Bur. Standards Sci. Paper* 514 (1925).
(7) *Ibid.*, 563 (1927).
(8) Oberhoffer, P., *Stahl u. Eisen*, 46, 1045 (1926).
(9) Oberhoffer and Hessenbruch, *Rev. Mét.*, 26, 93 (1929).
(10) Oberhoffer, Pfeiffer, and Schiessl, *Stahl u. Eisen*, 44, 113 (1924).
(11) Reeve, *Trans. Am. Inst. Mining Met. Engrs.*, 113, 82 (1934).
(12) Seth, R. von, *Jernkontorets Ann.*, 112, 113 (1928).
(13) Shepherd and Ledig, IND. ENG. CHEM., 19, 1059 (1927).
(14) Strauch and Oberhoffer, *Stahl u. Eisen*, 45, 1559 (1925).
(15) Vacher and Jordan, *Bur. Standards J. Research*, 7, 375 (1931).
(16) Washmut and Oberhoffer, *Arch. Eisenhüttenw.*, 2, 829 (1929).
(17) Ziegler, *Trans. Electrochem. Soc.*, 62, 109 (1932).

RECEIVED July 11, 1935

A. S. T. M. Activities in Ferrous Metals

The Steel Committee has under way the development of new specifications and revisions in some existing standards. Requirements for fabricated reinforcement material, wire mesh, wire mats, etc., are being developed and separate specifications for steel castings for marine use are under consideration. The committee has decided to standardize requirements for 4 to 6 per cent chromium steel still tubes and heat-exchanger and condenser tubes. In the high-temperature field a draft of requirements for nut material for use in bolting for high-temperature or high-pressure service has been circulated in the committee and action will be taken thereon during the year. Progress has been made in the study on specifications for high-strength structural rivets and revisions in the existing standard specifications for structural nickel steel (A8–29) are under way.

Colorimetric Determination

LOREN C. HURD AND HARRY O. ALLEN
University of Wisconsin, Madison, Wis.

IT HAS long been known and appreciated that the thiocyanate–stannous chloride method for molybdenum yields concordant results only when standard and sample are treated in exactly the same manner. The similarity of the reaction to the Geilmann reaction of rhenium and the profound effect which slight changes in concentrations of reagents have upon the rhenium color (*1*) led the authors to believe that a study of the actual effect of the variables involved might yield results of value to the analyst.

The Eastman universal colorimeter (*3*, *4*) was used to follow all color changes. As in the case of rhenium, it was found that the color could be duplicated in the field by means of the blue wedge, provided slight corrections were made with the other wedges.

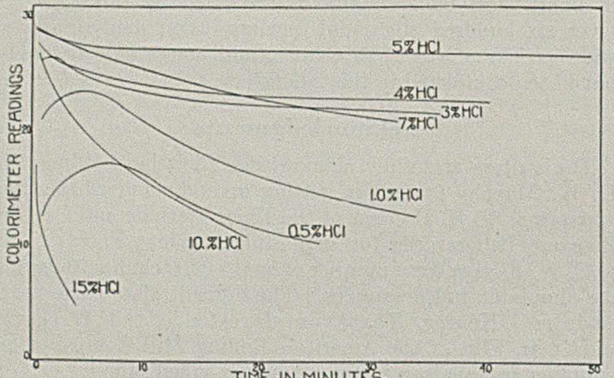


Figure 1

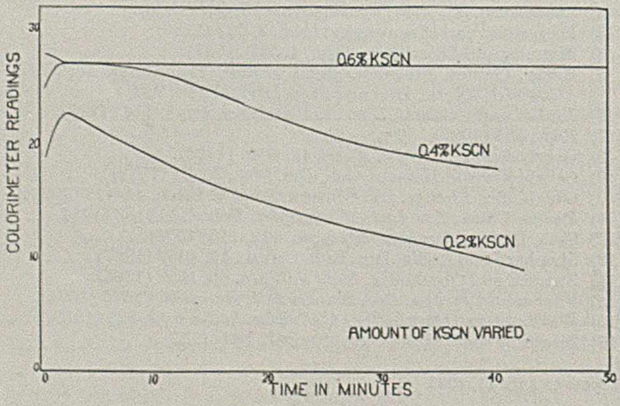


Figure 2

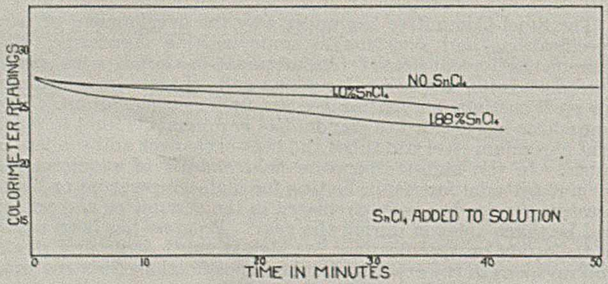


Figure 3

A stannous chloride solution was prepared from reagent quality salt, standardized, and adjusted so that it contained 2.0 per cent of $SnCl_2$. The hydrochloric acid content of the solution was 2.3 per cent. A 10.0 per cent potassium thiocyanate solution was prepared from the recrystallized salt. The hydrochloric acid solution was prepared by diluting constant-boiling acid with water. Pure molybdic acid was converted to the sodium salt with a minimum amount of sodium hydroxide and dissolved in water to yield a solution containing 10γ per ml. The method followed was first to add to the colorimeter tube the desired amount of molybdenum and then follow this with a mixture of hydrochloric acid, stannous chloride, potassium thiocyanate, and water. The final volume in every case was 50 ml. The time at which the reagents were added to the molybdenum was taken as zero. Colorimeter recordings were made at intervals, the magnitude of which was determined by the rate of color change.

Figure 1 illustrates the effect of various hydrochloric acid concentrations upon the color developed in a solution containing 100γ of molybdenum, 1.0 per cent of potassium thiocyanate, and 0.80 per cent of stannous chloride. When the hydrochloric acid concentration was low—i. e., 0.5 per cent—the color reached a maximum at the end of 8 minutes and faded to less than its initial value at the end of 25 minutes. As the concentration increased, the maximum shifted toward zero time and less fading was evident until a concentration of 5 per cent was exceeded. In higher concentrations of acid the fading was marked.

The effect of varying the potassium thiocyanate concentration is shown in Figure 2. The colors were developed in 5.0 per cent of hydrochloric acid and 0.8 per cent of stannous chloride. In solutions containing less than 0.6 per cent of potassium thiocyanate the fading was marked. Above this value there was little or no change produced.

The molybdenum thiocyanate reaction, unlike the Geilmann reaction, is not particularly sensitive to fluctuations in

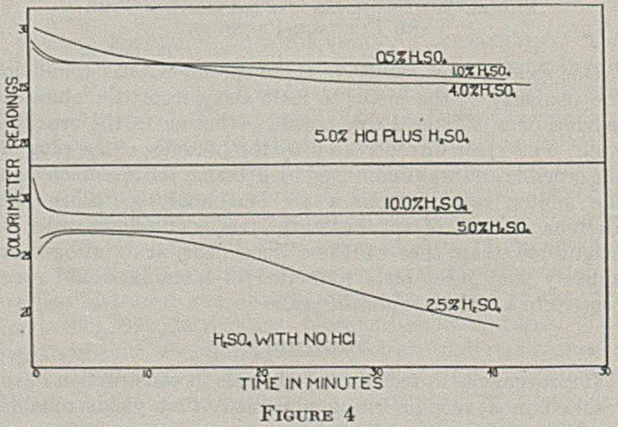


Figure 4

# of Molybdenum

A Study of Variables Involved

stannous chloride concentration. With 100γ of molybdenum it was found that a 0.04 per cent concentration produced a color concentration equal to that of a twenty-fold excess. No great differences were detected in either the speed of development or the rate of fading. In actual practice the determination is usually carried out in the presence of large amounts of ferric iron, which is reduced by the stannous ion with the production of stannic chloride. The effect of stannic chloride, as is to be seen in Figure 3, was to promote a slight fading of the color. After the first few minutes the effect was not marked even in concentrations as high as 1.88 per cent. Sulfuric acid in low amounts caused a rapid initial decrease, whereas higher concentrations contributed to fading (Figure 4). In the absence of hydrochloric acid (except for 0.46 per cent added with the stannous chloride) maximum color was not reached below 10 per cent of sulfuric acid and at this concentration initial fading was rapid. In 5 per cent solution the color was unusually stable.

Nonaqueous Extractors

The effect of saturating petroleum ether–ethyl ether (*5*) mixtures by shaking the solvent with the reagents before extraction is shown in Figure 5. The curves were constructed from observations made upon 35 per cent petroleum–65 per cent ethyl ether solutions containing 100γ of molybdenum. The initial intensities were about the same and both passed through minima at the end of 1 hour, after which the change was too gradual to be of great consequence.

Cyclohexanol (*2*) when saturated with the reagents exhibited practically no fading over a period of a few hours (Figure 6), but on long standing the color slowly became deeper (Figure 7). It is interesting to note that the color produced by a given amount of molybdenum is more intense when dissolved in cyclohexanol than in ether. Cyclohexanol is, however, difficult to handle, separates slowly from aqueous solutions, and sometimes develops a turbidity.

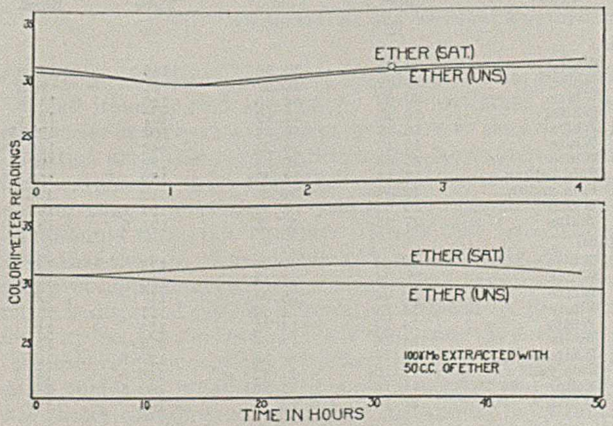


Figure 5

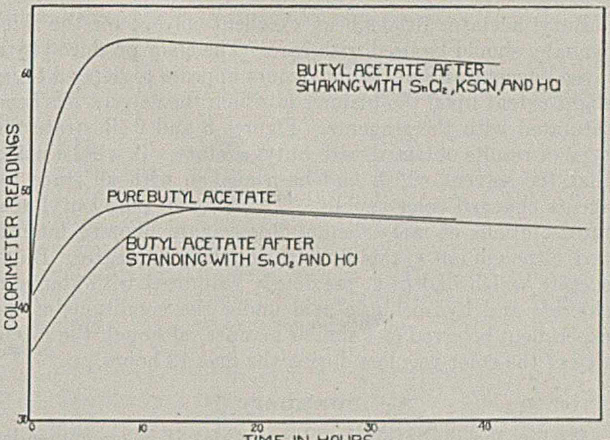


Figure 9

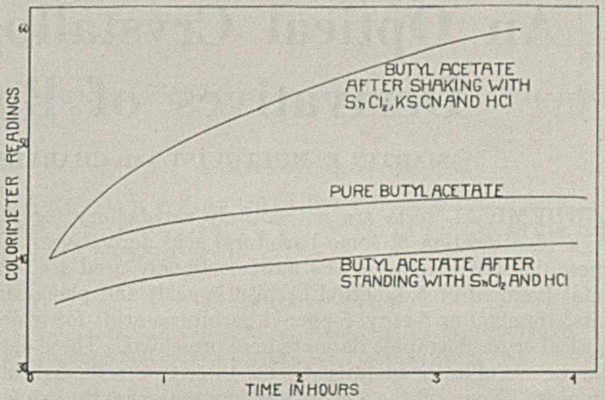


Figure 8

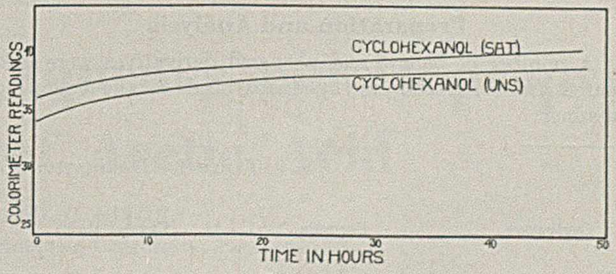


Figure 7

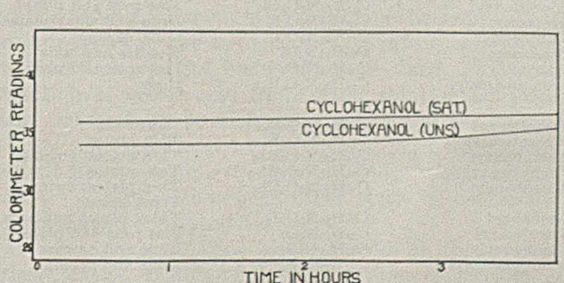


Figure 6

Butyl acetate, although an excellent solvent for the thiocyanate, should be used with care. The color produced by a given concentration of molybdenum appears to depend to no slight extent upon the manner in which the solvent has been saturated with the reagents. Figures 8 and 9 illustrate the type of results obtained with butyl acetate. It will be noted that the solvent which had been shaken with all three reagents changed color rapidly. The color of pure butyl acetate solutions of molybdenum thiocyanate likewise intensified, although not so rapidly or to so marked a degree. Butyl acetate which had been previously saturated with stannous chloride and hydrochloric acid under the conditions of the experiment behaved in a similar manner, although the intensity of the color was less during the first 12 hours.

Summary

Within the limits of the observations it is recommended that in the determination of molybdenum the concentration of hydrochloric acid be held at 5.0 per cent, potassium thiocyanate at 0.6 per cent, and stannous chloride above 0.1 per cent. Under some conditions sulfuric acid exerts an appreciable influence upon the color formation. Extraction of the complex should be made 5 minutes after adding the reagents. The behavior of the thiocyanate in ether, cyclohexanol, and butyl acetate has been studied. Anomalous color effects obtained with butyl acetate indicated that in general it was not as satisfactory an extractor for molybdenum as ether or cyclohexanol.

Literature Cited

(1) Hurd and Babler, unpublished paper.
(2) Hurd and Reynolds, Ind. Eng. Chem., Anal. Ed., 6, 477 (1934).
(3) Jones, *Am. Dyestuff Reptr.*, 13, 121 (1924).
(4) Jones, *J. Optical Soc. Am.*, 4, 421 (1920).
(5) Malowan, *Z. anorg. Chem.*, 108, 73 (1919).

Received August 15, 1935. From the senior thesis of Harry O. Allen, University of Wisconsin, 1935.

An Optical Crystallographic Study of Some Derivatives of Barbital and Luminal

MARTIN E. HULTQUIST AND CHARLES F. POE, University of Colorado, Boulder, Colo.

CHEMICAL tests are not entirely satisfactory for the identification of some barbituric acid derivatives. Of these derivatives, two of the most commonly used are barbital (veronal or 5,5-diethyl barbituric acid) and phenobarbital (luminal or 5-ethyl-5-phenyl barbituric acid) for which optical crystallographic data are here presented. These data can be useful in the identification of these two medicinal substances. None of the derivatives presented in this paper, however, have been reported in the literature with the exception of the *p*-nitrobenzyl compounds, which have been prepared by Lyons and Dox (*3*), Hargreaves and Nixon (*1*), and Jesperson and Larsen (*2*).

Preparation and Analysis

A number of benzyl and phenacyl derivatives were prepared from barbital and phenobarbital in the following manner:

Equivalent amounts of the barbituric acid and potassium or sodium carbonate were dissolved in a little more than enough boiling water to make a saturated solution. This solution was added to a solution of the benzyl or phenacyl halide (two molecular quantities) dissolved in an amount of alcohol twice as large as the amount of water used to dissolve the barbituric acid salt. The resulting mixture was refluxed until the reaction was completed.

The *o*-chlorobenzyl and the phenacyl derivatives of phenobarbital were prepared, but were obtained in the form of oily liquids which could not be made to crystallize. The *p*-chlorobenzyl derivative of phenobarbital occurs in two forms, depending on the method used for purification. If crystallization is caused to take place from a hot saturated solution, form A (Tables I and II) is obtained; but if the crystallization takes place slowly from a less saturated solution, we obtain form B.

Each new compound was analyzed for halogens or nitrogen. The melting points were run by both the tube method and the "Bloc Maquenne" method. Water of crystallization was not present in any of the compounds prepared.

Table I. Derivatives of Barbital and Phenobarbital

Derivative	Formula	Crystal Habit	Color	Halogen Calcd.	Halogen Found[a]	Melting Point Uncorrected Tube	Melting Point Uncorrected Block
				%	%		
			Barbital				
o-Bromobenzyl	$C_{22}H_{22}N_2O_3Br_2$	Thick rods	White	30.62	30.50	140	141
m-Bromobenzyl	$C_{22}H_{22}N_2O_3Br_2$	Thin plates	White	30.62	30.57	91	90
p-Bromobenzyl	$C_{22}H_{22}N_2O_3Br_2$	Flat rods and plates	White	30.62	30.65	146	147
o-Chlorobenzyl	$C_{22}H_{22}N_2O_3Cl_2$	Long rods	White	16.37	16.49	127	125
m-Chlorobenzyl	$C_{22}H_{22}N_2O_3Cl_2$	Thin plates	White	16.37	16.34	102	100.5
p-Chlorobenzyl	$C_{22}H_{22}N_2O_3Cl_2$	Flat rods and plates	White	16.37	16.32	142	144
p-Iodobenzyl	$C_{22}H_{22}N_2O_3I_2$	Rods and thick plates	White	40.55	40.48	122	123
m-Nitrobenzyl	$C_{22}H_{22}N_4O_7$	Long needles	Pale yellow	12.34[b]	12.27[b]	159	160
p-Nitrobenzyl	$C_{22}H_{22}N_4O_7$	Needles and rods	Pale yellow	12.34[b]	12.29[b]	192	193
Phenacyl	$C_{24}H_{24}N_2O_5$	Flat rods and plates	White	6.67[b]	6.72[b]	191	192
p-Bromophenacyl	$C_{24}H_{22}N_2O_5Br_2$	Rods	White	27.65	27.55	191.5	193
			Phenobarbital				
o-Bromobenzyl	$C_{26}H_{22}N_2O_3Br_2$	Short rods	White	28.04	27.98	116	113
m-Bromobenzyl	$C_{26}H_{22}N_2O_3Br_2$	Thin plates	White	28.04	28.14	130	130
p-Bromobenzyl	$C_{26}H_{22}N_2O_3Br_2$	Thin plates, twinned	White	28.04	28.05	117	118
m-Chlorobenzyl	$C_{26}H_{22}N_2O_3Cl_2$	Thin plates	White	14.74	14.90	111	111
p-Chlorobenzyl	$C_{26}H_{22}N_2O_3Cl_2$ A	Thin plates, twinned	White	14.74	14.63	111	111
	B	Thick plates	White	14.74	14.64	113	114
p-Iodobenzyl	$C_{26}H_{22}N_2O_3I_2$	Thick plates and rods	White	37.77	37.90	127–8	127
m-Nitrobenzyl	$C_{26}H_{22}N_4O_7$	Flat rods and plates	Pale yellow	11.16[b]	11.17[b]	149.5	151
p-Nitrobenzyl	$C_{26}H_{22}N_4O_7$	Rods and needles	Yellow	11.16[b]	11.20[b]	182.5	184
p-Bromophenacyl	$C_{28}H_{22}N_2O_5Br_2$	Rods and needles	White	25.53	25.65	164	167

[a] Average of two determinations.
[b] Per cent nitrogen.

Table II. Optical Crystallographic Data for Derivatives of Barbital and Phenobarbital

(All monoclinic)

Derivative	Optical Characteristic (Sign)	Sign of Elongation	Refractive Indices at 25° Alpha	Beta	Gamma	Rhombic Dispersions	Extinction Angle, Degrees
			Barbital				
o-Bromobenzyl	−	+	1.556	1.640	1.663	None	16
m-Bromobenzyl	−	+	1.577	1.679	1.693	None	30
p-Bromobenzyl	+	−	1.556	1.577	1.698	None	4
o-Chlorobenzyl	−	+	1.548	1.649	1.696	None	20
m-Chlorobenzyl	−	+	1.538	1.640	1.690	None	23
p-Chlorobenzyl	+	−	1.545	1.563	1.664	None	33
p-Iodobenzyl	+	−	1.531	1.642	$>\mathrm{CH_2I_2}$	None	34
m-Nitrobenzyl	−	−	1.487	1.626	1.715	Strong $\nu > \rho$	7
p-Nitrobenzyl	±	+	1.510	1.606	1.706	Strong	14
Phenacyl	−	+	1.587	1.626	1.634	Moderate $\rho > \nu$	42
p-Bromophenacyl	−	+	1.599	1.642	1.649	None	32
			Phenobarbital				
o-Bromobenzyl	+	±	1.605	1.620	1.720	Moderate $\nu > \rho$	36
m-Bromobenzyl	−	−	1.599	1.668	1.698	None	7
p-Bromobenzyl	[a]	+	1.563	[a]	$>\mathrm{CH_2I_2}$	[a]	9
m-Chlorobenzyl	−	−	1.580	1.660	1.681	None	5
p-Chlorobenzyl A	[a]	+	[a]	1.568	$=\mathrm{CH_2I_2}$	[a]	8
B	+	±	1.585	1.593	1.730	None	15
p-Iodobenzyl	−	±	1.580	1.730	$>\mathrm{CH_2I_2}$	Moderate $\nu > \rho$	34
m-Nitrobenzyl	−	+	1.538	1.652	1.715	Moderate $\nu > \rho$	25
p-Nitrobenzyl	−	+	1.534	1.666	$=\mathrm{CH_2I_2}$	Strong $\nu > \rho$	17
p-Bromophenacyl	+	−	1.599	1.656	1.703	Strong $\nu > \rho$	36

[a] Since no optic axis interference figure could be seen, these values could not be determined.

Eleven derivatives of barbital and nine derivatives of phenobarbital were prepared, purified, and analyzed. The results are presented in Table I.

Optical Crystallographic Data. The optical properties of each compound listed in Table I were determined by methods used in a similar study for compounds of strychnine (*4*) and cinchonine (*5*), and are presented in Table II. The optical properties of the derivatives of barbital differ sufficiently from those of phenobarbital to allow the use of the optical data in the identification of the original barbituric acid.

Summary

Ten new derivatives of barbital and eight new derivatives of phenobarbital have been prepared and described. The optical crystallographic data for twenty benzyl and phenacyl compounds of barbital and phenobarbital have been determined.

Acknowledgment

The authors wish to thank the Winthrop Chemical Company, Inc., New York, N. Y., for kindly furnishing the barbital and phenobarbital.

Literature Cited

(1) Hargreaves and Nixon, *J. Am. Pharm. Assoc.*, 22, 1250 (1933).
(2) Jesperson and Larsen, *Dansk. Tids. Farm.*, 8, 212 (1934).
(3) Lyons and Dox, *J. Am. Chem. Soc.*, 51, 288 (1929).
(4) Poe and Sellers, *Ibid.*, 54, 249 (1932).
(5) Poe and Swisher, *Ibid.*, 57, 748 (1935).

Received July 8, 1935.

Surface Tension between Aqueous and Isopropyl Ether Solutions of Acetic Acid

F. M. BROWNING and J. C. ELGIN
Department of Chemical Engineering, Princeton University, Princeton, N. J.

THE factors determining the rate of extraction of acetic acid from aqueous solution by isopropyl ether and the efficiencies of types of equipment applicable to the extraction operation are under investigation in this laboratory. These form one phase of an investigative program directed toward the development of methods and data for the rational design of liquid-liquid extraction systems. Results thus far obtained show that the rate of extraction and, consequently, the efficiency of liquid-liquid contact equipment in which one solvent phase is dispersed may be primarily influenced by the interfacial surface tension between the two solvents. It is apparent that this result is logically explained by the fact that for a given volume of liquid the degree of dispersion and droplet size (hence contact area) are determined primarily by interfacial surface tension. Since the concentration of the soluble component distributing itself between two immiscible solvents in contact may exert a very considerable influence on their interfacial surface tension, the extent or efficiency of extraction in a given equipment is a function of the respective solute concentrations in the two phases, operating conditions and concentration gradient being otherwise fixed. Thus, in the extraction of acetic acid from water solution by isopropyl ether, the capacity coefficients in a tower of the spray type and the plate efficiencies of a bubble plate column are dependent upon the respective acid concentration of the two phases. A similar result for other types of contacting devices is also to be expected.

To permit a correlation of the results on this system the surface tension of different concentrations of aqueous acetic acid against isopropyl ether of varying acetic acid concentra-

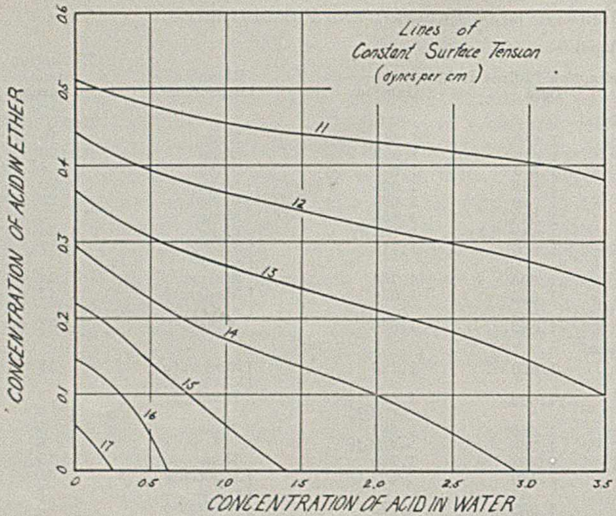


Figure 1. Surface Tension between Water and Isopropyl Ether Phases Containing Acetic Acid

Concentrations in gram molecules per liter.

tion has been measured. Inasmuch as this system is the basis of an industrial process for the recovery of acetic acid and no previous data on its surface tension appear to be available, it was thought that the present measurements would be of industrial as well as scientific interest.

Experimental Method

The "drop weight" method of determining surface tension was employed. The procedure followed was based on suggestions advanced by Harkins and Brown (*2*). This method combines simplicity (*1*) with a degree of accuracy commensurate with that to be expected from any usual applications of the results.

The apparatus consisted of a 5-cc. buret attached through a suitable stopcock to a 10-cm. length of 7-mm. capillary tubing. The tip of this was carefully ground, and its diameter accurately determined to be 0.377 mm. The denser phase was placed in the buret and permitted to drop through the less dense at the rate of approximately one drop every 3 minutes. From accurate measurements of the volume of the drops, the densities, and the size of the tip surface tensions were calculated from the usual relation as given in the International Critical Tables.

The accuracy yielded by the apparatus as constructed was checked by comparing values of the surface tensions of water, benzene, and benzene-water obtained with it with the corresponding values reported in the literature. That substantial agreement was obtained may be seen from Table I.

Table I. Surface Tension Comparison

(Temperature 20° C.)

System	Drop Volume	Density	Surface Tension Observed	Surface Tension Accepted value (*3*)
	Cc.	*G./cc.*	*Dynes/cm.*	*Dynes/cm.*
Water-air	0.1070	0.9972	73.46	72.75
Benzene-air	0.0485	0.8746	28.49	28.80
Benzene-water	0.4500	H_2O-0.9968 C_6H_6-0.8738	34.50	35.00

In making the measurements presented herein aqueous acetic acid of different concentrations was placed in the buret and drops were permitted to form in isopropyl ether solutions of various concentrations. Purified isopropyl ether from the Eastman Kodak Company, distilled water, and U. S. P. acetic acid were employed. Each phase was mutually saturated with the other by agitation for a prolonged period in a thermostat at 20° C. before making measurements. The solutions were removed from the thermostat into a room at approximately 20° C. immediately prior to each determination.

With solutions of different concentrations the drop weight method is superior to the ring method. The latter requires a large surface and consequently allows variation in the respective solution concentrations during measurement due to diffusion across the interface. Use of the drop weight method greatly reduces this effect. Reproducible results were readily obtained by permitting fresh drops to form continuously in a large volume of solution.

Results

The surface tension results obtained are recorded in Table II. Corresponding densities of the aqueous and isopropyl ether solutions of acetic acid employed, each solvent mutually saturated by the other, were also determined since their knowledge was necessary for the calculation of surface tension values. (As reported by the Carbide and Carbon Chemicals Corporation commercial isopropyl ether at 25° C. is soluble in water to the extent 0.65 per cent by volume, water being soluble in the ether to the extent of 0.025 per cent by volume. Pure isopropyl ether is undoubtedly considerably less soluble.) Inasmuch as no previous data on these have been reported the authors' values are also included in the table.

Table II. Values of Surface Tension between Aqueous and Isopropyl Ether Solutions of Acetic Acid at 20° C.

Ether Concentration	Water Concentration	Density Ether	Density Water	Drop Volume	Surface Tension
G. moles/l.	*G. moles/l.*	*G./cc.*	*G./cc.*	*Cc.*	*Dynes/cm.*
0.0044	0.0001	0.7246	0.9951	0.0940	17.56
0.0583	0.0001	0.7262	0.9951	0.0914	17.08
0.1718	0.0001	0.7296	0.9951	0.0843	15.66
0.5239	0.0001	0.7399	0.9951	0.0624	10.90
0.0060	0.2519	0.7247	0.9977	0.0900	16.97
0.0581	0.2519	0.7262	0.9977	0.0882	16.54
0.1710	0.2519	0.7295	0.9977	0.0825	15.28
0.5134	0.2519	0.7396	0.9977	0.0604	10.65
0.0092	0.6234	0.7247	1.0008	0.0836	15.95
0.0584	0.6234	0.7262	1.0008	0.0825	15.65
0.1709	0.6234	0.7295	1.0008	0.0776	14.55
0.5009	0.6234	0.7392	1.0008	0.0594	10.60
0.0140	1.5368	0.7249	1.0074	0.0761	14.84
0.0623	1.5368	0.7263	1.0074	0.0751	14.57
0.1716	1.5368	0.7296	1.0074	0.0712	13.73
0.4976	1.5368	0.7392	1.0074	0.0573	10.46
0.0212	3.2513	0.7250	1.0199	0.0676	13.69
0.0679	3.2513	0.7265	1.0199	0.0664	13.39
0.1724	3.2513	0.7296	1.0199	0.0637	12.69
0.4982	3.2513	0.7391	1.0199	0.0539	10.26

By plotting the surface tension exerted between solutions of various concentrations with acid concentration in the ether as ordinates and in water as abscissas as in Figure 1, lines of constant surface tension are obtained. From this graph the surface tension exerted between the two phases for varying acid concentrations may be readily obtained by interpolation.

It is evident that the surface tension between these two immiscible solvents is markedly dependent upon their respective acetic acid concentrations. Consequently, the dispersion of either phase in the other will vary greatly with their respective acid concentrations. These data are of value for predicting qualitatively where other variables are fixed, the area of contact and, consequently, the influence of acid concentration on the extraction efficiency to be expected for the various stages of extraction equipment operating this process.

Literature Cited

(1) Dorsey, *Bur. Standards Sci. Paper* 540, 563–95 (1926).
(2) Harkins and Brown, *J. Am. Chem. Soc.*, 41, 499 (1919).
(3) International Critical Tables, Vol. IV, p. 435 (1928).

Received March 21, 1935.

Preparation and Properties of Mono-, Di-, and Tricalcium Phosphates

H. W. E. LARSON, University of Wisconsin, Madison, Wis.

THE three common phosphates of calcium—namely, the mono-, di-, and tricalcium phosphates—are of great importance because of their usage as fertilizers, their presence in soils, and their use in numerous commercial products. Monocalcium phosphate is the essential constituent of superphosphate fertilizer, which is manufactured to the extent of about 15,000,000 tons annually, and valued at several hundred million dollars. Di- and tricalcium phosphates find a restricted use as fertilizers at present, but this use may increase. Notwithstanding the great importance of these phosphates, information regarding their preparation and properties in pure crystalline form leaves much to be desired. Because samples of pure crystalline material were often not at hand, the results of these determinations of their properties are in many cases open to question. It was for the purpose of preparing these phosphates in pure crystalline form and determining some of the more important properties of these pure forms that this investigation was undertaken.

General Laboratory Methods

Phosphorus was determined by both the colorimetric and gravimetric methods. The colorimetric method followed is that described by Truog and Meyer (*28*). The gravimetric method followed is essentially that given by Treadwell and Hall (*26*), except that a smaller sample (approximately 0.035 gram of P_2O_5) was used, 5 grams of ammonium nitrate were added to each solution previous to precipitation, and the ammonium molybdate solution used was prepared according to official methods (*1*). The colorimetric method was used whenever the amount of phosphorus involved was so small that the gravimetric method could not be used conveniently.

Calcium was determined by precipitation as the oxalate and titration with potassium permanganate.

The loss of water by the salts at different temperatures was determined by heating 1-gram samples in an electric oven for the temperature range of 40° to 185° C., in an electric furnace equipped with a pyrometer for the temperature range of 190° to 800° C., and over Bunsen and Méker burners for temperatures above 850° C.

The carbon dioxide-free water used in solubility studies was prepared by drawing carbon dioxide-free air through distilled water for approximately 48 hours. Throughout this paper, water so treated will be designated as "water." The carbon dioxide-saturated water was prepared by passing carbon dioxide through distilled water until it attained a pH of 3.8.

The solubility studies, unless stated otherwise, were conducted by shaking the suspensions for the designated period, after which they were allowed to stand with intermittent shaking for 24 hours in a water bath maintained at 25° C.

The pH of water solutions of the three phosphates was determined with the hydrogen electrode.

Monocalcium Phosphate Monohydrate

PREPARATION. A review of the literature pertaining to the preparation of pure crystalline monocalcium phosphate monohydrate shows that the ratio of P_2O_5 to CaO (*2*, *24*), temperature at which crystallization takes places (*2*), and kind of washing liquids used (*24*, *25*) are factors to be considered.

Clark (*10*) attempted to prepare the pure salt by dissolving the commercial product in water and evaporating until crystallization had proceeded for some time. Then the mixture was cooled to 50° C. and centrifuged. The ratio of P_2O_5 to CaO of his product was slightly higher than the theoretical, due to the presence of free acid.

In some preliminary trials, the writer was unable to obtain pure crystalline products from solutions evaporated at 40° C. when the ratios of P_2O_5 to CaO were 3 to 1 and 4 to 1. With a ratio of 5 to 1, a pure crystalline product was finally obtained when prepared in the following manner:

To 3 liters of water containing 332 grams of P_2O_5 as phosphoric acid, calcium hydroxide equivalent to 66.4 grams of CaO was added. The filtered solution was evaporated at 35° to 40° C., using an air current to hasten evaporation. The solution was stirred several times a day, and any salt crystallizing on the side of the beaker was pushed down into the solution to dissolve. Crystallization began when the volume had been reduced from 3 liters to approximately 850 cc. The temperature was then lowered to 30° to 33° C. When the volume had been reduced to 500 cc., the supernatant liquid was decanted, the crystalline mass crushed somewhat to liberate occluded phosphoric acid, and the excess liquid removed by suction, using a Büchner funnel. The crystalline mass was washed once by decantation with 800 cc. of absolute alcohol, then transferred to a Büchner funnel with absolute alcohol, and washed six times with 125-cc. portions of absolute alcohol. The suction was stopped before each addition until the alcohol had become well distributed. The crystals were finally washed, similarly, three times with absolute ether, spread onto a sheet of paper, and maintained at a temperature of approximately 25° C. until the ether had evaporated. The salt was ground to pass a 20-mesh sieve, the yield being about 66 per cent of the theoretical. The salt did not take on a tarry odor during a period of one year, which Clark (*10*) found to be the case when he used alcohol and ether for washing his product.

COMPOSITION AND CRYSTAL PROPERTIES. The results of analyses for phosphorus and calcium of the prepared monocalcium phosphate monohydrate are given in Table I, as are also results of analyses of di- and tricalcium phosphates. These analyses show that the salt prepared was pure and a monohydrate. The crystals were white and rhomboidal in shape.

TABLE I. ACTUAL AND THEORETICAL COMPOSITION OF THREE PHOSPHATES PREPARED

	Composition					
	By analysis of those prepared			Theoretical		
Phosphate	P_2O_5	CaO	$\frac{P_2O_5}{CaO}$	P_2O_5	CaO	$\frac{P_2O_5}{CaO}$
	%	%		%	%	
$CaH_4(PO_4)_2 \cdot H_2O$	56.65 56.60	22.40 22.25	2.54	56.30	22.12	2.54
$Ca_2H_2(PO_4)_2 \cdot 4H_2O$	41.46 41.14	32.90 33.20	1.25	41.27	32.48	1.27
$Ca_3(PO_4)_2 \cdot H_2O$	42.40 42.50	51.20 51.20	0.83	43.30	51.10	0.84

Results of petrographic examination are given in Table II. The crystals are very finely twinned, but not of the same orientation, thus necessitating the choosing of single crystals for optical work. The x-ray diffraction pattern is represented in Figure 1, and differs markedly from those of di- and tricalcium phosphates, the lines being more prominent than those of the latter phosphate but less so than those of the former.

LOSS OF WATER AND TRANSFORMATION ON HEATING. Results of the effect of heating monocalcium phosphate monohydrate at different temperatures for short and long periods of time on loss of weight are given in Table III. Prolonged

TABLE II. CRYSTAL PROPERTIES OF MONOCALCIUM PHOSPHATE MONOHYDRATE AND DICALCIUM PHOSPHATE TETRAHYDRATE

Phosphate	Properties of Crystals: System	Sign	Value of $2V$	Refractive indices using "D" light: N_g	N_m	N_p
Monocalcium phosphate monohydrate	Triclinic	Minus	70°	1.5292	1.5176	1.4932
Dicalcium phosphate tetrahydrate	Monoclinic	Minus	83°	1.5516	1.5457	1.5394

heating at 100° C. caused a loss in weight equivalent to 0.96 molecule of water (variation from 1 molecule is within limit of error), showing that the molecule of water is lost at a lower temperature than is reported by some investigators (*4*, *14*), and that the anhydrous salt is quite stable when heated for long periods of time at this temperature. It is also stable when heated for 5-hour periods over a temperature range of 103° to 153° C.

When the salt was heated at 200° to 205° C. for nearly 10 weeks, it gradually lost weight equivalent to 2.5 molecules of water. This loss can be accounted for by the formation of a mixture of calcium pyrophosphate and metaphosphoric acid in accordance with the equation given by Stoklasa (*24*):

$$2CaH_4(PO_4)_2.H_2O = Ca_2P_2O_7 + 2HPO_3 + 5H_2O \uparrow$$

The mixture thus obtained was dissolved in water acidified with sulfuric acid, and the presence of one or both compounds in solution was shown by the formation of a white precipitate when silver nitrate was added. Pyrophosphate was shown to be present in the mixture by the formation of a white precipitate when zinc sulfate was added in excess to the solution at approximately pH 5.4. A few drops of a water extract of the mixture caused coagulation of a solution of albumin, indicating the presence of metaphosphate.

In order to confirm further the presence of metaphosphate and pyrophosphate, the relative rate of hydrolysis to orthophosphate in boiling water of the mixture obtained by heating and of pure calcium pyrophosphate was investigated.

The relative rate of hydrolysis was studied by boiling 0.05-gram samples in 500 cc. of water for the given period. After cooling, aliquots were filtered and analyzed for orthophosphate by the colorimetric method. The remainder of the unfiltered aliquot was then boiled for the next desired period. The mixture at first hydrolyzed much more rapidly than did a sample of pyrophosphate. The velocity of hydrolysis of the mixture became much slower after an amount of phosphorus equivalent to the calculated amount of metaphosphoric acid had hydrolyzed. This slower velocity was similar to the velocity of hydrolysis of the calcium pyrophosphate alone. This test confirmed the presence of pyrophosphate and metaphosphate in accordance with the reaction just given.

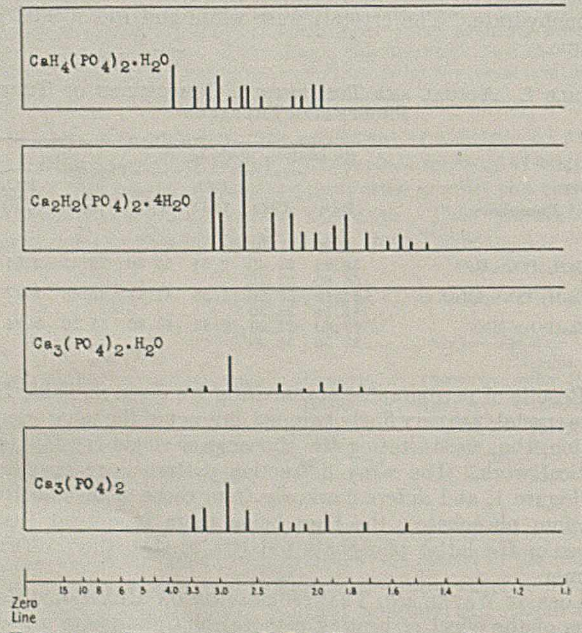


FIGURE 1. DIAGRAMS OF X-RAY PATTERNS OF PHOSPHATES

Length of lines indicates estimated intensity of diffraction spectra lines Mo. radiation. $\lambda = 0.712$ Å. $R = 20$ cm.

TABLE III. EFFECTS OF TEMPERATURE AND PERIOD OF HEATING ON LOSS OF WEIGHT OF MONOCALCIUM PHOSPHATE MONOHYDRATE

(Loss of 7.14 per cent is equivalent to 1 mole water)

Temperature of Heating	Period Heated	Loss of Weight on Hydrated Salt Basis
° *C.*	*Hours*	%
99 to 101	27	6.32
90 to 101	256	6.93
90 to 101	334	6.93
103	5	6.73
109	5	7.14
119	5	7.25
134	5	7.31
147	5	7.39
151	5	7.41
203	1	10.83
203	3	11.66
203	18	13.74
203	63	14.91
203	158	15.66
203	254	15.90
203	373	16.27
203	492	16.30
203	587	16.33
203	730	16.40
203	855	16.81
203	974	17.54
203	1165	17.59
203	1362	17.60
203	1658	17.60
325	204	21.78
900 to 910	1/3	22.40
900 to 910	4	23.16
950 to 970	7	23.80
950 to 970	30	33.47
950 to 970	49	36.77
950 to 970	82	40.56
950 to 970	127	42.07
950 to 970	170	42.35
950 to 970	176	42.34

When the monocalcium phosphate monohydrate was heated at 325° C. for 204 hours, a loss in weight equivalent to 3 molecules of water took place. This loss can be accounted for by a complete change from orthophosphate to metaphosphate in accordance with the following equations:

$$2CaH_4(PO_4)_2.H_2O = Ca_2P_2O_5 + 2HPO_3 + 5H_2O$$
$$Ca_2P_2O_7 + 2HPO_3 = Ca_2P_2O_7 + P_2O_5 + H_2O$$
$$Ca_2P_2O_5 + P_2O_5 = 2Ca(PO_3)_2$$

To study the effect of higher temperatures for short and long periods of time, samples of the salt were heated for about 20 minutes, and also for 4 hours, over a Bunsen burner at approximately 900° to 910° C., and then for longer periods over Méker burners at approximately 950° to 970° C. until the weights were constant. The data obtained (Table II) show that at the temperature of a Bunsen burner the equivalent of 3 molecules of water is removed in about 20 minutes, and when the temperature is raised to that of a Méker burner, the equivalent of approximately 3 more molecules of water is removed gradually over a period of 170 hours. The total loss was equivalent to 6 molecules of water. A loss in weight (49.6 per cent) equivalent to 7 molecules of water can be accounted for by the equation:

$$2CaH_4(PO_4)_2.H_2O + \text{heat} = Ca_2P_2O_7 + P_2O_5 \uparrow + 6H_2O \uparrow$$

in which case both phosphoric anhydride and water are removed. This is in disagreement with Hinds (*18*), who states that metaphosphate is the final product when monocalcium and dicalcium phosphate are heated. A further loss in weight equivalent to 1 molecule of water might have taken place at a higher temperature.

SOLUBILITY AND REACTION. For a review of the literature pertaining to the solubility of monocalcium phosphate monohydrate, the reader is referred to articles by Cameron and Hurst (*7*), Sanfourche and Focet (*22*), Seidell (*23*), and Stoklasa (*24*).

The effect of shaking for different periods of time on the solubility was studied first. The salt was added to water and carbon dioxide–saturated water at the rate of 25 and 50 grams per liter, respectively. The suspensions were placed on a shaker, and aliquots taken after 3, 9, 24, and 48 hours, filtered, and then analyzed for phosphorus. The results are given in Table IV. These data indicate that shaking for 3 hours was sufficient for equilibrium to take place in both solvents.

TABLE IV. EFFECTS OF PERIOD OF SHAKING AND AMOUNT OF SALT ADDED ON SOLUBILITY OF MONOCALCIUM PHOSPHATE MONOHYDRATE IN WATER AND CARBON DIOXIDE–SATURATED WATER

(Ratio of P_2O_5 to CaO in salt is 2.53)

Solvent	Period of Shaking	Salt Added	Salt Dissolved According to: Phosphorus in solution		Calcium in solution		Ratio of P_2O_5 to CaO in Solution
	Hours	*G./l.*	*G./l.*	%	*G./l.*	%	
Water	24	10.0	9.92	99.2	10.00	100.0	2.52
	24	12.0	10.80	90.0	11.80	98.3	2.32
	24	20.0	18.90	94.5	18.70	93.5	2.55
	3	25.0	23.85	95.5	...	...	..
	9	25.0	23.85	95.5	...	...	..
	24	25.0	23.85	95.5	...	...	..
	48	25.0	23.85	95.5	...	...	..
	3	40.0	36.60	91.5	...	...	..
	24	100.0	87.17	87.2	79.90	79.9	2.78
CO_2–saturated water	3	14.0	13.97	99.7	13.82	98.8	2.56
	3	14.5	14.50	100.0	14.00	96.5	2.64
	3	16.0	15.40	96.7	15.80	99.0	2.48
	3	17.0	17.00	100.0	16.65	98.0	2.59
	24	20.0	17.80	89.0	19.40	97.0	2.33
	14	25.0	24.70	98.7	23.20	93.0	2.71
	3	50.0	46.80	93.5	...	...	..
	9	50.0	46.80	93.5	...	...	..
	24	50.0	46.80	93.5	...	...	..
	48	50.0	46.80	93.5	...	...	..
	24	75.0	62.00	82.5	61.00	81.3	2.58
	24	100.0	86.70	86.7	77.00	77.0	2.86

The influence of ratio of salt to solvent on solubility was studied by adding 10 to 100 grams of salt to a liter in the case of water, and 14 to 100 grams in the case of carbon dioxide–saturated water. The results of analyses for phosphorus and calcium in solution are given in Table IV, and show that all the added phosphate dissolved when 10 grams of salt were added per liter of water at 25° C. Beyond this, the percentage of salt which dissolved decreased, but the actual amount increased greatly.

In the case of carbon dioxide–saturated water, all the added phosphate dissolved at 25° C. when 14 grams of salt per liter were added. The percentage of salt that dissolved decreased as the quantity of salt added was increased, while the actual amount increased. As the amount of salt added to both solvents increased, the ratio of P_2O_5 to CaO in the solution increased, showing that some decomposition was taking place, and that a more insoluble calcium salt was being formed and left out of solution. Stoklasa (*24*) believed that the process of decomposition could be represented as follows:

$$X\ CaH_4(PO_4)_2.H_2O + H_2O = (X - 1)\ CaH_4(PO_4)_2.H_2O + CaHPO_4 + 2H_2O + H_3PO_4$$

When X equals 4, the undecomposed quantity would be 75 per cent, and the decomposed 25 per cent.

The effect of concentration of monocalcium phosphate monohydrate in filtered water solutions on reaction is shown in Table V. The solution having the highest ratio of P_2O_5 to CaO had the lowest pH. The acidity increased with increasing concentrations of dissolved salt.

TABLE V. REACTION OF WATER SOLUTIONS OF THE THREE PHOSPHATES

Phosphate	Salt Added	Salt Dissolved, Based on Phosphorus in Solution	pH of Solution
	G./l.	*G./l.*	
Monocalcium phosphate monohydrate	10.0	9.92	3.62
	100.0	87.17	2.49
Dicalcium phosphate tetrahydrate	0.5	0.196	6.00
	1.0	0.16	6.55
Tricalcium phosphate monohydrate	0.5	0.0137	6.22
	5.0	0.0307	6.41

Dicalcium Phosphate Tetrahydrate

PREPARATION. A review of the literature pertaining to the preparation of dicalcium phosphate tetrahydrate indicates that the temperature at which evaporation takes place (*3*, *6*) and the use of proper washing solutions (*13*) are the most important factors to be considered.

The writer prepared the pure crystalline salt in accordance with the method outlined by DeSchulten (*13*). Anhydrous commercial dicalcium phosphate was dissolved in 25 per cent acetic acid solution at 50° C. The filtered solution was evaporated at 25° to 33° C. under a hood, where circulation was aided with a fan. The salt which collected on the side of the beaker was pushed down into the solution. When about 75 per cent of the added salt had crystallized, the crystals were crushed somewhat and the liquid filtered off. The crystalline mass was then washed by decantation ten times with absolute alcohol and finally five times with absolute ether. After drying at room temperature, the crystals were ground to pass a 20-mesh sieve and the product used for determinations of properties.

COMPOSITION AND CRYSTAL PROPERTIES. The results of analyses of the dicalcium phosphate tetrahydrate for phosphorus and calcium are given in Table I, and agree well with the theoretical values of the tetrahydrate salt.

The crystals were pale yellow rhomboidal plates with the sharper corners broken off in many instances, which is in agreement with the observations of DeSchulten (*13*). Results of examination of the crystals under the petrographic microscope are given in Table II, and check very closely with those of Koehler (*19*).

The x-ray diffraction pattern of this salt represented in Figure 1 had more prominent lines than those of the other salts, and it also differed in position of the lines.

LOSS OF WATER AND TRANSFORMATION UPON HEATING. Results of the effect of heating dicalcium phosphate tetrahydrate for long periods of time at temperatures of 40°, 75°, 110°, 200°, and 950° to 970° C. are given in Table VI. When the salt was heated for approximately 690 hours at 40° C., a loss equivalent to 0.6 molecule of water resulted. The salt gradually lost 1.5 molecules of water when heated at 108° C. for approximately 270 hours. Almost maximum loss occurred within 5 hours when it was heated at 200° C., only a slight additional loss occurring upon further heating, which shows that the salt reaches a stable point quickly at this temperature. When it was heated at 950° to 970° C. for 27 hours, a loss equivalent to nearly 5 molecules of water occurred, which can be accounted for by transformation to the pyrophosphate.

The salt was also heated for short periods—that is, for 5 hours—at temperatures ranging from 40° to 325° C. The results are given in Table VI. There was a gradual loss of water with rise in temperature. The partially hydrated salt was not stable over any temperature range between 40° and 200° C. The first 2 molecules of water were gradually

TABLE VI. EFFECTS OF TEMPERATURE AND PERIOD OF HEATING ON LOSS OF WEIGHT OF DICALCIUM PHOSPHATE TETRAHYDRATE

(Loss of 5.23 per cent is equivalent to 1 mole of water)

Temperature of Heating	Period Heated	Loss of Weight on Hydrated Salt Basis
° *C.*	*Hours*	%
40	5	0.08
40	48	0.60
40	96	0.78
40	192	1.89
40	312	2.35
40	621	3.23
40	687	3.57
66	5	1.32
75	15	2.08
75	36	2.70
75	60	3.07
75	108	3.58
75	352	3.52
85	5	2.15
95	5	3.95
105	5	4.87
108	5	5.57
108	11	5.81
108	57	6.41
108	151	7.04
108	270	7.56
108	335	7.60
110	5	6.07
134	5	7.70
150	5	10.45
175	5	13.66
184	5	19.80
200	12	19.57
200	24	19.63
200	49	19.70
230	5	19.80
255	5	19.97
277	5	20.03
310	5	20.25
325	5	20.41
950 to 970	1	25.61
950 to 970	9	25.76
950 to 970	27	25.80

driven off over the temperature range of 40° to 150° C. There was some indication that the third and fourth molecules are removed at the same temperature, or at least within a narrow range of temperature. The first molecule of water was driven off at approximately 108° C., the second at 150° C., and the third and fourth at 150° to 185° C. Dragunov (*14*) reported a loss equivalent to nearly 4 molecules of water by heating the dry salt at 150° C. for only 20 minutes. Davies (*12*) also observed that there was no definite temperature at which the salt lost its water of crystallization.

SOLUBILITY AND REACTION. For a review of the literature pertaining to the solubility of dicalcium phosphate tetrahydrate, the reader is referred to the articles by Cameron and Seidell (*8*), and Cameron and Hurst (*7*).

The effect of duration of period of shaking on solubility was studied first. The salt was added to water and to carbon dioxide-saturated water at rates of 0.12 and 1 gram per liter, respectively. The suspensions were placed on the shaker and aliquots taken after 3, 9, 24, 48, 72, and 96 hours. Results of analyses for phosphorus in the filtered solutions are given in Table VII. Equilibrium was attained after the solutions had been shaken for 72 hours, which is a much longer period than was required by monocalcium phosphate.

The influence of ratio of salt to solvent on solubility was next investigated. Different amounts of salt ranging from 0.12 to 1 gram per liter were added to water, and amounts ranging from 0.266 to 5 grams per liter were added to carbon dioxide-saturated water. The results of analyses for phosphorus and calcium in filtered solutions are given in Table VII. Maximum solubility in water at 25° C. was attained with only 0.5 gram of salt per liter. The ratios between the amounts of phosphorus and calcium which dissolved show that some hydrolysis took place. Approximately 0.2 gram per liter of the salt is soluble in water according to the phosphorus determination. These results are higher than those reported by Seidell (*23*), and lower than those reported by Comey and Hahn (*11*).

The solubility of the salt in carbon dioxide-saturated water was found to be highest when 3 or 4 grams of salt were added per liter. A slightly lower solubility was found when 5 grams per liter were added. Slightly larger proportionate amounts of calcium than of phosphorus were dissolved. These results differ from those obtained in water where larger proportionate amounts of phosphorus than of calcium were dissolved. It is not apparent why the solubility was less when 5 grams of salt were added per liter than when 3 or 4 grams were added. These results for carbon dioxide-saturated water are higher than those given by both Seidell (*23*) and Comey and Hahn (*11*). The ratio of P_2O_5 to CaO in solution agreed better with the formula requirements in the case of carbon dioxide-saturated solutions than in the case of water solutions, indicating less hydrolysis in the former.

TABLE VII. EFFECTS OF PERIOD OF SHAKING AND AMOUNT OF SALT ADDED ON SOLUBILITY OF DICALCIUM PHOSPHATE TETRAHYDRATE IN WATER AND CARBON DIOXIDE-SATURATED WATER

(Ratio of P_2O_5 to CaO in salt is 1.27)

Solvent	Period of Shaking	Salt Added	Salt Dissolved According to: Phosphorus in solution		Calcium in solution		Ratio of P_2O_5 to CaO in Solution
	Hours	*G./l.*	*G./l.*	%	*G./l.*	%	
Water	3	0.12	0.037	30.8	....	..	..
	9	0.12	0.044	36.7	....	..	..
	24	0.12	0.057	47.5	....	..	..
	48	0.12	0.061	50.7	....	..	..
	72	0.12	0.067	55.7	....	..	..
	96	0.12	0.067	55.7	....	..	..
	72	0.50	0.179	36.0	0.139	27.8	1.65
	72	0.50	0.196	39.2	0.128	25.6	1.94
	72	1.00	0.160	16.0	0.135	13.5	1.50
CO_2-saturated water	3	0.266	0.132	49.5	0.133	50.0	1.26
	3	0.570	0.219	38.5	0.243	42.7	1.14
	3	1.0	0.513	51.3	....	..	..
	9	1.0	0.610	61.0	....	..	..
	24	1.0	0.750	75.0	....	..	..
	48	1.0	0.660	66.0	....	..	..
	72	1.0	0.777	77.7	....	..	..
	96	1.0	0.777	77.7	....	..	..
	72	3.0	0.820	27.3	0.8400	27.9	1.24
	72	4.0	0.818	20.5	0.8460	21.1	1.23
	72	5.0	0.685	13.7	0.7200	14.4	1.21

The effect of concentration of dicalcium phosphate in water solutions on the reaction is shown in Table V. The solutions of highest concentration had the lowest pH. Another factor that probably affected the values was the ratios of P_2O_5 to CaO in solution. The pH values of dicalcium phosphate solutions, as would be expected, are much higher than those of the monocalcium phosphate. Zinzadze (*31*) obtained a pH of 7.5 for a freshly prepared solution.

Tricalcium Phosphate Monohydrate

PREPARATION. A review of the literature pertaining to the preparation of tricalcium phosphate monohydrate shows that a pure salt will precipitate in an alkaline solution when the theoretical ratio of P_2O_5 to CaO is present (*29*, *30*), and in an acid solution but above pH 5.5 if a very low ratio of P_2O_5 to CaO is present (*5*).

Tricalcium phosphate monohydrate was prepared as follows in approximately 15-gram quantities:

Sixteen and four-tenths grams of disodium phosphate ($Na_2HPO_4.12H_2O$) were dissolved in 2 liters of water contained in a 3-liter round-bottomed flask. An equivalent quantity of calcium chloride was dissolved in 750 cc. of water and placed in a separatory funnel connected to the mouth of the flask. The stopcock of the funnel was so adjusted that the contents flowed into the flask in about 48 hours. The flask was supported in a water bath maintained at 65° to 70° C., and the contents were kept agitated by means of a stream of carbon dioxide-free air which entered through a fine capillary that extended to the bottom of the flask. During the course of a day, approximately 500 cc. of water evaporated, necessitating the addition of a like amount. Special care was taken to maintain the pH between 7 and 8 by adding dilute ammonium hydroxide as required. At the end of 48 hours, the precipitate was allowed to settle and the supernatant liquid poured off. Twelve portions were prepared in this manner, mixed together, and the mass washed free of chlorides by decantation, using small quantities of water. The salt was air-dried and ground to pass a 20-mesh sieve, and then used for determinations of its properties.

COMPOSITION AND CRYSTAL PROPERTIES. Results of analyses for phosphorus and calcium of tricalcium phosphate monohydrate are given in Table I, and agree well with the theoretical values of the monohydrate.

The crystals were too small for petrographic study, but x-ray diffraction patterns of both freshly prepared salt and of salt which had been heated for 25 hours at 950° to 970° C. were obtained, and are represented in Figure 1. The lines in the pattern of the heated salt were closer together and were also more prominent than those of the freshly prepared salt, which shows that the molecular planes in the crystal were brought closer together when the crystal was heated. Since in these patterns a number of the prominent lines of mono- and dicalcium phosphate were absent the crystalline properties exhibited were not due to admixtures of mono- and dicalcium phosphates. The exhibition of crystalline properties by tricalcium phosphate monohydrate is in agreement with the work of Zinzadze (*31*) and Gerlach (*17*). Cameron and Seidell (*8*), working prior to the advent of the x-ray method, were unable to establish the crystalline nature of this salt. These patterns, as would be expected, differ from those which Tromel (*27*) obtained for oxyapatite and hydroxyapatite.

LOSS OF WATER AND TRANSFORMATION ON HEATING. Results of heating tricalcium phosphate monohydrate for short and long periods of time are given in Table VIII. When the salt was heated for 5-hour periods at 65° and 100° C., the loss in weight was very small. This stability of the salt at temperatures around 100° C. was also observed by Zinzadze (*31*). The salt lost weight equivalent to 0.91 molecule of water when heated at 950° to 970° C. for 5 hours. An additional loss of only 0.06 water molecule took place when the same samples were heated for 21 hours more at this high temperature, which is in agreement with the results of Sanfourche (*21*).

TABLE VIII. EFFECTS OF TEMPERATURE AND PERIOD OF HEATING ON LOSS OF WEIGHT OF TRICALCIUM PHOSPHATE MONOHYDRATE

(Loss of 5.48 per cent is equivalent to 1 mole of water)

Temperature of Heating	Period Heated	Loss of Weight on Hydrated Salt Basis
° C.	*Hours*	*%*
65	5	0.60
108	5	0.96
325 to 335	24	3.03
950 to 970	5	4.96
950 to 970	14	5.15
950 to 970	21	5.24
950 to 970	25	5.24

SOLUBILITY AND REACTION. The influence of ratio of salt to solvent on solubility of tricalcium phosphate monohydrate was studied by Cameron and Seidell (*9*), and Cameron and Hurst (*7*), while Gaarder (*16*), and Osugi et al. (*20*) studied the effect of reaction of the solution on solubility of the salt.

In order to study the effect of period of shaking on solubility, the salt was added to water and to carbon dioxide–saturated water at rates of 0.008 and 0.3 gram per liter, respectively. The suspensions were shaken and samples taken after 3, 9, 24, 48, 72, 96, and 120 hours, filtered, and then analyzed for phosphorus. The results are given in Table IX. The water solutions and the carbon dioxide–saturated solutions came to equilibrium at the end of 96 and 3 hours' shaking, respectively.

TABLE IX. EFFECTS OF PERIOD OF SHAKING AND AMOUNT OF SALT ADDED ON SOLUBILITY OF TRICALCIUM PHOSPHATE MONOHYDRATE IN WATER AND CARBON DIOXIDE–SATURATED WATER

(Ratio of P_2O_5 to CaO in salt is 0.84)

Solvent	Period of Shaking	Salt Added	Salt Dissolved According to: Phosphorus in solution		Calcium in solution		Ratio of P_2O_5 to CaO in Solution
	Hours	*G./l.*	*G./l.*	*%*	*G./l.*	*%*	
Water	3	0.008	0.0015	18.7	....	...	..
	9	0.008	0.0018	22.5	....	...	..
	24	0.008	0.0024	30.0	....	...	..
	48	0.008	0.0036	45.0	....	...	..
	72	0.008	0.0040	50.0	....	...	..
	96	0.008	0.0048	60.0	....	...	..
	120	0.008	0.0048	60.0	....	...	..
	24	0.111	0.0097	8.7	....	...	..
	120	0.500	0.0137	2.7	0.0237	4.7	0.49
	48	1.110	0.0158	1.4	....	...	..
	120	5.000	0.0307	0.61	0.0241	0.48	1.06
CO_2–saturated water	24	0.121	0.058	48.0	0.060	49.5	0.81
	3	0.300	0.1480	49.3	....	...	..
	9	0.300	0.1480	49.3	....	...	..
	24	0.300	0.1480	49.3	....	...	..
	24	0.300	0.1420	47.4	0.145	48.5	0.82
	3	0.500	0.1480	29.6	0.149	29.8	0.84
	24	1.000	0.1970	19.8	0.204	20.4	0.82
	24	2.000	0.2010	10.1	0.217	10.8	0.79
	24	4.000	0.2300	5.75	0.235	5.9	0.82

The influence of ratio of salt to solvent on solubility was studied by adding from 0.008 to 5 grams of salt in the case of water, and 0.12 to 4 grams in the case of carbon dioxide–saturated solutions. The results of analyses for phosphorus and calcium are given in Table IX. The maximum solubility of the salt at 25° C. in water was 0.031 gram per liter on the basis of the phosphorus in solution, when 5.0 grams of salt per liter were added. Since more phosphorus than calcium dissolved, the residue, of necessity, became a more basic phosphate than tricalcium phosphate. Cameron and Hurst (*7*) obtained similar results.

The maximum solubility of tricalcium phosphate monohydrate in carbon dioxide–saturated water was approximately 0.23 gram of salt per liter on the basis of the phosphorus in solution, and slightly higher on the basis of the calcium in solution. This solubility was attained when 4 grams of salt were added to a liter of carbon dioxide–saturated water. The ratio of P_2O_5 to CaO in solution was very close to that of the formula. The solubility obtained is within the limits given by Seidell (*23*).

The effect of concentration of the salt in water solutions on reaction is given in Table V. These solutions had higher pH values than solutions of the monocalcium phosphate, but approximately the same as solutions of dicalcium phosphate. The values obtained are slightly lower than those of Zinzadze (*31*), who observed a pH of 6.8 in water solution.

Additional Comments on Reactions of the Three Phosphates

Contrary to first thought, it is to be noted that, depending on the conditions of the test, tricalcium phosphate may apparently give a slightly more acid reaction than dicalcium phosphate. This may be due to the formation of intermediate products or to insufficient time for equilibrium to be established. In order to obtain some further data on the reaction of these phosphates as they are commonly obtained, samples of such commercial products and others as were at hand were tested. In making these tests, 0.2 gram of the phosphate was placed in 20 cc. of carbon dioxide–free water, the suspension shaken 2 minutes, centrifuged, and the pH determined colorimetrically on 5 cc. of the clear supernatant liquid. The results are given in Table X. The pH of the different samples of the mono- and dicalcium phosphates did not vary greatly, as did the samples of tricalcium phosphate. Here again, the samples of tricalcium phosphate usually reacted more acid than did those of dicalcium phosphate.

Table X. Reaction of Various Samples of Three Phosphates

Monocalcium Phosphate	pH
Author's preparation	4.3
Commercial preparation No. 1	3.3
Commercial preparation No. 2	3.0
Research laboratory preparation	3.1
Dicalcium Phosphate	
Author's preparation	7.3
Commercial preparation No. 1	7.2
Commercial preparation No. 2	6.9
Commercial preparation No. 3	6.8
Commercial preparation No. 4	7.0
Research laboratory preparation	6.8
Tricalcium Phosphate	
Author's preparation	6.6
Commercial preparation No. 1	3.6
Commercial preparation No. 2	5.4
Commercial preparation No. 3	6.6
Research laboratory preparation	6.9

Summary

The purpose of this investigation was to prepare mono-, di-, and tricalcium phosphates in pure crystalline form, and to establish the more important properties of these pure forms. The results are summarized as follows:

1. Crystalline monocalcium phosphate monohydrate was prepared by evaporating at 33° to 40° C. a water solution of phosphoric acid and calcium hydroxide having a P_2O_5 to CaO ratio of 5 to 1. The values of the refractive indices N_g, N_m, and N_p were found to be 1.5292, 1.5176, and 1.4932, respectively. It became anhydrous at 109° C., became a mixture of pyrophosphate and metaphosphate on heating for a long period at 203° C., was transformed into metaphosphate at 325° C., and lost weight equivalent to 6 molecules of water at 950° C. The solubility at 25° C. was 10 and 14 grams per liter in water and carbon dioxide–saturated water respectively, when the amount of salt added was limited to that which dissolved completely. However, when more salt was added than would dissolve, hydrolysis was evident. The pH of a water solution containing 10 grams of salt per liter was 3.62.

2. Dicalcium phosphate tetrahydrate was prepared according to the method of DeSchulten—that is, crystallization of the salt at 30° C. from a 25 per cent acetic acid solution to which anhydrous dicalcium phosphate had been added. The refractive indices N_g, N_m, and N_p were found to be 1.5576, 1.5457, and 1.5392, respectively. Heating the salt for 5-hour periods at 108°, 150°, and 150° to 185° C. caused a loss equivalent to 1 molecule, 2 molecules, and 3 to 4 molecules of water, respectively. It was transformed into pyrophosphate at 950° to 970° C. The solubility in water at 25° C. was in the range of 0.16 to 0.196 gram per liter, and in carbon dioxide–saturated water, 0.62 to 0.82 gram per liter. The pH values of water solutions containing 0.196 and 0.160 gram of salt per liter were 6.00 and 6.55, respectively.

3. Tricalcium phosphate monohydrate was prepared by the slow addition of calcium chloride solution to a constantly agitated alkaline solution of disodium phosphate, maintained at 65° to 70° C. An x-ray diffraction pattern indicated the product to be crystalline, but the crystals were too small for petrographic study. The salt was stable at 100° C. When heated at 325° C. for 24 hours and at 950° to 970° C. for 5 hours, it lost weight equivalent to 0.6 and 1 molecule of water, respectively. The solubility in water at 25° C. varied with the ratio of salt to water from less than 0.005 to more than 0.03 gram per liter, and in carbon dioxide–saturated water from 0.058 to 0.23 gram per liter. The pH values of water solutions containing 0.0132 and 0.0307 gram of salt per liter were 6.22 and 6.41, respectively.

Acknowledgment

The writer wishes to express his appreciation for the helpful suggestions and criticisms tendered by Professor Truog, under whose general direction this work was done.

The writer is indebted to Robert B. McCormick of the Department of Geology for making the x-ray patterns, and particularly to G. W. Volk, working under the direction of Dr. Emmons, for his painstaking efforts and much time in determining the crystal forms and optical properties according to the method described by Emmons (*15*).

Literature Cited

(1) Assoc. Official Agr. Chem., "Official and Tentative Methods of Analysis," 3rd ed., 14 (1930).
(2) Bassett, Henry, Jr., *Chem. News*, **95**, 21 (1907).
(3) Bassett, Henry, Jr., *J. Chem. Soc.*, **22**, 315 (1906).
(4) Bassett, Henry, Jr., *Z. anorg. Chem.*, **59**, 1–55 (1908).
(5) Britton, T. S., *J. Chem. Soc.*, **130**, 614–30 (1927).
(6) Cameron, F. K., and Bell, J. M., *J. Am. Chem. Soc.*, **32**, 869–73 (1910).
(7) Cameron, F. K., and Hurst, L. A., *Ibid.*, **26**, 885–913 (1904).
(8) Cameron, F. K., and Seidell, A., *Ibid.*, **26**, 1454–63 (1904).
(9) *Ibid.*, **27**, 1503–12 (1905).
(10) Clark, N. A., *J. Phys. Chem.*, **35**, 1232 (1932).
(11) Comey, A. M., and Hahn, D. A., "Dictionary of Chemical Solubilities, Inorganic," 2nd ed., pp. 683–8, New York, Macmillan Co., 1921.
(12) Davies, H. E., *Chem. News*, **64**, 287 (1891).
(13) DeSchulten, M. A., *Bull. soc. franç. minéral.*, **26**, 11–17 (1903).
(14) Dragunov, S. S., *Udobrenie i Urozhai*, **2**, 409–16 (1930).
(15) Emmons, R. C., *Am. Mineral.*, **14**, 441–60 (1929).
(16) Gaarder, T., *Medd. Vestlandets forst. Forsøkssta.*, No. **14** (1930).
(17) Gerlach, Max, *Landw. Vers.-Sta.*, **46**, 407–60 (1896).
(18) Hinds, J. I. D., "Inorganic Chemistry," 2nd ed., p. 493, New York, John Wiley & Sons, 1905.
(19) Koehler, A., *Tschermak's mineralog. petrog. Mitt.*, **37**, 93–4 (1926).
(20) Osugi, S., Yoshie, S., and Nishigaki, N., *Bull. Agr. Chem. Soc. Japan*, **7**, 84–5 (1931).
(21) Sanfourche, A., *Compt. rend.*, **196**, 935–6 (1933).
(22) Sanfourche, A., and Focet, B., *Ibid.*, **184**, 1652–5 (1927).
(23) Seidell, A., "Solubilities of Inorganic and Organic Compounds," 2nd ed., pp. 1, 210–12, New York, D. Van Nostrand Co., 1919.
(24) Stoklasa, I., *Listy Chem.*, **13**, 203–10, 240–3, 273–83; Abs. in *J. Chem. Soc.*, **58**, 695–6 (1890).
(25) Thorpe, E., "Dictionary of Applied Chemistry," pp. 1, 608, New York, Longmans Green & Co., 1912.
(26) Treadwell, F. P., and Hall, W. T., "Analytical Chemistry. II. Quantitative Analysis," pp. 380–2, New York, John Wiley & Sons, 1928.
(27) Tromel, Von G., *Phosphorsäure*, **2**, 116–24 (1932).
(28) Truog, E., and Meyer, A. H., Ind. Eng. Chem., Anal. Ed., **1**, 136 (1929).
(29) Vanino, I., "Handbuch der Preparation Chemie, p. 459, Stuttgart, Ferdinand Enke, 1925.
(30) Warrington, R., *J. Chem. Soc.*, **26**, 983–9 (1873).
(31) Zinzadze, Ch. R., "Recherches sur la Nutrition Artificielle des Plantes Cultivées. Nouveaux Mélanges Nutritifs à pH Stable," Paris, Jouve & Cie, 1932.

Received August 28, 1934. Part of a thesis submitted to the faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of doctor of philosophy. Published with the permission of the director of the Wisconsin Agricultural Experiment Station.

Determination of Total and Free Selenium in Vulcanizates

E. CHERASKOVA AND L. VEISBRUTE, Scientific Institute of Rubber Industry, Moscow, U. S. S. R.

THE use of selenium as a vulcanizing agent in rubber stocks has increased considerably during the last few years. Only a small portion of the selenium combines with rubber, whereas the greater part remains free. When analyzing compounds containing selenium, it is interesting to determine selenium in both states. In spite of the available literature, there exist few specific methods of analyzing rubber containing selenium and no method of determining free selenium. The purpose of this paper is to give a method of determining free and total selenium in rubber compounds.

Determination of Total Selenium

Most methods of determining selenium involve treatment of the compound with oxidizing agents, such as hydrogen peroxide, nitric acid, or a mixture of hydrochloric and nitric acids. The selenious acid obtained is reduced to metallic selenium which may be determined by gravimetric, volumetric, or colorimetric methods.

The work of Blake (*2*) and of Shaw and Reid (*4*) outlines methods of determining selenium in rubber. The first involves oxidizing the rubber according to Carius and determining the selenium by iodometric titration. In the second method the rubber is oxidized by fusion with a mixture of sugar, potassium nitrate, and sodium peroxide.

In unpublished work, E. N. Korsunskaya has determined selenium in rubber compounds by oxidizing with nitric acid and reducing the selenious acid with hydrazine sulfate. The latter method seemed to be the simplest, and has been tested on a rubber stock of the following composition:

Formula of Rubber Stock No. 1

Smoked sheets	100
Zinc oxide	5
Stearic acid	1.5
Captax	0.7
Selenium	3
Sulfur	0.5
	110.7

The determination was accomplished in the following manner:

Two grams of rubber, cut into small pieces, were placed in a 250-cc. Erlenmeyer flask connected to a reflux condenser by a ground joint. Nitric acid (specific gravity 1.4) was introduced in portions of 3 to 4 cc. The flask was heated carefully with a small flame until complete destruction of rubber took place. After cooling, the solution was diluted with water to 150 to 200 cc. The precipitate (nitrosites) formed during this operation was filtered and washed several times with hot water. The filtrate was neutralized with 10 per cent aqueous ammonia and acidified slightly with hydrochloric acid (according to Wagenmann and Triebel, *5*, precipitation with hydrazine sulfate is more satisfactory in dilute hydrochloric acid). The flask containing the solution was then connected with a reflux condenser and 75 to 100 cc. of saturated aqueous hydrazine sulfate were added. For complete precipitation a small excess must be used.

The mixture was carefully heated until the selenium was converted to the black modification. After standing overnight the residue was filtered on a glass Schott's filter and washed with hot water until free of chloride and sulfate, then with alcohol and ether, and afterwards dried at 75° to 80° C. to constant weight (15 to 20 minutes).

The results of the experiments are shown in Table I, experiment A.

As shown in Table I, the results of parallel determinations check. Experimentally, this method is very simple, but the use of the large amounts of hydrazine sulfate is expensive. Besides hydrazine sulfate, such reducing agents as tin chloride, sulfur dioxide, etc., may be used. In using these reducing agents, nitric acid must first be removed. The work of Barkovsky and Babalova (*1*) shows that no losses of selenium occur in evaporating nitric acid from such a solution. The authors have checked this.

After the destruction of the rubber by nitric acid, the mixture was washed into a porcelain cup and evaporated on a water bath until nearly dry. The residue was diluted with 100 cc. of hot water. After being cooled, the solution was filtered and placed in a 500-cc. Erlenmeyer flask. Two hundred and fifty cubic centimeters of hydrochloric acid (specific gravity 1.19) were added, and to this solution crystalline sodium sulfite was introduced in small portions. After each addition the flask was closed by a watch glass. A small surplus of sodium sulfite was introduced when the solution began to turn red. The flask was connected to a reflux condenser, heated to 40° to 50° C., and allowed to stand overnight. Considerable sodium salts precipitate but owing to their ready solubility in water, the determination of selenium is not affected.

The solution was poured through a filter and hot water added to the precipitate of selenium and sodium salts to dissolve the latter. Further filtration, washing, and drying were performed in the regular way.

Table I, experiment B, shows the results obtained by this method.

TABLE I. DETERMINATION OF SELENIUM IN COMPOUND 1

Experiment	Method of Precipitation	Amount of Selenium Calculated	Amount of Selenium Found
		%	%
A	Reducing with hydrazine sulfate	..	2.66
		2.71	2.68
B	Reducing with sulfur dioxide	..	2.58
		..	2.62
		..	2.69

Determination of Free Selenium

In developing a method of determining free selenium, detailed studies of the solubility of selenium were made. The authors tested chloroform, ether, benzene, acetone, carbon bisulfide, and carbon tetrachloride, with negative results.

Selenium dissolves in aqueous potassium cyanide, sodium sulfide, and sodium sulfite, giving chemical compounds. Potassium cyanide gives potassium selenocyanide. Sodium sulfide forms a selenosulfide and sodium sulfite gives a compound of the hyposulfite type. Selenium can be separated easily in its elementary state from each of the above solutions.

Potassium cyanide was discarded because of its poisonous character.

Sodium sulfide solutions had a tendency to separate free sulfur, which necessitated the use of a long and involved procedure.

One hundred cubic centimeters of sodium sulfite solution dissolve 0.1 gram of selenium after refluxing for 2 hours. The filtered and cooled solution on acidification with hydrochloric acid precipitates selenium which may be separated and weighed. In treating rubber in this manner free sulfur is also extracted, which precipitates with the selenium on acidification with hydrochloric acid. The authors have tested with success the possibility of using formalin for the selective precipitation of selenium. The use of sodium sulfite and formalin permits simultaneous determination of free selenium and free sulfur, the latter by the method of Bolotnikof and Gurova (*3*), which consists of iodometric titration of the hyposulfite formed.

This method has been tested on three mixtures of commercial selenium and sulfur, with the results shown in Table II.

Table II. Determination of Selenium and Sulfur in Mixtures

Selenium Taken	Selenium Found		Sulfur Taken	Sulfur Found	
Gram	*Gram*	%	*Gram*	*Gram*	%
0.1514	0.1492	98.5	0.0648	0.0605	93.4
0.1442	0.1431	98.8	0.0201	0.0190	94.5
0.1700	0.1685	99.1	0.0190	0.0180	94.5

The method of determining free selenium by means of extracting it with sodium sulfite has been checked by the authors on several rubber stocks, compounds 1, 2, and 3. The rubber was milled and cut into pieces 1 mm. square with scissors. Two different curves of No. 1 were used.

	Rubber Formulas	
	No. 2	No. 3
Smoked sheets	100	100
Zinc oxide	5	...
Synthetic rubber	...	100
Stearic acid	1	3
Captax	0.5	1.4
Selenium	3	6
Sulfur	2	1
	111.5	211.4

When using the authors' method of degradation, approximately 30 hours are required to extract free selenium from rubber, the greater part of the selenium being extracted during the first 12 hours.

For determining free selenium, about 1 gram of rubber was placed in a 500-cc. Erlenmeyer flask, 200 cc. of 10 per cent sodium sulfite solution were added, and the mixture was boiled under reflux for 30 hours. A second treatment of the rubber was made with a fresh portion of sulfite solution to insure complete extraction. After cooling, the solution was filtered and the rubber washed with hot water. The flask containing the filtrate was again connected with the condenser, 75 cc. of formalin were added, and the solution was boiled for about an hour. After settling, the selenium was filtered on a Schott's filter and rinsed with water. The filtrate was transferred to another flask and the free sulfur determined. The residue on the filter was washed with hydrochloric acid and hot water until free of chlorides, then with alcohol and ether, and dried to constant weight.

Table III gives a summary of the determination of free selenium in these rubber compounds.

Table III. Determination of Free Selenium in Rubber Stocks

Rubber	Time of Cure	Selenium (Calculated)	Free Sulfur Found	Free Selenium Found	Combined Selenium by Difference
	Min.	%	%	%	%
1	15	2.71	..	2.38	0.33
		2.71	..	2.36	0.35
	40	2.71	..	2.17	0.54
		2.71	..	2.15	0.56
2	..	2.69	0.15	2.29	0.40
			0.16	2.30	0.39
3	..	2.84	0.15	2.27	0.57
			0.18	2.15	0.69

Conclusions

The total selenium in rubber compounds may be determined by disintegrating with nitric acid and then separating the selenium by reducing the nitric acid solution with hydrazine sulfate, or by reducing with sulfurous acid after evaporation of the nitric acid. Free selenium is determined by extracting the rubber with aqueous sodium sulfite, from which selenium is precipitated by formalin.

Free sulfur is determined volumetrically by iodometric titration after precipitating selenium from sulfite solution.

Literature Cited

(1) Barkovsky, A. A., and Babalova, A. A., J. Plant Laboratory (U. S. S. R.), 4, 306 (1934).
(2) Blake, J. T., Ind. Eng. Chem., 22, 737, 740, 744, 748 (1930).
(3) Bolotnikof, V., and Gurova, V., *J. Rubber Ind.* (U. S. S. R.), **10**, 61–2 (1933).
(4) Shaw, E. H., Jr., and Reid, E. E., *J. Am. Chem. Soc.*, **49**, 2330 (1927).
(5) Wagenmann and Triebel, *Chem. Zentr.*, **II**, 273 (1930).

Received June 19, 1935.

Colorimetric Determination of Manganese in the Presence of Titanium

GEORGE J. HOUGH, Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

THE manganese content of crystalline rocks, according to Hillebrand (*1*), rarely exceeds 0.3 per cent. Long experience with soils in this laboratory shows the manganese content in the average soil of the United States to be about 0.05 to 0.06 per cent. When present in such small quantities manganese is usually determined by a colorimetric method, and the procedure generally used is oxidation to permanganic acid by means of ammonium persulfate. The method for soils commonly used in this laboratory (*2*) is as follows:

One gram of the soil is ignited in a small platinum dish to destroy organic matter, and is then digested on the hot plate with 25 cc. of hydrofluoric acid and 5 cc. of sulfuric acid until white fumes appear. It is cooled, diluted with water, warmed gently until all salts are in solution, and then filtered through a close filter to insure a perfectly clear solution. The filtrate is transferred to a 100-cc. volumetric flask, 1 cc. of 0.5 per cent silver nitrate solution is added, and then 1 gram of ammonium persulfate. The flask is put on the steam bath for 20 to 30 minutes until the color is fully developed. It is then cooled, made up to volume, and compared with a suitable standard in a colorimeter.

Another convenient way to prepare the sample is to fuse, after ignition, with about 10 grams of potassium pyrosulfate and 1 gram of sodium fluoride; heat to fumes for some time, cool, extract with hot water, boil, filter, and treat as above with persulfate. The standard manganese solution is best prepared from c. p. manganese sulfate, and for soils and rocks should have a value of about 0.0002 gram MnO per cubic centimeter.

It is not good practice to take the theoretical percentage of manganese in the manganese sulfate as purchased, as the amount of water held by the salt is variable. Therefore the actual percentage of manganese should be determined gravimetrically, preferably as the phosphate.

It is perhaps not generally known that if titanium oxide is present in the solution in amounts exceeding 1 per cent, the persulfate method is useless, as no color is developed unless excessive amounts of reagents are used, and even then one cannot be certain that the full color has developed. This was observed recently during the analysis of some soils that were unusually high in titanium (2 to 12 per cent). In making the determination of manganese by the persulfate method no color developed at first, although there was good reason for believing that the samples contained some manganese. When more reagents were added, to an excess of four or five times the usual amount, the color finally appeared.

In order to verify the interference of titanium, which also reacts with persulfates, a sulfuric acid solution containing 54 mg. of titanium oxide and 0.2 mg. of manganese oxide was treated in the usual manner, using 1 gram of ammonium persulfate; no color developed. It should be noted here that ammonium persulfate, with or without silver nitrate, produces the characteristic brown color with titanium only in concentrated solutions strongly acid with sulfuric acid.

When it was found that titanium interfered seriously with the ammonium persulfate method, an attempt was made to eliminate the titanium to avoid its interference. Certain textbooks state that titanium is volatilized by evaporation with hydrofluoric acid unless sulfuric acid or some other acid is present. This statement is not entirely accurate, as shown by the following experiments:

A solution containing 28 mg. of titanium oxide was precipitated by ammonia, filtered, and washed; the precipitate was then evaporated twice to dryness with 20 cc. of hydrofluoric acid. The residue was redissolved in acid, and the titanium determined gravimetrically; 24.2 mg. of titanium oxide were found.

One gram of a soil colloid sample which contained 4.51 per cent of titanium oxide (determined by the color method) was evaporated twice to dryness with 25 cc. of hydrofluoric acid. The residue was then fused with potassium pyrosulfate, and titanium determined gravimetrically by the sulfurous acid method; 4.63 per cent of titanium oxide was found.

One hundred milligrams of finely ground rutile were evaporated three times to dryness with 25 cc. of hydrofluoric acid. The residue was then fused with potassium pyrosulfate, and the titanium determined as above; 100 mg. of titanium oxide were found.

Finally, a given weight of pure potassium titanium fluoride containing 70 mg. of titanium oxide was taken, and evaporated twice to dryness with 20 cc. of hydrofluoric acid. When the residue was analyzed gravimetrically, 68.5 mg. of titanium oxide were found.

These tests show that while hydrofluoric acid alone may have a tendency to volatilize titanium, the effect is so slight, even on pure, freshly precipitated material, that it would be useless as a method of eliminating titanium for the purpose of preventing its interference in the persulfate color method.

It is recommended that potassium periodate be used as the oxidizing agent in the presence of much titanium. Sodium bismuthate can also be used successfully, as there is no interference with the development of the manganese color.

Literature Cited

(1) Hillebrand, W. F., *U. S. Geol. Survey Bull.* 305 (1906).
(2) Robinson, W. O., *U. S. Dept. Agr. Circ.* 139 (1930).

RECEIVED August 2, 1935.

Determination of Selenium in Organic Matter

K. T. WILLIAMS AND H. W. LAKIN

Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

IN 1934 Robinson, Dudley, Williams, and Byers (*2*) published a series of methods for accurate estimation of small quantities of selenium, which included a modification suggested by Van Kleeck for vegetation. This modification has been found generally satisfactory and perhaps the best hitherto available. Several thousand determinations have been made by its use (*1*). The method provides for the preparation of the sample by digestion with concentrated sulfuric acid as in the Kjeldahl method for nitrogen and subsequent distillation with concentrated hydrobromic acid and bromine. There are two unsatisfactory features in this procedure: In order to estimate quantities of selenium as low as 1 to 2 parts per million it is necessary to digest 10 grams of the air-dry vegetation, and even with the aid of mercuric oxide as a catalyzer this requires 6 to 8 hours for completion. Also, unless the digestion is carefully regulated the evolution of gases—carbon dioxide, sulfur dioxide, and water vapor—is so rapid that there is danger of loss of small quantities of selenium which are not absorbed by the bromine trap. The modification described below has been found to be much more rapid in execution, lends itself to routine work more readily, and is, when properly executed, free from all danger of selenium loss.

TABLE I. SELENIUM CONTENT OF VEGETATION AS DETERMINED BY KJELDAHL AND WET-COMBUSTION PROCEDURES

Lab. No.	Material	Selenium Content Kjeldahl digestion P. p. m.	Selenium Content Wet combustion P. p. m.
B14447	Astragalus grayii	1200 1180	1280 1260
14448	Mixed vegetation	12 12 14	15 15
14481	Corn	3 2	5 5
14482	Corn	10 7	10 10
14796A	Tium racemosum	450	460
14853	Stanleya bipinnata	460	530
14733A	Tium racemosum	45	70
14718A	Tium racemosum	150	160
16187	Diholcos bisulcatus	370	550
16190	Vegetation, not identified	7	18
16193	Sunflower	3	7
16197	Wild aster	220	310
16199	Corn	4	4

To prepare a sample of air-dry vegetation it is first ground to pass a 2-mm. mesh sieve, then mixed and quartered. A weighed sample, usually 10 grams, is stirred into a mixture of 50 cc. of concentrated sulfuric acid and 100 cc. of nitric acid in a 600-cc. Pyrex beaker. The mixture is stirred with a thermometer until it becomes homogeneous, after the first few minutes with gentle heating, without allowing the temperature to rise above 100° C. After all frothing has ceased, the temperature of the mixture is raised to a maximum of 120° C. until all evolution of nitrogen peroxide has ceased. The end of the operation is marked also by an incipient carbonization of the mixture, although longer heating at or below 120° C. does little harm. After the mixture is cooled it is transferred to an all-glass distilling flask, 100 cc. of hydrobromic acid and 1 cc. of bromine are added, and 75 cc. of distillate are collected. Care is taken that the first portion of the distillate contains a small excess of bromine.

The further procedure—filtration to remove wax, precipitation with sulfur dioxide and hydroxylamine hydrochloride, and subsequent estimation by color or weighing—is as previously described. The only important precaution to be observed is to remove the nitric acid, completely, by digestion. If this is not done the distillate will contain nitroxyl tribromide, which is not decolorized by sulfur dioxide and requires excessive quantities of hydroxylamine hydrochloride. If the temperature be allowed to rise until fumes of sulfur trioxide are evolved, certain loss of selenium will ensue. In Table I are given the results obtained upon identical samples by the procedure suggested and by the Kjeldahl digestion.

TABLE II. SELENIUM CONTENT OF VEGETATION

(Comparison by treatment with nitric and sulfuric acids to incipient carbonization after removal of nitric acid at 120° C. and by subsequent heating for half an hour.)

Lab. No.	Material	Selenium Content by Wet Combustion Method: Incipient carbonization P. p. m.	Selenium Content by Wet Combustion Method: Heated 0.5 hr. after carbonization P. p. m.
B15942	Wheat grass	10	5
15944	Side oats grama	2	2
15946	Wild aster	210	195
15948	Wild aster	8	6
15950	Little blue stem	1	1

In Table II are given five determinations made by wet digestion heated to incipient carbonization and for half an hour after carbonization has occurred but without allowing the temperature to rise above 120° C. It will be observed that while a rather minor loss of selenium is produced by heating beyond carbonization, such practice is inadvisable.

By contrast when standard sample B14447, Table I, was heated with nitric and sulfuric acid until white fumes of sulfur trioxide were evolved, the quantities of selenium found were, in two samples, 770 and 710 parts per million. It is therefore essential that during the wet-combustion process the temperature be kept low.

Small as is the modification suggested, it is of importance if large numbers of determinations are to be made, since the time required to prepare a sample for distillation is but 2 hours as against 6 to 8 for the Kjeldahl digestion. It is also more accurate, particularly for large quantities of selenium. By the use of this procedure an experienced operator with suitable equipment may readily effect distillation of twenty-four samples in an 8-hour day.

Literature Cited

(1) Byers, H. G., *U. S. Dept. Agr. Tech. Bull.* 482 (1935).
(2) Robinson, W. O., Dudley, H. C., Williams, K. T., and Byers, H. G., IND. ENG. CHEM., Anal. Ed., 6, 274–6 (1934).

RECEIVED September 2, 1935.

Quantitative Analysis of Solutions by Spectrographic Means

O. S. DUFFENDACK, F. H. WILEY,[1] AND J. S. OWENS,[2] University of Michigan, Ann Arbor, Mich.

A method for determining the amounts of metallic elements in a solution of their salts is described. An uncondensed spark in air between a suitably chosen solid electrode and the solution under analysis is photographed, and, from measurements on the relative intensities of chosen spectral lines, the analysis is made by reference to previously determined working curves. An internal standard is employed. Two methods for correcting for the influence of the presence, in varying amounts, of one element on the intensity of the spectral lines of another are described. The method has been applied in the determination of sodium, potassium, magnesium, and calcium in solutions of mixtures of their salts in concentrations varying over the range of their occurrence in human urine. The accuracy of analysis of an unknown is, in general, such as to give an error of about 2 per cent of the amount of the test element present.

METHODS for quantitative analysis by spectroscopic means have been developed to such a degree of reliability that it seemed desirable to investigate the feasibility of applying them to the determination of the inorganic bases in biological materials. The Department of Internal Medicine of the university became interested in the problem and it has been carried out as a joint investigation by this department and the Department of Physics. In this paper, the general technic for making quantitative analyses for metallic elements in a mixture of their salts will be described. The fundamental method employed is the same as that described by Duffendack, Wolfe, and Smith (*1*), except that a different spectroscopic source was demanded.

The particular problem that had to be solved was that of making correct determinations of the several metallic elements in the presence of each other when the amounts of the elements present in different solutions of the same salts varied over considerable ranges. As the presence of one element or ion oftentimes markedly affects the intensities of the spectral lines of another, corrections had to be found for such of these effects as appeared. Two methods were devised for making corrections for the effect of variations in the abundance of one element on the analysis for another. The technic has been worked out for the determination of sodium, potassium, magnesium, and calcium in solutions of mixtures of their salts over the ranges of abundance in which these elements occur in urine.

Spectroscopic Source

A number of spectroscopic sources were tested before one satisfactory for the purpose was found. It is essential that the solution under test be vaporized in such a way that the vapor shall contain the elements in amounts representative of their concentration in the solution. Hence the vaporization of the solution must not change the nature of the solution not yet used, and the solution must be fed into the spectroscopic source continuously, any part of it not volatilized being immediately removed.

The source found to be most satisfactory is an uncondensed spark in air between a suitable solid electrode and an electrode consisting of the solution itself. The material of the solid electrode should be one that permits ready and complete cleaning and has no spectral lines close to those used for the analyses. Silver was used in the present investigation. The solution is volatilized by the electric discharge.

The sparking apparatus, Figure 1, is a modification of one described by Twyman and Hitchen (*3*). *S* is the solid electrode. The solution is fed from the reservoir, *R*, through a capillary, *C*,

---

[1] Now at Haskell Laboratory of Industrial Toxicology, Wilmington, Del.
[2] Now at The Dow Chemical Co., Midland, Mich.

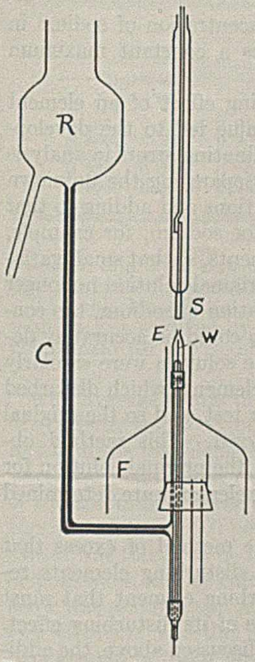


Figure 1. Spark Gap for Solutions

into the electrode, *E*. The capillary regulates the rate of flow, which must be sufficiently rapid so that a considerable excess of the solution overflows into the waste receiver and only a small percentage is volatilized by the discharge. A flow of 2 cc. per minute was found to be satisfactory for the source employed. Electrical contact with the liquid electrode is afforded by a platinum wire, *W*, introduced into the electrode from below and kept 2 or 3 mm. below the surface, so that the spark does not pass directly to the wire.

A draft of air around the spark prevents the reëntry of any spray or vapor into the spark. This draft was achieved by blowing compressed air from a glass nozzle up through a funnel, *F*, surrounding the liquid electrode. The rate of flow of air can be easily regulated in practice by means of a water manometer.

The electrical connections for the spark are shown in Figure 2. The spark gap, *G*, was 11 mm. in length. The spark employed was excited by a 1-kva. 25,000-volt transformer, *T*, supplied with 110-volt 60-cycle current and regulated by means of the water-cooled rheostat, *R*. The ammeter, *P*, and the milliammeter, *S*, measured the primary and secondary currents, respectively. The secondary current was 32 milliamperes. A high-frequency spark generated by a Hartley oscillating circuit was also satisfactory.

The chief precautions to be observed with the source in order to obtain consistent analyses are to maintain constant the rate of flow of the solution, the strength of the air draft, and the amount of the spark current. A screen was interposed between the source and the split of the spectrograph in such a manner that light from only the lower half of the spark entered the spectrograph. A deposition of material from the solution was observed to accumulate on the upper electrode and the spectral lines of this material appeared in the portion of the spark adjacent to this electrode. As it was found that all of the materials in the solution are not proportionately represented by their spectral lines from this deposited material, it is better to avoid the use of this portion of the spark.

Fixing Excitation Conditions

The complete development of the method of analysis consists of three parts, (*a*) fixing the excitation conditions, (*b*) determining the working curves, and (*c*) analyzing the unknown specimen. These steps are in every way analogous to those of the method of Duffendack, Wolfe, and Smith (*1*), and obviously steps *a* and *b* need be done only once for a given kind of solution.

After the lines to be used for the analysis are definitely selected, the variation of the relative intensities of these lines with changes in the spark current and other factors in the source should be investigated and those conditions of excitation chosen that are easily maintained practically constant. The conditions should be such that small variations in them, especially the spark current, do not produce appreciable variations in the relative intensities of the selected lines. It is important also that the spectrum be excited without any background.

Selection of Spectral Lines. Many factors require consideration in the selection of the spectral lines. Sometimes, of course, one is limited, as in this case, to the very few lines that appear in the spectrum of the material to be analyzed, but oftentimes more lines can be brought out by changing the excitation conditions and usually there is considerable choice of lines. With a spark source, it is safer to use only arc lines or only spark lines for the analysis and not compare arc and spark lines, as the relative intensities of lines of such radically different classes may vary rapidly with changes in the excitation conditions. For the case under consideration, only arc lines were used, and the spark was operated so as to be as arc-like as possible. The lines to be compared should lie close together in the spectrum, and, if a number of elements are to be estimated from a single spectrogram, all the selected lines, including those of the standard, should lie in a region of constant contrast of the photographic plate. For the solutions described above, the following lines, or unresolved multiplets, were selected: sodium 3302 Å., potassium 4046 Å., magnesium 2852 Å., and calcium 4226 Å. Cadmium was used as the internal standard and its lines at 3261 Å., 3466 Å., and 3610 Å. were chosen for comparison. All these lines were separated far enough from other lines and the water vapor bands so that their densities could be accurately measured. Their relative intensities were determined by the method of Thomson and Duffendack (*2*).

Determination of Working Curves

The basic principle of this method of analysis is that the relative intensities of spectral lines emitted by different elements in a spectroscopic source are determined by functions of their relative abundance. Then, if some element, the standard, is present in known concentration, the concentrations of the other elements can be determined if the correct functions can be discovered. These functions are determined empirically by a set of control measurements on solutions made up synthetically and, hence, of known composition. These functions plotted graphically constitute the working curves for the analysis of the unknowns. For convenience, the logarithms of the relative intensities of lines of a test element and of the standard are plotted against the percentage of the test element in the solution, as shown in Figure 3.

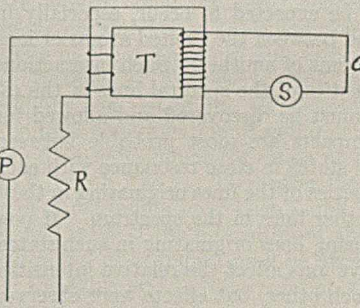


Figure 2. Electric Circuit

Unfortunately, the relative intensity of a line of a test element with respect to a line of the standard may vary with the concentration of another element in the solution. When the disturbing element varies in concentration, corrections have to be made for its effects on the analysis of the test element. Methods for making these corrections to the working curves are described below. Working curves and corrections for the effects of the several metals on the analyses of one another have been determined for mixtures of the salts of sodium, potassium, magnesium, and calcium with cadmium as the internal standard over the following ranges of percentage composition: sodium 0.1 to 1.2 per cent, potassium 0.1 to 1.2 per cent, magnesium 0.0025 to 0.015 per cent, and calcium 0.04 to 0.15 per cent. The cadmium was maintained at a known concentration.

Effect of Presence of One Element on Analysis for Another. The effect of one element on the determination of another arises from several causes, which may be separated into two groups—changes in the characteristics of the solution, and changes in the nature of the vapor and in the interactions

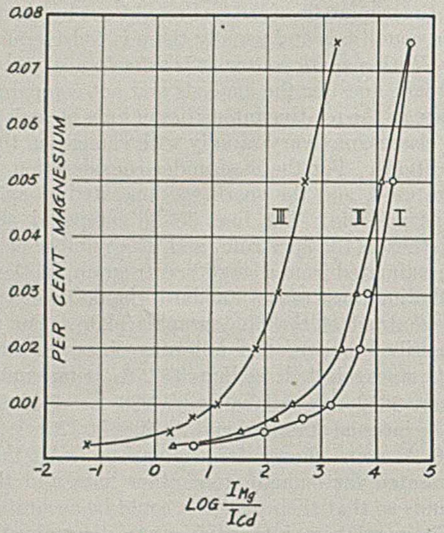


FIGURE 3. WORKING CURVES FOR ESTIMATION OF MAGNESIUM

I. Mg 2852 Å., Cd 3261 Å.
II. Mg 2852 Å., Cd 3466 Å.
III. Mg 2852 Å., Cd 3610 Å.

within the vapor. Variations in the amount of one of the salts of the solution may be expected to alter the electrical conductivity and volatility of the solution. If the volatility of the solution is changed, the character of the vapor, its density, its composition, and its electrical conductivity will likewise change.

In the vapor excited by the electric spark, interactions between the elements may be expected to occur, especially in impacts of the second kind between the excited atoms or ions of one kind and normal atoms of another. Such interactions markedly affect the intensities of the spectral lines of the reacting elements, and so must be discovered and allowed for in the results. These impacts are most probable between atoms which have energy states in close resonance with each other and affect the intensities of the lines originating in these states much more than other lines in the spectrum. If possible, it is best to avoid using lines originating in such states.

Not only do the positive ions affect the relative intensities of the spectral lines of each other, but effects were observed from the negative ions as well. The chloride ion was found to enhance the intensities of all the lines without, however, appreciably changing their relative intensities. The sulfate and phosphate ions, on the other hand, were observed to decrease the relative intensities of the lines of all the elements in the solutions used with respect to the lines of cadmium. The phosphate ion has a greater effect in this way than the sulfate ion. On account of these effects, it is necessary for accurate determinations first to convert all the salts to a single acid radical by appropriate chemical processes.

Method of Excess

In the case of the solutions tested, sodium, potassium, and magnesium were each found to decrease the relative intensity of the spectral line of each of the other elements with respect to those of cadmium. Calcium slightly increased the relative intensities of the lines of potassium and magnesium with respect to those of cadmium, but decreased that of sodium. Investigation revealed that the amount of the effect increased with an increase in the concentration of the disturbing element or elements, but reached an approximately constant value at relatively high concentrations. An example of this effect is given in Figure 4, which shows the change in the intensity of the calcium line relative to the cadmium lines brought about by increasing the concentration of sodium in the solution. The effect approaches a constant maximum value.

The observation that the disturbing effect of an element approached a constant maximum value led to the development of the method of excess for eliminating errors in analysis due to such disturbing effects. By separating the unknown solution to be analyzed into four portions and adding to that portion of the solution under test for sodium, for example, excess amounts of the disturbing elements, so that small variations in their concentrations in the original solution no longer produced variations in the determination of sodium, the concentration of sodium in the unknown could be accurately determined. The other portions of the solution were similarly treated with excess amounts of the elements which disturbed the determination of the metal under test, and so the original solution could be completely analyzed. This method obviously demands a larger amount of the original solution for analysis than one in which all of these elements are determined from a single spectrogram.

It was observed in the use of the method of excess that sometimes an excess of one of the disturbing elements reduced the amount of another disturbing element that must be added to eliminate the variations of its disturbing effect. Thus, in the analysis of the solution discussed above, the addition of 1 per cent of sodium and 1 per cent of potassium rendered the disturbing effects of both the elements on the determination of magnesium constant, whereas 2 per cent of either alone was required to eliminate variations due to the single element.

The analysis of solutions of mixtures of the salts used as an illustration in this paper was accomplished by the method of excess as follows:

For the determination of magnesium, there were added to a portion of the unknown 2 per cent of cadmium for internal standard and 1 per cent of sodium, 1 per cent of potassium, and 0.5 per cent of calcium.

For the determination of sodium, there were added to another portion of the unknown 1.5 per cent of cadmium for internal standard and 2 per cent of potassium, 0.25 per cent of magnesium, and 0.25 per cent of calcium.

For the determination of potassium, there were added to a third portion of the unknown 1 per cent of cadmium for internal standard and 2 per cent of sodium, 0.25 per cent of magnesium, and 0.25 per cent of calcium.

For the determination of calcium, there were added to a fourth portion of the unknown 0.5 per cent of cadmium for internal

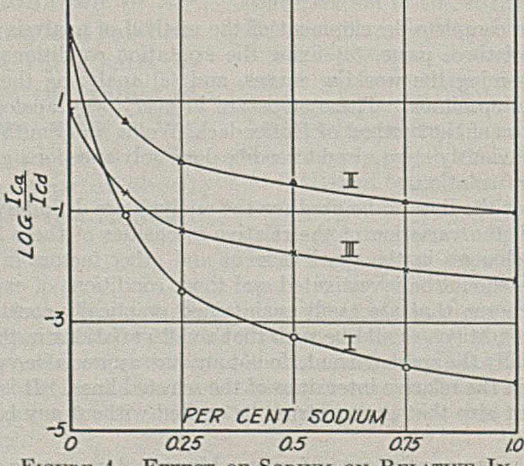


FIGURE 4. EFFECT OF SODIUM ON RELATIVE INTENSITIES OF CALCIUM AND CADMIUM LINES

I. Ca 4226 Å., Cd 3261 Å.
II. Ca 4226 Å., Cd 3466 Å.
III. Ca 4226 Å., Cd 3610 Å.

Table I. Analyses of Solutions by Method of Successive Approximations

Sodium				Potassium				Magnesium				
Spectrographic			Actual	Spectrographic			Actual	Spectrographic				Actual
%			%	%			%	%				%
0.198,	0.198,	0.214	0.200	0.207,	0.200,	0.206	0.200			0.0076,	0.0076	0.0075
0.408,	0.394,	0.404	0.400	0.408,	0.393,	0.386	0.400		0.0097,	0.0098,	0.0099	0.010
0.594,	0.581,	0.588	0.600	0.612,	0.603,	0.592	0.600	0.0147,	0.0157,	0.0154,	0.0156	0.0155
0.753,	0.762,	0.749	0.800	0.784,	0.790,	0.759	0.800			0.0199,	0.0203	0.020
0.993,	0.988,	0.983	1.000	0.946,	0.932,	0.905	1.000		0.0311,	0.0293,	0.0295	0.030

standard and 2 per cent of sodium, 2 per cent of potassium, and 0.25 per cent of magnesium.

The chlorides of the metals were used in all cases and the solution was acidified by adding 2.5 cc. of concentrated hydrochloric acid per 100 cc. of solution.

The average errors in analyzing by this method a number of synthetic solutions, of composition unknown to the analyst, in which the test elements varied over the ranges given above were: for magnesium 1.9 per cent and for sodium 1.2 per cent of the amounts of these elements present. The maximum errors were 2.8 and 2.0 per cent, respectively. The method of excess was found to be not so accurate for the determination of potassium and of calcium. In the latter case the average error was about 5 per cent. The lack of accuracy with these two elements was due to the development of a continuous background in the region of the potassium and calcium lines when an excess of sodium was added to the solution. Furthermore the excess of potassium necessary for the calcium determination produced a marked weakening of the calcium line and consequent difficulty in the measurement of its intensity relative to that of the standard cadmium line.

Method of Successive Approximations

Since the use of excessive quantities of interfering elements did not give sufficiently accurate determinations for potassium and calcium, and since this method requires that each element be determined separately, other methods for correcting for the effect of the elements on each other were sought. One method which involves the use of successive approximations was found satisfactory. The solutions used in establishing the working curves were made up so that the curves might be used for the analysis of urine directly.

These solutions were made by adding the desired amount of each element in the form of a rather concentrated solution of the chloride salt (chlorides being used owing to the insolubility of calcium sulfate) to a volumetric flask. To this mixture were then added sufficient hydrochloric and sulfuric acids so that after dilution the total concentration of the chloride ion would be 0.5 *N* and the concentration of the sulfate ion would be 0.5 *N* plus the sum of the hydrogen equivalents of the bases present. Sufficient cadmium chloride solution was then added so that the concentration of cadmium in the final volume would be 1.5 per cent, and the solution was diluted to volume. Thus to use the curves obtained with these solutions for urinary analyses it would be necessary to remove the phosphates from the urine, ash the filtrate with sulfuric acid until the excess acid was removed, dissolve the ash with 10 cc. of 5 *N* hydrochloric acid or its equivalent, add to this solution 5 cc. of 10 *N* sulfuric acid, and 10 cc. of a solution of cadmium chloride containing 15 per cent of cadmium, and dilute to 100 cc.

It was found that, in the quantities present, sodium and potassium had the predominant effects on the analyses. Thus, by this method, it was necessary to correct the sodium determinations for the presence of potassium only and vice versa. The magnesium estimations had to be corrected for both sodium and potassium. Calcium occurs in such small quantities in the urine that the authors have not been able as yet to get sufficiently accurate determinations of its concentration in synthetic solutions in its normal range of occurrence in urine.

Sodium and potassium may be estimated in the following manner: Working curves for each element are determined in the presence of the internal standard element and of the acids only. For a number of concentrations of each element, the relative intensities of the selected pairs of spectral lines, one of the element in question and the other of the internal standard element, are determined with varying concentrations of the interfering element. These relative intensities are then set up in table form for each of the elements. The analysis of a solution of unknown composition for sodium and potassium is then carried out as follows:

From the working curves, a first approximation of the concentration of each element present can be determined. Using the concentration, so determined, of each element as the concentration of the interfering element, a second approximation may be obtained for the concentration of each, by the use of their respective correction tables. This procedure is continued until the desired degree of precision is obtained. Usually the third approximation has been found sufficient.

After the concentrations of sodium and of potassium have been determined, that of magnesium may be obtained. Since the effects of sodium and of potassium on the relative intensity of the spectral lines of magnesium and of cadmium are almost equal for equal concentrations, this process is relatively simple. A table was prepared of the relative intensities of the magnesium and cadmium lines for several concentrations of magnesium and varying concentrations of sodium and potassium. The headings of the columns give the total concentration of sodium and potassium; under each are three subcolumns for ratios of sodium to potassium of 1 to 3, 1 to 1, 3 to 1. Thus after the concentrations of sodium and of potassium have been found, the experimentally determined ratio of the intensities of the spectral lines of magnesium and of cadmium may be applied to the proper column in the table and by interpolation the amount of magnesium can be obtained.

In Table I are given the representative precision and accuracy of the analyses of solutions of the class described above for sodium, potassium, and magnesium. Each spectrographic value was obtained from a single spectrum.

The errors in the analyses of unknowns of the character described by the method of successive approximations are, on the average, for sodium 2 per cent, for potassium 3 per cent, and for magnesium 2 per cent of the amounts of these elements present.

Acknowledgment

The writers wish to express their gratitude for a grant-in-aid from The Faculty Research Fund of the University of Michigan which enabled them to carry out this investigation.

Literature Cited

(1) Duffendack, Wolfe, and Smith, Ind. Eng. Chem., Anal. Ed., 5, 226–9 (1933).
(2) Thomson and Duffendack, *J. Optical Soc. Am.*, 23, 101–4 (1933).
(3) Twyman and Hitchen, *Proc. Roy. Soc.* (London), A133, 72–92 (1931).

Received January 10, 1935.

Determination of True Free Sulfur in Vulcanized Rubber

A Modification of the Thiocyanate Method

SYUKUSABURÔ MINATOYA,[1] ITIRÔ AOE, AND IDUMI NAGAI
The Electrotechnical Laboratory, Department of Communications, Tôkyô, Japan

For the determination of true free sulfur in vulcanized rubber a method has been proposed by Davis and Foucar, whereby the acetone extract of the original sample is treated with boiling alcohol and a small lump of potassium cyanide to convert the free sulfur into potassium thiocyanate and the latter titrated with a standard solution of silver nitrate. The application of this method, however, always meets with difficulty due to an excess of cyanide going into solution together with the thiocyanate formed, rendering the end point of the final titration indistinct. In this paper are given the results of experiments which were carried out by the present authors to overcome this difficulty through the successful separation of cyanide from thiocyanate by their difference of solubility in acetone.

IT IS WELL known that the acetone extract of vulcanized rubber contains not only free sulfur, but in some cases also certain sulfur compounds which can be converted into sulfate by oxidation. Davis and Foucar (*2*) proposed a method to determine the true free sulfur contained in acetone extract of vulcanized rubber, as follows:

> The sample of the rubber stock is extracted by acetone as usual, the acetone is driven off from the extract, and the dried mass is heated under a reflux condenser with alcohol and a small lump of potassium cyanide. The free sulfur contained in the extract is converted into potassium thiocyanate. The solid cyanide remaining is removed, and alcohol is driven off by evaporation. The residue is treated with water, and a slight excess of nitric acid and some iron alum are added. The characteristic blood-red coloration of ferric thiocyanate appears. Titration is then carried out with a standard solution of silver nitrate until the red color disappears.

In applying this method, however, difficulty was always found in that some of the potassium cyanide used for the conversion of free sulfur into the form of thiocyanate goes into solution, rendering the end point of the final titration indistinct. To eliminate this difficulty, a modification was proposed by Castiglioni (*1*), consisting of shaking the mixture of cyanide and thiocyanate with a 20 per cent solution of formaldehyde to convert the cyanide into glycolic acid and hexamethylene tetramine, neither of which is considered to have any influence upon the final titration.

The present authors, however, found that there was much left to be desired in Castiglioni's method, because sufficient cyanide always remained unreacted to render the end point of the titration indistinct, and they were led to the idea that it is better to eliminate the cyanide completely by the use of a suitable solvent. Acetone was found eminently suitable for this purpose. It does not dissolve potassium cyanide to any appreciable extent, but at 22° C. dissolves 17.2 per cent of its weight of potassium thiocyanate (*3*).

To determine the suitability of acetone for this purpose, the following preliminary experiments were carried out:

1. Test for the insolubility of potassium cyanide in acetone.
2. Test for the limit of amount of cyanide influencing the end point of the titration of thiocyanate by silver nitrate solution.
3. Test for the separation of cyanide from thiocyanate by means of acetone.

Preliminary Experiments

TEST FOR THE INSOLUBILITY OF CYANIDE IN ACETONE. Various quantities of an alcoholic solution containing 0.00048 gram of potassium cyanide per cc. were accurately measured into flasks. The alcohol was distilled off and each residue digested with 20 cc. of acetone by gentle warming on the water bath under the reflux condenser for 30 minutes. After complete cooling, the acetone was filtered through a filter paper as quickly as possible and the filter washed several times with cold acetone. The cyanide on the filter and that adhering to the inside wall of the flask were dissolved with water, the solutions united, and then titrated with 0.01 *N* silver nitrate, with a few drops of 10 per cent solution of potassium iodide as indicator.

For comparison, the experiments were also carried out with the original alcoholic solution of cyanide without digestion with acetone. The results are shown in Table I.

TABLE I. ANALYSIS OF POTASSIUM CYANIDE BEFORE AND AFTER DIGESTION WITH ACETONE

No.	KCN Alcoholic Solution Taken	KCN in Alcoholic Solution Taken	0.01*N* $AgNO_3$ Solution Used	KCN Found
	Cc.	*Gram*	*Cc.*	*Gram*
1 Digested with acetone	5.0	0.0024	3.6	0.0023
2 Digested with acetone	10.0	0.0048	7.1	0.0046
3 Digested with acetone	20.0	0.0096	14.1	0.0091
4 Not digested with acetone	10.0	0.0048	7.3	0.0047
5 Not digested with acetone	20.0	0.0096	14.6	0.0094

The differences between the results for samples 2 and 3 which were digested with acetone and 4 and 5 which were not, are so slight that they may be regarded as within the limit of experimental error.

TEST FOR THE LIMIT OF AMOUNT OF CYANIDE INFLUENCING THE END POINT OF THE TITRATION OF THIOCYANATE WITH THE SOLUTION OF SILVER NITRATE. Several 5-cc. portions of a 0.107 *N* aqueous solution of purified potassium thiocyanate were accurately measured into conical flasks, to which various amounts of a 0.1016 *N* aqueous solution of potassium cyanide were added. The contents of the flasks were diluted with water up to about 25 cc. and acidified with a few cubic centimeters of 30 per cent nitric acid. Titration was carried out with a 0.05 *N* solution of silver nitrate, using a 5 per cent solution of ferric nitrate as indicator. The results are shown in Table II.

The results in Table II show that no influence appeared until the content of cyanide reaches to the amount of experiment No. 6 or about 0.0005 mole of potassium cyanide in about 35 cc. of solution at the end of the final titration. Indistinctness of the end point was always observed when the concentration of cyanide exceeded this limit, increasing as the concentration of cyanide increased.

---

[1] Present address, Rubber Laboratory, Heisen Trading Co., Ogu, Tôkyô, Japan.

TABLE II. INFLUENCE OF POTASSIUM CYANIDE UPON THE TITRATION OF POTASSIUM THIOCYANATE WITH SILVER NITRATE SOLUTION

No.	0.107*N* KCNS Solution Taken	0.1016*N* KCN Solution Added	KCN in Solution Added	0.05*N* $AgNO_3$ Solution Used	End Point
	Cc.	*Cc.*	*Gram*	*Cc.*	
1	5.0	0	0	10.7	Distinct
2	5.0	1.0	0.0066	10.6	Distinct
3	5.0	2.0	0.0132	10.6	Distinct
4	5.0	3.0	0.0198	10.6	Distinct
5	5.0	4.0	0.0264	10.5	Distinct
6	5.0	5.0	0.0330	10.8	Somewhat indistinct
7	5.0	10.0	0.0660	10.8	Somewhat indistinct
8	5.0	15.0	0.0990	10.8	Somewhat indistinct

TABLE III. TITRATING THIOCYANATE WITH SILVER NITRATE AFTER SEPARATING CYANIDE BY MEANS OF ACETONE

No.	0.0996*N* KCNS Alcoholic Solution Taken	Solid KCN Added	0.05*N* $AgNO_3$ Solution Used	End Point
	Cc.	*Gram*	*Cc.*	
1	10.0	0	19.9	Distinct
2	10.0	About 1	19.8	Distinct
3	10.0	About 1	19.9	Distinct

TABLE IV. COMPARISON, THROUGH ESTIMATION OF PURE SULFUR, OF RESULTS OBTAINED BY MODIFIED AND OXIDATION METHODS

Method Used	Sample of Sulfur Taken	Time of Boiling with KCN	$BaSO_4$ Found	Sulfur Found
	Gram	*Min.*	*Gram*	%
New modified method	0.0100	30	....	99.4
	0.0100	40	....	99.4
	0.0100	60	....	99.4
Oxidation method	0.0100	..	0.0727	99.9
	0.0158	..	0.1149	99.9

TEST FOR THE SEPARATION OF CYANIDE FROM THIOCYANATE BY MEANS OF ACETONE. Ten cubic centimeters of a 0.0996 *N* alcoholic solution of purified potassium thiocyanate were accurately measured into a 100-cc. flask and diluted with alcohol up to about 50 cc. To this solution was added about 1 gram of potassium cyanide and the flask was heated under a reflux condenser for half an hour. The solution was evaporated to dryness, 30 cc. of acetone were added to the residue and the flask was shaken for a few minutes, while being gently warmed. On cooling, the contents of the flask were quickly filtered and washed several times with acetone. The filtrate was received in a 300-cc. flask and the acetone distilled off. The residue in the flask was dissolved in water, and 5 cc. of 30 per cent nitric acid were added. Titration was carried out with 0.05 *N* solution of silver nitrate, with 5 per cent solution of ferric nitrate as indicator. The results are shown in Table III.

These results show that acetone is a suitable solvent for removing cyanide and giving a distinct end point to the titration of thiocyanate with the solution of silver nitrate. From this fact, the method proposed by Davis and Foucar may be successfully modified and the difficulty of indistinct end point eliminated.

Procedure of Modified Method

Heat the dried acetone extract of vulcanized rubber for half an hour with 25 cc. of absolute alcohol and a small lump of potassium cyanide under a reflux condenser on a water bath, distill off the solvent, shake the dried mass with about 30 cc. of acetone for a few minutes, remove the undissolved residue by filtration, and wash with acetone. After evaporating the filtrate on the water bath, dissolve the dried substance with 50 cc. of water, add 5 cc. of 30 per cent nitric acid and a few drops of 5 per cent solution of ferric nitrate; shake the solution vigorously, and titrate with 0.1 *N* solution of silver nitrate until the blood-red coloration of ferric thiocyanate has disappeared.

Calculate the free sulfur content in original rubber sample as follows:

$$\text{Percentage of free sulfur} = \frac{0.003206 \times \text{cc. of } 0.1\,N\ AgNO_3 \text{ solution used for titration}}{\text{weight of sample (grams)}} \times 100$$

Application of Modified Method

ANALYSIS OF PURE SULFUR. To test the accuracy of the modified method, it was applied to the estimation of sulfur purified by means of sublimation in a glass retort, the purified sulfur being monoclinic crystal with a melting point of 119.0°–119.2° C. and leaving no trace of ash when incinerated. The results were also compared with those obtained by the ordinary oxidation method whereby the sample is oxidized into sulfate by means of bromine and fuming nitric acid. The results obtained by the two methods are almost concordant with each other, as shown in Table IV.

ANALYSIS OF RUBBER STOCKS. For exemplifying the application of the modified method, the rubber compounds given in Table V were prepared, and the ordinary oxidation method was also applied to the same samples for comparison. The results are shown in Table VI.

Table VI indicates that samples 1 and 3 give the same results by both methods within the limit of experimental error; on the other hand, sample 2 gives somewhat higher results by the oxidation method than by the modified method. This is probably due to the fact that the acetone extract of sample 2 contains an undervulcanized portion of the incorporated brown substitute containing some combined sulfur which can be oxidized to sulfate.

Applications were also made for the analysis of rubber insulation of a flexible joint wire manufactured by a Japanese cable maker, and a stamp mat employed in the post office. The results are shown in Table VII.

For the rubber insulation, the results of both methods are very close. For the stamp mat, however, the difference in results is rather remarkable.

Summary

The limit of quantity of potassium cyanide was determined as regards the interference with the end point of the titration of potassium thiocyanate with silver nitrate solution.

Acetone was found to be a suitable solvent for the separation of potassium cyanide from potassium thiocyanate.

TABLE V. COMPOSITION OF RUBBER STOCKS FOR ANALYSIS

No.	Composition					Vulcanization	
	Standard smoked sheet	Zinc oxide	Sulfur	D. P. G.	Brown substitute	Steam pressure	Time
						Kg./sq. cm.	*Min.*
1	100	5	5	1	0	2.81	30
2	100	5	5	1	5	2.81	30
3	100	5	40	1	0	4.22	300

TABLE VI. RESULTS OF ANALYSIS OF PREPARED RUBBER STOCKS

No.	Free Sulfur Found	
	New modified method	Oxidation method
	%	%
1	2.66	2.76
	2.66	2.77
2	1.17	1.30
	1.17	1.31
3	0.21	0.27
	0.21	0.28

TABLE VII. ANALYSIS OF FREE SULFUR IN COMMERCIAL RUBBER GOODS

Kind of Sample	Free Sulfur Found	
	New modified method	Oxidation method
	%	%
Rubber insulation	0.13	0.17
	0.13	..
Rubber stamp mat	1.01	1.20
	1.01	1.20

A new modified method was proposed for the determination of true free sulfur in vulcanized rubber, by the use of acetone to remove the cyanide which renders obscure the end point of the titration of thiocyanate with silver nitrate solution. The proposed method was applied to the analysis of pure sulfur and some rubber goods, and was ascertained to be accurate and easy to carry out, requiring no special apparatus.

Acknowledgment

The authors wish to express their sincerest thanks to W. Ogawa, head of the Fifth Division of the Electrotechnical Laboratory, Department of Communications, for his advice and encouragement given to this research and permission to publish this paper. They also acknowledge their great indebtedness to D. Nishida for his kind suggestions concerning the publication of the paper.

Literature Cited

(1) Castiglioni, A., *Z. anal. Chem.*, 91, 32 (1932); *Rubber Chem. Tech.*, 6, 412 (1933).
(2) Davis, C., and Foucar, L. J., *J. Soc. Chem. Ind.*, 31, 100 (1912); W. A. Caspari, "India-Rubber Laboratory Practice," p. 116, London, Macmillan Co., 1914.
(3) Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Auflage 5, Bd. 1, S. 729, Berlin, Julius Springer, 1923.

Received May 21, 1934.

Determination of the Fineness of Nitrocellulose by Dye Absorption

A. J. PHILLIPS, Picatinny Arsenal, Dover, N. J.

THE purification of nitrocellulose used in the manufacture of smokeless powder, lacquers, etc., customarily includes wet grinding in one or more types of beaters, for the purpose of mechanically liberating occluded acidity as well as reducing the particle size of the nitrocellulose. The control of the final particle size at the end of the beating process is of considerable importance in some cases.

When only one type of beater is used, practical control of the fineness may be obtained by the use of a simple settling test. However, different types of beaters have distinctly different actions. Any one type of beater may produce fibers of a type in which chopping, crimping, fibrillation, flattening, or crushing is the major action. Types of these fibers are shown in Figure 1. In addition, the type of fiber produced will vary according to whether wide or narrow blades are used in the beating engine. Because of this difference in beater effects, nitrocellulose subjected to beating in different types of machines may be of the same degree of fineness as judged by a settling test, but differ considerably in specific surface, which must be considered to be representative of true fineness.

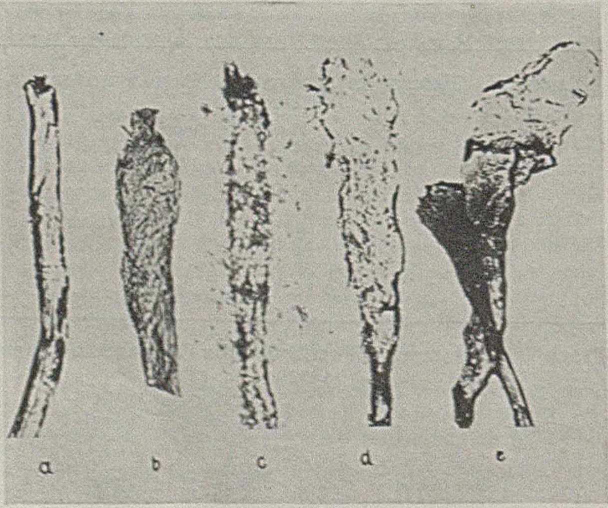


Figure 1. Types of Beaten Fibers

a, chopped; *b*, crimped; *c*, fibrillated; *d*, crushed; *e*, flattened

The specific surface is of importance with regard to the rate of purification in the boiling and poaching processes as well as in the rate of gelatinization by a solvent. It was therefore considered desirable to develop a test involving surface, in order that some numerical value might be given to the amount of specific surface produced, as beating progressed. Such a test would permit comparisons to be made between different types of beating engines and also furnish information with respect to the relation between consistency of pulp and type of beaten fiber obtained.

The method developed was the result of a large number of tests made to establish a relationship between increasing surface and increasing dye absorption. Tests by single dyeing, nonaqueous dyeing, and mordant dyeing methods were made, but no dye was found which did not penetrate the nitrocellulose and dye the fibers internally as well as externally. However, a satisfactory procedure was developed on the basis of the work of Pelet and Grand (*7*) and of Haller (*5*), who found that basic dyes may be quantitatively precipitated by acid dyes with the formation of weakly associated compounds.

If nitrocellulose fibers are dyed with either a basic or acid dye, washed, and treated with a dye of opposite sign, a definite amount of the latter is taken up as an insoluble precipitate on the surface of the dyed fibers. The amount of dye taken up should therefore be a measure of the specific surface.

Choice of Dyes

Since the excess of the first dye must be washed out of the fibers before the second dye is applied, it was thought that a choice might be made by dyeing nitrocellulose with different dyes, washing with water, and recording how many washes were necessary before a colorless filtrate was obtained. The dye or dyes which required the least washing would be most firmly fixed and thus tend to shorten the time required to carry out the complete process. These washing tests are recorded in Table I, and indicate that with regard to absence of bleeding Congo red, benzopurpurin, and acid violet negatively charged, and night blue positively charged, were superior to the rest.

The behavior of the dyes is in agreement with their molecular weights, the high molecular weight dyes being in the colloidal condition and tending to diffuse slowly. The low molecular weight compounds are designated as colloidal electrolytes and diffuse rapidly into or out of fibers.

TABLE I. WASHING OF DYED NITROCELLULOSE

Dye	Mol. Wt.	Charge	No. of Washings	Remarks
New fuchsin	337	+	4	Still bleeding
Tartrazine	468	−	2	Completely removed from nitrocellulose
Chrysoidine	248	+	4	Still bleeding
Martius yellow	234	−	2	Completely removed from nitrocellulose
Acid violet	757	−	3	Colorless filtrate
Naphthol yellow	390	−	3	Completely removed from nitrocellulose
Benzopurpurin	724	−	3	Colorless filtrate
Alkali blue		−	2	Colorless filtrate
Methylene blue	319	+	4	Still bleeding
Congo red	696	−	3	Colorless filtrate
Malachite green	364	+	4	Still bleeding
Night blue	575	+	3	Colorless filtrate
Crystal violet	443	+	4	Colorless filtrate
Methyl violet	373	+	4	Still bleeding

The first dye chosen was the negatively charged Congo red, because of its peculiar behavior in dyeing cotton fibers. It has a greater affinity for the lumen than for the walls of the fiber and tends to concentrate at the center rather than at the surface of the hair. Bright (*3*) recommends Congo red for distinguishing between damaged and undamaged fibers because it penetrates the damaged portion and stains the lumen deeply. This was exactly the property desired, since the concentration of Congo red at the center tends to prevent the penetration of an oppositely charged dye to the same region.

A study of Knecht and Hibbert's (*6*) titration methods, using titanium trichloride, showed that some dyes required back-titration, some a boiling temperature, and others the addition of alcohol, sodium tartrate, Rochelle salt, etc., while methylene blue alone could be titrated directly at room temperature. In addition it was found that the bleeding of methylene blue, as shown in Table I, could be prevented by washing the dyed fibers with a buffer solution instead of pure water. Methylene blue was therefore chosen as the positively charged dye to be used.

PREPARATION OF DYE AND BUFFER SOLUTIONS. For the dye solutions, 0.5 gram of Congo red or methylene blue was dissolved in 150 cc. of water, brought to a boil, cooled to room temperature, and centrifuged for 10 minutes at 1500 r. p. m. The supernatant liquid was decanted and made up to 500 cc. The methylene blue contained much insoluble matter and the solution was therefore less than 0.1 per cent in strength.

For the buffer solutions, 37.875 grams of powdered sodium tetraborate were made up to 1 liter in boiled distilled water, and 10.9618 grams of granular C. P. sodium chloride and 46.515 grams of crystallized boric acid were dissolved in boiled distilled water and made up to 1 liter. Five cubic centimeters of the borax solution added to 5 cc. of the boric acid–sodium chloride solution gave a mixture having a pH of 7.9, as tested colorimetrically with LaMotte color standards, using phenol red as an indicator.

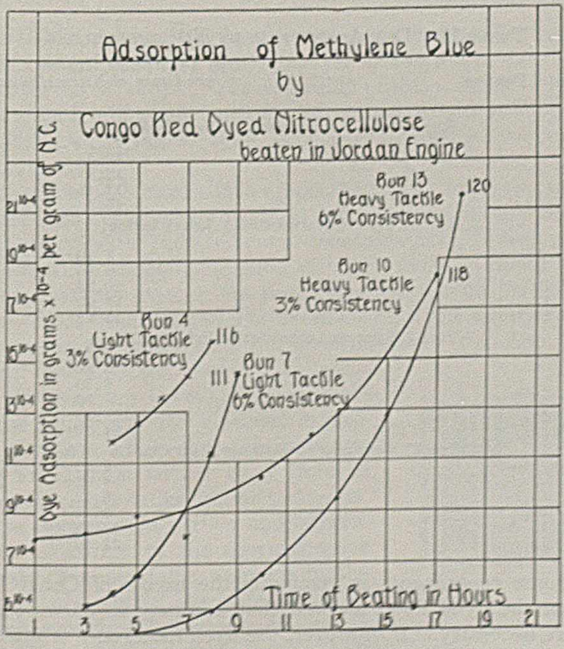


FIGURE 2

FIGURE 3. PHOTOMICROGRAPH OF RUN 4

Light tackle, 3 per cent consistency, 150 ×

Ten grams of the mixed solution were evaporated to dryness in a glass capsule and dried for 2 hours at 140° C. From the weight obtained, the necessary dilution was made to secure a 3 per cent solution.

STANDARDIZATION OF TITANIUM TRICHLORIDE SOLUTION. The standardization was carried out in an atmosphere of carbon dioxide, according to the method of Knecht and Hibbert (*6*). The following value was found:

1 cc. of $TiCl_3$ = 0.001426 gram of methylene blue

Experimental Procedure

Three grams of nitrocellulose were placed in a 250-cc. beaker containing 150 cc. of a borax–boric acid–sodium chloride buffer solution with a pH of 7.9 and a salt concentration of 3 per cent, soaked, and stirred until all the lumps are broken up. Five cubic centimeters of 0.1 per cent Congo red solution were added, the beaker was placed in a boiling water bath, and the contents were mechanically stirred and heated for exactly 15 minutes. The beaker was then removed from the bath and the contents were filtered through a platinum Gooch crucible. The nitrocellulose was removed from the crucible, placed in the beaker, and washed four times by decantation with 40-cc. portions of the buffer solution at 50° to 60°. A final 40-cc. portion was used to transfer the nitrocellulose back to the crucible and wash out the beaker. The crucible was sucked dry with vacuum, the contents were transferred to the original beaker, and 150 cc. of buffer solution added, a portion of the solution being used to clean out the platinum crucible. Then 12 to 15 cc. of 0.1 per cent methylene blue solution were added, heating and stirring carried out for 15 minutes, and the contents of the beaker filtered through the crucible, which was sucked dry. The filtrate was transferred to a 250-cc. flask, acidulated with 10 cc. of concentrated hydrochloric acid, saturated with carbon dioxide, and titrated with titanium trichloride solution. A blank without Congo red was run on the nitrocellulose and buffer solution.

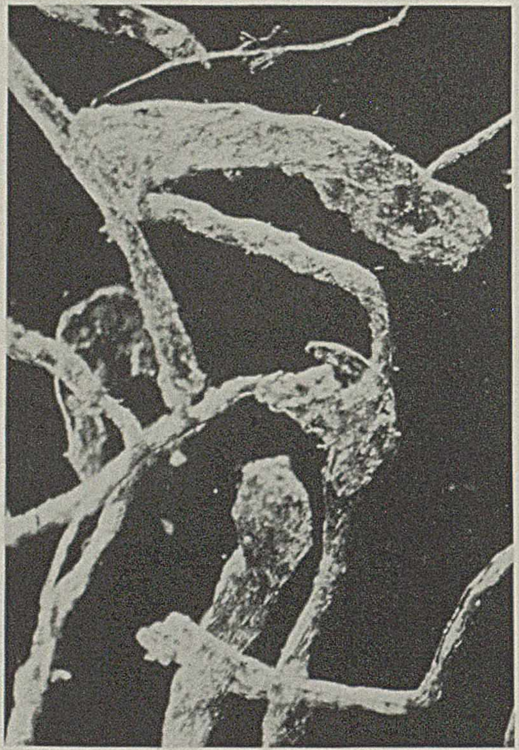


Figure 4. Photomicrograph of Run 10

Heavy tackle, 3 per cent consistency, 150×

The amount of methylene blue absorbed on the Congo red dyed fibers was determined as follows:

Blank titration: 150 cc. of buffer solution boiled with 3 grams of nitrocellulose, filtered, 15 cc. of methylene blue solution added, and titrated with titanium trichloride.

$0.011426 \times$ cc. $TiCl_3$ (titration) = methylene blue in 15 cc. $= A$

$A/15$ = methylene blue in 1 cc. $= B$

$B \times$ cc. methylene blue added to unknown = total methylene blue $= C$

$0.001426 \times$ cc. $TiCl_3$ used for titrating excess methylene blue $= D$

$\frac{C - D}{3}$ = amount of methylene blue absorbed by 1 gram of nitrocellulose

Dyeing from Buffered Solutions

It has been pointed out by Birtwell, Clibbens, and Ridge (*2*) and by Bancroft (*1*), that dye absorption varies very markedly with the pH of the solution. Since nitrocellulose is beaten under conditions in which there may be absorption of either acid or alkali, the necessity for running the test in a solution of definite pH becomes apparent. Again, Congo red is negatively charged and consequently has but little affinity for nitrocellulose which is likewise negatively charged in water. But if a soluble inorganic cation is present, such as the sodium ion of sodium chloride, the positive charge of the sodium ion partially neutralizes the negative charge on the nitrocellulose, causing the negatively charged dye to be more readily absorbed and more firmly fixed. Finally with respect to evenness of dyeing, it was found that sodium chloride, sodium acetate, and sodium sulfate increased the depth of shade on the fibers without promoting evenness. Night blue was distinctly worse, with respect to evenness of dyeing, than methylene blue, crystal violet, or methyl violet. Six citric acid–sodium phosphate buffer solutions were prepared according to directions by Clark (*4*) having pH values of 2.1, 2.9, 4, 4.9, 6, and 6.8 and used in the dyeing tests. It was found that as the pH of the solutions changed from acid to neutral to alkaline conditions, the depth of color and uniformity increased up to a pH of 6. Above this figure there was no gain in evenness of dyeing while the depth of color continued to increase.

Microscopic Examination for Evenness of Dyeing. Examination of the fibers with a dark-field condenser was unsatisfactory, as the fibers usually appeared to be of a brilliant white color. Examination with reflected light in a metallurgical microscope showed no traces of color, but a black fiber. Transmitted light with the fibers air-mounted gave poor results and the best results were secured by immersion in a liquid of 1.52 refractive index. An 8-mm. objective was used with a 15 × eyepiece, the slide being oiled to the condenser with cedar oil.

Filtration and Washing of Dyed Nitrocellulose. In the first tests a porcelain Gooch crucible was used for filtration of the nitrocellulose after dyeing. It was found, however, that very finely divided nitrocellulose in a colloidal condition was being carried through into the filtrate and coagulated when the solution was acidified. A glass crucible with a porous, fritted glass bottom was tried but absorbed dye so strongly that it became necessary to wash it with acid after each filtration. In addition, it became choked with finely divided nitrocellulose and filtration was very slow. Recourse was made to a Munroe platinum Gooch crucible, as described by Snelling (*8*). This proved to be efficient and rapid.

Effect of Temperature

It was known from the literature that the best results in dyeing with Congo red were secured at boiling temperature, but conflicting statements were found as to what temperature was best for methylene blue. Accordingly, a series of tests at different temperatures was run with methylene blue in a buffered solution, the excess dye being titrated with titanium trichloride. The results follow:

Temperature	30°	50°	70°	80°	90°
$TiCl_3$ required for excess dye, cc.	2.4	2.2	1.5	1.1	0.7

This test indicates that under the same conditions with regard to concentration and pH of the solution, a larger amount of dye is deposited upon the fibers as the temperature of the dye solution is raised.

Table II. Dye Adsorption by Nitrocellulose

Time of Beating *Hours*	Dye Adsorption, Grams $\times 10^{-4}$ per Gram of Nitrocellulose
	Run 4, 3 per cent consistency, light tackle
4	11.7
5	12.5
6	13.4
7	14.46
8	15.7
	Run 10, 3 per cent consistency, heavy tackle
1	7.85
3	8.20
5	8.90
10	10.35
12	11.92
17	18.28
	Run 7, 6 per cent consistency, light tackle
3	5.22
4	5.80
5	6.50
7	7.96
8	11.20
9	14.50
	Run 13, 6 per cent consistency, heavy tackle
5	4.10
7	4.92
10	6.62
13	9.35
15	12.78
18	21.40

Some experiments in removing the excess of Congo red from the dyed fibers showed that as many as 36 washings were necessary. If, however, the dyed material was washed with the buffer solution, five washings with a total of 200 cc.

were sufficient to remove the excess dye. It was also found that if the buffer solution was used at a temperature higher than that employed for dyeing, the dye would bleed from the cotton. A temperature of 95° C. for dyeing followed by washing with buffer solution at a temperature of 50° to 60° C. was finally adopted.

Relation between Surface and Dye Adsorption

The results of dye adsorption tests on nitrocellulose beaten in a Jordan engine are recorded in Table II and shown in the form of adsorption curves in Figure 2. Two consistencies or slurries were used, 3 and 6 per cent, and two sets of beating blades in the engine, narrow blades (light tackle) and wide blades (heavy tackle).

The fineness of each batch, as shown by settling tests in a 250-cc. graduated cylinder, is shown on Figure 2, the smaller the number the finer the material. Three of the samples showed approximately the same fineness—116, 118, and 120—but differed widely in their dye adsorptions. Microscopic examination of the 3 per cent consistency material, as shown in Figures 3 and 4, showed the reason for the difference in dye adsorption and indicated the superiority of such a test over the usual fineness test.

The difference in the development of specific surface for dye adsorption is due to the fact that when nitrocellulose is beaten, the pulp becomes thin and watery with the passage of time. The beating rolls cannot be set down rapidly and beating efficiency drops off. This is more noticeable with the thin than with the thick consistencies, which explains why a 6 per cent consistency as shown in run 13 develops a greater surface for dye adsorption than a 3 per cent consistency beaten for approximately the same length of time, as in run 10. The fineness test does not indicate this difference, the microscope discriminates but furnishes no quantitative information, while the dyeing test yields quantitative comparisons.

Summary

A double dyeing method for estimating the increase in specific surface of beaten nitrocellulose is described. The method involves dyeing the fibers with a negatively charged dye (Congo red) and the deposition of a positively charged dye (methylene blue) at and near the surface of the Congo red dyed fibers. Dyeing is carried out in a borax–sodium chloride–boric acid buffer solution of 3 per cent concentration, with a pH of 7.9, at 95° C. The dyeing tests, which were confirmed by microscopic analysis, indicate that products not only from different beaters but from the same beater may be differentiated. Such differentiation cannot be made by the standard fineness test.

Literature Cited

(1) Bancroft, W. D., Sixth Colloid Symposium Monograph, p. 73, New York, Chemical Catalog Co., 1928.
(2) Birtwell, C., Clibbens, D. A., and Ridge, B. P., *J. Textile Inst.*, 14, 297 (1923).
(3) Bright, C. G., *Ibid.*, 17, 396 (1926).
(4) Clark, W. M., "Determination of Hydrogen Ions," 2nd ed., p. 116, Baltimore, Williams and Wilkins Co., 1923.
(5) Haller, R., *Zeit. Chem. Ind. Kolloide*, 11, 110–15 (1912), et seq.
(6) Knecht, E., and Hibbert, E., "New Reduction Methods in Volumetric Analysis," 2nd ed., p. 101, N. Y., Longmans Green & Co., 1925.
(7) Pelet and Grand, L., *Rev. gén. mat. color.*, 11, 225 (1907).
(8) Snelling, W. O., *J. Am. Chem. Soc.*, 31, 456 (1909).

RECEIVED August 23, 1935. Published by permission of the Chief of Ordnance, U. S. War Department.

Application of the Spectrograph to the Determination of Carbon in Steel

FREDERIC H. EMERY WITH HAROLD SIMMONS BOOTH, Western Reserve University, Cleveland, Ohio

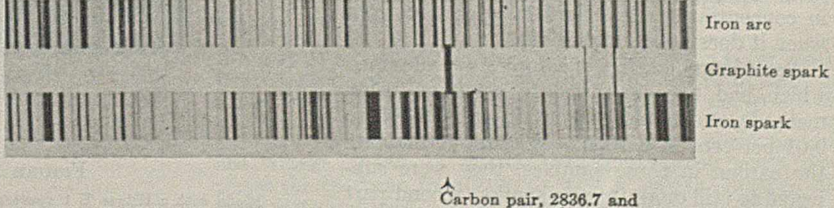
CHEMICAL analysis by the emission spectrum has been successful in the determination of the lesser metallic constituents of alloys. The extension of this method to the determination of small amounts of carbon would result in considerable saving in time, especially as against vacuum fusion methods.

To accomplish quantitative spectrographic analysis, the wanted element must be made to produce light in amounts which vary with the element's concentration. Before an element will emit light, its outer electrons must be raised to higher quantum states. As the charge on the nucleus increases from lithium's three to fluorine's nine, the number of electrons in the outer quantum level increases from one to seven; hence outer electrons in negative elements are enveloped by a more intense field than outer electrons in positive elements. It is therefore easier to force an electron farther away from its nucleus in elements like lithium and boron, than in elements like carbon and oxygen.

The problem of the spectrographic analysis of nonmetallic elements in the presence of metallic elements is one of putting enough potential into the arc or spark flame to excite atoms having their outer shells subjected to powerful nuclear fields. The difficulty is further increased by the probability that the metallic elements will do most of the work of current transfer in the spark flame, at a potential so low that the outer electrons of the nonmetals will not be disturbed.

The internal standards method of Gerlach and Schweitzer (*4*) has been successfully applied to the quantitative analysis of practically all of the minor constituents of steels except carbon (*10*).

The authors applied the same method to the determination of carbon in steel. The relative line intensities of carbon and iron were determined by the logarithmic wedge sector (*9, 11*), rotated before the slit of a Hilger E 1 Littrow quartz



Carbon pair, 2836.7 and 2837.6 Å.

FIGURE 1

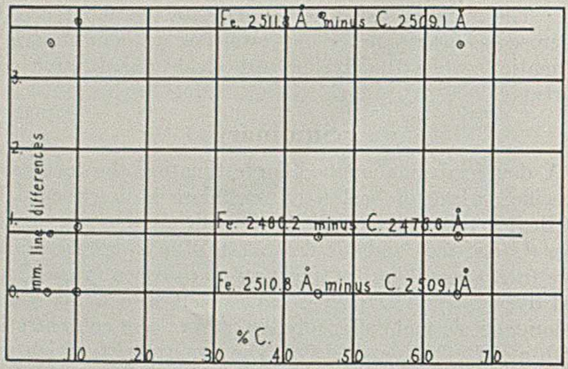


FIGURE 2. RELATION BETWEEN PERCENTAGE OF CARBON IN STEEL AND DIFFERENCE IN LENGTH OF SELECTED IRON AND CARBON WEDGE SPECTRUM LINE PAIRS

spectrograph. The instrument was set to take the region between 2250 and 2850 Å. According to Kayser and Konen (*6*), the following lines are given by carbon in the ultraviolet:

Å.[a]	Estimated Intensity	
	Spark	Arc
2992.6	1	–
2837.6	3	1
2836.7	7	1
2747.3 2746.5	3 diffuse	–
2512.0	5	1
2509.1	4	1
2478.6	10	10
2296.8	8	1

[a] The carbon line 2641 Å. given by Kayser (*5*) and the carbon lines 2547.8, 2402.4, and 2401.77 Å. given by Fowler (*3*) were not found in a graphite spark spectrogram.

All these lines appear in a graphite spark, but only three were found in sparks from samples of steels: at 2296.8, 2478.6, and 2509 Å. The line at 2296.8 Å. coincides with a faint iron line, which is of constant intensity and so faint that it will not interfere with the use of this carbon line at 2296.8 Å. for quantitative analysis of carbon in steel. The carbon line at 2478.6 is interfered with by the Geisler tube oxygen line at 2478.5 Å. Oxygen will not interfere, provided the oxygen lines at 2445.5 and 2433.6 Å. are not visible. The carbon line at 2509.1 Å. has no listed interferences. Although unmarked iron lines are very close, the carbon II pair 2836.7 and 2837.6 Å. are shown by the comparison spectrum in Figure 1 to be absent from the iron spark. This is remarkable, since the carbon III line at 2296.8 Å. is easily seen.

A series of steel samples varying in carbon content from 0.05 to 1.02 per cent was subjected to various combinations of sparking and arcing conditions. These experiments (Table I) amply demonstrate that carbon in steel shows no concentrational variation by ordinary spectrographic methods (Figures 2 and 3). The spectrograph frequently brings out variations in concentrations less than 0.05 per cent, even when it does not in higher ones.

Accordingly a series of samples was obtained which had been analyzed by vacuum fusion methods, and found to contain from 0.005 to 0.01 per cent of carbon. In order to activate the carbon in these samples, they were subjected to still more intense sparks (second part of Table I). The 0.005 per cent carbon sample, which shows an increase in carbon line in-

TABLE I. SPECTROGRAPHIC DETERMINATION OF CARBON IN STEEL

Method	Conclusions
Carbon content 0.05 to 1.02 per cent	
Equal weights of wires of varying carbon content were completely burned in 200 seconds in a 3-ampere arc. Upper electrode negative and of magnesium. Lower electrode positive and a measured length of the sample. Upper electrode made large enough so that it did not melt or burn.	Intensity of carbon lines relative to iron lines varied solely with the gap length, becoming weaker with longer gaps. No concentrational variation.
Spark between two electrodes of the sample. Gap 1.5 cm.; 1-kw. 15,000-volt transformer; 10-microhenry inductance; 0.009- to 0.036-microfarad capacity. Resistance up to 50 ohm.	Intensity of carbon lines relative to iron lines decreased with increasing inductance and resistance. Increasing capacity increases intensity of carbon lines relative to iron lines. No concentrational variation.
Carbon content 0.005 to 0.01 per cent	
Tesla coil spark 1-kw. 15,000-volt transformer, 0.018-microfarad capacity, fed primary of Tesla coil. Sample attached to secondary with 0.009-microfarad shunt, 2.5-cm. gap.	Long exposures (15 to 30 minutes) required. Carbon at 2478.6 Å. and oxygen at 2445.5 and 2433.6 Å. stronger than iron lines. No concentrational variation between 0.005 and 0.1 per cent carbon.
Aperiodic spark 1-kw. 15,000-volt transformer, 0.009-microfarad condenser. Inductance in oscillating circuit equaled that of leads which were about 30 cm. long. 2-cm. gap.	Spectra similar to that from Tesla coil, but more intense. Carbon line at 2478.6 Å. shows concentrational variation relative to iron lines. The line at 2478.6 Å. is stronger in the sample having the lowest amount of carbon (0.005 per cent).
Aperiodic spark in argon Same electrical conditions as above. Spark atmosphere consisted of 99.8 per cent argon which had been scrubbed with BaO, NaOH, and phosphorus pentoxide.	Carbon lines stronger relative to iron lines than by any other method. Wandering of spark makes equivalent exposures impossible.

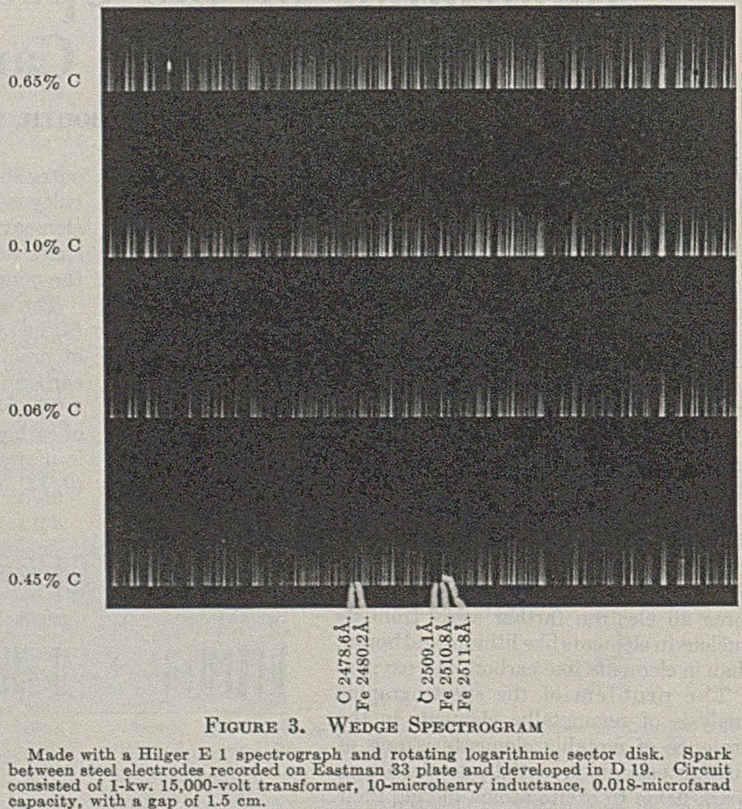


FIGURE 3. WEDGE SPECTROGRAM

Made with a Hilger E 1 spectrograph and rotating logarithmic sector disk. Spark between steel electrodes recorded on Eastman 33 plate and developed in D 19. Circuit consisted of 1-kw. 15,000-volt transformer, 10-microhenry inductance, 0.018-microfarad capacity, with a gap of 1.5 cm.

tensity, had been treated with iron oxide and is higher in oxygen. An oxygen line appears at 2478.5 Å., and increases the intensity of the carbon line from which it is not separated. The oxygen lines at 2445.5 and 2433.6 Å. also show an increase in intensity as compared with higher carbon samples. The aperiodic spark is therefore capable of detecting concentrational variations in oxygen content, but these variations must be much greater than those normally experienced in steels. A sample of iron containing less than 0.005 per cent of carbon and low oxygen was made available. This sample was of high purity, and had been treated with wet hydrogen at 1495° C. for 61 hours. It probably contained about 0.001 per cent of carbon. Using the aperiodic spark, this sample was compared with a sample of steel containing 0.1 per cent of carbon. The carbon lines in the two samples are of equal intensity.

Conclusions

Although the aperiodic spark detects gross changes in oxygen content, it apparently does not have potential enough to bring out either small or large variations in carbon content. The problem of the spectrographic analysis of nonmetallics in metals may be solvable by using excitation which will ionize a high percentage of the metal atoms. Means of more intense excitation than the aperiodic spark are available in the exploded wire (*1*), the vacuum spark (*2*), and electric furnace arc (*7*, *8*) methods.

Acknowledgments

This work was made possible by a grant given by the National Smelting Co., Cleveland, Ohio, and was carried out on this company's spectrographic equipment. The following companies donated analyzed steel samples: The Cleveland Twist Drill Co.; Newburgh Works, American Steel and Wire Co.; and the Illinois Steel Co. Low-carbon samples were obtained from the Naval Research Laboratory and the Carnegie Institute of Technology.

Literature Cited

(1) Anderson, *Astrophys. J.*, 51, 37 (1920).
(2) Baly, E. C. C., "Spectroscopy," 3rd ed., Vol. II, p. 124, London, Longmans Green and Co., 1927.
(3) Fowler, A., *Proc. Roy. Soc.*, A105, 299 (1924).
(4) Gerlach and Schweitzer, "Foundations and Methods of Chemical Analysis by the Emission Spectrum," London, Adam Hilger, 1932.
(5) Kayser, H., "Tabelle der Hauptlinien der Linienspektra aller Elemente," Berlin, Julius Springer, 1926.
(6) Kayser and Konen, "Handbuch der Spectroscopie," Vol. 8, Part 1, p. 274, Leipzig, S. Hirzel, 1933.
(7) King, *Astrophys. J.*, 37, 119 (1913).
(8) King, *Ibid.*, 38, 315 (1913).
(9) Scheibe, G., and Neuhäusser, A., *Z. angew. Chem.*, 41, 1218 (1928).
(10) Twyman and Fitch, *J. Iron Steel Inst.*, 88, 289 (1930).
(11) Twyman, F., and Simeon, F., *Trans. Optical Soc.*, 31, 169 (1930).

RECEIVED March 24, 1934.

Spectrographic Microdetermination of Zinc

Preliminary Note

LEWIS H. ROGERS, Florida Agricultural Experiment Station, Gainesville, Fla.

INTEREST of biologists in the physiological effects of small amounts of zinc on plants and animals has prompted a study of the applicability of spectrography to the quantitative determination of this element.

For the spectrographic detection of zinc, various workers have used three lines in the zinc spectrum—namely, those occurring at 4810.534, 3345.0, and 2138.5 Å. Early in this investigation, it was found that zinc was not detected in many of the samples which were examined when only the first two of these lines were used, because they are not sufficiently sensitive to give an observable density on the photographic plate with very small concentrations of zinc. The 2138.5 Å. zinc line, however, proved to be quite sensitive. Since calcium and strontium are common constituents of plant materials, a spectrograph with good dispersion is necessary to separate the 4810.534 Å. zinc line from the 4811.86 Å. strontium line, and the 3345.0 Å. zinc line from the 3344.49 Å. calcium line.

For the 2138.5 Å. zinc line to register on the photographic plate, it is necessary to sensitize it in some manner. A plate sensitized by spreading ordinary mineral oil over the emulsion is satisfactory, but the Eastman spectroscopic plate, Type III-O, with ultraviolet sensitization is more convenient.

Of the various methods of quantitative spectrum analysis, it was decided to follow that of Nitchie and Standen (*2*), substituting a nonrecording microphotometer for the recording instrument used by them.

Procedure

A base, free of zinc, and approximating a representative plant ash, was synthesized as follows (after first running a qualitative spectrographic analysis on the ingredients to insure absence of zinc): three grams of H_3PO_4, 3.5 grams of Na_2CO_3, 5 grams of $MgCl_2 \cdot 6H_2O$, 10 grams of $CaSO_4 \cdot 2H_2O$, and 32 grams of K_2CO_3 were dissolved in water where possible, then evaporated while stirring, to insure homogeneity. After drying, the mixture was thoroughly pulverized.

It was decided to use tellurium as the "internal standard" of the method, since a sensitive line of tellurium occurs at 2143.0 Å. Accordingly, 5 grams of $H_2TeO_4 \cdot 2H_2O$ were dissolved in 1 liter of water, filtered, and added to all samples and standards in the proportion of 1 ml. of solution to 1 gram of sample.

For a stock zinc solution, 0.8797 gram of $ZnSO_4 \cdot 7H_2O$ was dissolved in 1 liter of water. Five milliliters of this solution were added to 1 gram of the synthetic ash, plus 1 ml. of the tellurium solution, dried, then thoroughly pulverized and mixed to give a standard containing 0.1 per cent of zinc. Other mixtures, prepared by adding 5 ml. of the proper dilution of the stock zinc solution and 1 ml. of the tellurium solution to 1-gram portions of synthetic ash, gave standards containing 0.05, 0.01, and 0.005 per cent of zinc.

Each standard was spectrographed in quintuplicate under the following conditions:

About 20 mg. of the standard were placed in the lower (positive) electrode of Acheson graphite rod 0.63 cm. (0.25 inch) in diameter and 3.8 cm. (1.5 inches) long, bored to a depth of 0.32 cm. (0.125 inch) with 0.436-cm. (0.172-inch) drill, and burned to completion with an arc drawing 9 amperes and a direct current line voltage of 125. A quartz Leiss spectrograph which disperses the spectrum from 2100 to 8000 Å. on one 22.5-cm. (9-inch) plate was used. A rotating sector wheel with adjustable aperture was inserted between the arc and the slit of the spectrograph to reduce the exposure 75 per cent.

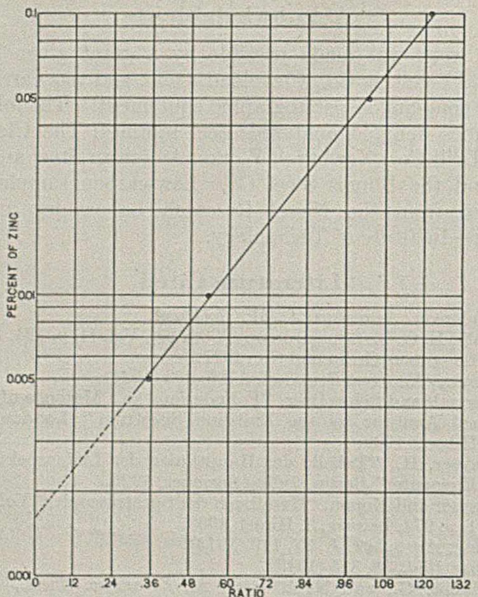


Figure 1. Calibration Curve

The spectrograms were photometered on a Bausch & Lomb density comparator. The ratios of the densities of the 2138.5 Å. zinc line and the 2143.0 Å. tellurium line for the various standards thus determined were averaged and plotted on semi-logarithmic coördinate paper with the result shown in Figure 1.

Preparation of Samples. In preparing the plant samples for analysis, they were first dried, and then ashed at less than 450° C. in platinum, at which temperature, according to Thompson (*3*), zinc is not volatilized. Tellurium solution was added to the ash, then it was dried, pulverized, mixed thoroughly, and spectrographed in quintuplicate under the same conditions as given for the standards.

Time for Analysis. Neglecting the time required for ashing the samples, adding tellurium solution, drying, and homogenizing, 2 hours are ample for making ten spectrograms—i. e., two samples in quintuplicate—developing, fixing, washing, and drying the plate, and an additional 1.5 hours are sufficient for photometering and conversion of the ratios to percentages.

Limits of Method

The upper limit of the method is not 0.1 per cent although at about 1 per cent the 2138.5 Å. zinc line begins reversing; hence for percentages greater than this, other lines would have to be used, probably that line occurring at 4810.534 Å. The lower limit is not necessarily 0.005 per cent, for assuming that the calibration relation holds below this concentration, extrapolation of the calibration curve would indicate sensitivity to about 0.002 per cent.

Interference

When appreciable iron is present in the sample, an iron line may occur at 2138.587 Å., which would be unresolved by most spectrographs from the 2138.5 Å. zinc line and thus lead to erroneous results. Preliminary tests indicate that from 0.5 to 1 per cent of iron is required to give an observable density of this iron line on the photographic plate. Burns and Walters (*1*) assign an intensity of three to this iron line, and to another iron line at 2132.011 Å. they assign an intensity of four. In this work, therefore, the plates were always examined for the presence of the iron line at 2132.011 Å., and since it has never appeared in any spectrogram of any sample, the possibility of an iron interference has been neglected. The study of this interference and the development of a method to permit allowance for the presence of iron is to be undertaken (probably using the ratio of intensities between the 2132.011 Å. iron line and the 2143.0 Å. tellurium line).

Accuracy

The large deviation from the mean of the last analysis in Table I is due either to lack of homogeneity of the sample or to the use of the extreme end of the calibration curve. The maximum deviation from the mean in most cases is less than one part in five. Handling all samples and standards in solution will probably reduce this deviation. Further study of the method is proposed to determine probable error. The influence (if any) of synthetic ashes of different composition is also to be studied.

Table I. Quintuplicate Analyses of Several Samples

Ratio	Per Cent
0.471	0.0078
0.438	0.0070
0.415	0.0065
0.415	0.0065
0.451	0.0073
	Av. 0.0070 ± 0.0008
0.73	0.019
0.73	0.019
0.71	0.017
0.69	0.016
0.73	0.019
	Av. 0.018 ± 0.002
1.22	0.10
1.12	0.07
1.24	0.11
1.22	0.10
1.16	0.08
	Av. 0.09 ± 0.02

Summary

A quantitative spectrographic method for determining zinc in plant material when present in concentrations between 0.1 and 0.005 per cent, employing tellurium as an internal standard, has been studied. Iron interferes with the determination when present in concentrations of about 1 per cent, and a procedure for making allowance for this interference is suggested. The maximum deviation of the analyses from the mean in most cases is less than one part in five. Further study of the method is proposed to determine the probable error and influence of other factors on the procedure.

Literature Cited

(1) Burns, K., and Walters, F. M., *Pub. Allegheny Observatory Univ. Pittsburgh*, 6, No. 11, 159–211, especially 180 (1929).
(2) Nitchie, C. C., and Standen, G. W., Ind. Eng. Chem., Anal. Ed., 4, 182–5 (1932).
(3) Thompson, P. K., *J. Ind. Hyg.*, 7, 358–70 (1925).

Received June 7, 1935. Based upon a part of a Master of Science thesis submitted to the graduate council of the University of Florida, August, 1934, which was carried out under the direction of R. C. Williamson, University of Florida, and L. W. Gaddum, Florida Agricultural Experiment Station.

Correction

In the article on "Constituents of Pyrethrum Flowers" by Haller and Acree [Ind. Eng. Chem., Anal. Ed., 7, 343 (1935)] an error was made in citing the page in the first of the literature references given. The correct reference is Butt, C. A., J. Ind. Eng. Chem., 7, 130 (1915).

The Determination of Small Quantities of Selenium in Sulfur

GEORGE G. MARVIN WITH WALTER C. SCHUMB

Massachusetts Institute of Technology, Cambridge, Mass.

THE determination of very small quantities of selenium in various materials is becoming of increasing importance, as shown by recent articles on the determination of small amounts of selenium in pyrites, shales, soils, and agricultural products (*2*, *4*, *6*). In addition, the appearance of selenium in the 18-8 type steels in small percentages makes particularly desirable a reliable method for the determination of small amounts of this element. In this paper, the determination of small quantities of selenium in sulfur is reported over the range from 0.1 to 0.001 per cent. Smaller percentages could no doubt be determined by the use of a larger sample for analysis, but the range below 0.001 per cent was not investigated in the present work. A later communication will describe a convenient method for the determination of selenium in steels.

The present method was developed as a result of an investigation of Beattie, Benedict, and Blaisdell upon the intercomparison of the international and thermodynamic temperature scales from 0° to 444.6° C. (*1*). Sulfur vapor was used in this investigation, and it became necessary to know the amount of selenium present, if any, because of the effect upon the boiling point of sulfur. The method, as developed, requires a minimum amount of apparatus, and an analysis may be completed in about 3 to 5 hours; the detection and quantitative determination of 1 mg. of selenium in 100 grams of sulfur are possible. The method is applicable to all kinds of sulfur and sulfur-containing materials; arsenic and tellurium cause no interference; and large samples may be used, thereby allowing the determination of small percentages.

Most previous methods for the detection of selenium in sulfur have required the complete solution of the sulfur (*5*), which necessarily limits the size of the sample and therefore limits the determination of very small percentages of selenium. The only other method in the literature which is similar to the one given here and which employs a similar apparatus is a rather long and complicated procedure, with expensive equipment, and involves the use of concentrated solutions of potassium cyanide (*3*). Furthermore, this method has been found to be of questionable accuracy.

Experimental

In the proposed method, the sample is burned in a 45-mm. Pyrex glass tube 60 cm. (2 feet) long, and the selenium is caught in a suitable solid filtering medium and then converted into selenium dioxide, which is titrated by the iodometric method:

$$SeO_2 + 4HI \rightarrow Se + 2H_2O + 2I_2$$
$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

The sulfur used was the purest obtainable grade of sublimed sulfur. The selenium dioxide used was prepared from crude selenium dioxide by digestion with concentrated nitric acid, filtering, evaporating, crystallizing, and then subliming to give clear crystals of selenium dioxide. A standard solution of selenious acid (containing about 1 mg. of selenium per cc.) was prepared from this selenium dioxide, and standardized iodometrically against a carefully prepared solution of thiosulfate which had been checked against Bureau of Standards arsenic trioxide. In addition, the selenious acid solution was standardized by precipitation as selenium from a concentrated hydrochloric acid solution by means of sulfur dioxide. The two methods of standardization checked each other.

Tellurous acid solution was prepared by dissolving crystalline tellurium in concentrated sulfuric acid. This solution was diluted to a definite volume and standardized gravimetrically by precipitation of tellurium by means of sulfurous acid and hydrazine.

In order to obtain a definite quantity of selenium, the following procedure was used:

A 10-cc. pipet of standard selenious acid solution was delivered into a 250-cc. beaker, 25 cc. of concentrated hydrochloric acid were added, followed by 25 cc. of hydrochloric acid saturated with sulfur dioxide, and the solution was allowed to stand at least 24 hours. At the end of this time, the red modification was completely precipitated and had settled out upon the bottom of the beaker. This precipitated selenium was then filtered upon asbestos or a layer of sulfur about 3.8 cm. (1.5 inches) thick. The red selenium was dissolved from the asbestos or sulfur pad by means of concentrated nitric acid, the solution concentrated to small volume, made alkaline with ammonium hydroxide to precipitate ferric hydroxide, and, after filtration, again acidified with nitric acid. Urea was added to destroy nitrous acid, the solution cooled, an excess of potassium iodide added, and the liberated iodine titrated with standard sodium thiosulfate. Using the same pipet in order to obtain the same quantity of selenious acid, hydrochloric acid and potassium iodide were added and the mixture was titrated with standard sodium thiosulfate solution. The two procedures required the same amount of sodium thiosulfate solution.

Of the reagents which might be used for the solution and oxidation of selenium to selenium dioxide, concentrated nitric acid was found to be the most satisfactory. Nitric acid solutions of selenium may be concentrated to a small volume with no loss of selenium, a fact which was checked by numerous experiments. None of the selenium is oxidized to selenic acid by either dilute or concentrated nitric acid. The one necessary precaution is the elimination of nitrous acid from the nitric acid just previous to the addition of potassium iodide and titration. Urea was found to be entirely satisfactory for this purpose. All experiments using urea gave excellent check results in varying concentrations of nitric acid.

The asbestos used for the plug in the end of the tube must be of the best quality and the usual laboratory grade requires further purification to eliminate iron. The procedure used to eliminate iron was to digest the asbestos fibers with concentrated hydrochloric acid for 4 to 5 hours, filter, wash, and dry at 110° C. This treatment reduced to a minimum the amount of iron that might later be extracted by the hot nitric acid.

A boat large enough to hold 100 grams of sulfur was required. To prepare this, Pyrex tubing of about 34-mm. bore and about 20 cm. (8 inches) long was closed at both ends and the upper part removed by melting away in an oxygen flame, thus producing a glass boat (Figure 1).

It was found after several experiments that the selenium dioxide gas badly attacked the rubber stopper used at the inlet end of the large tube. The best method for eliminating such attack was found to be that shown in the diagram. The oxygen gas passes in through the neck of the small, round-bottomed flask, thence through a hole in the neck of the flask into an oxygen chamber, and from there into the main combustion chamber. This arrangement prevented any action upon the rubber stopper, even after months of usage.

Of the different filtering mediums tried, by far the most satisfactory proved to be asbestos fibers which had been treated by concentrated hydrochloric acid, as described above. Liquid absorbents were found to be inadequate.

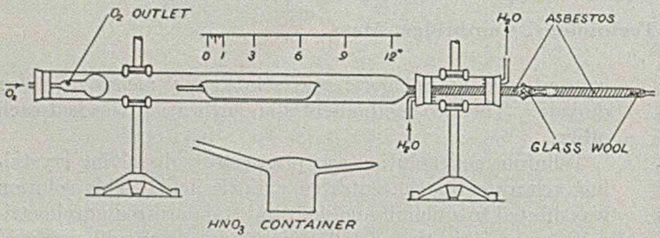


FIGURE 1

Constriction of the main tube at the exit end to a diameter of about 12 mm. permitted the use of an asbestos pad as long as 15 to 20 cm. (6 to 8 inches), without the use of an excessive amount of asbestos. At the end of the small tube the pad of glass wool prevented the possibility of blowing the asbestos out of the end. The constricted exit tube was cooled externally by means of a water jacket.

To the end of the small tube was attached an auxiliary tube filled with asbestos, a ground-glass joint between. This arrangement was found to be very useful whenever it became necessary to test the efficiency of any particular filtering medium. At the end of a run, the auxiliary tube could easily be examined for traces of selenium.

Another procedure, which proved useful in tracing the selenium at the end of the run, was developed. By passing sulfur dioxide gas through concentrated hydrochloric acid and then through the entire system, the selenium is almost completely precipitated in the red form, in which modification very minute quantities may be readily observed, a fact which proves to be very useful in testing the efficiency of different filtering mediums.

The color of the filtering mediums at the end of an ordinary run was a light green. After development of the red form, the efficiency of any particular filtering medium became evident from the extent of penetration of the red color through the mass of the filter.

A container suitable for handling hot, concentrated nitric acid was prepared from an ordinary 400-cc. tall-form beaker.

Procedure

The procedure adopted in the analysis of the seleniferous sulfur was as follows:

About 10 to 20 grams of the sulfur were placed upon a filter plate within a tall-form Gooch funnel, and tamped down to form a compact mass about 3.8 cm. (1.5 inches) thick. Upon this sulfur was filtered the known quantity of selenium, which had been precipitated from a concentrated hydrochloric acid solution by sulfur dioxide at least 24 hours previously. The filtered selenium was washed with hydrochloric acid, water, alcohol, and then ether. By pushing a stirring rod up through the stem of the funnel, the entire mass of sulfur, with selenium upon the surface, moved out through the straight sides of the funnel, cleaning the sides as it went. After drying at room temperature a few hours, the sulfur and selenium were mixed and transferred to the Pyrex boat. The small end chamber was prepared with the glass wool and asbestos filter. The apparatus was always tested with oxygen before starting a run, to be sure the asbestos was not too compact to prevent ready passage of gases. Furthermore, it was found desirable to have the main combustion chamber full of oxygen before placing the lighted sulfur in position.

The sulfur in the boat was lighted in a small spot, the boat immediately pushed into position, the chamber closed, and oxygen allowed to pass. The heat of combustion of the sulfur carries the reaction to completion. At the end of a run on a 100-gram sample of sulfur containing selenium, a small residue of a few milligrams would remain, and about 2 or 3 cc. of an oily, green solution of selenium in sulfur trioxide collected in the bottom of the chamber. The entire chamber was allowed to cool, with oxygen passing to sweep out excess sulfur dioxide. The boat was removed and rinsed off with hot, concentrated nitric acid into a beaker. The combustion tube was then placed in a vertical position upon a suitable filter flask, suction applied, and hot, concentrated nitric acid run down the inside of the chamber through the asbestos, followed by hot wash water. The asbestos filter pad remained in position and a clear, yellow solution of nitric acid containing selenious acid was obtained. To this solution were added the washings from the boat, and the entire solution was concentrated to a volume of about 10 cc. This was cooled and ammonium hydroxide added to precipitate ferric hydroxide, which was filtered off and washed. The solution was neutralized with nitric acid, and 10 cc. of concentrated nitric acid were added. The solution was diluted to 50 cc., about 3 grams of urea were added, and the solution was gently heated for 2 to 3 minutes, cooled, and diluted to 300 cc. Three grams of potassium iodide were added, and the solution was stirred for 1 to 2 minutes and titrated with the standard sodium thiosulfate.

Table I contains the results obtained by this procedure, when decreasing quantities of selenium were added to increasingly large quantities of pure sulfur.

TABLE I. ANALYSIS OF SELENIFEROUS SULFUR

Sulfur Taken	Selenium Added	$Na_2S_2O_3$ Required	
		Theoretical	Actual
Grams	*Mg.*	*Cc.*	*Cc.*
10	11.4	40.3	40.50
10	11.4	40.3	40.40
25	11.4	40.3	40.20
25	11.4	40.3	40.50
50	11.4	42.90	43.00
50	11.4	42.90	43.10
100	11.4	42.90	43.10
100	11.4	42.90	43.10
100	5.6	22.30	22.40
100	5.6	22.30	22.40
100	1.14	4.40	4.50
100	1.14	4.40	4.50

In addition, the following experiments were carried out on sulfur specimens from different sources, using the same procedure as previously described:

One hundred grams of commercial grade Texas sulfur (flowers of sulfur) were burned and no selenium was found present.

One hundred grams of crude Louisiana sulfur containing an appreciable amount of oil and hydrocarbons gave no selenium.

A 30-gram sample of crystal sulfur from Garginti, Sicily, gave no selenium.

Five-gram samples of seleno-sulfur of volcanic origin (Sicilian deposit) gave check results at 10.00 and 10.10 cc. of sodium thiosulfate, from which the selenium content was calculated to be 0.054 per cent. This sample contained a large percentage of arsenic, which caused no trouble.

EFFECT OF ARSENIC. The effect of arsenic upon the determination of selenium was tried by adding a definite amount of Bureau of Standards arsenic trioxide to a mixture of selenium and sulfur. The results obtained are shown in Table II where the amount of arsenic trioxide added was of the same magnitude as the selenium present, the same procedure being followed as before. These results led to the conclusion that moderate amounts of arsenic caused no trouble in the titration for selenium.

TABLE II. SULFUR CONTAINING SELENIUM AND ARSENIC TRIOXIDE

Sulfur	Selenium	As_2O_3	$Na_2S_2O_3$ Required	
			Theoretical	Actual
Grams	*Mg.*	*Mg.*	*Cc.*	*Cc.*
25	11.4	10	42.90	43.10
25	11.4	10	42.90	43.20

EFFECT OF TELLURIUM. The selenium was precipitated in the usual manner and the tellurium was precipitated from a definite amount of prepared tellurous acid solution by means of sulfurous acid and hydrazine.

The tellurium and selenium were filtered on a mat of sulfur, and the mixture was burned in the usual manner. When tellurium was present, the inside of the combustion tube was coated over with an opaque deposit of tellurium dioxide. The entire tube was washed out with hot nitric acid, as described above. The combined filtrates were evaporated to a volume of 10 cc. and carefully neutralized with ammonium hydroxide to the appearance of a precipitate of tellurium dioxide. Six cubic centimeters of 6 *N* nitric acid and 3 grams of urea were added and diluted to a volume of 300 cc. Three grams of potassium iodide were added, allowed to stand 7 minutes, 75 to 100 cc. of water were added, and the solution was titrated with sodium thiosulfate in the usual manner.

The end point was very satisfactory, but not as sharp as with selenium alone. The concentrations as given were found to be the proper ones to allow a titration of the selenium alone, without interference from the tellurium present. Variation of the acid concentration, iodide concentration, or time from those specified gave varying results, due to interference by the tellurium.

Table III. Effect of Tellurium

Sulfur	Selenium	Tellurium	$Na_2S_2O_3$ Required Theoretical	$Na_2S_2O_3$ Required Actual
Grams	*Mg.*	*Mg.*	*Cc.*	*Cc.*
25	11.4	12.4	42.90	43.00
25	11.4	12.4	42.90	43.10

Summary

A procedure is described whereby amounts of selenium in sulfur ranging from 0.1 to 0.001 per cent may be accurately determined. Quantities of arsenic and tellurium present in magnitude equivalent to that of the selenium were found to cause no interference. The apparatus required is simple in construction, the number and quantity of reagents used are a minimum, and the total time required is a matter of a few hours. The reproducibility of results is quite satisfactory, if the usual precautions of analysis are observed.

Literature Cited

(1) Beattie, Benedict, and Blaisdell, M. I. T. doctorate thesis, unpublished, 1935.
(2) Dudley and Byers, Ind. Eng. Chem., Anal. Ed., 7, 3 (1935).
(3) Klason and Mellquist, *Z. angew. Chem.*, 25, 514 (1912).
(4) Robinson, Dudley, Williams, and Byers, Ind. Eng. Chem., Anal. Ed., 6, 274 (1934).
(5) Smith, W., J. Ind. Eng. Chem., 7, 849 (1915).
(6) Williams and Byers, *Ibid.*, Anal. Ed., 6, 296 (1934).

Received August 21, 1935. Publication 50, Research Laboratory of Inorganic Chemistry.

Boron Content of Sea Water of the North Atlantic Coast

NORRIS W. RAKESTRAW and HENRY E. MAHNCKE
Woods Hole Oceanographic Institution, Woods Hole, Mass.

SOME time ago Moberg and Harding published a brief account of determinations of the boron content of sea water (*1*). Their samples were for the most part drawn from the Pacific. Because of the part which boric acid presumably plays in the buffer mechanism of sea water it is important to know how uniformly it is distributed, and it was therefore thought desirable to make similar determinations on water of the North Atlantic coast. Accordingly, the same method used by Moberg and Harding (a modification of the differential electrometric titration described by Wilcox, *2*) was applied to some 75 samples from different depths at eight stations along the Atlantic coast, within cruising range of Woods Hole.

The stations may be divided into two groups: Nos. 1731, 1732, 1734, and 1739 to the south of Cape Cod in the direction of Bermuda, at which the water is of generally southern origin; and Nos. 1747, 1767, 1775, and 1781 in the Gulf of Maine, at which the water is of generally northern origin. The average boron concentration in the 39 samples from the southern stations is almost identical with that in the 36 samples from the northern stations, being 4.73 mg. per kg. in the former and 4.75 mg. per kg. in the latter. This compares with an average of 4.50 mg. per kg. found by Moberg and Harding.

More important, however, is the ratio of boron to chloride (or total halide). The average ratio, B/Cl, at the southern stations was 0.000240, almost identical with 0.000239 found by Moberg and Harding in their fifty samples. At the northern stations a B/Cl ratio of 0.000255 was found, indicating a slightly higher percentage of boron in the dissolved solids of the water of this region.

There seems to be no significant regularity in the vertical distribution of boron.

Table I. Boron in Sea Water

Depth	Boron	Ratio
M.	*Mg./kg.*	B/Cl
Station 1731 38° 06′ N., 68° 54′ W.		
0	4.69	0.000236
30	4.64	0.000234
50	4.85	0.000243
60	4.85	0.000243
80	4.82	0.000241
100	4.93	0.000244
150	4.87	0.000240
200	4.92	0.000244
355	4.92	0.000250
530	4.87	0.000251
700	4.88	0.000252
860	4.79	0.000247
1020	4.82	0.000249
1175	4.77	0.000246
1320	4.71	0.000243
1685	4.74	0.000245
Station 1732 37° 21′ N., 68° 31′ W.		
0	4.45	0.000224
50	4.55	0.000229
100	4.67	0.000233
1050	4.62	0.000238
1725	4.67	0.000241
2710	4.52	0.000234
3830	4.58	0.000238
Station 1734 36° 27′ N., 68° 38′ W.		
0	5.07	0.000254
50	5.01	0.000243
87	4.97	0.000245
175	4.76	0.000236
365	4.72	0.000234
550	4.61	0.000229
730	4.56	0.000230
915	4.68	0.000239
1550	4.48	0.000232
2000	4.66	0.000241
3500	4.47	0.000231
Station 1739 40° 18′ N., 70° 22′ W.		
10	4.58	0.000250
30	4.31	0.000237
40	4.56	0.000250
60	4.31	0.000237
75	4.54	0.000247
Av.	4.73	0.000240
Station 1747 42° 41′ N., 69° 29′ W.		
0	4.42	0.000252
10	4.46	0.000255
28	4.42	0.000249
47	4.48	0.000250
73	4.54	0.000252
110	4.60	0.000253
150	4.74	0.000256
185	4.78	0.000255
240	4.73	0.000251
Station 1767 44° 11′ N., 66° 51′ W.		
0	4.48	0.000249
10	4.52	0.000251
30	4.59	0.000254
50	4.67	0.000256
80	4.83	0.000264
125	4.84	0.000261
175	4.83	0.000259
Station 1775 43° 13′ N., 65° 38′ W.		
0	4.40	0.000257
10	4.46	0.000259
20	4.48	0.000257
30	4.61	0.000265
40	4.57	0.000260
50	4.69	0.000264
Station 1781 41° 52′ N., 65° 10′ W.		
0	5.00	0.000261
20	4.90	0.000252
40	4.89	0.000251
59	4.94	0.000252
100	5.00	0.000254
150	4.97	0.000251
200	5.02	0.000254
300	4.92	0.000252
400	4.92	0.000254
600	5.02	0.000260
1000	4.95	0.000256
1395	4.86	0.000251
1800	4.94	0.000256
2000	5.06	0.000262
Av.	4.75	0.000255

Literature Cited

(1) Moberg, E. G., and Harding, M. W., *Science*, 77, 510 (1933).
(2) Wilcox, L. V., Ind. Eng. Chem., Anal. Ed., 4, 38 (1932).

Received September 11, 1935. Contribution 87 from the Woods Hole Oceanographic Institution.

Detection of Adulteration in Maple Sirup

A Simplified Rapid Method Based on Electrical Conductivity

AUGUSTUS CONLIN, Cary Maple Sugar Company, Inc., St. Johnsbury, Vt.

IN HANDLING large commercial volumes of maple sirup, the detection of adulteration is difficult because of (1) the smallness of the unit volume to be sampled, never over 55 gallons and often as little as 5 gallons; (2) the length of time required for chemical determinations, such as ash values, malic acid value, and even lead numbers; and (3) the wide variations in the values found in pure maple sirups.

Of the various official methods by means of which the purity of maple products can be determined, only one is suited for rapid manipulation with little loss in accuracy. This is the measurement of electrical conductivity, introduced by Snell (*3*), who pointed out that maple sirup showed a maximum conductivity when diluted with two volumes of water. The official method (*1*) adopted specified that the sample used be 22 grams of dry matter in a volume of 100 cc. This weight was subsequently changed to 25 grams (*2*) in order that a portion of the same sample might be used for Canadian lead number determination. The limitations of electrical conductivity methods have been described by Snell (*3*).

Method and Apparatus

The method proposed here was designed primarily to detect adulteration with white sugar, and is similar to the original method of Snell (*3*) except that the apparatus consists of a Leeds & Northrup sugar ash bridge and conductivity cell. No constant-temperature bath is necessary with this apparatus, since a knob on the bridge provides for variations in cell temperatures between 10° and 35° and variations in cell constant from 0.14 to 0.16, and all results are automatically corrected to 20°. The sirup is diluted with three volumes of water instead of two because the sample bottles in which the sirups are graded for color and in which they are received by the laboratory contain approximately 25 cc. This volume, diluted to 100 cc. with water, is sufficient both for rinsing the electrodes of the cell and filling the cylinder in which the electrodes are inserted. Density variations in the sirups and the presence of suspended "niter" may be neglected.

The rapidity of the method is its most important feature, and makes it particularly useful when a large number of samples must be examined. The method outlined above is far more rapid than any previously described. Two operators, one preparing the samples and the other taking measurements, can easily examine 400 or more samples per day.

PROCEDURE. Place 75 cc. of water in a 100-cc. graduated cylinder, add 25 cc. of sirup, and mix thoroughly. Rinse off the electrodes with approximately 40 cc. of this solution, pour the remainder into the testing cylinder, and insert the electrodes and thermometer. Adjust the temperature-compensating knob on the bridge to correspond with the cell reading, place the resistance plug in the proper setting (usually the 1000-ohm block), press the alternating current button, and turn the main slide-wire knob until the galvanometer balances. Take the dial reading. The product of this value and the plug setting is specific conductance multiplied by 10^6 and reduced to 20°. Since the conductivity value is defined as the specific conductance multiplied by 10^5, the product is 10 times the desired figure. The official method (*1*) also specifies 25° as the temperature for taking measurements, but 20° is fully as satisfactory provided the difference in conductance caused by the 5° change is taken into consideration.

ACCURACY OF METHOD. That the accuracy of conductivity measurements is not impaired by not weighing the sirup sample or reducing all sirups to a standard density was pointed out by Snell (*3*) and is further demonstrated by the following figures, showing the difference in conductivity values of sirup samples containing 25 grams of dry matter and 25 cc. of sirup (about 22 grams of dry matter) in a total volume of 100 cc. at 20°.

TABLE I. CONDUCTIVITY VALUES

25 Grams of Dry Matter	25 Cc. of Sirup
138	136
129	127
110	109
140	136
124	121
126	124

There is, of course, a considerable difference between the conductivity value measured at 20° and at 25°, but all values obtained at the same temperature are comparable among themselves and with the minimum standard chosen for that temperature. Measurements made at 25° average about 13 per cent higher than those made at 20°.

Range of Values

Because of the varying nature of maple products, it is impossible absolutely to define the two limits between which the conductivity values of pure maple sirups will fall. Snell (*3*) originally adopted 110 as the lower limit and 200 as the upper, but later (*4*) found values as low as 96 and as high as 230. His measurements were made at 25° on sirups known to be genuine. For the present study of over 7200 samples obtained from nearly all important producing sections in the United States and Canada the author has adopted for the method outlined above a minimum value of 100. However, a number of sirups with conductivity values lower than 100 were found which, by other methods, were considered either pure or doubtful. It should be emphasized here that sirups showing conductivity values near the minimum should always be examined by other standard tests before drawing conclusions regarding their genuineness. Since there was no guarantee of genuineness with any of the samples tested, the collected data cannot be used to help define the conductivity limits of pure maple sirup. Values found ranged from 40 in highly adulterated sirups up to 200, which corresponds closely to the maximum of 230 at 25° found by Snell.

TABLE II. CONDUCTIVITY VALUES

Source	No. of Samples Averaged	Grade	Conductivity Value
Canada (Quebec)	400	Mixed	144
United States:			
Maryland, Pennsylvania, New York, Vermont, and New Hampshire	500	Mixed	130
Maryland, Pennsylvania, and western New York	250	Mixed	135
Vermont, New Hampshire, and eastern New York	250	Mixed	124
Southeastern Vermont	100	Fancy and No. 1	130
Vermont and New York	250	Fancy	118
Vermont and New York	250	No. 3	137
New York	150	Mixed "Buddy"	142

Table II gives average values for various grades of sirups from various localities. These figures were selected at random from the large number at hand. All measurements were made at 20°.

Conclusions

The average conductivity value of Canadian sirups is higher than that of American sirups.

Sirups originating in Maryland, Pennsylvania, and southwestern New York show higher average conductivities than those from eastern New York, Vermont, and New Hampshire, with the exception of those from southeastern Vermont.

The average value for light-colored sirups is lower than that for the darker sirups.

"Buddy" sirups, regardless of color, usually show higher conductivity values than normal sirups.

Literature Cited

(1) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, 2nd ed., p. 204 (1925).
(2) *Ibid.*, 3rd ed., p. 393 (1930).
(3) Snell, J. F., J. Ind. Eng. Chem., 5, 740 (1913).
(4) *Ibid.*, 8, 331 (1916).

Received August 30, 1935.

Bismuthate Method for Manganese. II

BARTHOLOW PARK, Michigan College of Mining and Technology, Houghton, Mich.

IN THE reaction between arsenite and permanganate in acid solution used in the bismuthate method for manganese, the manganese is not reduced to the bivalent state (*4, 5, 7, 9, 10, 14, 17*).

Lang (*13*) has shown that a dilute solution of potassium iodate catalyzes this reaction and causes it to proceed according to the equation $2Mn^{+++++++} + 5As^{+++} \rightarrow 2Mn^{++} + 5As^{+++++}$ if the permanganate is added to the arsenite in either sulfuric or hydrochloric acid solution. Cantoni (*1*) proposed the addition of one drop of 0.1 per cent potassium iodide solution as catalyst. Lang (*12*) studied this procedure. Swift and Gregory (*16*) make use of iodine monochloride in hydrochloric acid solution. Gleu (*6*) proposed the use of 0.01 *M* osmium tetroxide in sulfuric acid solution.

Because the bismuthate method is usually carried out in nitric acid solution, it was thought advisable to test these catalysts in its presence. For this work an electrotitration outfit similar to that described by Kassner, Hunze, and Chatfield (*11*) was set up with the following modification: The 201-A tube was replaced by a Cunningham C-33 tube, the two platinum electrodes were replaced by one platinum and one tungsten, and a milliammeter with a large scale was employed. This set-up was found to be extremely sensitive and it was very easy to determine the end point within one drop of the very dilute solutions used.

Preparation of Solutions

STANDARD ARSENITE. Bureau of Standards arsenious oxide No. 83 (1.8019 grams) was dissolved in water by the addition of a little sodium carbonate and diluted to 2 liters. The per cent purity of this sample, obtained by titration, is given on the certificate as 99.97. This figure is based on calculations made with the 1925 atomic weights. Recalculating on the basis of the 1935 weights gives a value of 99.93 per cent which was used.

STANDARD PERMANGANATE. A well-aged strong solution was diluted with distilled water in the ratio of 1 to 10 and then restandardized frequently with Bureau of Standards sodium oxalate No. 40a. The results obtained corroborate the work of Halverson and Bergeim (*8*). After standing only 15 minutes the dilute solution was 0.5 per cent weaker than the value calculated from the strong solution. Four days later it was 1 per cent weaker than the calculated value.

NITRIC ACID. Ordinary C. P. nitric acid was freed from oxides of nitrogen by blowing air through it as proposed by Cunningham and Coltman (*3*).

Experimental Results

All titrations were carried out electrometrically, the drop which caused the largest deflection being taken as the end point. Twenty-five cubic centimeters of arsenite solution were pipetted out and the volume was made up to about 200 cc. The other conditions were as noted in Table I. On the basis of this work a modification of the procedure for the bismuthate method in iron and steel is proposed.

After filtering out the excess bismuthate on a Jena glass filter No. 4, add the filtrate to a measured excess of standard arsenite solution containing 3 drops of 0.01 *M* osmium tetroxide and titrate with standard permanganate to the electrometric end point. (Cheishvili (*2*) has shown that washed and ignited asbestos reduces a small amount of permanganate when used as a filtering medium.) Bureau of Standards steel No. 65a was run by this method with the following results: found, 0.746 and 0.743 per cent of manganese. The certificate gives 0.746 per cent of manganese.

Bureau of Standards Norrie iron ore No. 28 was run by the bismuthate method as modified by Park (*15*), using arsenite with the addition of osmium tetroxide instead of ferrous ammonium sulfate. The results obtained were 0.442 and 0.438 per cent of manganese. The average value for manganese as given by the certificate for all methods is 0.465 per cent. Blum found 0.44 per cent by the bismuthate method.

TABLE I. EXPERIMENTAL RESULTS

Catalyst	Acid	Ratio Calculated	Ratio Determined	Difference, P. p. 1000
KIO_3[a]	10 cc. H_2SO_4	1.004[b]	Uncertain[c]	...
$KIO_3 + NaCl$[d]	10 cc. H_2SO_4	1.004	1.004	None
$NaCl$[e]	10 cc. H_2SO_4	1.004	1.006	+2
$NaCl + I_2$[f]	10 cc. H_2SO_4	1.004	Uncertain[c]	...
I_2[g]	10 cc. H_2SO_4	1.004	1.022	+18
OsO_4[h]	10 cc. H_2SO_4	1.004	1.0048	+0.8
$OsO_4 + NaCl$[i]	10 cc. H_2SO_4	1.004	1.0048	+0.8
KIO_3[a]	15 cc. HNO_3	1.008	Uncertain[c]	...
I_2[g]	15 cc. HNO_3	1.008	Uncertain[c]	...
OsO_4[h]	15 cc. HNO_3	1.008	1.010	+2

[a] One drop of 0.0025*M* solution.
[b] From weights of As_2O_3 and $Na_2C_2O_4$ standardization of $KMnO_4$.
[c] No determinable end point.
[d] One drop of 0.0025*M* solution plus 1 gram of NaCl.
[e] 1 gram of NaCl.
[f] 1 gram of NaCl plus small crystal of I_2.
[g] Small crystal of I_2.
[h] Three drops of 0.01*M* solution.
[i] Three drops of 0.01*M* solution plus 1 gram of NaCl.

Acknowledgment

The writer wishes to thank T. R. Maki of this college for setting up the electrotitration apparatus and assisting with the titrations.

Literature Cited

(1) Cantoni, O., *Ann. chim. applicata*, 16, 153 (1926).
(2) Cheishvili, P., *J. Russ. Phys. Chem. Soc.*, 42, 856 (1911).
(3) Cunningham, T. R., and Coltman, R. W., Ind. Eng. Chem., 16, 58 (1924).
(4) Geloso, Max, *Bull. soc. chim.*, 37, 641 (1925).
(5) Geloso, Max, *Compt. rend.*, 171, 1145 (1920).
(6) Gleu, K., *Z. anal. Chem.*, 95, 305 (1933).
(7) Hall, W. T., and Carlson, C. E., *J. Am. Chem. Soc.*, 45, 1615 (1923).
(8) Halverson, J. O., and Bergeim, O., J. Ind. Eng. Chem., 10, 119 (1918).
(9) Hollata, J., *Z. anorg. allgem. Chem.*, 168, 361 (1928).
(10) Ibbotson, F., *Chem. News*, 117, 157 (1918).
(11) Kassner, J. L., Hunze, R. B., and Chatfield, J. N., *J. Am. Chem. Soc.*, 54, 2278 (1932).
(12) Lang, Rudolf, *Z. anal. Chem.*, 85, 176 (1931).
(13) Lang, Rudolf, *Z. anorg. allgem. Chem.*, 152, 197 (1926).
(14) Oryng, T., *Ibid.*, 152, 197 (1926); *Roczniki Chem.*, 7, 334 (1927).
(15) Park, B., Ind. Eng. Chem., 18, 597 (1926).
(16) Swift, E. H., and Gregory, C. H., *J. Am. Chem. Soc.*, 52, 901 (1930).
(17) Travers, H., *Bull. soc. chim.*, 37, 456 (1925).

Received July 13, 1935.

Determination of Chlorine in Organic Compounds

I. A Rapid Lamp Method

WILLIAM MARIAS MALISOFF, School of Medicine, University of Pennsylvania, Philadelphia, Pa.

IN THE course of a study of the decomposition of organic sulfur compounds by means of aluminum chloride, it was noted that the sulfur values rose above 100 per cent as determined by the well-known lamp method for the determination of sulfur (*1*). Suspicion fell on chlorine as the cause, and led to the confirmation that many organic chlorine compounds form hydrochloric acid practically quantitatively on combustion under the conditions of the method. Under more restricted conditions other types form hydrobromic, hydriodic, and nitric acids along with the free halogen. This paper presents data with particular attention to carbon tetrachloride and phenyl chloride, which were used for studying the principal factors.

Experimental

GENERAL PROCEDURE. The organic compound is dissolved in a combustible solvent in various concentrations, preferably to produce 0.2 to 0.3 per cent chlorine, and is burned in the standard sulfur lamp following the precautions officially recommended by the A. S. T. M. (*1*). The titrations are made with precisely the reagents specified by the method with the same indicator. About 1 gram of solution is burned. The standard calculation may be used and a correction applied—namely, that 1 per cent of sulfur is equivalent to 2.216 per cent of chlorine.

TABLE I. DETERMINATION OF CHLORINE

Solvent	Compound	Halogen Calculated	Halogen Found	No. of Observations
		%	%	
Extraction naphtha	Phenyl chloride	0.069	0.069 ± 0.002	6
		0.121	0.121 ± 0.002	7
		0.124	0.123 ± 0.004	10
		0.276	0.273 ± 0.004	8
		0.524	0.504 ± 0.005	8
Methanol	Phenyl chloride	0.200	0.196 ± 0.003	4
Extraction naphtha	Carbon tetrachloride	0.072	0.073 ± 0.002	8
		0.130	0.132 ± 0.002	10
		0.260	0.263 ± 0.003	8
		0.390	0.394 ± 0.004	7
		0.520	0.522 ± 0.005	6
Methanol	Carbon tetrachloride	0.200	0.203 ± 0.003	4
Methanol	Ethylene Chlorohydrin	0.353	0.345 ± 0.005	2
Extraction naphtha	*o*-Chlorophenol	0.177	0.176	2
	Hexachlorobenzene	0.068	0.069 ± 0.007	4, crusts
	Epichlorohydrin	0.168	0.178 ± 0.005	2
	Ethylchloroacetate	0.256	0.270 ± 0.010	4, smoke
	Chloroacetone	0.162	0.168 ± 0.010	4, smoke
	Ethylene dibromide	0.427	0.277 ± 0.004	2
	Ethyl iodine	0.273	0.302 ± 0.005	2
	Hydrazobenzene	0.015	0.009 ± 0.002	2
Methanol	Isoamyl nitrite	0.195	0.163 ± 0.003	2

Discussion

The choice of a hydrocarbon solvent should fall on a petroleum fraction relatively free of sulfur and somewhat lighter than gasoline. The material used in this investigation contained 0.018 per cent sulfur. The analysis was checked at 5 points in the investigation, so that the value is an average of 10 determinations to within 0.001 per cent. This served as a blank correction. In the case of methanol the blank correction was zero.

The lamp method operates best in solutions less concentrated than 0.5 per cent, preferably at the 0.1 to 0.3 per cent level, where the determinations are good to 2 to 3 per cent. Therefore, since burning about 1 gram suffices, a determination can be carried out with only a few milligrams of a substance.

The results for phenyl chloride tend to be slightly low, the effect rising to about 4 per cent at the highest concentration used. The results for carbon tetrachloride are slightly high in every case, but to the extent of only 1 per cent, and this may be attributed to difference in volatility. The other chlorine compounds have not been studied in detail, but the author hopes that further experience will lead to better adjustments. For example, the low solubility of hexachlorobenzene in naphtha led to crust formation and some erratic results, a good average being, in his opinion, more or less of an accident. Furthermore, smoky experiments should probably be discarded, although they were included in this report.

The fact that check values have been obtained for the combustion of compounds containing bromine, iodine, and nitrogen, although they are quite different from the amounts actually introduced, raises some hope for further study of the proper conditions of combustion to insure complete conversion to acids. The addition of hydrogen peroxide to the carbonate absorber is a possible method in the author's opinion, judging from the known reducing action of peroxides on free halogens.

The author's 112 determinations are in general accord with 43 determinations reported by Wirth and Stross (*6*) on amyl chloride, amylene dichloride, benzyl chloride, butyl chloride, carbon tetrachloride, dichlorobenzene, ethylene dichloride, isopropyl chloride, isobutyl chloride, and propyl chloride, in gasoline to chlorine concentrations of 0.017 to 0.390 per cent, by the use of Mohr's method of titration with silver nitrate following the combustion. Bowman (*2*) also uses a combustion method, determining chlorine nephelometrically and finding it necessary to ash the wick. Miloslavsky and Vepritzkaya (*4*) have carried on some combustions of alcoholic solutions, catching the hydrochloric acid in silver nitrate and titrating the excess silver nitrate with potassium thiocyanate. Using a Kennedy lamp (*3*), similar to the standard, Smith (*5*) records a few satisfactory determinations of chlorine in pinene hydrochloride and in mono- and dichlorobenzene dissolved in turpentine, by a silver chloride determination of the absorbed products of combustion. The author's work indicates that a simple titration is sufficient when dealing only with chlorine. Specific applications must await empirical trial, since no general rule can be given on the basis of several compounds.

Literature Cited

(1) Am. Soc. Testing Materials, "Tentative Standards," 1927; *Bur. Mines Tech. Paper* 323B (1927).
(2) Bowman, S., *J. Inst. Petroleum Tech.*, 7, 334–8 (1921).
(3) Kennedy, IND. ENG. CHEM., 20, 201 (1928).
(4) Miloslavsky and Vepritzkaya, *J. Applied Chem.* (U. S. S. R.), 5, 860–7 (1932).
(5) Smith, W. C., IND. ENG. CHEM., Anal. Ed., 3, 354 (1931).
(6) Wirth, Chas., III, and Stross, M. J., *Ibid.*, 5, 85–7 (1933).

RECEIVED August 3, 1935. Presented before the Division of Organic Chemistry at the 89th Meeting of the American Chemical Society, New York, N. Y., April 22 to 26, 1935. Work done under grants of the Josiah Macy, Jr., Foundation.

Notes on the J. Lawrence Smith Fusion

MARK O. LAMAR, WALLACE M. HAZEL, AND WM. J. O'LEARY
Norton Company, Research and Chemical Laboratories, Worcester, Mass.

There have been pointed out several sources of possible disagreement between different analysts over the alkali content of the same material when using the standard J. Lawrence Smith fusion. Since different substances are not thereby decomposable to the same extent, it has been suggested that the samples first be ground to some standard size, that the fusions be made at a higher temperature than is now customary, that the calcium carbonate and ammonium chloride flux be mixed together by ball-milling, and that correction of the mixed chlorides for accompanying magnesium be appropriately emphasized. The suggested improvements have been applied in the analysis of so-called beta-alumina.

As MANY prominent analysts continually fail to agree on the alkali content of rocks, minerals, refractory substances, and the like, and report different results on one and the same material after preliminary treatment by the J. Lawrence Smith method of fusion, it has been thought worth while to describe some of the experiences met in the Norton Company Research Laboratories with the J. Lawrence Smith treatment of difficultly attackable materials, in the hope that the results may lead to some improvement of the method as now standardized.

All the better texts on analytical chemistry that have come to the authors' attention emphasize the danger of losing gases, oxidizing the sample, and picking up moisture by grinding the sample excessively, but none mentions the fairly obvious fact that the less subject to attack a material is the more finely it must be ground to insure decomposition. Washington (*18*) and Hillebrand and Lundell (*8*) are among the few who adhere to Smith's (*17*) original directions in stating that the sample for a Smith fusion should be ground to an impalpable powder, although Smith himself states that such is not always necessary. The degree of fineness of a material expressed by a term like "impalpable powder" can be very loosely interpreted, depending on the individual and on the amount of labor involved in grinding the sample; a sample through 100-mesh on 120-mesh may be quite impalpable to most people, but will not always be completely decomposed by a single fusion. A glass is more readily decomposable than a clay or a feldspar, but spectrographic examination of residues shows that lepidolites through 100-mesh are not completely decomposed by one fusion. Beryl and tourmaline are more difficult to attack, and such substances as fused alumina are far more difficult still.

Hillebrand and Lundell (*9*) claim that a second fusion is seldom necessary, but state in a footnote that appreciable amounts of alkalies can be recovered from a second treatment of even so amenable a substance as a diorite. This lends support to the contention of Dittrich (*4*), Mellor (*13*), and Connor (*3*) that several milligrams of alkalies are not recovered after one treatment; whether or not all of the alkalies are recovered in a single treatment depends on the nature, particle size, and fusibility of the sample.

A second point upon which many chemists disagree is the temperature of fusion. Most of them state that if heated too hot the subsequent leaching is accomplished with difficulty; Washington (*18*) even claims that some alkali chloride may be lost by volatilization. The latter assertion is possibly true in the case of rubidium and cesium, but the average analyst is seldom concerned with more than sodium and potassium.

A third point is the manner in which the sample is mixed with the ammonium chloride–calcium carbonate fusion mixture. The standard procedure is to add the ammonium chloride to the sample, and then to incorporate the calcium carbonate, a process that cannot always insure the uniform formation of an ammonium chloride–calcium carbonate fusion mixture.

Analysis of Highly Aluminous Materials

The authors' experience with the J. Lawrence Smith fusion has been confined mainly to highly aluminous minerals of low silica content, both raw and calcined, and to electric furnace products consisting principally of fused alumina; all these materials are inherently much more difficult to decompose with ammonium chloride–calcium carbonate than the highly siliceous materials, such as rocks, usually examined for alkalies. In analyzing them for sodium and potassium it has been found (1) that comparable disintegrations by the J. L. Smith method can be obtained only when the samples have been ground to a comparable, controlled size; (2) that highly aluminous samples low in silica must be ground so that all the sample passes 200-mesh, and that an "impalpable feel" is not a sufficient criterion to insure complete decomposition; (3) that the highest temperature of a Méker-type burner is preferable for the fusion, and occasions neither loss of alkali nor difficulty in leaching the cake; and (4) that complete decomposition of the sample is not effected unless the ammonium chloride and calcium carbonate have previously been intimately mixed before compounding with the sample.

Complete disintegration of a difficultly decomposable substance is almost always effected when the sample has been ground to pass 200 mesh; it has been found, however, when a sample of fused alumina through 100 mesh is treated by the J. Lawrence Smith method, that from 20 to 60 per cent of the sample remains undecomposed after the first treatment, and that several subsequent treatments are necessary to decompose the sample completely. Microscopic and spectroscopic examination of the residues of feldspars and lepidolites, which are comparatively amenable to decomposition, has shown that under approximately the same conditions of fusion there is from 1 to 5 per cent of the sample undecomposed with one fusion after passing 100 mesh; at 150 mesh there appeared to have been complete decomposition; and samples through 200 mesh, even beryl and fused alumina, were completely decomposed after the first treatment. The retention of lithium by the sinter after complete decomposition of the sample has no immediate bearing on the question; it is being investigated and will be reported upon later. Smith (*17*) himself says that complete decomposition is seldom effected with one fusion of an impalpable powder; Mellor (*13*) adduces numerical data on the incompleteness of decomposition of such substances as basalts, syenites, etc.

Grinding a substance to impalpability can afford no assurance that the entire sample has been reduced to the fineness of the few portions that are felt. A method of analysis that is adopted as standard cannot be expected to yield satisfactory results when variables are introduced, such as inherent resistance of sample to fusion, particle size of sample, and temperature of fusion. Accordingly, if the J. Lawrence Smith fusion be expected to afford concordant results on the same materials in the hands of different analysts, some recommendation should be made to subject the sample at least to a uniform treatment that will insure complete decomposition.

In spite of the assertion by Washington (*18*) that some alkali chloride may be volatilized by heating the fusion too strongly with a Bunsen burner, there appears in the authors' hands to be no loss of alkali whatever from Bureau of Standards samples of feldspars, glasses, or clays, contained in standard J. L. Smith crucibles set up in the standard way, and heated with the conventional proportion of flux for twice the prescribed period with the hottest flame obtainable from a Méker type burner. The ammonia is first gently fumed off, and the lower portion of the crucible is brought, over a period of 20 to 30 minutes, to between 1000° and 1100° C., and is kept at that temperature for another 90 minutes. These temperatures were measured on the outsides of the crucibles by means of an optical pyrometer. It is true that sodium and potassium chlorides have an appreciable vapor pressure (*15*) at their melting points when alone, but such does not seem to be the case during a J. L. Smith fusion. If chlorides are volatilized in the hot zone, they are no doubt condensed in the upper part of the crucible, for the crucibles are tightly covered, the upper part of the crucible is considerably cooler than the lower portion, and the heating at the high temperature is not done until the evolution of gases has ceased.

The authors have found that decomposition of the less siliceous materials is invariably incomplete unless such temperatures are attained, and that two or even three Bunsen burners do not raise the entire lower portion of the crucible to the temperature required.

Following the ignition, there is very seldom any trouble in disintegrating the sinter, provided the recommendation of Mellor (*14*) is followed of adding not more than 2 ml. of hot water to the cake, and allowing it to stand for 10 to 15 minutes before adding more water. The slaking of the lime exerts a powerful disintegrating action on the cake if there is no excess of water to absorb the heat evolved. If, however, the cake is allowed to stand too long before beginning to extract it, it shows a tendency to go colloidal. Most difficulties in leaching the cake can be traced to improper mixing of the flux with the sample and to insufficient or improper heating of the fusion mixture, both of which cause incomplete decomposition.

Decomposition will still not be complete in the case of a very resistant material, even on a properly sized and thoroughly ignited sample, unless the fusion mixture has been specially prepared.

Willard (*20*) suggested that the calcium carbonate and ammonium chloride be ball-milled together, as such a mixture causes much less fuming. The authors have found, however, that in addition to reducing the fuming, the two constituents become so intimately admixed by such a process that they exert a very much stronger disintegrating action than mixtures ground by hand in a mortar. The mixture is prepared by adding one part of resublimed ammonium chloride to eight parts of precipitated and washed calcium carbonate, and is ball-milled in a porcelain mill for 5 hours with flint balls. Although Hillebrand and Lundell (*10*) assert that the calcium carbonate should be kept by itself, and not mixed with the ammonium chloride, the ball-milled mixture is made up in the Norton laboratories and stored in large batches; it is just as effective and has the same blank after standing 12 months as when freshly prepared. Lundell, Hoffman, and Bright (*12*) now recommend this procedure.

The sample to be fused is thoroughly mixed by hand with nine parts of the ball-milled preparation, and is placed in the crucible directly, without any bottom or top layer of calcium carbonate; no loss is occasioned by omitting these "protecting" layers, even at the high temperature employed. This procedure has the further advantage that the leaching process after fusion is much more readily effected.

It is asserted by most authorities that complete solution of the residue in hydrochloric acid after leaching is conclusive proof that complete decomposition has been effected by the fusion. This statement must not be accepted too literally, because solution of the residue in acid cannot prove more than that decomposition has proceeded to a certain point. In many cases where the residue is completely soluble in acid it still retains tenaciously some alkali that cannot be leached out with water (*9, 13, 17*); spectrographic checks on the residues have confirmed these observations. The modifications of the J. L. Smith fusion suggested above reduce to a minimum this tendency of the residues to retain alkalies, but no fusion or leach should be considered complete until elementary precautions have been taken to ascertain that it is.

The above-mentioned considerations explain why so many analyses yield results lower than the true alkali values. In a careful analysis high results are seldom obtained, and if obtained are usually due to incomplete removal of calcium, to carelessly conducted blank determinations, and particularly to failure to provide for the removal of magnesium. Every text on the subject that the authors have seen states that the chief advantage of the J. L. Smith fusion is the elimination of magnesium from the start; while they repeat this statement (*10*), Hillebrand and Lundell nevertheless recognize elsewhere (*2, 11*) its inaccuracy and make provision for the magnesium that usually accompanies the alkalies, without, however, attaching to their proviso the importance it deserves. Magnesium will usually be found even in the blanks, and too much emphasis cannot be laid on the necessity of correcting the final weight of the alkali chlorides for it.

Analysis of Beta-Alumina

Perhaps the most interesting application of these modifications of the J. L. Smith fusion to a difficultly attackable substance is the analysis of so-called beta-alumina. This was prepared and described by Rankin and Merwin (*16*), analyzed for them by Washington (*19*), and was asserted to be entirely Al_2O_3 and therefore an allotropic modification of aluminum oxide. The authors have since found that beta-alumina can be prepared only if the aluminum oxide used contains sodium, and that beta-alumina is probably a sodium aluminate because it contains 4.82 per cent Na_2O. Table I shows a comparison of the analytical results obtained on typical specimens of this substance using the authors' modifications of the J. L. Smith fusion, and the results obtained by others, most of whom secured their samples of beta-alumina from the authors; detailed reasons for believing that this beta-alumina is really a sodium aluminate are being published elsewhere.

TABLE I. SODIUM CONTENT OF BETA-ALUMINA

Sample No.	Na_2O	Al_2O_3	Analyst
	%	%	
1	..	100	Washington (*19*)
2	..	100	R. Dalton for Hendricks and Pauling (*7, 21*)
3	2.56	....	H. Swanson for Gallup (*5*)
4	2.56	96.59[a]	E. Spuhrmann for Gottfried (*6*)
5	4.59	95.30[b]	Norton Co.
6	4.76	....	Norton Co.
7	4.87	....	Norton Co.

[a] Contains small amounts of other impurities.

[b] Contains small amounts of other impurities; sample was somewhat decomposed by acid treatment before analysis.

The only method other than Smith's for determining the alkali content of insoluble materials is that of Berzelius (*1*); but, if a material is not completely decomposable in acids, this method obviously fails. Alkalies are strongly adsorbed and tenaciously retained by many compounds, so any leaching process that does not afford complete decomposition of the sample cannot be accurate; if the alkali is present combined as a compound, there is no possibility of leaching it out without previous decomposition. These considerations may explain some of the discrepancies in the amounts of sodium found by different analysts in beta-alumina, listed in Table I. In some cases the J. L. Smith procedure was not employed.

Literature Cited

(1) Berzelius, J. J., *Pogg. Ann.*, **1**, 169 (1824).
(2) Bur. Standards Certificate of Analyses of Standard Sample No. 80 Soda-Lime Glass, p. 4, J-56072 (1927).
(3) Connor, M. F., Compte Rendu du Congrès Géologique International, XIIe sess., p. 885 (1913).
(4) Dittrich, M., *Neues Jahrb. Mineral. Geol.*, **II**, 69 (1903).
(5) Gallup, J., *J. Am. Ceram. Soc.*, **18**, 144 (1935).
(6) Gottfried, C., *Z. Krist.*, **66**, 393 (1928).
(7) Hendricks, S. B., and Pauling, L., *Ibid.*, **64**, 303 (1927).
(8) Hillebrand, W. F., and Lundell, G. E. F., "Applied Inorganic Analysis," p. 789, New York, John Wiley & Sons, 1929.
(9) *Ibid.*, p. 791.
(10) *Ibid.*, p. 788.
(11) *Ibid.*, pp. 518, 521, 790.
(12) Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., "Chemical Analysis of Iron and Steel," p. 586, New York, John Wiley & Sons, 1931.
(13) Mellor, J. W., "Treatise on Quantitative Inorganic Analysis," pp. 225, 247, London, C. Griffin & Co., 1913.
(14) *Ibid.*, p. 224.
(15) Mitscherlich, A., *J. prakt. Chem.*, [1], **83**, 485 (1861).
(16) Rankin, G. A., and Merwin, H. E., *J. Am. Chem. Soc.*, **38**, 568 (1916).
(17) Smith, J. L., *Am. J. Sci.*, [2], **50**, 269 (1871).
(18) Washington, H. S., "Chemical Analysis of Rocks," p. 193, New York, John Wiley & Sons, 1919.
(19) Washington, H. S., *J. Am. Chem. Soc.*, **38**, 570 (1916).
(20) Willard, H. H., private communication.
(21) Winger, R. E., private communication.

RECEIVED September 14, 1935.

Occurrence of Selenium in the Colorado River and Some of Its Tributaries

KENNETH T. WILLIAMS AND HORACE G. BYERS
Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

DURING the past few years the writers have been engaged upon an investigation of the occurrence of selenium in soils (*1*). In the fall of 1934, W. D. Collins, of the Quality of Water Division, U. S. Geological Survey, kindly furnished a composite sample of water from the Colorado and Gunnison rivers in western Colorado. This was found to contain 0.015 part per million of selenium. As a result, C. S. Howard, of the same division, in December, 1934, collected a series of water samples from the same area, as well as a series of soil incrustations. In the spring (May, 1935) C. S. Howard, John T. Miller, and H. G. Byers collected a further series of samples of soils and water.

The samples collected have been analyzed by K. T. Williams. The methods employed were essentially those described by Robinson and others (*2*). The results obtained are given below in tabular form. Table I contains the data concerned with the water samples themselves and Table II the analyses of certain soils and soil incrustations which emphasize the conclusions reached concerning the sources of the selenium.

TABLE I. SELENIUM CONTENT OF WATER SAMPLES FROM COLORADO RIVER AND RELATED SOURCES

Lab. No.	Field No.	Location	Selenium
			P. p. m.
B14417	1	Colorado River near Cameo	0.000
14423	8	Gunnison River near Cimarron	0.000
15197	3	Uncompahgre River 5 miles south of Ouray	0.000
15196	2	Uncompahgre River 13 miles south of Colona	0.000
15198	4	Bear Creek 3 miles south of Ouray	0.000
15200	6	Cow Creek at Highway Bridge	0.002
15201	7	Uncompahgre River at Colona (1935)	0.002
14422	7	Uncompahgre River at Colona (1934)	0.003
14425	10	Uncompahgre River 0.75 mile west of Delta	0.220
14427	12	Gunnison River 0.5 mile north of Delta	0.007
14420	4	Gunnison River near Redlands	0.080
14420A	5	Colorado River near Grand Junction	0.030
	31	Dolores River near Cisco, Utah	Trace
	32	Green River at Green River, Utah	Trace
	33	Colorado River near Topock, Ariz.	0.030
14421	6	Drainage ditch in Montrose	0.700
14426	11	Relief drainage ditch, 2 miles east of Delta	0.320
14424	9	Main lateral 1 mile south of Chipeta	1.050
14419	3	Main drain 1.5 miles east of Loma	0.630
15203	9	Surface drainage 1 mile north of Mack	0.007
15204	10	Surface drainage near Loma	0.003
14418	2	New drain 4 miles north of Mack (1934)	1.980
15202	8	New drain 4 miles north of Mack (1935)	2.680

The data of Tables I and II are of interest not only because of the demonstration of the presence of selenium in river water, a fact not heretofore recorded, but because they indicate very clearly the sources of the selenium found. The Colorado river water is diverted near Cameo, Colo., to irrigate a large tract of land in the vicinity of Grand Junction in Mesa County. The Gunnison water is diverted near Cimarron, Colo., to provide a portion of the water used on the Uncompahgre irrigation project in Montrose and Delta Counties. The Uncompahgre river water is diverted near Colona for the same project. Examination of the data in Table I (Field Nos. 1, 7, and 8) reveals the fact that at these diversion points the Colorado and Gunnison contain no selenium, at least none in excess of one part per billion. The Uncompahgre at Colona, however, contained 3 parts per billion in December, 1934, and 2 parts per billion in May, 1935. These streams receive the surplus irrigation water as well as the surface and subsurface drainage water at points further down the streams. The Gunnison river near Delta, at the lower end of the Uncompahgre irrigation tract, has a selenium content of 0.007 part per million. Near its point of junction with the Colorado, after receiving drainage from the irrigated area near Whitewater and a part of the Grand Junction tract, its selenium content has increased more than tenfold. The Uncompahgre, near its mouth at Delta, has increased its selenium seventy-fold over that at Colona. The Colorado has no selenium until it receives drainage from the irrigated area, but at Grand Junction it has a selenium content of 30 parts per billion. The other tributaries of the Colorado examined contain negligible quantities of selenium, but it seems evident that sources other than the Gunnison exist, since otherwise dilution would have decreased the selenium content by the time Topock, Ariz., is reached. The selenium content of the Uncompahgre at Colona is 2 parts per billion, and is zero above the mouth of Cow Creek, and between Cow Creek and Colona there is a fairly large irrigated area. Whether any irrigation is practiced along Cow Creek is not known to the writers.

That the chief source of selenium is the drainage of the

TABLE II. SELENIUM CONTENT OF SOILS AND SOIL INCRUSTATIONS IN THE VICINITY OF MONTROSE AND GRAND JUNCTION, COLO.

Lab. No.	Field No.	Location	Material	Selenium *P. p. m.*
B14412	18	Near main lateral 1 mile south of Chipeta (near B14424, Table I)	Salt crust	100.0
14413	19	Near main lateral 1 mile south of Chipeta (near B14424, Table I)	Ooze in ditch	4.0
14414	20	Bar in Uncompahgre River (near B14425, Table I)	Sandy clay	9.0
14415	21	Relief drainage ditch, 1 mile east of Delta (near B14426, Table I)	Ditch deposit	28.0
14416	22	Drainage ditch (near B14427, Table I)	Ditch deposit	1.5
14442	28	Main drain 1.5 miles east of Loma (near B14419, Table I)	Salt crust	16.0
14439	25	6.5 miles east of Fruita	Salt crust	260.0
15003	2	6 miles east of Montrose, Montrose County	Clay soil 0–6 inch	3.5
15022	8	2.5 miles east of Montrose, Montrose County	Gypsiferous shale	3.5
15054	4	Sec. 26, T.15 S, R.95 W., Delta County	Chipeta clay 0–12 inch	3.0
15060	5	Sec. 19, T.15 S., R.95 W., Delta County	Billings clay 0–12 inch	4.0
15075	1	Sec. 10, T.9 S., R.103 W., Mesa County	Billings clay loam 0–12 inch	2.0
15078	1	Sec. 10, T.9 S., R.103 W., Mesa County	Billings clay loam 36–48 inch	8.0
15079	2	Sec. 15, T.9 S., R.103 W., Mesa County	Billings clay loam 0–12 inch	2.0
15082	2	Sec. 15, T.9 S., R.103 W., Mesa County	Billings clay loam 36–48 inch	5.0
B15085	4	Sec. 15, T.9 S., R.103 W., Mesa County	Alkali crust	52.0
15102	13	1.25 miles east of White Water	Billings clay loam 0–12 inch	3.0
12104	M27x	4.5 miles north of Loma, Mesa County	Mancos shale	2.0
12109	M27x	5.5 miles north of Loma, Mesa County	Mancos shale	6.0
15022	8	2.5 miles east of Montrose, Montrose County	Gypsiferous shale	3.5
15065	5	8 miles north of Delta, Delta County	Mancos shale	2.0

irrigated lands is made clearly evident by the data on the drainage waters examined. All the drainage waters examined from this section of Colorado contain selenium. The most striking examples are furnished by Nos. B14421 and B14424, both in the Uncompahgre area, and by B14419 and B14418, both in the Grand Junction area. The source of the selenium in the drainage water is clearly evident through consideration of the data of Table II. On the banks of the drainage ditches occur salt incrustations and these are in effect seepage deposits. They range in selenium content from 16 to 260 parts per million. Even the ooze (B14413 and B14416, Table II) in the ditches has a selenium content, and also a mud bar in the Uncompahgre river (B14414).

The soils of the whole area concerned in this investigation are derived from shales which contain selenium. The selenium content of representative shales is shown in Table II by Nos. B12104, B12109, B15022, and B15065. The quantity found in the soils varies considerably over the area. A few examples only are given in Table II.

Of special interest are samples B15075, B15078, B15079, B15082, and B15085 of Table II because of their relation to samples B14418 and B15202 of Table I. The new drainage ditch 4 miles north of Mack was sampled by C. S. Howard only a few weeks after its completion and before any great amount of drainage had taken place. It was sampled again after it had been in operation for about 6 months, when it was delivering a small flow of water. The water it contained was seepage through the soil, represented by samples B15079 and B15082 (Table II). The nonirrigated area adjacent to it is represented by samples B15075 and B15078 (Table II). Sample B15085 is a seepage incrustation near the ditch.

These observations have a practical aspect aside from their scientific interest, in that they indicate clearly the possibility of improvement of seleniferous land by irrigation and drainage where such management is practicable.

Literature Cited

(1) Byers, H. G., *U. S. Dept. Agr. Tech. Bull.* 482 (1935).
(2) Robinson, W. O., Dudley, H. C., Williams, K. T., and Byers, H. G., IND. ENG. CHEM., Anal. Ed., 6, 274–6 (1934).

RECEIVED September 2, 1935.

Semi-Micro-Kjeldahl Determination of Nitro and Azo Nitrogen

ROBERT A. HARTE, 315 East 80th St., New York, N. Y.

SEMI-MICRO adaptations of the classical Kjeldahl method, suitable for the estimation of nitrogen in combination as amine, amide, or imide, have been reported by Hitchcock and Belden (*3*) and Northrop (*4*). By modifying the method of Elek and Sobotka (*2*) for the determination of nitro nitrogen in micro- and macrosamples, a successful technic for the estimation of nitro and azo nitrogen on the semimicro scale has been devised.

Procedure

An accurately weighed sample of the dried substance, to contain from 2 to 5 mg. of nitrogen, is introduced into a dry 100-ml. Kjeldahl flask having a constriction about halfway up the neck, avoiding, as far as possible, deposition on the neck of the flask. Three hundred milligrams of C. P. dextrose, 1 to 1.5 grams of potassium sulfate, about 20 mg. of small copper sulfate crystals, and a few bits of well washed alundum (grain size 14, boiled out 5 to 6 times with distilled water until the washings showed no change of pH), are added to the flask whose neck is then washed down with 4 ml. of concentrated sulfuric acid (sp. gr. 1.84), care being taken to leave the neck entirely free of adhering particles. The mixture is digested over a shielded microburner with the flask in a nearly horizontal position, the heat being applied through a 2.5-cm. (1-inch) hole in an asbestos board. As soon as the digestion mixture has become homogeneous one drop of selenium oxychloride is added. Heating is continued until the solution is clear and for 15 to 20 minutes thereafter. The time of digestion varies from 35 to 45 minutes.

To the cooled solution 35 ml. of distilled water are added, and, just before distillation, the solution is made alkaline with 12 ml. of a clear 50 per cent sodium hydroxide solution, in the usual fashion. The distillation apparatus is the same as that described by Hitchcock and Belden (*3*). The distillate is received in 25 ml. of 0.02 *N* hydrochloric acid, and the excess acid is titrated with 0.02 *N* barium hydroxide, using as indicator the mixture of methyl red and methylene blue described by Andersen and Jensen (*1*). Blank values on the reagents vary from 0.10 to 0.20 ml. of 0.02 *N* solution. Typical analytical data are shown in Table I.

TABLE I. SEMI-MICRO-KJELDAHL DETERMINATION OF NITRO AND AZO NITROGEN

Substance	Weight of Sample	Nitrogen Found		Theory
	Mg.	*Mg.*	%	%
p-Nitroaniline, Kahlbaum	20.4	4.13	20.2	20.29
	20.4	4.14	20.3	
p-Aminoazobenzene, Kahlbaum	23.1	4.90	21.2	21.32
	22.5	4.78	21.2	
3-Nitro-5-carboxyphenylglycyl sulfanilic acid	21.8	2.30	10.5	10.63
3-Nitro-5-carboxyphenylglycyl aniline	23.6	3.11	13.2	13.33
Helianthine	19.9	2.72	13.7	13.77
	19.8	2.72	13.7	
Benzeneazoresorcinol	26.5	3.44	13.0	13.08
p-Nitromalanilic acid	30.8	3.38	11.0	11.02
p-Nitrobenzoÿl tyrosine ethyl ester	24.3	1.88	7.8	7.83

It is extremely important that the flask be thoroughly dried before the sample is introduced, since the presence of more than the traces of moisture contained in the reagents causes excessive foaming which prevents satisfactory completion of the digestion.

The method described permits of economy of time and substance with retention of a high degree of accuracy and precision. It has been used for more than a year for the routine analysis of new preparations with continued satisfaction. No special balance is required, a fine analytical balance being completely adequate.

Literature Cited

(1) Andersen, A. C., and Jensen, B. N., *Z. anal. Chem.*, 83, 114–20 (1931).
(2) Elek, A., and Sobotka, H., *J. Am. Chem. Soc.*, 48, 501–3 (1926).
(3) Hitchcock, D. I., and Belden, R. C., IND. ENG. CHEM., Anal. Ed., 5, 402 (1933).
(4) Northrop, J. H., *J. Gen. Physiol.*, 13, 774 (1929–30); 16, 320 (1932–33).

RECEIVED May 27, 1935.

Continuous Production of Distilled Water Free from Carbon Dioxide and Ammonia

FREDERICK G. STRAUB, Chemical Engineering Division, University of Illinois, Urbana, Ill.

THIS laboratory was recently faced with the necessity of continuously producing high-grade distilled water free from ammonia and carbon dioxide and having a specific conductance of 0.5 × 10^{-6} mho. or less. Tap water and steam were available (Tables I and II). When tap water was used in a hardwater type of Barnstead gas-fired still the best distillate obtained had a specific conductance of 5.0 × 10^{-6} mho. This was obtained with very little bleeding through a continuous overflow and with the condenser venting free steam.

TABLE I. ANALYSIS OF TAP WATER AVAILABLE

	P. p. m.
SiO_2	14.1
Ca	66.9
Mg	31.4
NH_3	5.3
Na	34.8
SO_4	1.2
Cl	4.0
Alkalinity: phenolphthalein, 0; methyl orange	37.6

TABLE II. ANALYSIS OF CONDENSED STEAM

	Condensate Leaving Condenser	
	At 20° C.[a]	At 100° C.[b]
CO_2, p. p. m.	9 to 16	0.7 to 1.0
NH_3, p. p. m.	10 to 12	
pH	6.0 to 6.5	8.0 to 9.0

[a] Specific conductance 16.6 × 10^{-6} to 12.5 × 10^{-6} mho.
[b] Specific conductance 6.6 × 10^{-6} mho.

The conductance was determined by passing a small amount of the distilled water through a totally enclosed type of conductivity cell. The resistance was determined by means of a dial type of Wheatstone bridge and a pointer type of alternating current galvanometer using 60-cycle current. The cell constant was about 20. The water leaving the still passed through a tin pipe.

The still was rearranged so that condensed steam from the steam heating system was used as make-up to the still, but again the best distillate produced had a specific conductance of 5.0 × 10^{-6} mho. The still was modified so that air, free from carbon dioxide and ammonia, could be added just below the water level and passed through the condenser with the condensing steam. The quality of the distillate remained the same and it was found to contain no carbon dioxide but appreciable amounts of ammonia.

The condenser used to condense the steam from the steam-heating system was then modified so that the condensate left the condenser at 100° C. with appreciable amounts of uncondensed steam flashing to the atmosphere. Table II shows the composition of the condensate after being collected in this manner. The carbon dioxide was low, but the ammonia had not been materially reduced. With such water being fed to the still, the ammonia would be carried with the steam and remain in the distillate. Tests were then run after continuously adding various amounts of sulfuric acid mixed with sodium dichromate to the condensed steam being fed to the still and with the still arranged so that a constant level was maintained by an overflow (Figure 1). When no air was being fed to the still the distillate from the still had a conductance of 1.0 × 10^{-6} mho. and

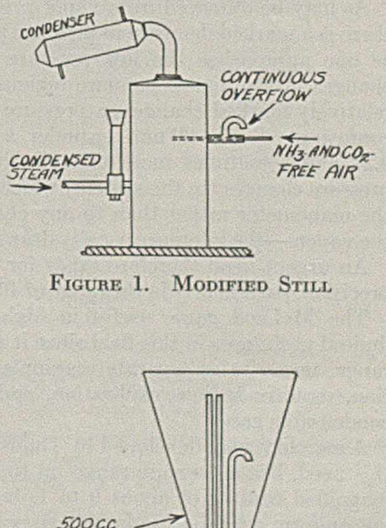


FIGURE 1. MODIFIED STILL

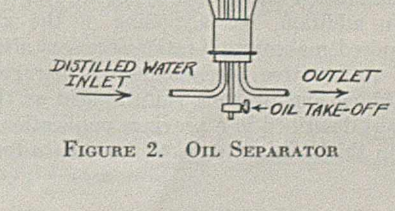


FIGURE 2. OIL SEPARATOR

a pH value (using a glass electrode) of 6.0. When air free from ammonia and carbon dioxide was blown through the still, the conductance changed to between 0.5×10^{-6} and 0.3×10^{-6} mho. with a pH value of 6.8. Variation of the acid feed showed that the best results were obtained when the pH value of the overflow water from the still was around 3.5.

After running with this type of treatment for several months, the still was found to be in very good condition. A black coating appeared below the water level but the tin coating was still intact beneath it.

A typical balance of acid feed and distilled water generated is as follows: The acid chromate solution was made up with 9 cc. of concentrated sulfuric acid and 10 grams of sodium chromate to 5 liters of water. This was added by means of a continuous feeding device at the rate of 30 cc. per minute. About 15 liters per hour of condensed steam were mixed with the acid feed and fed to the still, the excess above the amount distilled overflowing to waste. Nine liters per hour of distilled water were generated. The water overflowing from the still had a pH value of about 3.5.

The steam from the heating system contained a small amount of oil, giving a faint opalescence to the condensed steam, but the distillate from the still was perfectly clear. The oil appeared to carry over and deposit in the tin piping and from time to time globules of oil about 0.16 cm. in diameter came through with the water. A separator shown in Figure 2 was installed. The oil collected on the top of the solution and was drawn off through a valve, so that the resulting water was free from oil.

Received July 3, 1935. Presented before the Division of Industrial and Engineering Chemistry at the 90th Meeting of the American Chemical Society, San Francisco, Calif., August 19 to 23, 1935. Part of the research conducted in coöperation with the Utilities Research Commission, Chicago, Ill. Published by permission of M. L. Enger, Director, Engineering Experiment Station, University of Illinois.

A Precision Oil Gage

S. PALKIN, Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

INCREASING application of vacuum practice to fractional distillation has stimulated the development of a variety of pressure control devices (*2, 3, 5, 6*). Marked progress in this direction has been made in recent years, and control devices capable of a high order of precision have been developed (*3, 6*). Progress has lagged, however, in the development of gages capable of measuring the small pressure changes often involved—changes of a magnitude comparable with the precision control now possible by the improved devices.

The ordinary mercury manometer of the U-tube type, the most widely used in laboratory practice, permits a wide range of absolute pressure measurements but is comparatively coarse and insensitive. Pressure changes less than 0.25 mm. cannot be read with any reasonable degree of accuracy.

As may be observed from vapor pressure curves generally, there is a marked decrease in pressure per unit of temperature as one approaches the low pressure region. Temperature changes in the higher pressure regions generally conform to relatively marked changes in pressure and are not apt to be confusing. But at 20 mm. or under, a temperature change of 0.2° and sometimes more in a distillation may be due to pressure changes (in the system) which cannot be detected on the manometer rather than to any change in composition of the vapors—the inference usually drawn.

An urgent need therefore exists for pressure gages of high precision, particularly in the range of 40 mm. or less.

The McLeod gage, useful in high-vacuum work, has a limited usefulness in this field since it provides a very narrow range, necessitates separate manipulation for each observation, requires tedious calibration, and cannot be used with condensable gases.

A mercury gage developed by Dubrovin (*1*) intended to fill this need, has a pressure range up to 20 mm. and permits a magnified reading of about 9 to 1, but the magnification is not uniform over the 20-mm. range, so that for precision work calibration throughout the entire range is here also necessary. In addition, reconditioning of the gage, occasionally required, makes recalibration necessary after each reconditioning.

A sensitive U-manometer constructed of large diameter tubing and utilizing sulfuric acid as the manometric liquid was described in a previous publication (*6*). One millimeter on this manometer is equivalent to less than 0.125 mm. of mercury. The high absorptive capacity of strong sulfuric acid for olefin, terpene, and other unsaturated vapors, however, renders this manometer, in the course of time, unreliable when used in distillations involving these compounds. Even with efficient trapping devices, occasionally "reboiling" out of this instrument becomes necessary.

Oil Gages

The magnified reading and consequent increased precision that is possible with light liquids such as butylphthalate has long been recognized. But, as is well known, these liquids can only be used in the U-type manometers of the open-arm form, such as the Hickman gage (*4*), because of the impossibility of dislodging the liquid from the closed end. To provide the necessary reference vacuum, therefore, the Hickman gage utilizes a butylphthalate condensation pump as an integral part of the gage assembly. Its operation is necessarily a continuous function of the gage while the latter is in use.

In this paper, an improved gage is described which utilizes oil or other light nonvolatile medium as the manometric liquid and does not require a high-vacuum condensation pump for either its preparation or its use. For purposes of preparing or conditioning the gage a good laboratory pump, usually the same one used in connection with the vacuum distillation, is sufficient. After that, it functions much like any other type of gage, independent of the pump. Production of a reference vacuum, comparable to the Torricellian vacuum of the ordinary U-tube type, is made possible primarily by the construction of the gage.

With reasonable safeguards, the reference vacuum can be maintained for a long time and the gage can be used either continuously or intermittently without the need for reconditioning, although conditioning is, in itself, a very simple process and can be repeated for checking purposes as often as desired.

With paraffin oil as a manometric liquid, a pressure difference of 1 mm. oil level is equivalent to less than 0.067 mm. of mercury. Assuming an accurate reading of 0.5 (mm.) division, pressure changes of 0.033 mm. of mercury may therefore be read with precision. The oil level is, furthermore, very responsive to small pressure changes, no tapping, etc., as in mercury manometers, being required.

The gage is in effect a double U-tube type manometer in which both oil and mercury are employed, the latter serving, however, only as a mobile "backing" medium for the oil column.

Reservoirs 30, 31, and 32 are joined hermetically, as indicated, by thick-walled capillary tubes of approximately 1.5-mm. bore for the tube between reservoirs 30 and 31, and 2.5 mm. between reservoirs 31 and 32. Reservoir 30 serves as the mercury reservoir, 32 as the oil, and 31 as a temporary common reservoir for both, also as a degassing chamber and as a space for the Torricellian vacuum, comparable to the closed end of the simple U-type mercury manometer.

Stopcocks 33 and 34 directly below reservoirs 30 and 32, respectively, serve to lock the two liquids, mercury and oil, as necessary. The three-way stopcocks, 35 and 36, serve primarily to establish communication with the pumping system, the atmosphere, or the system whose pressure is to be measured, and for manipulating the movement of the liquid during preparation for use as explained below.

The three-way stopcock, 37, provides a means for selective communication either directly with the pumping system or with the gas system whose pressure is to be measured, as the case may be. The relative position of the reservoirs, their dimensions, etc., are in general as indicated in the illustration. The position of 30 must, however, be such as to insure against a differential mercury height in excess of 76 cm. (barometric height), so as to make possible free movement of the mercury through the whole apparatus when so desired. Thus, the greater the oil reading range desired, the higher the mercury reservoir 30 must be set up.

In order to maintain a Torricellian reference vacuum, the oil or other light liquid must be suitable for manometric work, have a very low vapor pressure and reasonably low viscosity, and be free from volatile impurities, to insure against the filling of reservoir 31 with vapors.

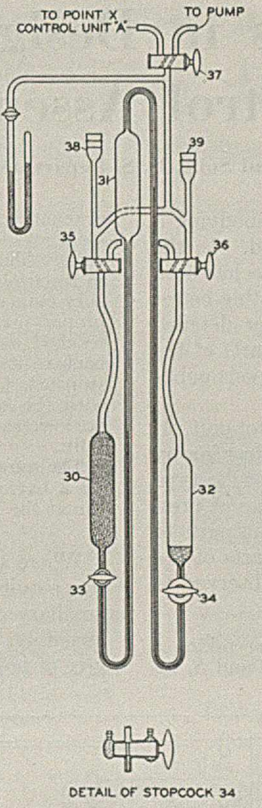


Figure 1. Diagram of Gage

Conditioning Gage for Use

The requisite quantity of purified mercury is introduced into reservoir 30 by way of opening 38 (ordinarily kept closed with rubber stopper) and stopcock 35 by applying slight suction through 37 and is allowed to fill the capillary tube up to bottom of reservoir 31. The mercury is then locked in position by stopcock 33. The rest of the system (reservoirs 31, 32, capillary, etc.) is then evacuated by communication with the pump by way of stopcocks 34, 36, and 37. Stopcock 36 is then locked and the requisite quantity of oil or other nonvolatile manometric liquid is introduced through opening 39 and drawn into reservoir 32 through stopcock 36 and thence into reservoir 31. By proper manipulation of appropriate stopcocks the mercury layer and its overlying oil layer are then allowed to rise in reservoir 31 to a point about one-half or two-thirds full. Stopcock 33 is then locked. Suction is applied to both sides of the system by way of the pump and pumping continued until no further gas evolution is evident. Heat may be applied to hasten the degassing process. Reservoir 30 is then opened to the atmosphere by way of stopcock 35 and by careful manipulation of stopcock 33, mercury and oil are pushed upward, the oil layer being sent through the capillary and the major part into reservoir 32 until the top of the mercury column is at the top of reservoir 31. The oil layer is then locked by stopcock 34 and, with the pump operating continuously, the three-way stopcock is turned to evacuate reservoir 30. When the pressure has been sufficiently lowered, the mercury thread will break at the mercury-oil juncture and the mercury column is then allowed to drop and empty reservoir 31. Stopcock 33 is then locked. There is thus produced a Torricellian vacuum between the mercury and oil. Moreover, since reservoir 31 is relatively large, the effect of any trace of residual gas in the mercury or oil that had not been removed in the degassing process is so minimized as to constitute a negligible factor. With the pump operating continuously, stopcock 34 is now opened, the oil column drawn over to a convenient level, locked again by 34, and is now ready for use. Communication with the system to be measured is made through stopcock 37. Stopcock 34 is opened and differential pressure read directly as in the ordinary mercury U-type manometer.

Special Stopcock 34. While any well-ground, long-barreled stopcock can be used, the mercury-sealed, or grease-sealed stopcock (shown in detail) is preferred. The grease should be "high vac" type, free from volatile matter.

The bores, respectively, of the tube below the stopcock, the plug, and the tube above the stopcock are progressively larger, as shown, in order to prevent the trapping of air bubbles.

Some indication may be had of the uniformity of behavior of the oil gage throughout its pressure range from the data in Table I. Comparative readings were made with the oil gage and a well-made simple U-type mercury manometer, using the pressure control unit (described in another paper, 6) to maintain constant pressure at the various points while making the observations. Readings were checked by T. H. Harris of this laboratory.

The mercury gage could probably be read at best to a fourth of a division (0.25 mm.).

The values given in column 3 of Table I were obtained by dividing the oil readings by 15.53, the ratio of the specific gravities of mercury and oil.

It was found that pressure readings could be made more rapidly and accurately by using the top of the wide meniscus (reservoir 32) for the 0 reference point and reading the distance between it and the bottom of the meniscus in the capillary rather than reading the distance between the bottom of the two menisci. The difference between top and bottom should, however, be determined as also the error due to capillarity. The latter is best determined on a separate piece of capillary tubing (2.5 mm.). These errors are compensating and their difference, which is generally within 1 mm. of oil (0.06 mm. of mercury), is applied as a correction for absolute pressure reading.

Table I. Comparative Readings

Reading on Oil Gage[a]	Reading on Hg U-Manometer[b]	Oil Reading Calculated[c] to Mm. Hg
Mm.	*Mm.*	
543	35	34.97
544	35	35.04
308.5	19.8	19.86
296	19+	19.06
155	10−	9.91
136	9−	8.76
82.5	5.3	5.31
29	2−	1.87
311	20	20.03
297	19+	19.12
233	15.2	15.03
155	10.0	9.91
77.2	5.0	4.97
25.5	1.7	1.64

[a] Oil used was Apiezon-B (J. Biddle and Co., Philadelphia), sp. gr. 0.8712 at 25/25°.

[b] Mercury manometer readings accurate to about 0.3 mm.

[c] Calculated values obtained by dividing oil readings by 15.53—the ratio of the specific gravity of mercury to that of the oil.

Literature Cited

(1) Dubrovin, U. S. Patent 1,928,096 (Sept. 26, 1933).
(2) Hershberg and Huntress, Ind. Eng. Chem., Anal. Ed., 5, 144 (1933). (Contains comprehensive bibliography to 1933.)
(3) *Ibid.*, 5, 344 (1933).
(4) Hickman and Weyerts, *J. Am. Chem. Soc.*, 52, 4714 (1930).
(5) Jacobs, Ind. Eng. Chem., Anal. Ed., 7, 70 (1935).
(6) Palkin and Nelson, *Ibid.*, 6, 386 (1934).

Received July 15, 1935. Presented before the Division of Agricultural and Food Chemistry at the 90th Meeting of the American Chemical Society, San Francisco, Calif., August 19 to 23, 1935.

Improvements in Design of Pressure Control Assembly

S. PALKIN, Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

IN A PREVIOUS publication (*2*) a design embodying a dual system of pressure control was described. In the new design shown in Figure 1 the control apparatus has been improved and its operation simplified, thus permitting better coördination with the distillation apparatus. For detailed measurements and construction of the essential parts of the control assembly, the reader is referred to the previous publication (*2*).

The low-pressure system both for the main control unit, *A*, and for the auxiliary unit, *C*, is indicated in the drawing by heavy dark lines. Both barometric and short U-tube type manometers are used in order to provide full range of pressure up to atmospheric and are distributed in various parts of the apparatus as shown, so that pressure in all parts of the assembly, including the auxiliary units, may be observed at any time.

The arrangement has been so simplified that after taking a fraction of distillate from 4 and locking stopcocks 5 and *S*, reevacuation of 4 is accomplished with the manipulation of but two stopcocks—*S* of the control unit and 5 of the distillate reservoirs. This is done as follows: Three-way stopcock *S* is opened to reservoir 4. The pump, thus automatically started by mercury manostat *V* and relay *r*, exhausts reservoir 4 and when the proper pressure (equal to the distillation pressure) has been reached, as indicated by manometer t_1 or t_2, stopcock *S* is turned back to its original position, open to low-pressure flask *K*, and stopcock 5 is opened to 6, bringing it back in communication with the column distillation system. No other manipulations are necessary, as all other operations are taken care of automatically.

The same simplicity of manipulation in taking a fraction holds for a battery of stills operated at the same time where all are run at the same pressure.

Where simultaneous operation of several pieces of apparatus requires pressures differing from one another, smaller auxiliary control units as shown in *C* may be joined to the assembly. Such auxiliary units do not possess the high degree of precision possible with the sulfuric acid manostat (*1*), but have been used satisfactorily, for example, for controlling the temperature of a column still jacket and for an Abderhalden drying apparatus. Here the desired temperature is obtained by boiling a suitable liquid at a set pressure controlled by the auxiliary unit.

The auxiliary unit is similar to the large unit, *A*, but simpler and consists of a capillary valve-manometer mechanism (set in the large test tube, 20) and a mercury manostat, 21. The magnet operating the valve receives the current from a 110-volt circuit (d. c.) in series with a 7.5-watt lamp, 22, which provides the necessary resistance. The mercury manostat, 21, acts both as a manostat and a switch, thus obviating the need for a relay. Stopcock 23 serves as a by-pass. Capillary stopcock 24 provides connection with the atmosphere when necessary.

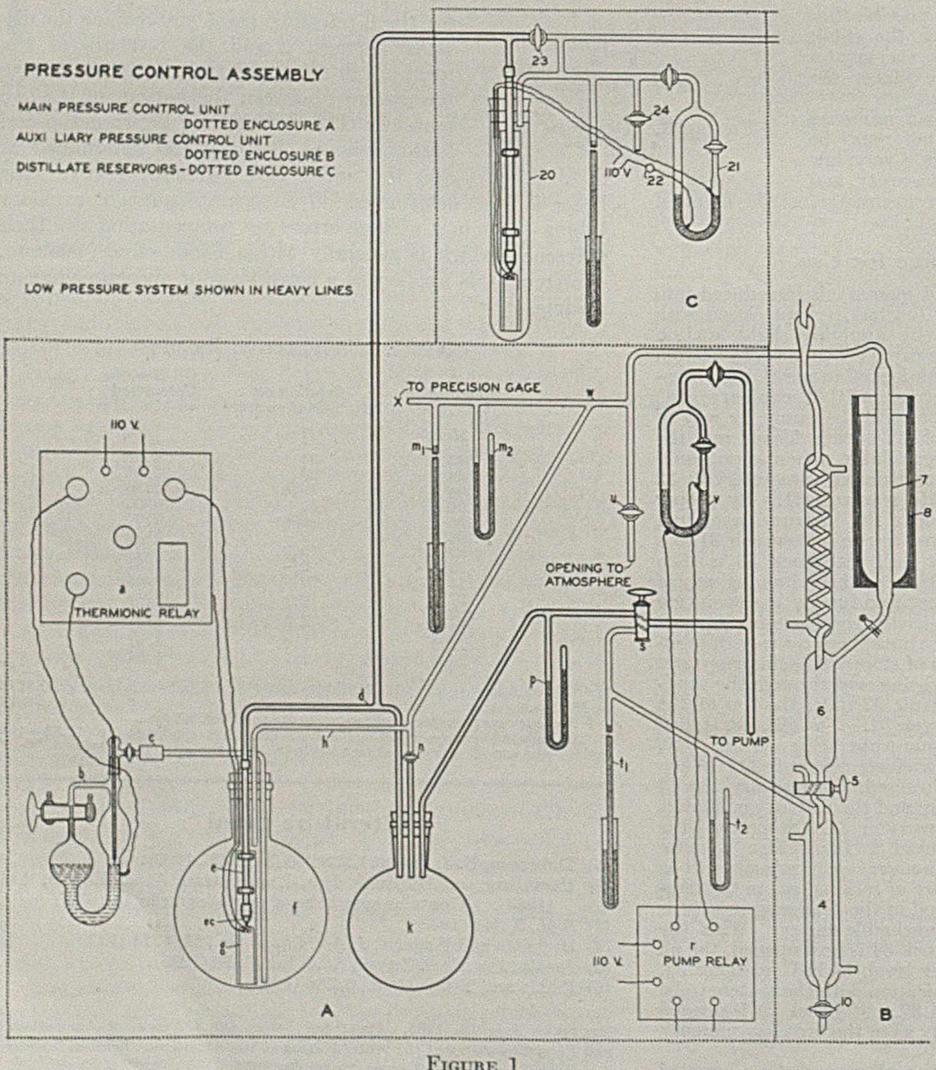


FIGURE 1

Literature Cited

(1) Hershberg and Huntress, Ind. Eng. Chem., Anal. Ed., 5, 344 (1933).
(2) Palkin and Nelson, *Ibid.*, 6, 386 (1934).

RECEIVED July 15, 1935. Presented before the Division of Agricultural and Food Chemistry at the 90th Meeting of the American Chemical Society, San Francisco, Calif., August 19 to 23, 1935.

A Convenient Absorption and Titration Flask for Carbon Dioxide Determination

ROBERT GARDNER, Colorado Agricultural College Experiment Station, Fort Collins, Colo.

A PRECISE method of determining carbon dioxide in air has been described by Thomas (*2*). A modified form of the absorption unit described, which has been found very useful for a variety of carbon dioxide determinations, consists of a 250-cc. Erlenmeyer flask with a side arm drawn down at the end for tube connection and a fritted glass disk sealed in the tube at the point where it begins to taper. The flask was made by blowing a hole in the end of a test tube, sealing on a small piece of tubing, and fusing a porous disk at *A* (Figure 1). The tube was then sealed into the side of the flask. The disk was made of 100- to 200-mesh glass and was prepared by the method described by Bruce and Bent (*1*).

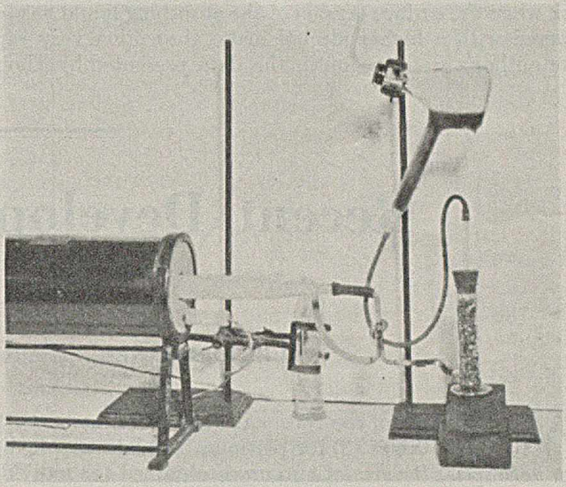


FIGURE 3. ASSEMBLY FOR DETERMINING TOTAL CARBON

To operate, 25 to 50 cc. of the absorbing solution with a few drops of normal butyl alcohol are placed in the flask, the side arm is attached by a rubber connection to the source of gas to be analyzed, and suction applied through a tube in the stopper. As soon as suction is applied, the flask is rotated so that the side arm is nearly vertical. Before the suction is removed and the pressure equalized, the side arm is brought to a horizontal position to prevent liquid passing through the disk. The contents are titrated through a tube in the stopper. For precise work, carbon dioxide is removed before starting a determination by filling with water and then replacing the water with carbon dioxide-free air through the side arm. Usually, a correction for the initial carbon dioxide in the flask, made from a blank determination, is sufficiently accurate.

Tenth normal sodium hydroxide is satisfactory as an absorbing solution. When absorption is complete, an excess of 10 per cent barium chloride solution is added through a tube in the stopper and the excess base titrated against 0.1 *N* hydrochloric acid. It is necessary to clean the porous disk occasionally with hydrochloric acid to prevent clogging with barium carbonate. The contents of the flask may be protected from contact with outside air by introducing all solution's through a rubber tube in the stopper, which is kept closed by a clamp except while the solutions are being introduced. Barium hydroxide is not suitable for an absorbent if much carbon dioxide is present, because the barium carbonate clogs the pores in the disk, but barium chloride may be added before titration.

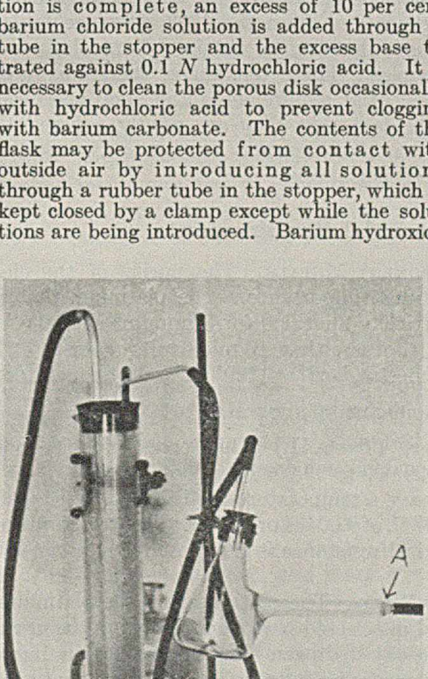


FIGURE 1. ASSEMBLED EQUIPMENT

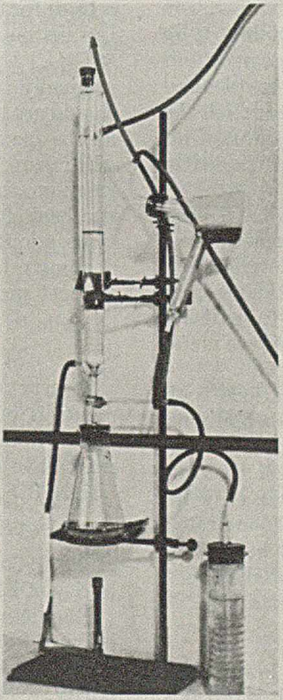


FIGURE 2. APPARATUS IN OPERATION

The equipment as assembled in Figure 1 has been used to determine carbon dioxide in the soil air and to measure the concentration of carbon dioxide in desiccators over a number of materials, including soil and cereals. When measuring carbon dioxide in the soil air, the side arm was connected directly to a tube inserted into the soil.

The device has been found very convenient in determining the carbonate and total carbon content of soils, particularly where the carbon content is low. Figure 2 shows the carbonate apparatus in operation.

The sample to be analyzed for carbonate is weighed into a wide-mouthed Erlenmeyer flask which is connected to a source of carbon dioxide-free air and through a condenser to the side arm of the absorber. Suction is applied by an aspirator pump. Acid is added to the soil through a large buret and the rate of gas flow regulated by the pump.

Total carbon may be determined conveniently by connecting the flask as shown in Figure 3, instead of the usual absorption train, to a combustion tube containing the sample. Titrating the contents of the flask takes no more time than weighing the absorption bulbs and is more accurate for small amounts of carbon. When determining total carbon in soil the sample is mixed intimately with manganese dioxide in a boat and placed in a combustion tube in the furnace. The gases from the tube pass through an absorber containing granular zinc to remove acids from the oxidation of sulfur and nitrogen compounds, through a sulfuric acid bulb (not shown in the figure, usually may be dispensed with) to remove any ammonia, and then to the carbon dioxide absorption flask. A stream of carbon dioxide-free oxygen is passed through the system during the determination and the furnace is run at about 900° C. About 10 minutes are required for a determination.

If the method is to be used for determining carbon in a variety of compounds, the chain preceding the carbon dioxide absorber would depend, of course, upon the composition of the material being studied. The zinc absorber does not remove nitric acid completely, but the error resulting is usually small with soils and, if necessary, can be corrected by a nitrate determination of the residue in the flask after titrating.

The extremely small bubbles produced by the porous glass disk when the surface tension of the absorbing liquid has been lowered with a higher alcohol make absorption very rapid. The author's results confirm the data presented by Thomas (*2*) which show that several hundred milliliters of air per minute can be passed through this type of absorber and still get very high absorption.

Literature Cited

(1) Bruce, W. F., and Bent, H. E., *J. Am. Chem. Soc.*, 53, 990 (1931).

(2) Thomas, M. D., Ind. Eng. Chem., Anal. Ed., 5, 193 (1933).

Received June 26, 1935.

Recent Developments in Platinum Thermocouples

BERT BRENNER, Sigmund Cohn, 44 Gold St., New York, N. Y.

WITH the use of the National Bureau of Standards 1933 reference tables (*3*) for platinum to platinum-rhodium thermocouples, the deviation curves obtained for individual couples have no points of inflection and are mostly linear. The improvement in these tables over those previously used is found principally at the higher temperatures, and particularly above 1200° C. (2200° F.). The accuracy of temperature measurements obtainable with such couples is now limited by the quality of the thermocouple wires and (unless corrections based upon an individual calibration of the actual couple used are applied to each reading) upon the limits within which the manufacturer can keep the deviations of the e. m. f. of his couples from the standard values. This situation seemed to make closer tolerances desirable.

In the past few years definite improvements have been made in the manufacture of platinum-rhodium thermocouples, increasing their effective life, their resistance to deterioration at high temperature, their homogeneity, and their reproducibility. The following data are presented to indicate what tolerances it is possible for a manufacturer of rare metal thermocouple wire to meet.

In 1934, this company adopted shop specifications with tolerances much closer than had ever been used for platinum and platinum-rhodium, and has been able to adhere rigidly to these specifications. While they may not represent the ultimate tolerances which might be met in special cases, they are significant in that they indicate the quality (as demonstrated by actual experience) which a manufacturer may be reasonably asked to maintain in the general run of his product.

General Considerations

Since the first effect in service is, in general, a lowering of the e. m. f. of a platinum-rhodium thermocouple, it is obvious that a couple which originally yields an e. m. f. lower than the standard will, in service, gradually depart further. It is, therefore, important to allow only positive deviations from the standard (N. B. S.) reference tables. Tests of high-grade thermocouples at the National Bureau of Standards by Neville in 1923 (*2*) have shown that during a service test of 25 hours at 1500° to 1600° C., the e. m. f. (measured at 1200° C.) of the platinum element decreased 5.5 microvolts while that of the alloy element decreased 14.5 microvolts. The e. m. f. of the couple consequently decreased 9 microvolts at 1200° C. Neville also found that the corresponding decrease in the e. m. f. of thermocouples then made commercially was from 4 to 12 times as great (36 to 120 microvolts). The author has observed an average drop in the e. m. f. in this company's thermocouples at 1200° C. of less than 10 microvolts (less than 1° C.) after 36 hours at 1500° C. (uniform electrical heating in air).

The ability of the best thermocouples to retain their original characteristics when subject to high temperatures furnishes a basis for deciding how far it is worth while to go in tightening up on specifications. The limit is indicated as about ±1° C. Upon this basis and keeping in mind the fact that originally negative deviations from the standard values should not be permitted, a tolerance of +2° to 0° C. at 1200° C. as the maximum deviations from the 1933 reference tables will insure the utmost that can be obtained from platinum-rhodium thermocouples. These tolerances, therefore, form the basis for the essential requirements and shop specifications adopted. The fact that they are rigidly adhered to demonstrates that manufacturers may be reasonably expected to meet such close specifications.

Essential Requirements

Purity of Component Metals. The purity of the elements is of the utmost importance. The platinum, drawn into wire and electrically annealed for 3 minutes at 600° C., must have an e. m. f. of less than 10 microvolts against Pt 27 (the N. B. S. platinum standard) at 1200° C., and a temperature coefficient for the fundamental interval 0° to 100° C., $\frac{R_{100} - R_0}{100R_0}$ of 0.00392 or higher. (Table II.) This corresponds (*1*) to a purity of between 99.999 to 99.9999 per cent.

Rhodium must have a temperature coefficient of resistance between 0° and 100° C. of 0.00434 or higher. The temperature coefficient of electrical resistance is the most reliable test for purity.

Preparation of Wire. The platinum and the platinum-rhodium are melted in selected pure lime, following the usual procedure, using an oxy-hydrogen blow torch (with platinum tip), with strongly oxidizing flame. They are cast into ingots, forged, rolled, swaged, and finally drawn through diamond dies to size. The utmost care must be taken throughout the entire procedure to keep the material absolutely clean if contamination is to be avoided. The finished wire must be sound, uniform, smooth, and round. The maximum tolerance in size at finish is ±0.0002 inch.

Interchangeability and Reproducibility. Platinum can be made to meet closer specifications for interchangeability than rhodium. The addition of slight impurities to pure platinum invariably makes it thermoelectrically more positive. The platinum is, therefore, practically always slightly positive to Pt 27 (the N. B. S. platinum standard). Occasionally a sample may be found which is 1 or 2 microvolts negative at 1200° C. to Pt 27 (indicating a purity very slightly higher than the Bureau's standard), but platinum is usually a few microvolts positive, although always by an amount less than 10 microvolts.

The e. m. f. of the platinum-rhodium wire, even when made up of impure constituents, can be adjusted for any one given temperature to any value within reason by changing the ratio of the constituents. At first sight this might seem to make high purity in the constituents a needless refinement. Such is not the case, however, for if impure constituents are combined in such a ratio that the resulting wire gives the e. m. f. in the standard table at 1200° C., it will not give the values in the standard table at other temperatures. It is for this reason that all the rhodium used by this company for thermocouple alloys is required to have a temperature coefficient of resistance, $\frac{R_{100} - R_0}{100R_0}$, of 0.00434 or higher.

The metals, both platinum and platinum-rhodium, must be homogeneous and as free from gases as possible. Homogeneity is much more easily achieved in platinum than in platinum-rhodium. In the latter, considerable segregation takes place and steps must be taken to reduce this to a minimum. The company's shop specification for homogeneity is that the difference in e. m. f., in either the platinum or the alloy wire, checked every 1.2 meters (4 feet) of the entire length of every coil (approximately 180 meters at 0.5 mm. diameter, 600 feet at 0.020 inch diameter) shall be less than 3 microvolts at 1200° C. Since the completed couple yields about 12 microvolts per degree Centigrade at 1200° C., this is the equivalent of 0.25° C.

The platinum-rhodium wire, of the degree of homogeneity specified above, is required to be between 0 and 24 microvolts plus to the company's standard alloy. This standard is one which combined with Pt 27 would exactly fit the standard table. Now, since the platinum is required to be between 0 and 10 microvolts plus to Pt 27, the deviation of the couple is always a quantity between 0 and 24 microvolts diminished by a quantity between 0 and 10. Thus if alloy wire is +12 microvolts and the platinum +6 microvolts, the completed couple will be +6 microvolts at 1200° C., or about 0.5° C. Numerous checks have shown the maximum deviation to average about 1° C. The maximum allowed for these departures on the completed thermocouple from the standard table is +24 to 0 microvolts or +2° to 0° C. at 1200° C. This figure represents the accuracy with which these couples can be used without calibration. Moreover the first effect of service is to decrease the e. m. f. and to bring the couple closer to the standard table.

Resistance to Contamination. Resistance to contamination of thermocouple wire during service is greatly affected by the temperature, time, and number of annealings before use. In service, the rate and extent of contamination of pure platinum annealed for 3 minutes at 1500° C. is about ten times that of 10 or 13 per cent rhodium-platinum similarly treated. Of the factors affecting the rate of contamination in service, temperature of anneal prior to use seems the most important.

The appearance under the microscope of highly annealed wire, especially pure platinum, is not dense but rather porous with large crystals, large open grain boundaries, and severe pitting. Such highly annealed wire is very susceptible to contamination in service. It seems that such wire is chemically or catalytically more active than wire annealed at lower temperatures. On the other hand the appearance of wire annealed at a low temperature is dense, not porous, and shows no recrystallization or grain boundaries. It is also mechanically much stronger, and less susceptible to contamination in service.

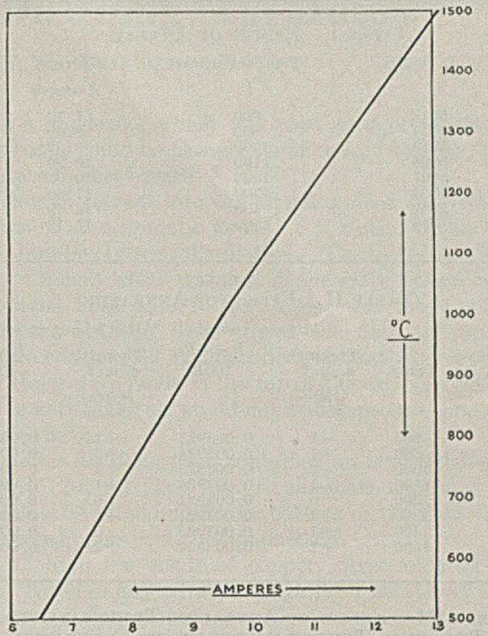


Figure 1. Temperature-Current Curve for Annealing Thermocouple Wire 0.05 Cm. Diameter

In the case of pure platinum and platinum-rhodium, the purpose of annealing is to normalize the wire. Knowing that wire annealed at a low temperature is less susceptible to contamination in service than wire annealed at a very high temperature, an investigation was started to determine the lowest possible temperature which would accomplish the desired result. It was found with pure platinum, annealed for 3 minutes at 600° C., that recrystallization takes place sufficiently to result in a constant e. m. f. and temperature coefficient of resistance. Magnification one hundred times does not show any visible signs of recrystallization. The grain size is considerably smaller than after annealing at higher temperatures and the density, strength, elongation, and general appearance of the wire are improved.

A similar condition exists for 10 per cent platinum and 13 per cent rhodium. Annealing for 2 minutes at 1200° C., instead of at 1500° C., as heretofore practiced, normalizes this wire sufficiently to produce constant e. m. f. values. The grain size of this wire also is considerably smaller than after annealing at higher temperatures. The strength, elongation, and general appearance also are improved.

Constancy of Calibration and Life

The usual procedure in making life tests is to suspend the wire between terminals and heat electrically to the desired temperature. The terminals should be close enough together to avoid putting the wire under any tension beyond that due to its own weight. Certain changes in e. m. f. values, general appearance, and mechanical properties appear after this annealing procedure. Thermocouples which are intended for accurate use should not be annealed at 1500° C., although a test at 1500° C. is a good criterion of their quality.

The wire which this company supplies commercially has been flash-annealed—that is, for 3 minutes—at 600° C., for the platinum and for 2 minutes at 1200° C. for the alloy. Before a melt is finally accepted, two samples, one from each end, are heated for 6 hours at 1500° C. and the maximum drop

Table I. Effect of Annealing

N. B. S. No.	Temperature	Current
	° C.	*Amperes*
5013	600	7.10
5014	800	8.30
5015	1000	9.52
5006	1100	10.20
5007	1200	10.93
5008	1300	11.66
5009	1400	12.39
5010	1500	13.12

Table II. Effect of Annealing

		5-Minute Anneal		After 1 hour at 1450° C.	
N. B. S. No.	Temp.	Thermal e. m. f.	$\frac{R_{100}-R_0}{100R_0}$	Thermal e. m. f.	$\frac{R_{100}-R_0}{100R_0}$
	° C.	*Micro-volts*		*Micro-volts*	
5013	600	−1	0.003923	+3	0.003922
5014	800	−1	0.003924	+3	0.003923
5015	1000	−2	0.003922	+3	0.003923
5006	1100	−1	0.003924	+1	0.003921
5007	1200	0	0.003921	0	0.003924
5008	1300	+1	0.003921	+1	0.003920
5009	1400	+1	0.003922	0	0.003920
5010	1500	+2	0.003922	+2	0.003920

Table III. Effect of Annealing Temperature and Time upon Tensile Strength and Elongation

Sample	Annealing		Tensile Strength[a]	Elongation
	° C.	*Min.*	*Kg.*	*%*
Thermocouple platinum	(Hard drawn, no anneal)		5.45	0.8
	600	3	2.95	36
	1000	3	2.61	34
	1200	3	2.50	34
	1500	3	2.27	32
	1500	1 hour	1.13	24
	1500	6 hours	.91	3.5
10% Rhodium platinum	(Hard drawn, no anneal)		11.80	0.6
	900	2	6.36	1.5
	1000	2	6.36	3.0
	1200	2	6.36	22.0
	1450	2	5.68	16.0
	1450	6 hours	2.72	6.0

[a] Kilograms at 0.5 mm. (0.020 inch) diameter.

from the flash-anneal to the 6-hour anneal at 1500° C. must not exceed 5 microvolts at 1200° C.

Experience has revealed an interesting phenomenon that occurs in such life tests. As time goes on the temperature near the terminals of the suspended wire becomes hotter, probably because of stretching due to the weight of the suspended wire and the fact that the rising currents of heated air make the temperature of the surrounding air hottest near the top. The ends, about 15 to 30 cm. (6 to 12 inches) are therefore disregarded. Samples of platinum wire annealed for 36 hours at 1500° C. show a drop of less than 5 microvolts and samples of 10 and 13 per cent alloy less than 10 microvolts under the same conditions (e. m. f. measured at 1200° C.). After 50 hours at 1500° C., the total drop of a thermocouple made of such wire is still less than 1° C. at 1200° C.

In order to determine the characteristics of pure platinum under different annealing conditions, a coil of wire of stock melt No. 26, 0.05 cm. (0.020 inch) in diameter was sent to the National Bureau of Standards. Eight samples of wire, each about 1.5 meters long, were cut from the coil and electrically annealed for 5 minutes in air, each wire at a selected temperature. These temperatures and the current required to bring the wire to the temperature in question, as reported by the National Bureau of Standards, are given in Table I, and plotted in Figure 1.

The e. m. f. versus Pt 27 and the temperature coefficients $\frac{R_{100} - R_0}{100\ R_0}$ were measured. All the samples were then heated electrically for 1 hour at 1450° C. and the e. m. f. and the temperature coefficient again determined. Table II gives the values reported by the National Bureau of Standards.

Each end of each sample was compared with Pt 27, and the Bureau of Standards reported that both ends gave identical results except in one case where the difference was 1 microvolt.

Mechanical Strength

Since the mechanical strength of the wire in service seemed to be very closely related to the annealing procedure before use, investigation was made to determine the best annealing practice. It was found that the lowest possible temperature for platinum is 600° C. and for platinum-rhodium 1200° C. These temperatures are sufficient to normalize the wire, and such wire has the greatest possible tensile strength (Table III) and also the greatest resistance to contamination in service.

Up to the present time, flashing at 1500° C. from 2 to 5 minutes and annealing at the same temperature from 1 to 6 hours has been generally believed to be essential and preferable, in order to establish the quality of thermocouples. It is possible to reduce the e. m. f. of platinum by such prolonged high-temperature treatment, but at the expense of the effective life in service. In the case of calcium contamination, for instance, it would be easily possible, by annealing at 1500° C., and faster yet at 1600° C., to reduce +25 microvolts to less than +10 microvolts against Pt 27, checked at 1200° C. The practice of burning out impurities, by prolonged high-temperature anneal, weakens the wire mechanically as well as renders it more susceptible to contamination, and such wire will not be nearly as satisfactory in actual service as platinum wire of less than 10 microvolts positive to Pt 27 at 1200° C., but which was annealed at the finish for 3 minutes at 600° C.

Conclusion

The tolerances of ±3 microvolts at 1200° C. for homogeneity within +2° to 0° C. for agreement with the standard values, and a maximum change of 5 microvolts at 1200° C., in the completed couple upon annealing for 6 hours at 1500° C. are, the author believes, the closest tolerances ever set up for thermocouples. Manufacturing experience with these tolerances demonstrates that they can be consistently met, however, and this fact should prove valuable to users of rare metal thermocouples as a guide in determining what performance they may reasonably demand.

Flash-annealing the platinum at 600° C. and the platinum-rhodium alloy at 1200° C. is sufficient to stabilize thermocouples of high quality. Intensive annealing does not materially change the e. m. f. and impairs the mechanical properties. Such annealing, moreover, renders the wire more susceptible to contamination during subsequent use.

Acknowledgment

Grateful acknowledgment is made for the helpful coöperation of H. T. Wensel and W. F. Roeser of the National Bureau of Standards for determining the data given in Tables I and II, and A. O. Ashman and C. F. Homewood of the New Jersey Zinc Company.

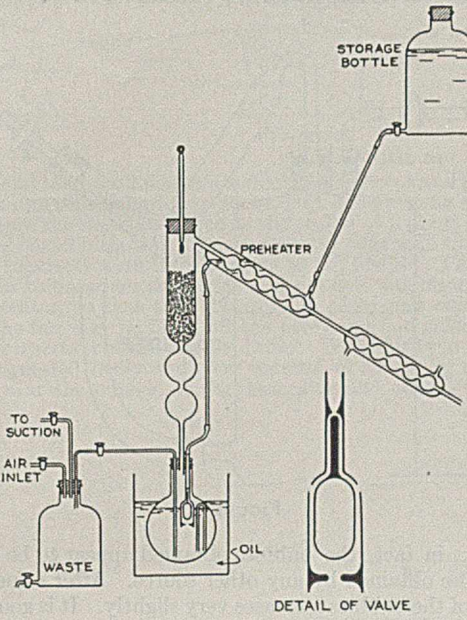
Literature Cited

(1) Caldwell, F. R., *Bur. Standards J. Research*, 10, 373 (1933).
(2) Neville, R. P., *Trans. Am. Electrochem. Soc.*, 43, 371 (1923).
(3) Wensel, H. T., and Roeser, W. F., *Bur. Standards J. Research*, 10, 275 (1923).

Received May 18, 1935.

An Economical Continuous Distilling Apparatus

FRANK M. SCHERTZ, 1305 Farragut St., N. W., Washington, D. C.



THE recovery of large quantities of solvents in isolating carotene, chlorophyll, and xanthophyll led to the development of the distilling apparatus illustrated. It was economical of heat and practically eliminated all danger of fire.

The storage bottle which contained the solvents to be distilled was elevated high enough so that gravity alone caused the liquids to flow into the distilling flask, after passing through a condenser which was used as a preheater. The storage bottle could be placed at a distance from the still and thus reduce the fire hazard.

The flow of solvent into the distilling flask was controlled by means of an automatic float (3.5 × 6 cm.) which kept it at a constant level during distillation. The end of the glass rod (5 mm. × 5 cm.) which was part of the valve was ground into the modified inlet tube, so that a seal was made when the liquid in the distilling flask caused the float to rise. The parts were constructed as illustrated, so that they would not stick. Holes were made in the top of the cage (4 × 8 cm.) of the valve so that the air would not be trapped and prevent the float from rising.

The 3-liter distilling flask contained an inverted U-shaped small-bore (2-mm.) glass tube to eliminate bumping as well as a glass tube extending to the bottom of the flask through which waste liquors could be siphoned off.

The oil bath was made of copper, silver-soldered at the seams. Nujol or any oil with a high flash point may be used in the bath. In recovering methanol or acetone from an aqueous solution the temperature of the bath often ran as high as 170° C.

Using a 1000-watt hot plate of the open type with a three-heat switch control, 2.5 liters of 95 per cent ethanol were distilled in 1 hour. Solvents with boiling points between 20° and 100° may be easily distilled or recovered.

Acknowledgments

Indebtedness is due Carl Rist for suggesting the use of a float for maintaining the constant level of the liquid in the distilling flask, Arthur Mack for its construction, and Mrs. Constance Sherry for the drawing.

RECEIVED June 29, 1935.

An Automatic Still Cut-Off

ARTHUR H. HALE AND FRED D. TUEMMLER
T. Jefferson Coolidge, Jr., Memorial Laboratory,
Harvard University, Cambridge, Mass.

A SIMPLE fool-proof automatic switch for breaking the circuit to an electrically heated Barnstead conductivity water still was needed to prevent any possibility of burning out the heating units by boiling the still dry.

Either an outside or inside float switch seemed impractical, since positive action might not always be certain in alkaline permanganate from which the water was distilled. By calibrating the rate of distillation on the glass level indicator in terms of the drop in the water level in 15-minute intervals, it was possible to use a time-clock switch to operate a magnetic switch controlling the still. However, if the magnet was controlled only by the clock switch, the still would turn on automatically at 12-hour intervals, or if the current stopped even momentarily, the clock would stop until started again manually but the still circuit would be closed again when the current returned without any possibility of being opened by the clock. In either case there was no protection against burning out the heating units.

To solve this problem the circuit in Figure 1 was used, the important feature of which is the momentary switch. Since the magnetic switch is held in contact through one of its own arms, a momentary interruption of the current will open it. To close the magnetic switch, the momentary switch is connected across the gap in the magnet circuit and only by pushing this switch can the still circuit be completed once it is opened. This circuit is applicable for use with any electrically operated machine which must not operate beyond a certain time limit and which must not again operate after the 12-hour interval of the clock.

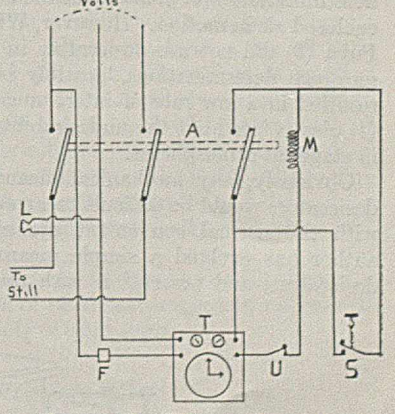


FIGURE 1. WIRING DIAGRAM

A. Magnetic switches
F. Fuse (110 volt)
L. Pilot light
M. Magnet
S. Momentary switch
T. Time-clock switch
U: Manual cut-off switch (ordinarily left closed)

RECEIVED September 21, 1935.

Carbon Dioxide from Dry Ice

WALTER S. IDE
Burroughs Wellcome and Company, U. S. A., Experimental Research Laboratories, Tuckahoe, N. Y.

IT HAS been found that carbon dioxide gas, generated from the solid in a convenient apparatus, is a very satisfactory source of carbon dioxide for use in the determination of nitrogen by the micro-Dumas method. Carbon dioxide snow is now becoming readily available in most laboratories.

The solid carbon dioxide in small pellets is placed in the mercury trap, which is a test tube 20 mm. in diameter and 20 cm. long, fused to another tube of like dimensions (Figure 1). The open end of the tube is fitted with a stopper containing a stopcock. A few minutes after introduction of the pellets the air in the trap will all be expelled. By closing stopcock *A*, the gas will be forced into the 8- to 10-liter aspirator bottle which has been filled with freshly boiled water and may be graduated to measure the quantity used. The water is forced out through special nitrometer tubing into a large thick-walled rubber bladder (heavy beach ball).

On setting up the apparatus, it is convenient to flush the aspirator bottle and bladder with carbon dioxide from a tank, filling the bladder with water before connecting to the bottle. The water will then flow into the bottle until it is filled and the bladder is deflated, ready to receive the carbon dioxide as it is generated. The bladder should be placed on a shelf approximately level with the top of the aspirator bottle. This height should be adjusted so that there will be positive internal pressure at all times.

The carbon dioxide should be released and replaced several times. This will insure very small microbubbles in the azotometer; in fact, the bubbles obtained appear to be smaller than those obtained by any other source. After some weeks the size of the bubbles increases very slightly. It is good practice to refill the generator about once each week during routine work to eliminate the possibility of this error.

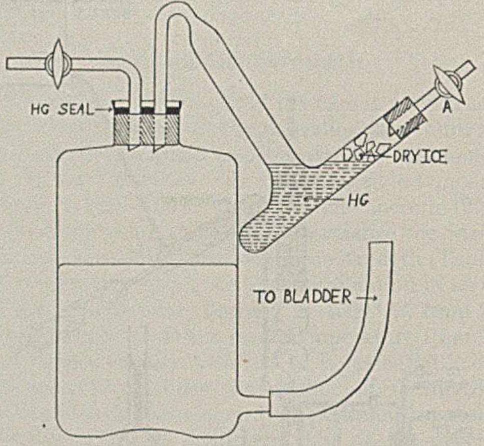


FIGURE 1

The method was suggested by J. S. Buck of this laboratory.

RECEIVED August 7, 1935.

Stirring Air within Desiccators

FRANK J. ZINK, Kansas Agricultural Experiment Station, Manhattan, Kan.

A NUMBER of investigators have used sulfuric acid solutions as a means of humidity control within small enclosed spaces. Wilson (*2*) suggested the use of desiccators for humidity chambers in conjunction with equilibria moisture determinations and pointed out the desirability of keeping the enclosed air in motion. However, Wilson (*2*) and Wilson and Fuva (*3*) did not use desiccators in their many equilibrium moisture determinations, possibly because the stagnant air resulted in a low rate of interchange of moisture. Lindsay (*1*) also pointed out the undesirability of such determinations in stagnant atmospheres.

Obviously, any mechanical means of stirring air within desiccators would be difficult to arrange and might interfere with the normal convenient use of the desiccator. The author has evolved a simple means of stirring air within desiccators, and presents it with the hope that others may find it useful in similar applications. Small fans mounted on pivots inside the desiccator were induced to rotate by a series of mechanically moved permanent magnets passing near the outside of the desiccator. The equipment was used in a series of investigations of equilibria moistures of forage hays and grains, in which 15 desiccators, each with enclosed fan, were used.

Figures 1, 2, and 3 illustrate the apparatus, the cost of which, exclusive of motor, was approximately $15. Many laboratories already have most of the apparatus available.

Metal desiccator plates were substituted for the usual porcelain plates. Small pivots were made, as illustrated in Figure 2, of steel wire about 0.0625 inch in diameter and 3 inches long and were soldered to the edges of the plates. The upper end was bent in such a manner as to offset it toward the center of the plate, so that the entire area of the plate would be free for moisture dishes. The ends of the pivots were sharpened to a point.

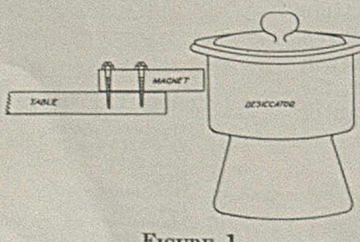


FIGURE 1

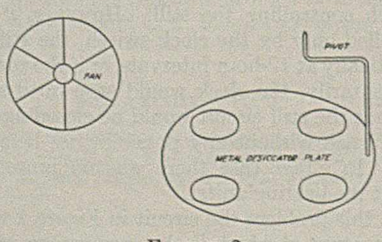


FIGURE 2

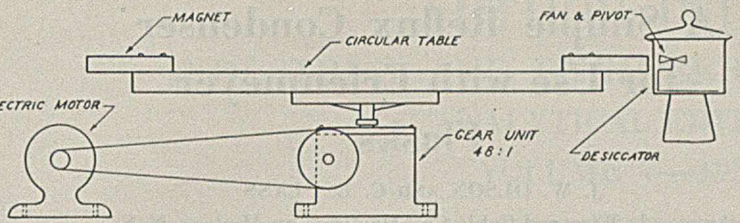


FIGURE 3

Sheet-metal tin disks 2.5 inches in diameter were cut and punched at the center with an ordinary center punch, care being used not to puncture the metal, to serve as the socket of a pivot bearing. Six radial cuts 1 inch deep were made in the edge with tin shears, and the segments were bent to serve as fan blades. These fans were then balanced on the pivots and the unit was placed inside the desiccator, so that the fans when in place just cleared the side. The fan may be lifted off the pivot and laid aside for removal or insertion of the sample dishes. With this type of pivot the fans rotated freely and were induced to rotate by magnets passing near the outside of the desiccator and on a level with the fan. The electromagnetic flux permeating the glass induced the fan to rotate, and no mechanical connection to the fan was necessary.

The motive power was furnished by a series of motor car magneto-magnets mounted on a circular platform, on a Boston Gear Company show window display unit of 48 to 1 ratio. An 1800-r. p. m., 0.125-h. p. electric motor was belted directly to the gear unit. A 2.5-foot diameter platform furnished ample space for 15 desiccators placed in a circle concentric with the platform and just outside the circle created by the passage of the magnets. The magnets were passed at the rate of 8 feet per minute and the more freely moving fans rotated at approximately 200 revolutions per minute.

Literature Cited

(1) Lindsay, D. C., International Critical Tables, Vol. 2, pp. 321–5 (1927).
(2) Wilson, R. E., J. IND. ENG. CHEM., 13, 326–31 (1921).
(3) Wilson, R. E., and Fuva, T., *Ibid.*, 14, 913–18 (1922).

RECEIVED September 17, 1935. Contribution No. 66, Department of Agricultural Engineering.

A Molecular Still

WILLIAM H. STRAIN AND WILLARD M. ALLEN
The University of Rochester, School of Medicine and Dentistry, Rochester, N. Y.

IN THE course of the purification of the corpus luteum hormone, progestin (*3*), it was found necessary to subject the highly purified concentrate to distillation in a molecular still. Since the described devices designed for use with small quantities were not entirely satisfactory for this purpose, a new type of apparatus modeled after the molecular still of Carothers and Hill (*1*) was designed. The still has the advantage that, in addition to being readily charged and cleaned, the temperature of distillation may be simply controlled.

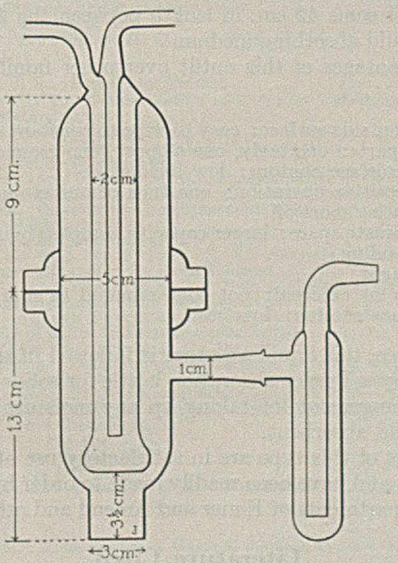


FIGURE 1

The still (Figure 1) was constructed from two pieces of old-style, flanged Pyrex pipe, 15 × 5 cm., the final dimensions being given in the diagram. After the apparatus was fabricated it was annealed and the surfaces ground for high-vacuum work. The still was heated by means of a small oil bath placed around the well of the apparatus.

In operation the thick oil to be distilled is dissolved in a small amount of ether and transferred by pipet to the well. The solvent is removed by cautious warming or by an air jet and the last traces by evacuation—first with a water pump and then with an oil pump. During this preliminary evacuation the condensing part of the apparatus is not used, the upper end being closed with a rubber stopper. Finally, when it is apparent that easily volatile substances have been removed, the stopper is replaced by the condenser, and the apparatus, including the trap, is attached to the intake of a mercury vapor pump. With the joints well greased and the mercury pump trapped with solid carbon dioxide, a vacuum of 0.0002 mm. is attained in a very short time, providing no distillation is taking place. By slowly heating the oil bath surrounding the well the distilling temperature is reached without any visible boiling and a waxy substance soon collects on the pestle from which it can be removed by immersion in benzene or other suitable solvent. A well of the size used will accommodate from 1 to 2 grams without difficulty. The detailed set-up of the high-vacuum apparatus and the technic of operation were essentially those described by Hickman and Sanford (*2*).

This same apparatus has been used for the purification of a number of other products of biological origin and appears to be adapted to a large variety of conditions.

Literature Cited

(1) Carothers, W. H., and Hill, J. W., *J. Am. Chem. Soc.*, 54, 1557 (1932).
(2) Hickman, K. C. D., and Sanford, C. R., *J. Phys. Chem.*, 37, 637 (1930).
(3) Wintersteiner, O., and Allen, W. M., *J. Biol. Chem.*, 107, 321 (1934).

RECEIVED August 29, 1935.

A Simple Reflux Condenser for Use with Erlenmeyer Flasks

J. W. OLSON AND C. E. PLASS
Anaconda Wire and Cable Co., Hastings-on-Hudson, N. Y.

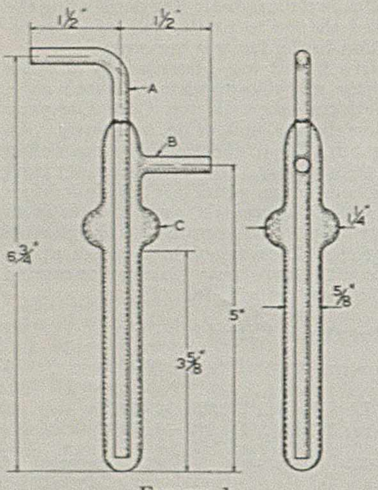


FIGURE 1

DURING the course of a study on the saponification number determination of oils the authors felt the need of a reflux condenser which could be conveniently used in an ordinary Erlenmeyer flask. Such a condenser as shown in Figure 1 was made up from an ordinary 150 × 16 mm. test tube and 8-mm. glass tubing and proved so satisfactory that others of like construction have been used for boiling various solutions under refluxing conditions.

The condensers can be made by anyone familiar with glassblowing technic by taking an ordinary test tube of such diameter that it will loosely fit in the Erlenmeyer flask to be used, and sealing in tube *A*. Section *C* is then enlarged as shown to act as a support for the condenser in the flask and tube *B* sealed in. The condensers can be used individually, or in series as shown in Figure 2 by means of appropriate rubber tubing connections. The dimensions shown in Figure 1 are suitable for condensers for standard Erlenmeyer flasks of 250-cc. capacity. Other sizes can be used for flasks of different dimensions.

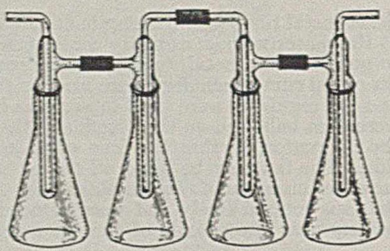


FIGURE 2

RECEIVED September 9, 1935.

An Improved Liquid Absorption Tube

W. D. TURNER, Columbia University, New York, N. Y.

AN IMPROVED absorption bulb for dry absorbents, such as ascarite, recently described (*1*), has now been supplemented by a similar tube for liquid absorbents. The new unit consists of the solid absorption tube, to which has been added the familiar Friedrichs gas absorption principle, in the form of a helical coil. This unit possesses all the advantages of the original dry absorber, besides offering a contact path of some 42 cm. in length between the gas bubbles and the liquid absorbing medium.

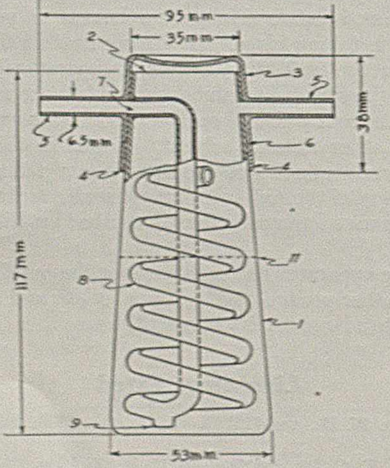


FIGURE 1. LIQUID ABSORPTION BOTTLE

Round glass body 1, 2; external stopper, 3, 4; lateral tubes, 5; ground joint, 6; tube and coil attached to inner side of body neck, 7, 8; open foot of coil, 9; hole communicating with top interior, 10; liquid level in charging, 11.

The advantages of this outfit over other familiar designs are:

Minimal outside surface: easy to wipe to constant weight.
Minimal parts: one body, one stopper, one ground joint.
Minimal surface contour: low breakage.
Simple, positive operation: one turn of one stopper shutting inlet and outlet short off.
Minimal waste space: larger capacity completely utilized.
Stable standing.
Light weight.
Ground joint external: not contaminated in charging.
Simple construction: low cost.

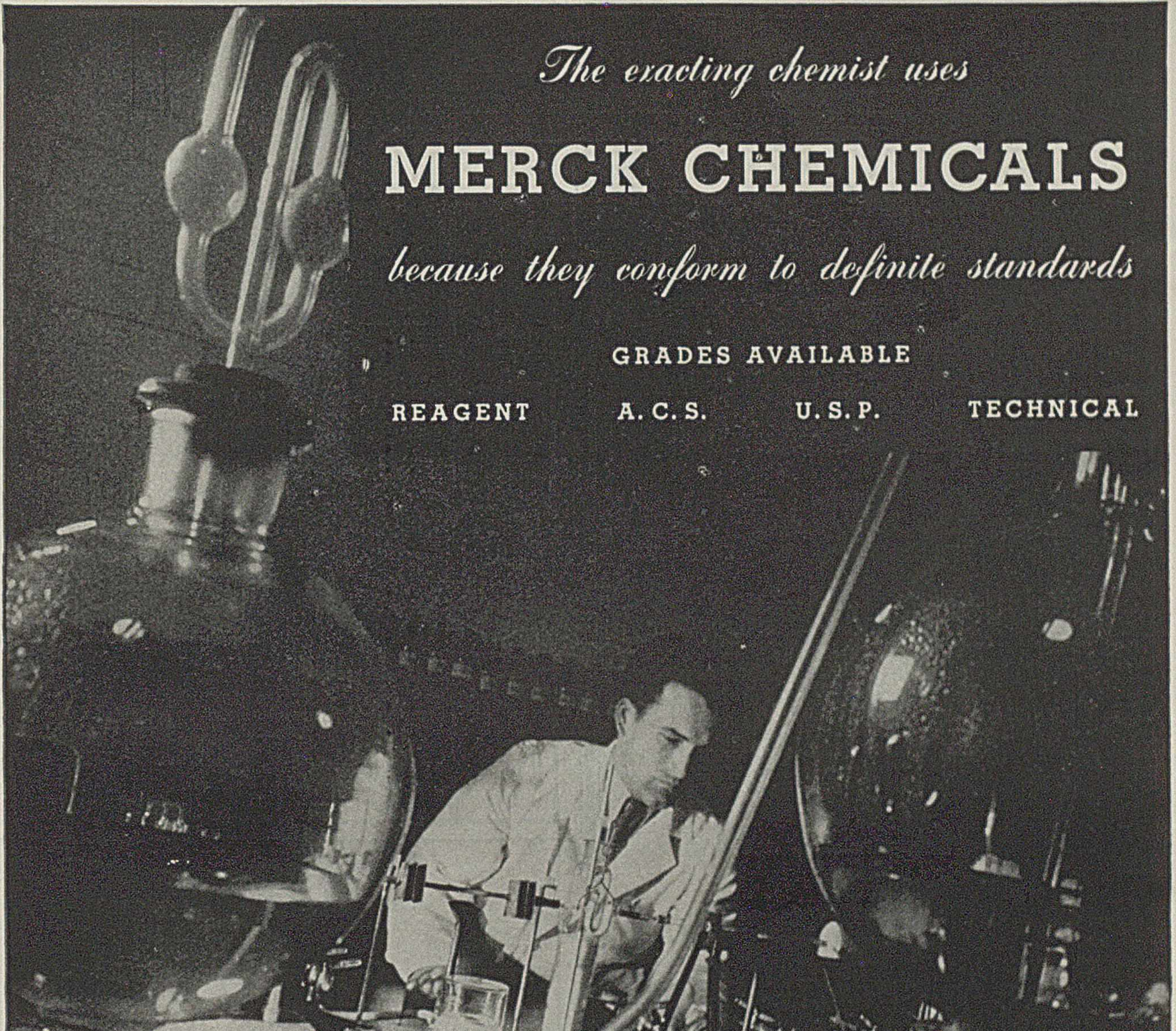
In practice, this liquid absorber is followed in the combustion train by a Turner absorption bottle for solids in the customary arrangement for taking up any moisture volatilized from a liquid absorbent.

Absorbers of this type are in satisfactory use at Columbia University, and have been readily made to order by the glassblowing departments of Eimer and Amend and others.

Literature Cited

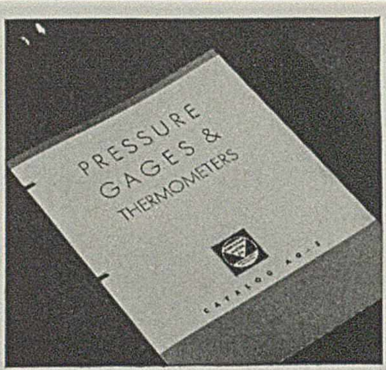
(1) Turner, W. D., IND. ENG. CHEM., Anal. Ed., 3, 63 (1931).

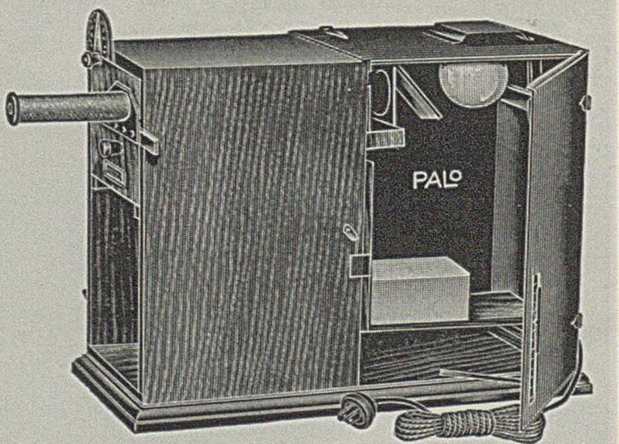
RECEIVED November 1, 1935.



The exacting chemist uses
MERCK CHEMICALS
because they conform to definite standards
GRADES AVAILABLE
REAGENT
A.C.S.
U.S.P.
TECHNICAL


HUX


PRESSURE GAGES & THERMOMETERS
CATALOG AG-5


PALO

New Beauty •

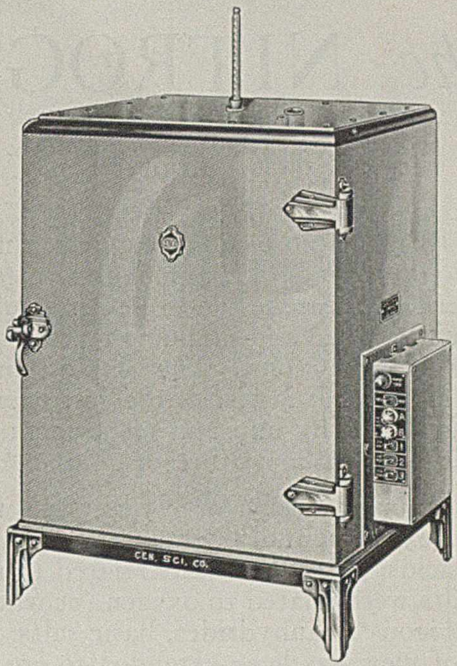
Easier Adjustment •

In the Reliable—Time Tested

Electrically Heated and Controlled

Constant Temperature

Laboratory Drying Oven



The Improved
CENCO-DeKHOTINSKY TRIPLE-WALLED OVENS

retain the patented triple-wall construction, upon which their enviable reputation for uniformity of temperature distribution in the heating chamber has been built. New features, in addition to a modern, highly attractive exterior design and finish, are: an inner lining of monel metal; a side port with shutter to permit rapid changing of the interior air, when desired; a full glass inner door; a compact, fully-enclosed heat regulating system, conveniently located within easy reach of the operator's right hand; and two pilot lamps to indicate both the operation of the main and auxiliary heat regulating units. At the present prices, these ovens are the best values obtainable in precision constant and uniform temperature ovens.

No. 95100A
Inside dimensions: 14¾ x 12 x 11¾ inches
For 110 volts—$140.00

No. 95105A
Inside dimensions: 19¾ x 17 x 14 inches
For 110 volts—$200.00

These Ovens and Many Other Improved Devices for the Chemical Laboratory are completely described in the New Cenco Catalog of Laboratory Apparatus.

Reserve Your Copy of Catalog J135 Now.

BOSTON—
79 Amherst St., Cambridge, Sta. A.

CHICAGO—
1700 Irving Park Blvd.

CENTRAL SCIENTIFIC COMPANY
LABORATORY CENCO SUPPLIES
Apparatus Chemicals
NEW YORK - BOSTON - CHICAGO - TORONTO - LOS ANGELES

Dr. Edward Curtis Franklin's New Book

The NITROGEN SYSTEM *of* COMPOUNDS

PROBABLY no element exhibits a more diverse chemistry than does nitrogen. The multiplicity of types of compounds formed by this element is such that, despite the many volumes of recorded researches on these compounds, there still awaits the formulation of a point of view sufficiently broad and simple to reach a systematic classification of them and a rational interpretation of their reactions. The simplest and most powerful tool yet devised for the accomplishment of the above ends is that of the "nitrogen" system of compounds as formulated by E. C. Franklin and developed by him and his students. The present monograph embraces the life-long work of Franklin and constitutes a unique American development of chemical thought.

Beginning nearly forty years ago with simple inorganic nitrogen compounds, Franklin was able to experimentally demonstrate that many of these compounds were to be regarded as ammono acids, bases, and salts related to nitrogen (or ammonia) as the more familiar acids, bases, and salts were related to oxygen (or water). Other nitrogen compounds were to be looked upon as analogous to anhydrides, basic salts, salts of amphoteric bases, etc. More recently this same point of view has been extended to organic nitrogen compounds where it promises to be of tremendous value in correlating the reactions of such diverse materials as the amines (ammono alcohols and ethers), ethylidene imine (ammono aldehyde-alcohol), hydramides (ammono aldehyde-acetals), Schiff's bases (aldehyde-ethers), amidines (ammono fatty acids), nitriles (fatty acid anammonides), cyanamide, guanidine (ammono carbonic acids), etc., as well as the nitrosamines, diazo compounds, and the nitrogen heterocycles.

A very desirable feature of the book is the appendix on the experimental manipulation of liquid ammonia.

No student of nitrogen chemistry nor investigator in this field can afford to be without this monograph.

● CONTENTS ●

Introduction
Properties of Liquid Ammonia
Reactions in Liquid Ammonia
The Nitrogen System of Bases, Acids and Salts
Nomenclature
Augmentation and Reduction in Liquid Ammonia
Ammono Bases and Basic Nitrides
Alkali Metal Salts of Amphoteric Metallic Amides and Imides
Ammonobasic Salts
Mercury Nitrogen Compounds
Ammono Carbonic Acids
Aquo-Ammono Carbonic Acids
Ammono Carbonous Acid
Amides and Imides of Silicon, Titanium, Germanium, Zirconium, Tin and Thorium
Hydrazoic Acid
Aquo-Ammono Nitric Acid
Ammono and Aquo-Ammono Phosphoric and Phosphorous Acids
Aquo-Ammono Sulfuric Acid
Ammono Sulfurous Acid, Ammono-Thio Sulfuric Acid, Aquo-Ammono Sulfurous Acid and Sulfazylic Acid
Ammono Hypochlorous Acids
Mixed Acids
Acid Anammonides
Acid Anhydride-Anammonides
Acid Chlorides
Hydrogen Peroxide, Hydrazine and Hydroxylamine
Ammono Alcohols
Aldehyde-Alcohols, Aldehyde-Ethers, Aldehyde-Acetals and Aldehyde-Esters
Ketone-Alcohols and Ketone-Ethers
Carbazylic Acids
Carboxazylic Acids
Hydrocyanic Acid and the Nitriles
Nitrosamines and Diazo Compounds
Nitrous Acid Hydrazides and Oximes
Aquo-Ammono Sulfonic Acids
Appendix

A. C. S. Monograph No. 68

339 Pages 33 Chapters Illustrated **$7.50**

REINHOLD PUBLISHING CORPORATION
Successor to The Chemical Catalog Company, Inc. • **330 West 42nd St., New York, U. S. A.**

DIPHENYLTHIOCARBAZONE

for the determination of LEAD

THE sensitive color reactions of diphenylthiocarbazone make it an interesting and valuable reagent for estimating small quantities of heavy metals. It is particularly useful in determining minute amounts of lead in biological materials. A cherry-red lead complex is formed, the color of which can readily be compared to known standards. Interference from other heavy metals is prevented through the use of an ammoniacal cyanide solution.

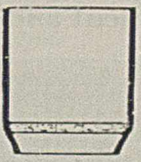
Eastman Diphenylthiocarbazone, 3092, has been prepared especially for such analytical purposes. A bibliography of recent articles on its use will be promptly forwarded upon request. Eastman Kodak Company, *Chemical Sales Division*, Rochester, N. Y.

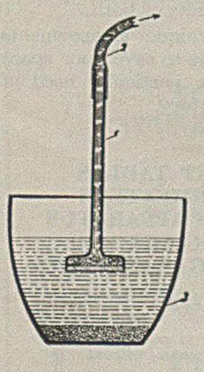
EASTMAN ORGANIC CHEMICALS

ROYAL BERLIN PORCELAIN

PORCELAIN FILTERING CRUCIBLES
ACCORDING TO KOENIG
U. S. PATENT, 1,567,654

Made in two porosities of the best glazed Royal Berlin Hard Porcelain, with porous bottom, equally resistant to heat as the vessel. Ignition does not alter rate of filtration. No loss of weight.



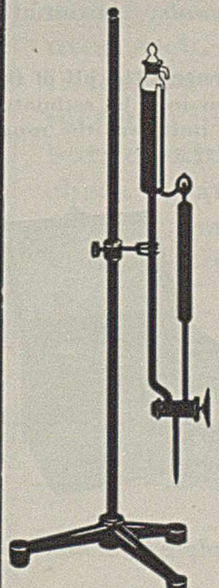


Specially recommended for quantitative determination of all crystalline precipitates such as barium sulphate, etc.

Royal Berlin Porcelain Immersion Filter Tubes, according to Emich, for use by immersion into liquids to be filtered, particularly for gelatinous precipitates and such which must be ignited.

FISH-SCHURMAN CORPORATION
230 EAST 45TH ST. NEW YORK CITY
U. S. AGENTS

NEW
ALL GLASS AUTOMATIC PRECISION PIPETTE



FOR RAPID MEASUREMENTS

SINGLE STOPCOCKS CONTROL

SELF-FILLING
ALL SIZES 2ml. to 25 ml.

NEW AUTO-PIPETTE RINSER PRICE $3.75
FOR THE BUSY LABORATORY
CLEANS AND WASHES ALL PIPETTES AUTOMATICALLY

GENERAL LABORATORY GLASS INSTRUMENTS
WE SOLICIT YOUR INQUIRIES

ERICK F. STEELE

135 East 26th Street, New York, N. Y.
ESTABLISHED 1915
MAKERS OF FINE PRECISION GLASS INSTRUMENTS

Revolutionary

The Beckman pH Meter (*Glass Electrode*) Has Arrived!

Possesses all of the marked advantages of the glass electrode. Unaffected by oxidizing or reducing agents, colloids, color or viscosity. Registers the pH of any solution in a *few seconds*. Automatic temperature compensator.

Simple—only 2 controls; requires no training to operate. The pH is read directly from dial.

Accurate—The pH of the solution may be estimated to 0.01 unit over the range of 0 to 12.5

Compact-Portable—Self-contained in attractive walnut carrying case. No external equipment.

Rugged—No special precaution needed in carrying the instrument; designed and built to withstand hard usage. Not affected by vibration.

Economical—A time and effort saving device. Can be used with equal effectiveness in plant or laboratory.

Write Department I-11 for complete information.

BRAUN
CORPORATION

2260 East 15th St., Los Angeles, Calif.

San Francisco
Braun-Knecht-Heimann-Co.

Seattle, Washington
Scientific Supplies Co.

For PURE WATER

**Typical Analysis of Distillate*

	Parts per 100,000
Total Solids	0.28
Volatile Solids	0.16
Inorganic Solids	0.12
Nitrogen as	
Free Ammonia	0.0035
Albuminoid Ammonia	0.0000
Nitrates	0.0000
Nitrites	0.00
Chlorine	0.00
Dissolved Oxygen	0.06
Free Carbon Dioxide	0.12
pH Value at 20° C	5.7
Total Bacteria per cc.	None

** Made and certified by Arthur D. Little, Inc.*

The *NEW* STOKES Water Still

produces an exceptional distillate—see typical analysis above—at low cost.

Features

which safeguard purity of distillate and increase convenience of operation.

Pyrex Glass Cover—makes operation visible and cleaning easy.

Triple Vapor Baffle—prevents entrainment.

Solid Block-tin Condenser Tube—not merely block-tin lined.

Gas Eliminator—Hot Well—where temperature, practically boiling, releases dissolved gases before distillation.

Deconcentrator—reduces foaming and scaling tendencies; vital in hard water districts.

Patented Heating Unit—in electric models—embodies dual-purpose protective device.

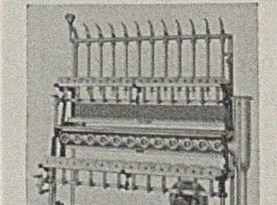
Capacity—One Gallon per Hour.

Steam-, Gas- and Electrically-heated. Wall-bracket and Floor-stand types.

FJSTOKES MACHINE CO.
Process Equipment Since 1895
5944 Tabor Road Olney P. O. Philadelphia, Pa.

10 Years of Specializing
in complete units of
Kjehldahl Nitrogen Apparatus

Has developed our superior equipment and a demand for its installation in the better laboratories.



¶ Combination digestion and distillation units in capacities 6 to 24. Separate units in capacities 6 to 48. All electric, all gas or units of both.

¶ Many unique arrangements are available to save floor space and fit the particular need of your laboratory.

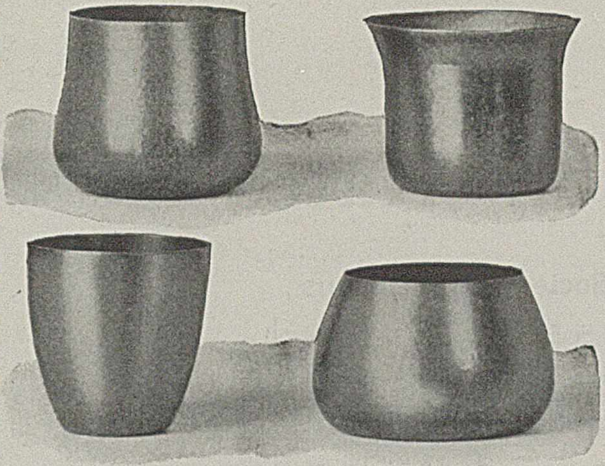
Also

LABORATORY EQUIPMENT TABLES
"GOLDFISCH" ELECTRIC HEATERS
"GOLDFISCH" EXTRACTION APPARATUS
CRUDE FIBRE APPARATUS
"LABCONCO" *WIDE RANGE* GAS BURNERS

Catalogue on Request

Your inquiry is invited. No trouble to submit proposals on your requirements and, of course, without obligation to you.

Laboratory Construction Company
1113 Holmes Street Kansas City, Missouri



For Maximum Service
Use APW
PLATINUM WARES

To provide the necessary requisite accuracy for your analytical work, A.P.W. Wares are made of Platinum refined to a state of extreme purity, under the strict supervision of our Research Laboratories. Proper construction methods and skilled workmanship of the metal—hand-hammering—are used to give our wares the maximum strength and stability so essential in their continual usage over a long period of time. They are always constant in weight—always dependable. We list some of these:

Regular style of crucibles and dishes, in Platinum and Platinum-Rhodium, also with A.P.W. Offset Rim and special heavy bottoms on request

Crucibles with capsule covers
Gooch Crucibles (all styles)
Capsule Crucibles
Interchangeable and Combination Crucibles
Micro Crucibles and Boats
Dishes for Iron and Steel Analyses
Dishes for Fertilizer Analyses
Dishes for Sugar, Water, Milk Analyses
Gold and Silver Crucibles and Dishes

Whether you want some new A.P.W. Platinum, or if any of your present stock of ware needs remaking or exchanging into either identical or different forms, let us give you more detailed information.

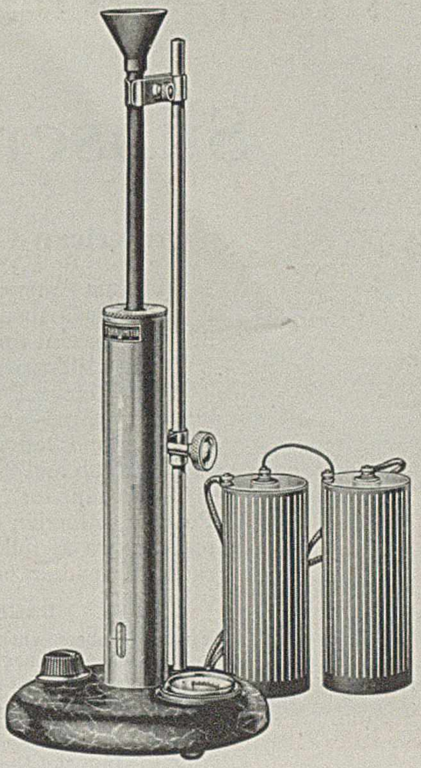
APW

PLATINUM, PALLADIUM, IRIDIUM, RHODIUM, RUTHENIUM, OSMIUM

We gladly supply anything you need in Platinum or Platinum Metals.

Ask for Catalog E-16 describing our regular line of Platinum Laboratory Wares.
For Micro-Chemical Wares ask for folder "F. M."

The AMERICAN PLATINUM WORKS
N. J. R. R. AVE. at OLIVER ST.
NEWARK, N. J.



Determinations by means of the

PARR TURBIDIMETER

may be made in less than five minutes each. The instrument is not intended to replace gravimetric methods in precise laboratory work, but, due to its speed and ability to check gravimetric results within 0.2%, it has found wide use in the routine estimation of the following:

SULPHUR IN FUELS
SULPHUR IN RUBBER
SULPHATE IN BOILER WATER
SULPHATE IN CHROMIUM PLATING SOLUTIONS
SO_3 IN PORTLAND CEMENT

Write for Bulletin E-24

PARR INSTRUMENT CO.
MOLINE, ILLINOIS

Subscription Rates

American Chemical Society Publications

1. Journal American Chemical Society	$ 8.50
2. Chemical Abstracts	12.00
3. Industrial and Engineering Chemistry.	
a. Industrial Edition	$5.00
b. News Edition	1.50
c. Analytical Edition	2.00
3a and 3c together	6.00
3a, 3b and 3c (i. e., complete journal)	7.50

10% discount for combinations of 1, 2 and (or) 3 (complete). Postage to foreign countries outside the Pan American Postal union extra as follows: 1, $1.50; 2 and 3 (complete), $2.10 each. Canadian postage one-third these rates.

BACK NUMBERS AND VOLUMES

	Single Numbers, when available, each major publication	$ 0.75
Back Volumes	J. Am. Chem. Soc., Vols. 23, 24, 28–56	9.00
	Chem. Abst., Vols. 1–28, incl. both Dec. Indexes	585.00
	Chemical Abstracts, Vols. 6, 8, 10, 14, 15, $20.00; Vols. 16–28, each	15.00
	Ind. and Eng. Chem., Vols. 9–26; each Vol.	9.00
	Ind. and Eng. Chem. Sets, Vols. 1–26*	234.00
	Index to Vols. 1–20, J. Am. Chem. Soc.	1.00
	Index to Chem. Abst., ordered separately each Vol.	2.50
	2nd Decennial Index to Chemical Abstracts—5 Vols.	50.00

Members, for personal use (sets excepted), are allowed a discount of 20%.

* *The News Edition and Analytical Edition are not included in back volume price for INDUSTRIAL and ENGINEERING CHEMISTRY. Price $2.00 and $3.00 each, respectively, when available. Single numbers 10 cents and 75 cents each, respectively.*

Advance payment is required in all cases and must be made by check or postal order payable in American exchange (dollars).

1. Journal American Chemical Society
   Proceedings, Vol. 2 and Vols. 16, 23, 24, 28–56, only available. Some single numbers of other volumes can still be supplied.
2. Chemical Abstracts
   Volumes 1–5, 7, 9, 11–13 will be sold as complete volumes only in sets of Vols. 1–28 including the 1st and 2nd Decennial Indexes.
3. Industrial and Engineering Chemistry
   Volumes 1 to 8 sold only as complete sets of Vols. 1–26, inclusive.

DOMESTIC SHIPMENTS. Single copies are sent by mail. Full volume, and sets are sent in the United States and Canada express collect.

FOREIGN SHIPMENTS. Foreign shipments will be sent by mail either at purchaser's risk or by registered mail at postage cost, plus 5% of invoice, additional for registry; minimum charge, 75 cents. Large shipments will be delivered, if desired, to responsible forwarding agents in New York free, further charges to be paid by the purchaser on receipt.

The Society will not be responsible for loss due to change of address unless notification is received one week in advance of issue.

Members or subscribers desiring their Journals or Abstracts forwarded from an old address should always notify their Postmaster and leave necessary postage.

The names of members and subscribers, whose Journals cannot be delivered by the Post-Office Department, will be cut off the mailing list at once, and will not be restored until correct addresses have been furnished.

In the absence of other information, the notices of change of address received from the Post-Office Department will be considered as correct, and the mailing list changed accordingly.

All communications relating to subscriptions or back issues should be addressed to
CHARLES L. PARSONS, Business Manager, Mills Building, Washington, D. C.

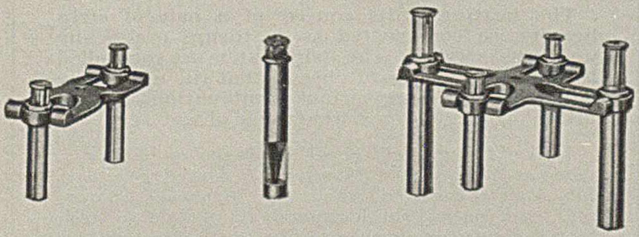
NEW!

MICRO CENTRIFUGE EQUIPMENT

International Centrifuges again show their adaptability to the demands of science. We are pleased to announce that the new heads and tubes for *microchemical analysis* are interchangeable with the regular heads of the "Clinical Model" Centrifuge.

"Clinical Model"

INTERNATIONAL CENTRIFUGE



MICROCHEMICAL HEADS and TUBES

International Microchemical Heads are made in three types, two place heads for either large or small metal tube holders (shown above at left) or four place combination heads (at right).

Standard glass tubes of 0.5, 2, 3 and 5 ml. capacities are now available. The small metal holder carries the three smaller glass tubes and the large holder the 5 ml. tube.

Bulletins and information gladly furnished upon request.

There is an International for any job

INTERNATIONAL EQUIPMENT CO.
352 Western Avenue Boston, Mass.
Makers of Fine Centrifuges

pH ....in the plant! or in the laboratory

Coleman pH Electrometer

• Self-contained • Direct Reading
Factory Sealed Glass Electrode

The heavy walled Glass, and also Reference electrode, are *filled and hermetically sealed* at the factory. The glass electrode may, of course, be used in practically any solution, gaseous, turbid, oily, colored, strongly alkaline or acid.

Direct pH readings are taken from a dial with nine-inch scale, graduated in $^1/_{10}$th pH, sensitive to $^1/_5$th of a division. The classic potentiometer circuit is retained and primary calibration is against enclosed Standard Cell. The electronic amplifying circuit is independent of vacuum tube characteristics or voltage variations. Temperature and asymmetric changes are corrected by built-in compensator.

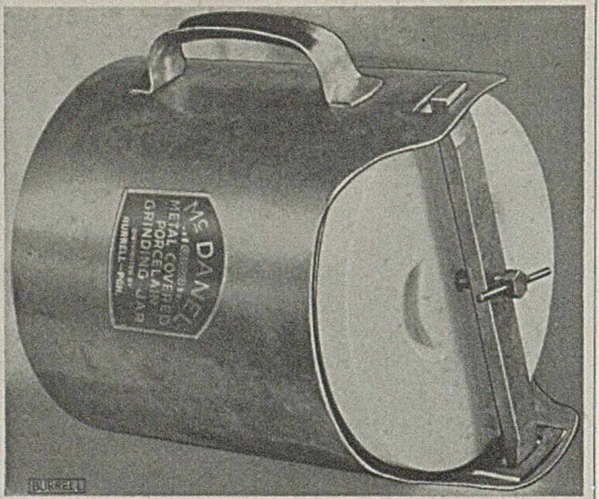
No Storage Battery Is Needed ....
No Reflecting Galvanometer Is Required

The Coleman pH Electrometer is readily portable, rugged and suitable for laboratory or plant. It is housed in a beautiful walnut cabinet 12" x 9" x 9", with leather handle and requires no accessories except distilled wash water.

SEND for Volume 2, WACO CATALYST, for more complete description . . . or we will gladly accept your order for a five-day free trial in your laboratory. It is No. 3535 E, costs $125.00 complete, ready for your most critical test. . . .

— DISTRIBUTOR —

WILKENS-ANDERSON COMPANY
111 N. CANAL STREET CHICAGO



Will fit "cradles" of all standard ball-mills.

McDanel

Steel-Jacketed Porcelain Grinding Jars

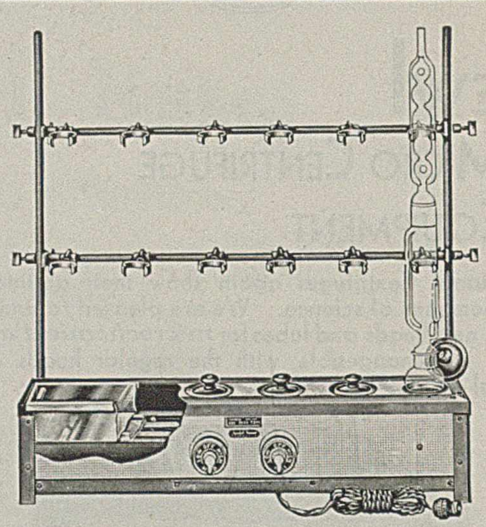
Fully described in New Burrell Bulletin 59-01

FEATURES OF DESIGN include the strong steel jacket with large comfortable handle; the heavy, straight-sided porcelain jar; the ground flat heavy porcelain cover with finger grips; the simple bar and screw for easy, positive closure and quick, unhampered opening.

FEATURES OF USEFULNESS include the insurance against breakage because of dropping from wet, slippery hands; the prevention of accumulations in the bottom corner because of the fillet; the convenience of a jar without a shoulder; and the longevity because all of the wall thickness, down to the steel jacket, is available for useful work. Prices are lower.

Burrell Pittsburgh stock includes a full line of scientific laboratory apparatus and chemicals

BURRELL
TECHNICAL SUPPLY COMPANY
1936-42 FIFTH AVE. PITTSBURGH, PA.



Combination Extraction Apparatus

This electrically heated, six-unit Combination Extraction Rack and Bath may be used for heating either by radiation or by immersion.

A Monel metal pan suspended within the rack, just above the heating units, allows for the heating of flasks by immersion when the pan is filled with water or oil. The entire top of the container may be removed and the pan lifted out if desired.

The heating units consist of a pair of strip heaters, so constructed as to insure practically unlimited service. The strip heaters are controlled by a pair of 3-heat switches so that the units may be used singly or in various combinations to permit of operation over a wide range of wattages.

Each of the six circular openings on the top of the container is fitted with a Monel metal flanged ring with Monel metal cover and knob. The removable support rods, both vertical and horizontal, are of stainless steel; special adjustable clamps are fitted with spring bronze clips.

Dimensions

Overall length	31"
Overall depth	6½"
Overall height	30"
Height to top of container	7"
Center distances between openings	5"
Dimensions of Monel metal pan	29x4, ¾x3"
Diameter of openings	2½"

Combination Extraction Apparatus, 6-unit, 1000 watts for connection to 110 volt lighting circuit. Complete as illustrated (excluding glassware) with 6 ft. of insulated cord and separable plug	**$100.00**
Combination Extraction Apparatus. As above, but 220 volts	**100.00**

WILL CORPORATION
LABORATORY APPARATUS AND CHEMICALS
ROCHESTER, N.Y.

POLITECHNIKA
BIBLIOTEKA GŁÓWNA